Studies in the coordination chemistry of some main group metals and metalloids

Stephen James Bryan

Bryan, Stephen James (1983) Studies in the coordination chemistry of some main group metals and metalloids. Doctoral thesis, Durham University.

STUDIES IN THE COORDINATION CHEMISTRY OF SOME MAIN GROUP METALS AND METALLOIDS

by

STEPHEN JAMES BRYAN B.Sc.
(Hatfield College)

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

Department of Chemistry
September 1983.

To my parents.

CONTENTS

PART 1

METHYLENEAMINO DERIVATIVES OF SOME MAIN GROUP METALS AND METALLOIDS.

CHAPTER 1

CHAPTER 2

PREPARATION AND CHARACTERISATION OF SOME ASSOCIATED METHYLENEAMINOBORANES AND RELATED STUDIES

Experimental Section

CHAPTER 3

REACTIONS OF LITHIUM TRIETHYLBOROHYDRIDE WITH SOME NITRILES; THE REACTIVITY OF LITHIUM t-BUTYL-, AND PHENYL-, METHYLENEAMINOTRIETHYLBORATE TOWARDS PHOSPHORUS TRICHLORIDE.

Experimental Section

Page

CHAPTER 4

SOME MONOMERIC DI-t-BUTYLMETHYLENEAMINO DERIVATIVES OF BORON

Experimental Section

CHAPTER 5

SOME METHYLENEAMINO DERIVATIVES OF ALUMINIUM

CHAPTER 6

^{15}N n.m.r. SPECTRA OF SOME METHYLENEAMINES AND METHYLENEAMINO DERIVATIVES

PART 2

STUDIES IN THE METAL-DERIVATIVE CHEMISTRY OF SOME BORANES AND CARBORANES

CHAPTER 7

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

Experimental Section

CHAPTER 8

ATTEMPTS AT THE PREPARATION OF SOME ICOSAHEDRAL-closo-DICOBALTABORANES

ACKNOWLEDGEMENTS

I should like to express my thanks to Professor K. Wade, under whose supervision this work was performed, for his encouragement and invaluable advice.

A number of other people have also provided considerable assistance during the course of this work. Five of the six crystal structures described here for the first time were determined by Dr. W. Clegg of the Institut für Anorganische Chemie der Universität, Göttingen, Federal Republic of Germany. The remaining structure was determined by Dr. J. Halfpenny, formerly of this University, and currently of Napier College, Edinburgh. The ^{15}N n.m.r. spectra were recorded by Dr. M.W. Cooper of PCMU, Harwell as part of a collaborative study with Dr. J. Mason of the Open University. I am grateful to Dr. R. Snaith and co-workers of Strathclyde University for the provision of some of the samples used in this ^{15}N n.m.r. study, and additionally to Dr. Snaith for the provision of the unpublished bond index data discussed in Chapter 4. Mr. B. Hall, of these laboratories, has provided occasional, though valuable, technical assistance, and I am grateful to Mrs. M. Chipchase for typing the text of this thesis.

Finally, the provision of a Science and Engineering Research Council maintenance grant is gratefully acknowledged.

S.J. Bryan.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1980 and September 1983. It has not been submitted for any other degree, and is the original work of the author except where acknowledged by reference.

Some aspects of this work have formed the basis of the following publications :

'Preparation and X-Ray crystal structures of the dimeric-aldiminoborane $(PhCH{=}NBMe_2)_2$ and monomeric paddle-wheel shaped tris(ketimino)borane $B(N{=}C^tBu_2)_3$', by J. Robert Jennings, Ronald Snaith, Muayyad M. Mahmoud, Stephen C. Wallwork, Stephen J. Bryan, Joan Halfpenny, Elizabeth A. Petch and Kenneth Wade, J. Organomet Chem., 1983, 249, Cl.

'Crystal Structure of the pentamethyldiethylenetriamine adduct of 1-Lithio-2-methyl-1,2-dicarba-closo-dodecaborane, $Li(C_2B_{10}H_{10}Me)(MeN(CH_2CH_2NMe_2))$, a compound containing a lithium atom terminally bonded to a six coordinate carbon atom', by William Clegg, David A. Brown, Stephen J. Bryan and Kenneth Wade, Polyhedron, in press.

During the course of his postgraduate study the author also contributed to the following publication :

'The Coordination chemistry of Acrylonitrile', by S.J. Bryan, P.G. Huggett, K. Wade, J.A. Daniels and J.R. Jennings, Coord. Chem. Rev., 1982, 44, 149.

'Studies in the coordination chemistry of some main group metals and metalloids'

by

S. J. Bryan B.Sc.

ABSTRACT

Part I of this thesis describes the preparation of some compounds containing methyleneamino ligands, $R^1R^2C{=}N-$ attached to lithium, boron, aluminium and phosphorus. The compounds were synthesised with the aim of providing detailed information on the structural and spectroscopic consequences of methyleneamino-ligand bonding to both valence-saturated, and unsaturated, metals and metalloids.

The syntheses of a number of associated methyleneaminoboranes of the type $(RCH{=}NBR'_2)_2$ are described, the crystallographically characterised derivative $(PhCH{=}NBMe_2)_2$ being typical of these compounds. Spectroscopic features of all the compounds are discussed in relation to the structural findings. In contrast, di-t-butylmethyleneaminoboranes of the form $({}^tBu_2C{=}N)_xBY_{3-x}$ have non-associated structures. The compound ${}^tBu_2C{=}NBPh_2$ is shown to possess a linear, allene-like, $C{=}N{\rightleftharpoons}B$ skeleton with extensive N(p)-B(p) dativeπbonding, while structural and spectroscopic features of a number of these compounds are discussed in conjunction with the results from theoretical studies. Additionally, the compound ${}^tBu_2C{=}NH_2{}^+BF_4{}^-$ has been structurally characterised. Methyleneaminoborates, RCH=N(BEt_3)Li (R=^{t}Bu,Ph) were prepared from the reaction of $LiBHEt_3$ and RCN, and their potential as synthetic reagents demonstrated by the preparation of some methyleneaminophosphines, $(RCH{=}N)_xPCl_{3-x}$. The reactivity of $LiBHEt_3$ towards CH_3CN is shown to be markedly different. Evidence of N(p)-Al(d) dative π bonding is seen in the structurally characterised methyleneaminoalane $((Ph_2C{=}N)_3Al)_2$, while the synthesis and spectroscopic properties of this and two further compounds, $((C_{12}H_8)C{=}NAlCl_2)_2$ and $LiAl(N{=}CPh_2)_4$, are discussed in relation to the conflicting findings of earlier studies of methyleneaminoalanes. The ^{15}N n.m.r. spectra of a number of methyleneamines, $R_2C{=}NH$, and methyleneamino derivatives $((R_2C{=}NMX_n))_z$, have been obtained. The ^{15}N shifts do not correlate with the ligand $C\hat{N}MX_n$ angle but may, in part, be explained in terms of paramagnetic shielding factors.

Part II of this thesis describes studies in the metal-derivative chemistry of some boranes and carboranes. The structurally-characterised compounds $Li(C_2B_{10}H_{10}Me)$(PMDETA) and $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2.C_7H_8$ contain unprecedented examples of group I and II metals covalently bonded to six-coördinate carbon atoms, while the concept of carboranyl cone angles is introduced to account for features of their structures. Finally, a number of unsuccessful attempts to synthesise 12-vertex *closo*-cobaltaboranes of the form $(L_3Co)_2B_{10}H_{10}$ are described.

PART 1

METHYLENEAMINO DERIVATIVES OF SOME MAIN GROUP METALS AND METALLOIDS

CHAPTER 1

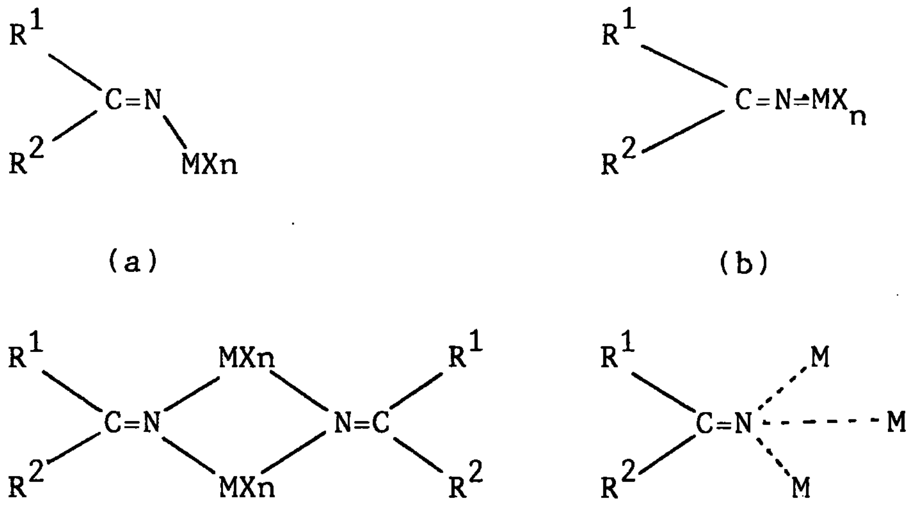
BONDING MODES OF METHYLENEAMINO LIGANDS

Over the last twenty years a large number of methyleneamino derivatives of main group metals and metalloids have been prepared and characterised, both in these laboratories and elsewhere. Interest in these compounds has stemmed largely from the realisation that the spectroscopic properties of the methyleneamino ligand $R^1R^2C=N-(R^1,R^2=\mathrm{alkyl,aryl,H})$, and in particular the infra red active stretching vibration $\nu(C=N)$, provide a convenient means of differentiating between the various bonding modes adopted by metal-attached nitrogen ligands. In more recent years however, increasing use has been made of X-ray crystallography, both to supplement the structural information available from spectroscopic studies and also to clarify the position in cases where the spectroscopic information has proved ambiguous. While no comprehensive review of methyleneamino derivative chemistry has been published, the theses of a number of workers in these laboratories, notably those of Petch (1) and Manning (2), have contained surveys of the synthetic chemistry and spectroscopic properties of such compounds. The aim of the present review is to provide a brief summary of the results from crystallographic studies performed on these compounds, and thus to supplement the work of these authors.

Methyleneamino ligands can bond to metals or metalloids in three main ways. When terminally attached as one-electron ligands to coordinatively saturated metals they adopt the angular $C{=}N{-}MX_n$ geometry that is familiar in the parent imines, $R^1R^2C{=}NH$, in oximes $R^1R^2C{=}NOH$, and in related systems, and that reflects the presence on the nitrogen atom of a stereochemically active lone pair of electrons (Figure I.1a). However, when bonded to a coordinatively unsaturated metal or metalloid the ligand may function as a source of three electrons for metal-nitrogen bonding.

Figure I.1

One and three electron bonding modes of methyleneamino ligands.



(a) (b)

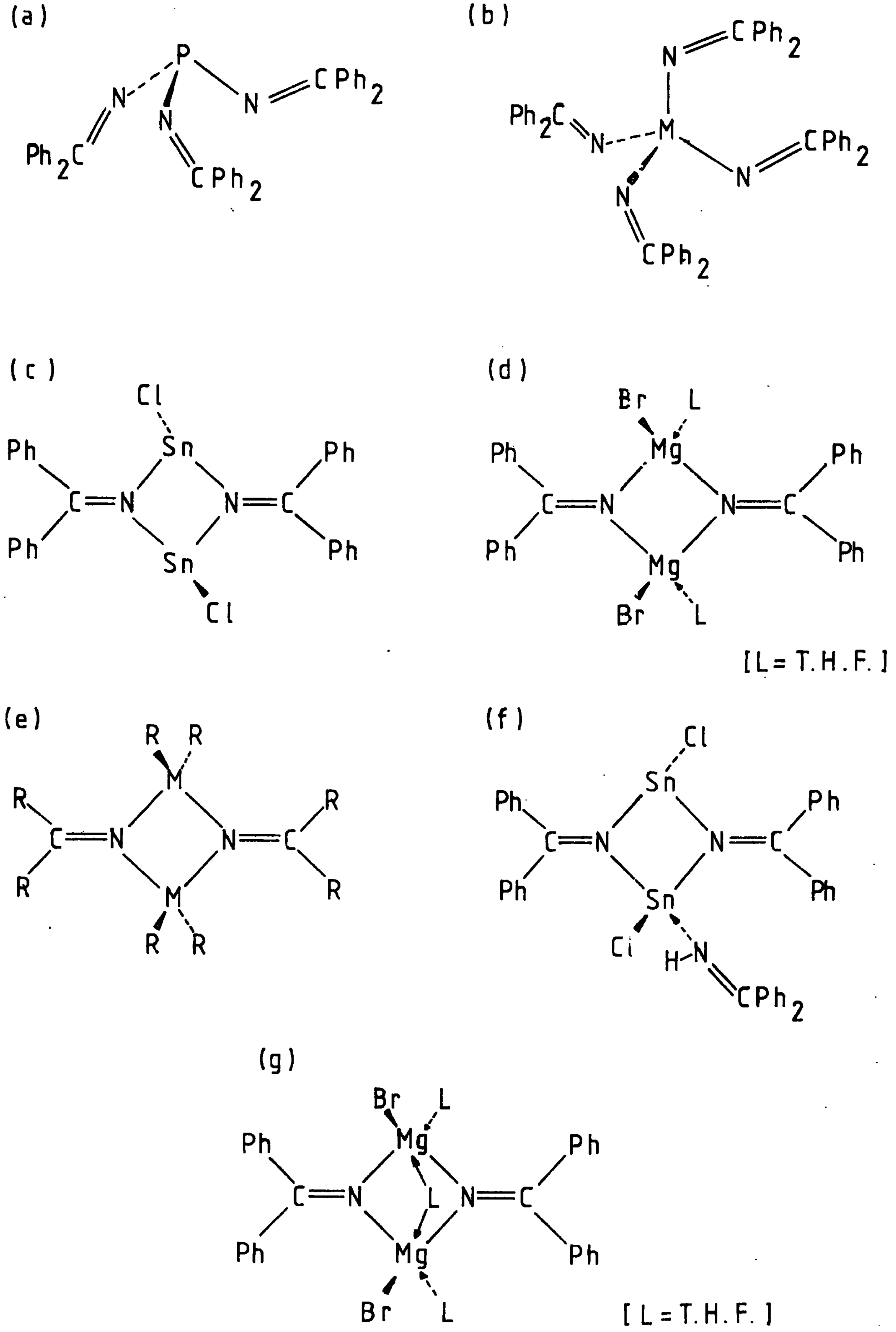
(c) (d)

In cases where association of the resulting imino derivative is prevented, notably by the bulk of the substituents R and X, dative $N \rightleftharpoons M$ π bonding will occur and the molecule will assume a linear, or near linear $C{=}N \rightleftharpoons MX_n$ skeleton (Figure I.1(b)) appropriate for the maximisation of such bonding. In the case of smaller substituents, R and

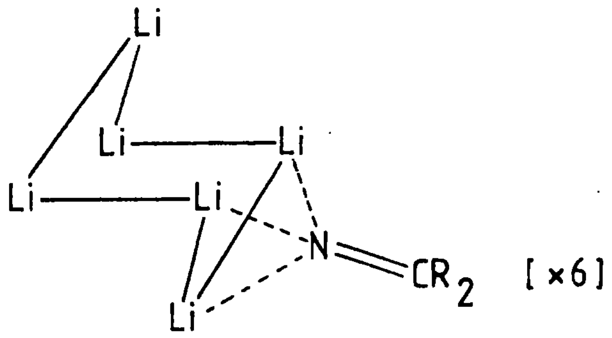
X, the energetically more favourable formation of two $N-MX_n$ bonds, rather than one σ and one π bond, will favour formation of a dimeric species (Figure I.1(c)) in which the imino ligand adopts a μ_2 bridging mode, even though the entropy term associated with such a process is unfavourable. A number of instances where the ligands adopt a μ_3 bridging mode (Figure I.1(d)) have also been found.

Examples of imino derivatives where a one-electron mode of bonding has been confirmed by crystallographic study include the imino-phosphorus III compound $(Ph_2C=N)_3P$(3) (Figure I.2(a)) and the series of group IV derivatives $(Ph_2C=N)_4M$ (M=Si,Ge,Sn) (4,5) (Figure I.2(b)). In the former an average $C\hat{N}P$ angle of 123° reflects the sp^2 character of the nitrogen atoms, and single bond character of the N-P bond, while the geometry around phosphorus is pyramidal. The group IV derivatives have the expected tetrahedral geometry around the metal or metalloid although the average $C\hat{N}M$ angle shows an increase in the sequence Sn(121.3°) $<$ Ge (127.0°) $<$ Si (137.1°). This is indicative of a slight, but progressive, departure of the ligand from a formal one electron bonding mode and has been interpreted as evidence of a degree of N(p) - M(d) dative π bonding involving the nitrogen lone pair and a suitable combination of vacant d orbitals on the metal or metalloid. The effect is most pronounced in the case of the silicon derivative where the energies of the lone pair and vacant

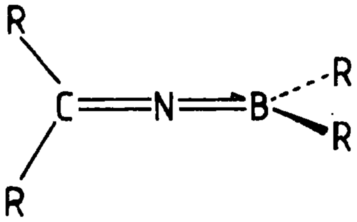
FIGURE I.2 Schematic representations of crystallographically characterised compounds illustrating methyleneamino-ligand bonding modes.



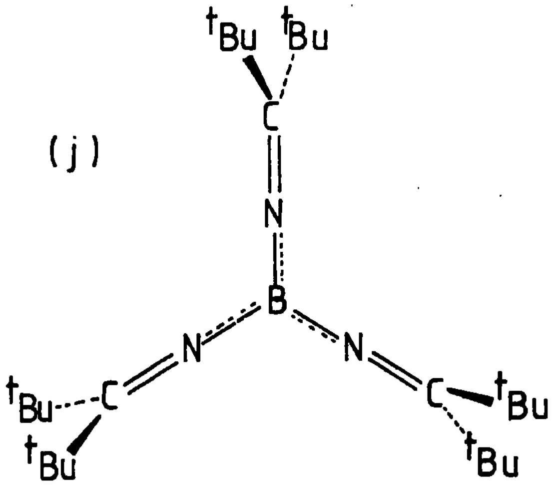
(h)


Li
Li
Li
Li
Li
Li
N
CR$_2$
[×6]

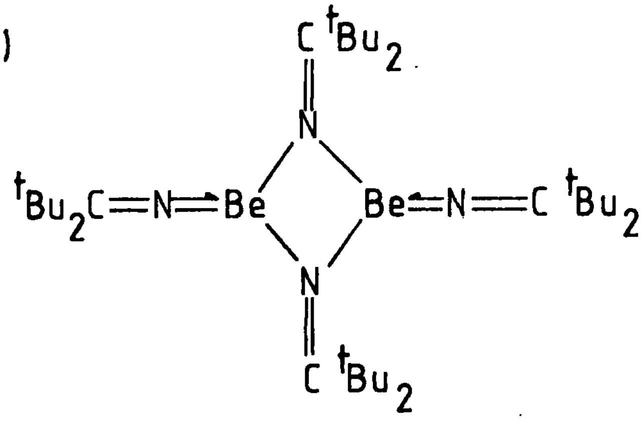
(i)


R
R
C
N
B
R
R

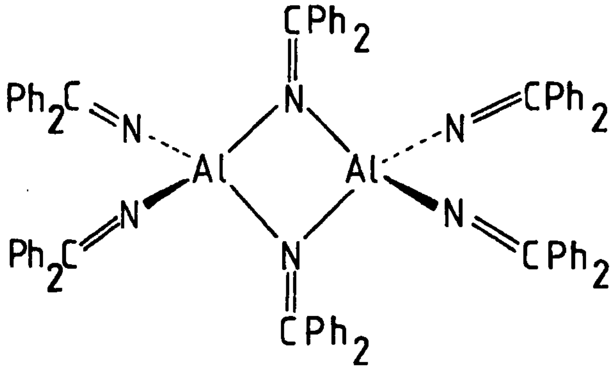
(j)


^{t}Bu
^{t}Bu
C
N
B
N
N
C
C
^{t}Bu
^{t}Bu
^{t}Bu
^{t}Bu

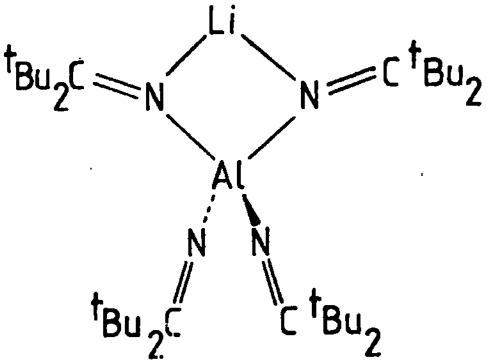
(k)


C ^{t}Bu$_2$
N
^{t}Bu$_2$C
N
Be
Be
N
C ^{t}Bu$_2$
N
C ^{t}Bu$_2$

(l)


CPh$_2$
N
Ph$_2$C
N
Al
Al
N
CPh$_2$
Ph$_2$C
N
N
CPh$_2$
N
CPh$_2$

(m)


Li
^{t}Bu$_2$C
N
N
C ^{t}Bu$_2$
Al
N
N
^{t}Bu$_2$C
C ^{t}Bu$_2$

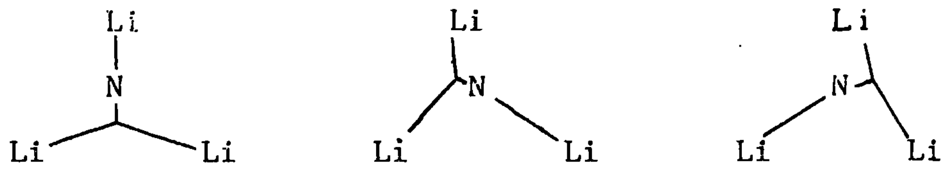
d orbitals are most nearly compatible, and therefore most favourable for dative bonding.

Examples of compounds where a structural determination has shown the methyleneamino ligand to be adopting a solely μ_2 bridging mode include the Sn^{II} derivative $(Ph_2C{=}NSnCl)_2$ (6) (Figure I.2(c)), the magnesium derivative $(Ph_2C{=}NMgBr)_2.3.T.H.F.$ (7) Figure I.2(d)) and the group III compounds $(RCH{=}NBMe_2)_2$ (R=Me(8), Ph(9))and $({}^tBuMeC{=}NAlMe_2)_2$ (8) (Figure I.2(e)). Structural features of the group III derivatives are discussed more fully in chapter 2. All the above compounds contain electron-precise $(NM)_2$ ring systems, the metal atoms contributing one electron apiece, and nitrogen atoms three electrons apiece, to give a total of six electrons which satisfies the requirement of four localised, two-electron, bonds. In consequence, metal-metal bonding interactions across the $(NM)_2$ rings should not be significant (c f. metal-metal bonding interactions across electron deficient rings (10,11)). The Sn atoms in $(Ph_2C{=}NSnCl)_2$ (Figure I.2(c)) may therefore be regarded as occupying a three-coordinate pyramidal environment, although the coordination state of one of the metal atoms may be expanded to four, as demonstrated by the structure of the imine-adduct derivative $Ph_2C{=}NH(Ph_2C{=}NSnCl)_2.C_7H_8$ (6) (Figure I.2(f)). By contrast, the magnesium atoms in $(Ph_2C{=}NMgBr)_2.3.T.H.F.$ (7) (Figure I.2(g)) have been shown to be formally five coordinate, in consequence of the bridging of the metal atoms by one of the three coordinated T.H.F. ligands. The length of the bridging Mg-O bonds however (2.453(3)Å). together with the fact that the $(MgN)_2$ ring is only slightly distorted from a planar configuration, is taken as evidence that the ether-ligand bridging interaction is of an only secondary nature; experimental work (7) has shown that the bridging T.H.F. molecule is easily removed to yield the compound $(Ph_2C{=}NMgBr)_2$ 2T.H.F. presumed to have a structure analogous to the group III derivatives $(R_2C{=}NM^{III}R'_2)_2$ (Figure I.2(e)).

Electron deficient, μ_3, bridging of metal atoms by a methyleneamino ligand is found in the compounds $(^tBu_2C{=}NLi)_6$ (12), $((Me_2N)_2C{=}NLi)_6$ (12), $(Ph(^tBu)C{=}NLi)_6$ (13) and $(Ph(Me_2N)C{=}NLi)_6$ (13), all of which have been the subject of crystallographic studies. All four structures are based on slightly folded, chair shaped, Li_6 rings (Figure I.2(h)), which are held together by the triply bridging $R_2C{=}N$ ligands, and are believed to be the first examples of electron deficient μ_3 bridging of Li_3 triangles by N-attached organic ligands. The mean dihedral angles between the chair 'seat' and 'back' vary between 78°, in $((Me_2N)_2C{=}NLi)_6$, and 85°, in $(^tBu_2C{=}NLi)_6$, while the imino ligands bridge the six smaller triangular faces, the nitrogen atoms being roughly equidistant from the three adjacent metal atoms. The bonding description of these compounds (12) requires each imino ligand to be a source of three electrons for use in metal-ligand bonding by using the three non-bonding electrons associated with the nitrogen atom. Together with the one valence electron which each metal atom can supply this results in a total of 24 electrons available to partake in the 18 Li-N bonding contacts within the molecule: each nitrogen atom thus has two electron pairs with which to bond to the three adjacent lithium atoms. The condition is therefore satisfied by the nitrogen atom partaking in one two-centre, and one three-centre, bond with the metal atoms, the bonds resonating between the three possible configurations (Figure I.3), and resulting in a mean Li-N bond order of $\frac{2}{3}$.

Figure I.3

Electron deficient μ_3 bonding mode of an imino ligand.



An alternative bonding description, in which each ligand contributes five electrons for ligand-cage bonding, and thus allows each nitrogen to form three localised N-Li bonds would require the use of the π bonding electrons of the C=N bond. Such a bonding mode is considered unlikely however in view of the shortness of the C=N bonds (1.30 - 1.24Å) which are near the length of c.a. 1.27Å generally found for a C=N double bond, while absorptions in the infra red between 1580cm^{-1} and 1625cm^{-1} provide further evidence, falling in the region 1570cm^{-1} to 1720cm^{-1} associated with three-electron imino bridging linkages.

The third general mode of imino-metal, or imino-metalloid bonding, dative N(p) - M(p) π bonding, has been found in a number of compounds, including the iminoborane derivatives $Ph_2C=NB(mesityl)_2$ (14,15). $^tBu_2C=NBPh_2$ (Figure I.2(i)) and $(^tBu_2C=N)_3B$ (9) (Figure I.2(j)). Features of the results obtained from crystallographic studies of these compounds are discussed more fully in chapter 4. In order to maximise the degree of dative π bonding these compounds adopt linear, or near linear, C =N=B linkages, analogous to the structure of the isoelectronic allene derivatives $R_2C=C=CR'_2$, and with a corresponding increase in the N-B bond order above unity. A similar near-linearity of the terminally attached imino ligands has been found in the case of the iminoberyllium derivative $((^tBu_2C=N)_2Be)_2$ (16) (Figure I.2(k)) where association of the molecule still leaves the sp^2 beryllium atoms in a coordinatively unsaturated state. The two metal atoms therefore retain vacant p orbitals available for dative π bonding with the terminally-bonded ligands, while maintaining the localised, electron precise, bonding of the $(BeN)_2$ ring.

Evidence of dative π bonding between the imino-nitrogen and metal atoms has also been found in the structurally characterised iminoaluminium derivatives $((Ph_2C=N)_3Al)_2$ (Figure I.2(l)) and $LiAl(N=C^tBu_2)_4$ (17) (Figure I.2(m)), discussed in chapter 5. In both these compounds two of the imino ligands adopt a three-electron μ_2 mode of bonding, the ligands bridging either two aluminium atoms, as in $((Ph_2C=N)_3Al)_2$, or a lithium and aluminium atom, as in

$LiAl(N{=}C^tBu_2)_4$. However, the remaining terminally attached ligands in both molecules adopt more nearly linear CNAl skeletons than would be associated with pure sp^2 hybridisation of the nitrogen atom, suggesting a substantial degree of N(p) - Al(d) dative π bonding, even though the aluminium atoms are formally coordinatively saturated. Such bonding as therefore analogous to that seen in the group IV derivatives $(Ph_2C{=}N)_4M^{iv}$, although the more nearly linear $C\hat{N}Al$ ligand bonding angles (175.2° for one ligand in $((Ph_2C{=}N)_3Al)_2$) can be taken as evidence that the effect is more marked in the aluminium derivatives.

CHAPTER 2

PREPARATION AND CHARACTERISATION OF SOME ASSOCIATED METHYLENEAMINOBORANES AND RELATED STUDIES

INTRODUCTION

This chapter describes the synthesis of some dimeric monoalkyl-, and monoaryl-, methyleneamino derivatives of boron, $(RCH{=}NBR'_2)_2$. The compounds were synthesised by the reaction of either tetramethyldiborane or triethylborane with the appropriate nitrile (see table II.1) and were fully characterised. Features of their infra red, ^{1}Hn.m.r., ^{13}Cn.m.r., ^{11}Bn.m.r. and mass spectra are discussed together with the results of a recent X-ray crystallographic study of one of them, $(PhCH{=}NBMe_2)_2$. The reactions of tetramethyldiborane towards Me_3SiCN and $(Me_2BCN)_n$ are also discussed.

EXPERIMENTAL SECTION

(i) Preparation of Trimethylborane

Trimethylborane was prepared by the reaction of boron trifluoride dibutylether complex with a dibutylether solution of methylmagnesiumbromide according to equation II.1, dibutylether being used to facilitate purification of the product (18). The reaction of boron trichloride and methyllithium had been found to be an unsatisfactory route to trimethylborane, owing both to the formation of large amounts of lithium tetramethylborate and the difficulty of removing diethylether from the product.

$$3MeMgBr + Bu^t{}_2O.BF_3 \rightarrow BMe_3 + Bu^t{}_2O + 3MgBrF \qquad II.1$$

Boron trifluoride dibutylether complex was slowly added to a previously prepared solution of methylmagnesiumbromide and the gas product swept into two traps cooled to -196° by a slow stream of nitrogen which was maintained throughout the experiment. The exhaust nitrogen gas was passed through an acetone bubbler to remove any remaining traces of trimethylborane. After completing the addition of boron trifluoride ether complex the reaction vessel was warmed to 70° to complete the reaction and the traps then removed to a vacuum line. Fractionation of the gas through a trapcooled by toluene slush (-95°) removed traces of dibutylether from the product, whose purity was checked by its vapour density and infra red spectrum (19).

(ii) Preparation of Triethylborane

Triethylborane was prepared by the reaction of boron trifluoride diethylether complex and ethylmagnesiumbromide in diethylether according to the equation

$$3EtMgBr + Et_2O.BF_3 \rightarrow BEt_3 + Et_2O + 3MgBrF \qquad II.2$$

II.2 Boron trifluoride diethylether complex was added under nitrogen to a previously prepared solution of ethylmagnesiumbromide in diethylether. After complete addition the reaction was refluxed for a period of half an hour and then filtered into a second vessel from which the product was distilled in the boiling range 94 - 97°. Repeated fractionation in a vacuum line failed to remove all traces of diethylether, final purification being effected by distillation of the product from aluminium trichloride The purity of the product was established on the basis of its infra red spectrum (20).

(iii) Preparation of Diborane

Diborane was prepared by the reaction of boron trifluoride dibutylether complex and sodium borohydride (21) according to the equation II.3.

$$3NaBH_4 + 4\ Bu_2O.BF_3 \longrightarrow 2B_2H_6 + 3NaBF_4 + Bu_2O \qquad \text{II.3}$$

A 50% excess of borontrifluoride dibutylether complex was added to a diglyme solution of sodium borohydride under N_2. The liberated gas was swept through two traps cooled to -196° by a slow stream of nitrogen which was maintained throughout the experiment, and the exhaust gas passed through an acetone bubbler to remove any trace amounts of diborane. After the boron trifluoride complex had been added the solution was warmed to complete the reaction and the traps removed to a vacuum line where the gas was fractionated through a trap cooled by ethanol slush (-117°). The gas purity was checked by vapour density measurements and by its infra red spectrum (22).

(iv) Preparation of Tetramethyldiborane

Tetramethyldiborane was prepared according to the equation II.4. Gas quantities were measured volumetrically,

$$4\ BMe_3 + B_2H_6 \longrightarrow 3\ Me_2BH_2BMe_2 \qquad \text{II.4}$$

with a 10% excess of trimethylborane over the theoretical amount being used, and the gases allowed to equilibrate over a period of days at room temperature (23). The excess of trimethylborane was included to suppress the formation of significant amounts of dimethyldiborane and trimethyldiborane, present in the product under equilibrium conditions.

The infra red spectrum of the product (24) showed the presence of some unchanged trimethylborane, no attempt being made to remove this prior to use.

(v) Reaction of Acetonitrile and Tetramethyldiborane (2:1).

Acetonitrile (0.70 g, 17.05 mmol.) and tetramethyldiborane (0.71 g, 8.47 mmol.) were condensed onto the wall of a 500 ml flask at -196°, the flask sealed and allowed to warm to room temperature. Over a period of one week colourless crystals grew on the wall of the vessel and a quantity of a colourless liquid collected. The contents of the flask were transferred to a vacuum distillation line and separated to yield trimethylborane (0.04 g) and unreacted acetonitrile (0.05 g). The remaining products were separated by repeated distillation from traps held between -10° and -15° (0.005 mmHg) and isolated as a colourless solid, (0.91 g), and a colourless liquid, (0.35 g).

The solid fraction was identified, by comparison with an earlier sample (25), as the anti isomer of methylmethyleneaminodimethylborane, $(MeCH{=}NBMe_2)_2$, m.p.t. 76°. (Found : C 58.1%, H 13.0%, B 13.4%, N 16.8% $C_8H_{20}B_2N_2$ requires : (57.9%, H 12.2%, B 13.0%, N 16.9%).ν_{max} (KBr disc) 2999(w) 2923(s) 2887(m) 2845(w) 2819(w) 1699(m,sh) 1694(s) 1612(vw) 1430(m) 1387(m) 1357(m) 1284(s) 1142(m) 1115(m) 1092(m) 1069(w,sh) 1051(m) 1041(m) 1020(m) 921(m) 847(m) 800(vw) 713(w) 610(w) 570(w) cm^{-1}. The compound was found to be stable to air.

The liquid fraction was identified, again by comparison with an earlier sample. (25) as the syn isomer of methylmethyleneaminodimethylborane, $(MeCH{=}NBMe_2)_2$, m.p.t. -5°. (Found : C 58.3%, H 13.5%, B 13.5%, N 16.7%, $C_8H_{20}B_2N_2$ requires : C 57.9%, H 13.0%, B 13.0%, N 16.9%). ν_{max} (liquid film) 3000(w) 2929(s) 2893(m) 2850(w) 2822(w) 1698(s) 1610(vs) 1431(m) 1397(m) 1358(m) 1289(s) 1144(m) 1116(m) 1093(m) 1071(w) 1037(mbr) 925(w) 847(w) 828(w) 771(vw) 714(vw) cm^{-1}. The compound was somewhat air sensitive, showing signs of decomposition after a few hours exposure to air.

Samples of both product fractions were sealed in glass tubes under vacuum and placed in an oven, held at 80°, for a period of four weeks. Upon subsequent opening the solid fraction was found to be unchanged anti isomer, the ^1H n.m.r. spectrum being identical to that recorded prior to thermolysis. The liquid fraction was found to have discoloured somewhat, showing a yellow colouration. Removal of the volatile material, shown by ^1H n.m.r. to be unchanged syn isomer, left a small amount, (10 mg), of an involatile yellow material which could not be positively identified.

(vi) Reaction of Propionitrile and Tetramethyldiborane (2:1)

Propionitrile (1.10 g, 19.97 mmol) and tetramethyldiborane 10.83 g, 19.81 mmol) were condensed onto the wall of a 500 ml flask at -196°, the flask sealed and allowed to warm to room temperature. After ten days the contents of the flask were transferred to a vacuum line and separated to yield trimethylborane, (0.03 g), and propionitrile, (0.01 g). The remaining product consisted of a colourless liquid of low volatility which was identified as a mixture of the *syn* and *anti* isomers of *ethylmethyleneaminodimethylborane*, $(EtCH{=}NBMe_2)_2$ m.p.t. -10° to --5°. (Found : C 62.1%, H 12.2%, B 11.2%, N 14.3%, $C_{10}H_{24}B_2M_2$ requires : C 61.9%, H 12.5%, B 11.2%, N 14.4%) ν_{max} (liquid film) 2972(m) 2927(s) 2892(m) 2820(m) 1702(msh) 1695(s) 1459(m) 1433(w sh) 1430(m) 1387(w) 1373(w) 1289(s) 1245(w) 1157(m) 1117(m) 1092(s) 1080(m) 1040(s) 1030(s) 1001(s) 913(m) 895(w) 862(w) 849(w) 710(w) cm^{-1}. The compound showed signs of gradual decomposition upon prolonged exposure to air.

Attempts to separate the mixture into its component parts by means of both vacuum distillation and chromatographic techniques failed, the mixture being recovered in its original state on each occasion.

A sample of the mixture, sealed in a glass tube under vacuum and placed in an oven at 80° for one week showed some sign of decomposition upon opening. The volatile materials consisted of a small amount of trimethylborane plus a quantity of the original isomeric mixture whose composition, as determed by ^1H n.m.r., appeared identical to that of the original sample. A small amount of an involatile yellow solid was also recovered but not identified.

(vii) Reaction of t-Butylcyanide and tetramethyldiborane (2:1).

Butylcyanide (1.35 g, 16.23 mmol), and tetramethyldiborane (0.68 g, 8.12 mmol) were condensed onto the wall of a 500 ml flask at -196°, the flask sealed, and allowed to warm to room temperature. Colourless crystals were observed to grow on the wall of the flask over a period of one week after which the contents were transferred to a vacuum distillation line. Separation of the volatile materials yielded trimethylborane (0.02 g), t-butylcyanide (0.06 g), and a colourless crystalline solid which was identified as the anti isomer of the compound t-Butylmethyleneaminodimethylborane ($(^{t}BuCH{=}NBMe_2)_2$ m.pt. 96.5° (Found : C 67.9%, H 13.3%, B 8.7%, N 11.3%, $C_{14}H_{32}B_2N_2$ requires: C 67.3%, H 12.9%, B 8.7%, N 11.2%) ν_{max} (KBr disc) 3000(w) 2964(s) 2952(s) 2925(s) 2890(m,sh) 2822(w) 1700(w,sh) 1695(m,sh) 1684(s) 1665(m,sh) 1473(w) 1460(w) 1421(w) 1384(w) 1363(w) 1358(w) 1292(s) 1285(s) 1208(w) 1113(m) 1087(m) 1049(m) 1024(s) 942(w) 923(w) 899(m) 845(w) 761(w) 727(w) 623(w) 572(w) cm^{-1}. The compound was found to be stable to air.

(viii) Reaction of Benzonitrile and Tetramethyldiborane (2:1).

Benzonitrile (1.18 g, 11.4 mmol) and tetramethyldiborane were condensed onto the wall of a 500 ml flask at -196°, the flask sealed, and allowed to warm to room temperature. Colourless crystals were observed to grow at the bottom of the flask over a period of a few hours.

After 48 hours the flask was opened to a vacuum line and the volatile material fractionated to yield trimethylborane (0.09 g) and a small amount (0.01g) of benzonitrile. The remaining non-volatile crystalline material was extracted from the flask with hot cyclohexane, from which crystals, identified as the anti isomer of Phenylmethyleneaminodimethylborane, $(PhCH=NBMe_2)_2$, were obtained upon cooling.m.pt. 170.5°. (Found : C 74.2%, H 9.5%, B 7.6%, N 9.6%. $C_{18}H_{24}B_2N_2$ requires : C 74.5%, H 8.3%, B 7.4%, N 9.7%) ν_{max} (KBr disc) 3095(w) 3072(w) 3055(w) 2926(s) 2892(w) 2821(w) 1654(s) 1638(m,sh) 1625(w,sh) 1597(w) 1584(w) 1576(w) 1530(w) 1493(w) 1449(m) 1434(w) 1404(m) 1313(m) 1293(s) 1283(s) 1220(w) 1203(m) 1107(m) 1083(s) 1035(m,sh) 1022(s) 1012 (m,sh) 988(m) 965(m) 917(w) 887(m) 759(m) 753(d) 728(w) 692(s) 633(w) 572(w) 493(m) 412(w) cm^{-1}. The compound was found to be stable to air.

(ix) Attempted reaction of Phenylmethyleneaminodimethylborane with Boron trichloride

Boron trichloride, (0.48 g, 4.10 mmol), was condensed into a Carius tube, of approximately 100 cm^3 capacity, containing phenylmethyleneaminodimethylborane (0.45 g, 1.55 mmol). The tube was sealed under vacuum and placed in an oven, maintained at 110°, for a period of six hours. After cooling the tube was opened to a vacuum line and the starting materials were recovered without sign of reaction.

(x) Reaction of Acrylonitrile with Tetramethyldiborane (2:1).

Acrylonitrile (0.70 g, 13.19 mmol) and tetramethyldiborane (0.55 g, 6.57 mmol) were condensed into a flask at -196°, the flask sealed, and allowed to slowly warm to room temperature. At approximately -20° a violent reaction occurred and a quantity of an orange material was deposited in the bottom of the flask. After two days the volatile materials were transferred to a vacuum line and fractionated to yield trimethylborane (0 03 g) and a trace amount (0.006 g) of acrylonitrile. The remaining product consisted of an involatile orange solid which was insoluble in a range of organic solvents and whose infra red spectrum was poorly resolved. It proved impossible to obtain consistent analytical data on the compound, the mass spectrum of which showed an almost continuous range of peaks below a mass cut off at $^m/e = 165$. The compound was resistant to water, dilute acid and dilute alkali at room temperature. Heating with 30% sulphuric acid at 100° under vacuum over a period of two days produced quantities of methane and ammonia as the only detectable volatile products.

A similar reaction between a 2:1 ratio of acrylonitrile and tetramethyldiborane in 20 ml of T.H.F. produced, upon workup, an involatile orange compound of apparently similar composition to that described above.

(xi) Reaction of Acrylonitrile and Tetramethyldiborane (1:1)

In a reaction similar to that described above, acrylonitrile (0.74 g, 13.95 mmol) and tetramethyldiborane (1.16 g, 13.84 mmol) reacted at below 0° to produce a quantity of orange solid material. Fractionation of the volatile materials resulting from the reaction yielded a mixture of trimethylborane and tetramethyldiborane (0.34 g) as the only volatile components. The orange solid possessed similar physical properties to that obtained from the 2:1 reaction of acrylonitrile and tetramethyldiborane, and again failed to give consistent elemental analyses. The mass spectrum showed a wide spread of peaks below a mass cut off at $^{m}/e = 122$, little of which could be conclusively assigned.

(xii) Reaction of Allylcyanide and Tetramethyldiborane (2:1)

Allylcyanide (1.28 g, 19.08 mmol) and tetramethyldiborane (0.80 g, 9.55 mmol) were condensed into a flask at -196°, the flask sealed, and allowed to warm slowly to room temperature. At room temperature a viscous orange oil was deposited over a period of two hours which did not change in appearance over a further period of 24 hours. The flask was opened to a vacuum line and the volatile materials removed by pumping on the flask at room temperature for a period of six hours. Fractionation of the volatile components yielded trimethylborane (0.06 g) plus a small amount (0.19 g) of a yellow viscous oil which could not be further purified and which decomposed upon heating to yield an orange solid material as the only identifiable product. Elemental analysis of the oil suggested it to be impure allylmethyleneaminodimethylborane, $(CH_2=CHCH_2CH=NBMe_2)_2$. (Found : C 62.3%, H 13.0%, B 9.1%, N 13.0%, $C_{12}H_{24}N_2B_2$ requires : C 66.1%, H 11.1%, B 9.9%, N 12.9%) ν_{max} (liquid film) 2928 (s) 2865 (m,sh) 2245(w) 1694(s) 1648(w) 1473(m) 1402(m) below 1400 cm^{-1} broad, ill defined.

The remaining, non volatile component of the reaction product was an orange solid, similar in physical appearance to the products obtained from the acrylonitrile reactions described above,and which again failed to give consistent elemental analysis.

(xiii) Reaction of t-Butylcyanide and Triethylborane (1:1).

t-Butylcyanide (0.90 g, 10.83 mmol) and triethylborane (1.06 g, 10.80 mmol) were sealed under vacuum in a Carius tube of approximately 100 cm^3 capacity and the tube heated to 135° for a total period of sixteen hours. Upon cooling the tube was opened to a vacuum line and a small amount of a non-condensable gas, which was not identified, pumped away. The remaining volatiles were separated by vacuum distillation to yield ethene (0.012 g), triethylborane (0.612 g), t-butylcyanide (0.627 g) and a white solid (0.635 g) which could be sublimed under vacuum (40°, 0.002 mmHg). A small amount of a non-volatile, yellow, resinous material remained in the tube and was not identified.

The white solid was identified as the anti isomer of t-butylmethyleneaminodiethylborane, $({}^{t}Bu\,CH{=}NBEt_2)_2$, m.pt. 76°. (Found : C 70.3%, H 14.0%, B 7.1%, N 9.1% $C_{18}H_{40}B_2N_2$ requires : C 70.6%, H 13.2%, B 7.1%, N 9.2%) ν_{max} (KBr disc) 3000(w) 2959(s) 2945(s) 2910(m,sh) 2867(s) 2715(w) 1663(s) 1654(m,sh) 1477(m) 1457(m) 1416(w) 1388(w) 1365(w) 1272(w) 1253(w) 1208(w) 1104(w,sh) 1081(m) 1055(s) 1029(w) 1010(w,sh) 949(w) 919(s) 888(w) 817(s) 777(w) cm^{-1}. The compound was stable to air.

(xiv) Reaction of Benzonitrile and Triethylborane (1:1)

Benzonitrile (0.87 g, 8.5 mmol) and triethylborane (0.83 g, 8.5 mmol) were condensed under vacuum in a Carius tube of approximately 100 cm^3 capacity and the tube was heated to 135° for a total period of eighteen hours. Upon cooling the tube was opened to a vacuum line and a small amount of a non-condensable gas pumped away. The remaining volatiles were separated by vacuum distillation to yield ethene (0.081 g), triethylborane (0.521 g), benzonitrile (0.542 g), and a white solid (0.450 g) which could be sublimed under vacuum (50°, 0.005 mmHg). A small amount of a yellow solid material remained in the bottom of the tube and was not identified. The white solid was identified as the anti isomer of phenylmethyleneaminodiethylborane, $(PhCH{=}NBEt_2)_2$ m.pt. 106°. (Found : C 76.8%, H 10.1%, B 6.3%, N 8.2%. $C_{22}H_{32}B_2N_2$ requires : C 76.3%, H 9.3%, B 6.3%, N 8.1%) ν_{max} (KBr disc) 3090(w) 3065(w) 3027(w) 2960(s) 2915(m,sh) 2895(m,sh) 2874(s) 2821(w) 1654(m,sh) 1648(m,sh) 1640 (s) 1600(w) 1578(w) 1527(w) 1489(w) 1451(m)

1407(w) 1313(w) 1267(m) 1245(m) 1203(m) 1090(w) 1072(s) 1047(s) 1027(sh) 958(w) 929(m) 910(m) 804(w) 748(s) 682(s) cm^{-1}. The compound was stable to air.

(xv) Reaction of Trimethylcyanosilane with Tetramethyldiborane (2:1).

Trimethylcyanosilane was prepared according to the method described by Evers et al. (26).

Trimethylsilylcyanide (1.23 g, 12.40 mmol) and tretamethyldiborane (0.52 g, 6.2 mmol) were condensed into a 500 ml flask at -196°, the flask sealed, and allowed to warm to room temperature. A reaction was observed below 0° which deposited a quantity of white solid at the bottom of the vessel, no further reaction being observed after three days at room temperature. The flask was opened to a vacuum line and the volatile products fractionated to yield trimethylborane (0.04 g), and a second fraction (0.89 g) which was identified, on the basis of its infra red spectrum, as trimethylsilane (27). The remaining product, a white involatile solid, was identified as dimethylcyanoborane, $(Me_2BCN)_n$ m.pt. 98° (dec.), Lit. value (28) 98°. (Found : C 52.4%, H 8.7%, B 15.9%, N 21.0%, Cl absent, Si absent C_3H_6BN requires : C 52.9%, H 9.0%, B 16.2%, N 20.9%) ν_{max} (nujol mull) 2278(s) 1301(s) 1116(w) 1004(s,br) 985(s,br) 805(m) 732(m,br) 651(w) 587(w) 550(w) 522(w,br) cm^{-1}. The compound was stable to air.

(xvi) Reaction of Trimethylcyanosilane with Dimethylboronchloride (1:1)

Dimethylboronchloride (2.02 g, 26.46 mmol), prepared from trimethylborane and boron trichloride by the method of Alford et al. (29),and trimethylsilycyanide (2.63 g, 26.46 mmol) were reacted under conditions similar to those described above for the reaction of trimethylsilylcyanide and tetramethyldiborane. The reaction proceeded at below 0° to yield trimethylchlorosilane, (2.77 g), and a white solid, (1.70 g) which was identified as dimethylcyanoborane, $(Me_2BCN)_n$, being in all respects identical to the sample described above.

(xvii) Reaction of Dimethylcyanoborane with Tetramethyldiborane (2:1).

Dimethylcyanoborane (0.28 g, 4.19 mmol) was dissolved in 40 ml of toluene and the solution frozen to -196°. Tetramethyldiborane (0.18 g, 2.15 mmol) was condensed onto the liquid surface, the reaction vessel let down to an atmosphere of nitrogen,and slowly warmed to 75°. After four hours the reaction vessel was cooled to room temperature and the volatile components removed to a vacuum line where all the tetramethyldiborane was removed by fractionation. The remaining involatile white solid (0.25 g) was identified as unchanged dimethylcyanoborane.

TABLE II.1 Summary of Reactions

Reactants	Conditions	Product(s)	Phase	m.pt.
$2MeCN + Me_2BH_2BMe_2$	Vapour phase/ Room Temp.	$(MeCH{=}NBMe_2)_2$	i Solid ii Liquid	76° -5°
$2EtCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	$(EtCH{=}NBMe_2)_2$	Liquid	-10° to -5°
$2{}^tBuCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	$({}^tBuCH{=}NBMe_2)_2$	Solid	96.5°
$2PhCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	$(PhCN{=}NBMe_2)_2$	Solid	170.5°
$(PhCH{=}NBMe_2)_2 + 2BCl_3$	Vapour phase/110°	No reaction	-	-
$2CH_2{=}CHCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	Not identified	-	-
$CH_2{=}CHCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	Not identified	-	-
$CH_2{=}CH\ CH_2CN + Me_2BH_2BMe_2$	Vapour phase/R.T.	$(CH_2{=}CHCH_2CH{=}NBMe_2)_2$ + Other	Liquid	-
${}^tBuCN + BEt_3$	135° 16 hrs	$({}^tBuCH{=}NBEt_2)_2$ $(+H_2C{=}CH_2)$	Solid	76°
$PhCN + BEt_3$	135°, 18 hrs.	$(PhCH{=}NBEt_2)_2$ $(+H_2C{=}CH_2)$	Solid	106°
$2Me_3SiCN + Me_2BH_2BMe_2$	Vapour phase/R.T.	$Me_2BCN(+\ Me_3SiH)$	Solid	98° (dec.)
$2ME_3SiCN + Me_2BCl$	Vapour phase/R.T.	$Me_2BCN\ (+\ Me_3SiCl)$	Solid	98° (dec.)
$Me_2BCN + Me_2BH_2BMe_2$	Toluene soln., 75°, 4 hrs.	No reaction	-	-

DISCUSSION

Prior to the present work a number of studies have investigated the formation of imino derivatives of boron, resulting from the reaction of a boron hydride compound with a nitrile. Early work established that diborane will react with two equivalents of either acetonitrile or propionitrile in the absence of solvent, to form an unstable nitrile-borane adduct, $RCN.BH_3$(30,31) which will then rearrange to form the corresponding borazine derivative (31,32) (Equation II.5). By contrast, reaction of two equivalents of

$$RCN + \tfrac{1}{2}B_2H_6 \rightarrow (RCN.BH_3) \rightarrow \tfrac{1}{3}(RCH_2NBH)_3 \quad R = Me, Et \qquad II.5$$

acetonitrile with tetramethyl-, or tetraethyl-, diborane, again in the absence of solvent, resulted in the addition of the B-H unit across the nitrile function to form the methyleneaminodialkylborane derivative (25) (Equation II.6) and

$$2CH_3CN + R_2BH_2BR_2 \rightarrow (CH_3CH{=}NBR_2)_2 \quad R{=}Me,Et \qquad II.6$$

without isolation of the adduct intermediate. Further, the reaction of acetonitrile with the unsymmetrical dimethyl-, and diethyl-, diboranes yielded mixtures of the iminoboranes and N,N',N'' trialkylborazines (Equation II.7) (25). An

$$2CH_3CN + R_2BH_2BH_2 \rightarrow \tfrac{1}{2}(CH_3CH{=}NBR_2)_2 + \tfrac{1}{3}(CH_3CH_2NBH)_3$$
$$R = Me,Et \qquad II.7$$

analogous reaction to that displayed by tetramethyldiborane (Equation II.6) occurred when dimethylaluminium hydride, $(Me_2AlH)_2$, was reacted with the organonitriles

RCN (R=Me, ^{t}Bu, Ph) (33,34). Addition of an Al-H unit across the nitrile function resulted in formation of the corresponding iminoalane (Equation II.8) while again no

$$2RCH + Me_2AlH_2AlMe_2 \rightarrow (RCH{=}NAlMe_2)_2 \text{ :R=Me, }^tBu\text{,Ph} \qquad II.8$$

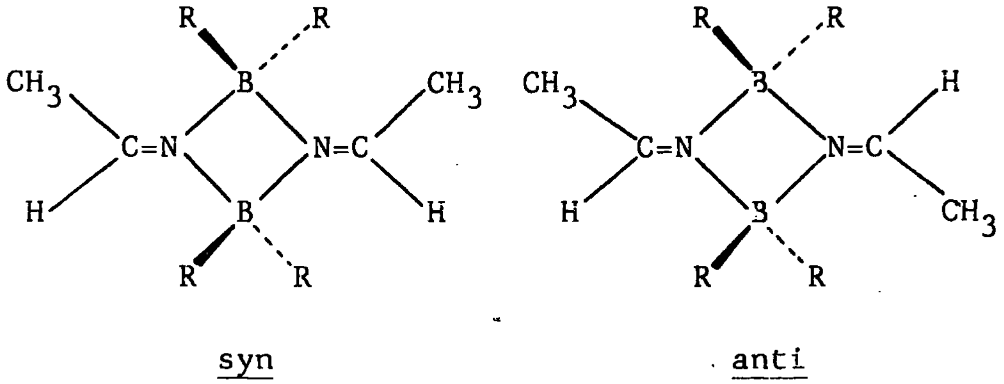
adduct could be isolated.

The methyleneaminodialkylboranes, $(CH_3CH{=}NBR_2)_2$, were characterised as isomeric mixtures of both syn and anti carbon-bonded methyl species (see Figure II.1) and were stable at room temperature. Other work (35) demonstrated that stable species of the form $(RCH{=}NBH^tBu)_2$

Figure II.1

Syn and anti isomers of the species

$(CH_3CH{=}NBR_2)_2$



could be prepared by the reaction of alkyl and aryl nitriles with the t-butylborane-trimethylamine complex in diglyme (Equation II.9). The resulting

$$H_2{}^tBuBNMe_2 + RCN \longrightarrow (RCH{=}NBH^tBu)_2$$
$$R = \text{alkyl, aryl} \qquad II.9$$

iminoboranes were stable up to their melting temperatures, showing no inclination to undergo a second hydrogen transfer across the C=N bond to form the borazine species. By contrast, trifluoro-, and trichloro-, acetonitrile failed to react with diborane at room temperature (36), either in the vapour phase or in ether solution. When heated, two equivalents of trifluoroacetonitrile reacted with diborane to form the borazine, $(CF_3CH_2NBH)_3$ (Equation II.10), while trichloroacetonitrile reacted to form the unstable iminoborane. $(CCl_3CH{=}NBH_2)_n$, whose state of associaton was not determined, and which subsequently decomposed to the corresponding borazine (36) (Equation II.11).

$$3CF_3CN \; + \; {}^3/2\; B_2H_6 \longrightarrow (CF_3CH_2NBH)_3 \qquad II.10$$

$$2CCl_3CN \; + \; B_2H_6 \longrightarrow {}^1/n\; (CCl_3CH{=}NBH_2)_2 \longrightarrow \tfrac{1}{3}(CCl_3CH_2NBH)_3 \qquad II.11$$

In recent years little further attention has been directed towards associated monoalkyl-, and monoaryl-, methyleneamino derivatives of boron. The current availability of a wider range of spectroscopic techniques, including ^{11}B and ^{13}C n.m.r., however prompted a further examination of such compounds, while the study was extended to include investigations of the reactivity of tetramethyldiborane towards Me_3SiCN, and the formation of associated iminoboranes from the reaction of nitriles with triethylborane.

Four new alkyl-, and aryl-, methyleneaminoboranes have been synthesised, during the present study, via the reaction of tetramethyldiborane and the corresponding nitrile (Equation II.12). They are: the _syn_ and _anti_ isomers of $(EtCH{=}NBMe_2)_2$, prepared as a liquid mixture.

$$2\ RC{\equiv}N + Me_2BH_2BMe_2 \rightarrow (RCH{=}NBMe_2)_2 \qquad \text{II.12}$$

$R{=}Et,\ {}^tBu,\ Ph$

m.pt. -10° to -5°, and which could not be separated, together with the anti isomers of the compounds $({}^tBuCH{=}NBMe_2)_2$, m.pt. 96.5°, and $(PhCH{=}NBMe_2)_2$, m.pt. 170.5°. In no case was evidence for the formation of the intermediate borane-nitrile adduct observed, although these may well have been formed as transitory species. All the listed compounds, together with the syn and anti isomers of $(MeCH{=}NBMe_2)_2$, were fully characterised. The products were either crystalline solids: anti $(MeCH{=}NBMe_2)_2$, $({}^tBuCH{=}NBMe_2)_2$ and $(PhCH{=}NBMe_2)_2$ or colourless liquids: syn/anti $(EtCH{=}NBMe_2)_2$ and syn $(MeCH{=}NBMe_2)_2$, and were thermally stable at room temperature. All the solids were unaffected by exposure to air while the two liquid fractions both showed some evidence of decomposition. An attempt to effect an exchange of boron substituents by reaction of $(PhCH{=}NBMe_2)_2$ with an excess of boron trichloride at 110° failed, the reactants being recovered unchanged. Elsewhere (37), the reaction of $({}^tBuCH{=}NBBu_2)_2$ with an excess of both boron trichloride and tribromide, has been shown to yield the compounds $({}^tBuCH{=}NBX_2)_2$ (x=Cl, Br)(Equation II.13). The difference in reactivity of the two compounds can be explained in

$$({}^tBuCH{=}NB^nBu_2)_2 + X.S.BX_3 \rightarrow ({}^tBuCH{=}NBX_2)_2 + XB^nBu_2,\ X_2B^nBu\ \text{etc.} \qquad \text{II.13}$$

X=Cl, Br.

terms of their state of association, and hence coordination state of boron, at reaction temperature. $(PhCH{=}NBMe_2)_2$ has been shown, by its mass spectrum, to remain associated in the vapour phase at temperatures in excess of 110°, while ^{11}Bn.m.r. and mass spectral evidence has shown $(^tBuCH{=}NB^nBu_2)_2$ to be nonomeric, in both the melt and vapour phase, above 70° (37). Such differences in reactivity of three and four coordinate boron are also observed in the differing resistance to hydrolysis exhibited by the species $^tBu_2C{=}NBCl_2$ and $(Ph_2C{=}NBCl_2)_2$ (38,39).

The reaction of acrylonitrile, $CH_2{=}CHCN$, and tetramethyldiborane did not produce the desired imino-borane species, but rather an involatile yellow-orange material of apparently high molecular weight, which could not be characterised. The material was insoluble in a range of organic solvents and resistant to hydrolysis at room temperature, while heating with concentrated acid over a period of days yielded methane and ammonia as the only volatile products. A second reaction between equimolar amounts of the reactants consumed only 70% of the borane and yielded more orange solid of similar appearance to that described above. Similar solids, again uncharacterised, were found to result from the reactions of diborane and two equivalents of acrylonitrile (31). Reaction of tetramethyldiborane and two equivalents of allyl cyanide, $CH_2{=}CH\,CH_2CN$, again produced insoluble orange solids, together with a small amount of an oily material which decomposed to yield more orange solid upon heating. It proved impossible to produce sufficient quantities of this material for full characterisation although its infra red spectrum contained a strong band at 1695 cm^{-1} which would be consistent with the bridging ν(C=N) stretch of dimeric allylmethyleneaminodimethylborane $(CH_2=CHCH_2CH=NBMe_2)_2$.

The reaction of tetramethyldiborane with two equivalents of the silyl analog of t-Butylcyanide, trimethylcyanosilane, Me_3SiCN, resulted, not in the formation of an imino-borane species, but in the liberation of trimethylsilane and deposition of a white involatile solid. The white compound, identified as dimethylcyanoborane, $(Me_2BCN)_n$, was also produced in the reaction of dimethylboron chloride and trimethylchlorosilane (Equations II.13, II.14). In both

$$Me_3SiCN + \tfrac{1}{2}Me_2BH_2BMe_2 \longrightarrow {}^1/_n(Me_2BCN)_n + Me_3SiH \qquad II.13$$

$$Me_3SiCN + Me_2BCl \rightarrow {}^1/_n(Me_2BCN)_n + Me_3SiCl \qquad II.14$$

cases reaction occurred below 0° and in the absence of solvent, no evidence for the formation of a stable nitrile-borane adduct being observed. Other studies have shown that diborane will react with both silylcyanide, H_3SiCN, and trimethylcyanosilane, Me_3SiCN, to form adducts which will thermally decompose above room temperature to form cyanoborane (27) (Equation II.14a), while boron trihalides

$$R_3SiCN + \tfrac{1}{2}B_2H_6 \rightarrow R_3SiCN.BH_3 \longrightarrow {}^1/_n(H_2BCN)_n + R_3SiH \qquad II.14a$$

$R = H_1Me$

(40) and di-n-butylboron chloride (41) react with diborane to form cyanoborane derivatives without isolation of the intermediate adducts (Equations II.15, 16).

$$R_3SiCN + BX_3 \rightarrow {}^1/_n(X_2BCN)_n + R_3SiX \qquad II.15$$

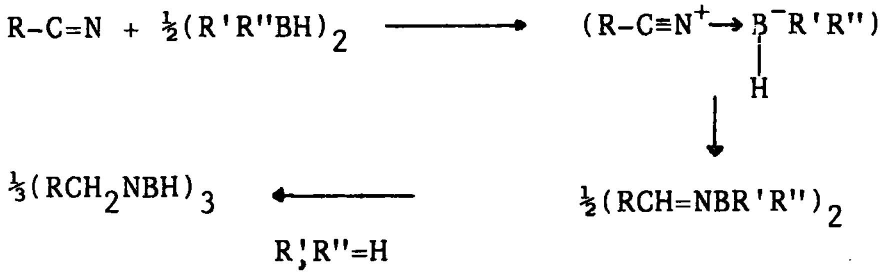
$R = H,Me$

$$Me_3SiCN + {}^nBu_2BCl \rightarrow {}^1/n({}^nBu_2BCN)_n + Me_3SiCl \qquad II.16$$

Trimethylborane, by comparison, did not react with trimethylcyanosilane to form dimethylcyanoborane, $(Me_2BCN)_n$, but instead yielded oily substances of varying composition which were not identified (26, 41).

The behaviour of boranes towards silylcyanides thus mirrors that towards organocyanides to the extent that diborane will initially form isolatable adducts with both groups of compounds (26, 30, 31) whereas tetramethyldiborane does not. The varying stability of the adduct species may be explained in terms of the decreasing Lewis acidity in the sequence $BH_3 > RBH_2 > R_2BH > R_3B$; diborane, being a stronger Lewis Acid, will form isolatable adducts whereas those formed by tetramethyldiborane are too unstable to be isolated. The end products from these borane-cyanide reactions differ however in that while diborane and tetramethyldiborane will react with silylcyanides to form cyanoboranes, $(R_2BCN)_n$ (R=H,Me), (Equations II.13, 15) the corresponding reactions with organocyanides yield either borazines (31,32) (Equation II.5) or iminoboranes (25) (Equation II.6).

In the case of organocyanides, RCN (R=alkyl, aryl) the reaction with boranes of the general form $(R'R''BH)_2$ (R',R''=H, alkyl, aryl) would seem to proceed via initial formation of the adduct species (Equation II.17) whose existence may, or may not, be only transitory. Subsequent reaction proceeds via a one-hydrogen shift across the C≡N function (32) to form the imino derivative which may



II.17

be isolated as a stable dimer, (RCH=NBR'R"), when R'=H and R"=alkyl or aryl (35), or when R' and R"=alkyl,aryl (25). In the case where both R' and R" are hydrogens a second hydrogen transfer spontaneously occurs and the isolated product is the borazine derivative $(RCH_2NBH)_3$ (31).

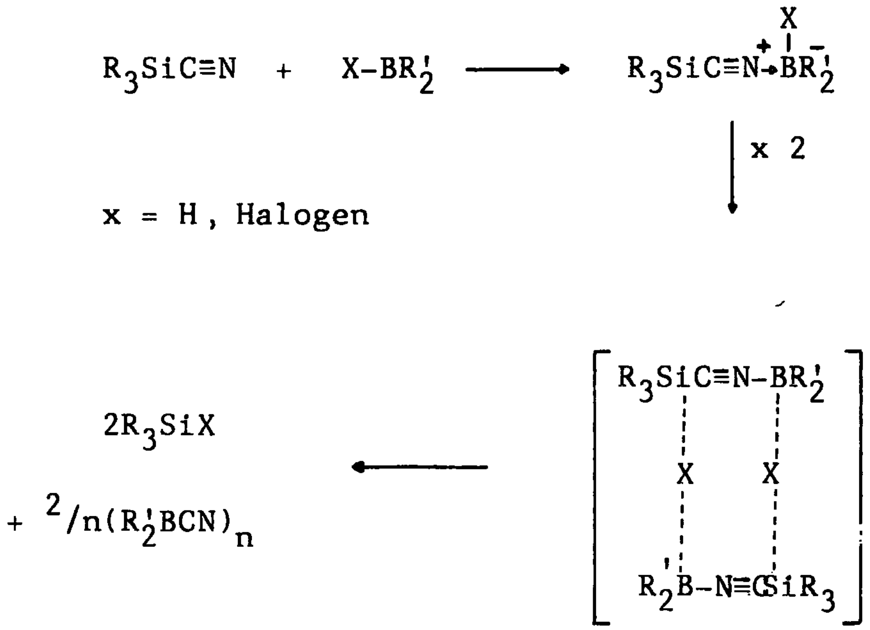
The reaction of boranes and silylcyanides to form cyanoboranes is less easily accounted for and it is only possible to speculate as to plausible mechanisms (Figure I .2). Once again it would seem likely that initial reaction involves formation of the adduct $R_3SiCN.BXR'_2$ (X= H,halogen), (26,40) while subsequent reaction could proceed by either an intermolecular or an intramolecular route. The intermolecular mechanism (A) would involve transfer of the species X from boron to silicon via the vacant 3d orbitals of silicon (28), with subsequent elimination of silane. A possibly more plausible intramolecular mechanism (B) would involve an initial 1,3 transfer of X, to form an intermediate imino-species, followed by spontaneous loss of the silane and subsequent association to form the cyanoborane.

The state of association of $(Me_2BCN)_n$ is uncertain and it is possible that a number of oligomers of differing

Figure II.2

Possible mechanisms for the reaction of boranes, R'_2BX, with silyl cyanides, R_3SiCN

A. Intermolecular (26).

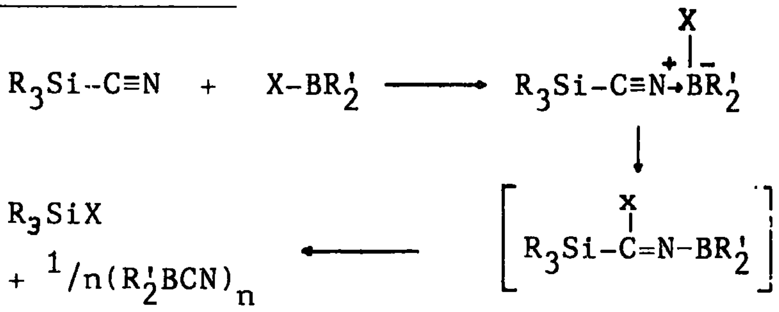


$$R_3SiC{\equiv}N + X{-}BR'_2 \longrightarrow R_3SiC{\equiv}\overset{+}{N}{\rightarrow}\overset{X}{\overset{|}{B^{-}}}R'_2$$

x = H, Halogen

$$\xrightarrow{\times 2} \left[\begin{array}{c} R_3SiC{\equiv}N{-}BR'_2 \\ X \quad X \\ R'_2B{-}N{\equiv}CSiR_3 \end{array}\right] \longrightarrow 2R_3SiX + {}^{2}/n(R'_2BCN)_n$$

B Intramolecular

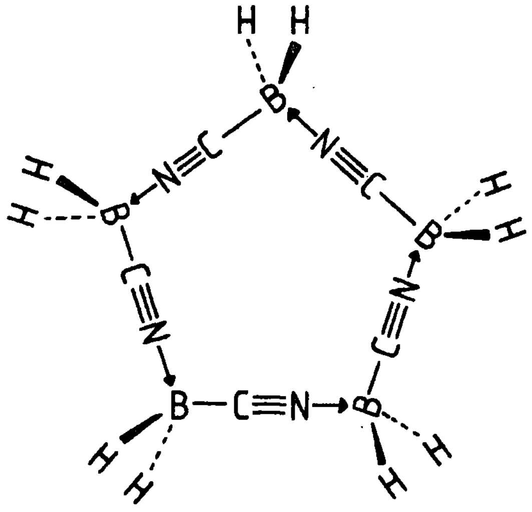


$$R_3Si{-}C{\equiv}N + X{-}BR'_2 \longrightarrow R_3Si{-}C{\equiv}\overset{+}{N}{\rightarrow}\overset{X}{\overset{|}{B^{-}}}R'_2 \longrightarrow \left[R_3Si{-}\overset{X}{\overset{|}{C}}{=}N{-}BR'_2\right] \longrightarrow R_3SiX + {}^{1}/n(R'_2BCN)_n$$

sizes are produced from the above reactions. The compound is air stable and resistant to hydrolysis by weak acid and alkali, while the infra red spectrum shows a single ν (C≡N) absorption at 2278cm^{-1}. This would be consistent with the compounds adoption of one or more cyclic structures, similar to those proposed for the analogous compound $(H_2BCN)_n$ (42), a study of which suggested $(H_2BCN)_5$ to be a major component in both the vapour and solution phases. Such a pentameric state of association would permit formation of a near planar structure (Figure II.3) involving the

Figure II.3

Proposed structure of $(H_2BCN)_5$



minimum distortion from the idealised, sp-hybridised, nitrogen bond angle of 180°, and sp^3 hybridised boron bond angle of 109.5°. In the present case the persistence of an oligomerised structure such as $(Me_2BCN)_5$ in solution would also account for its lack of reactivity towards tetramethyldiborane.

The reaction of benzonitrile, PhCN, and triethylborane at temperatures between 100° and 200° has been reported (43) to yield phenylmethyleneaminodiethylborane, $(PhCH{=}NBEt_2)_2$, while elsewhere (37) the reaction of t-butylcyanide, ${}^tBuCN$, and tri-n-butylborane, B^nBu_3, at between 150° and 200°, was shown to yield t-butylmethyleneaminodi-n-butylborane, $({}^tBuCH{=}NB^nBu_2)_2$ (Equations II.18, 19). Studies (33,34) on the analogous reactions

$$PhCN + BEt_3 \xrightarrow{100^\circ - 200^\circ} \tfrac{1}{2}(PhCH{=}NBEt_2)_2 + H_2C{=}CH_2 \qquad II.18$$

$$ {}^tBuCN + B^nBu_3 \xrightarrow{150^\circ - 200^\circ} \tfrac{1}{2}({}^tBuCH{=}NB^nBu_2)_2 + H_2C{=}CH_2 \qquad II.19$$

between a trialkylaluminium compound, R_3Al, and a range of nitriles R'CN (R'=alkyl, aryl) have shown that, when R=aryl, or alkyl other than ethyl, the reactions proceed to form iminoalanes, $(RR'C{=}NAlR_2)_2$, (Equation II.20) while the reaction between $AlEt_3$ and PhCN (44) yielded

$$R'CN + R_3Al \longrightarrow \tfrac{1}{2}(RR'C{=}NAlR_2)_2 \qquad II.20$$

a mixture of products (Equation II.21). Such anomalous

$$\begin{tikzcd}[column sep=small] & (PhEtC{=}NAlEt_2)_2 & \\ PhCN + AlEt_3 \arrow[ur] \arrow[dr] & & II.21 \\ & (PhCH{=}NAlEt_2)_2 + H_2C{=}CH_2 & \end{tikzcd}$$

behaviour of triethylaluminium towards benzonitrile prompted a re-examination of the reaction of BEt_3 and PhCN, and the performing of a second reaction with ^tBuCN.

Reactions between equimolar amounts of reactants (135° , 16-18 hours) resulted in approximately 40% yields of the iminoboranes, $(RCH{=}NBEt_2)_2$, ($R{=}Ph,{}^tBu$) together with corresponding amounts of ethylene. The compounds, white crystalline solids, were confirmed as being single species on the basis of their mass, ^{13}Cn.m.r., and ^{1}Hn.m.r. spectra. It was not possible to conclusively establish whether both syn or anti isomers were formed on the basis of their ^{1}Hn.m.r. spectra, due to difficulty in resolving the B-Et signals, but comparison with the analogous B-Me derivatives, together with the sharpness of their melting points, would suggest the exclusive formation of the anti isomers in these cases.

The mechanism involved in these reactions is uncertain and is obviously dissimilar to that occurring in the corresponding triethylaluminium reaction. It has been noted elsewhere (45) that trialkylboranes, R_3B, will dehydroborate at elevated temperatures to form terminal alkenes, $R'CH{=}CH_2$, and species of the form $(RBH)_2$. If such a process occurs under the conditions involved in the present reactions subsequent hydroboration of the nitrile will yield the iminoboranes (Equation II.22) in a similar manner to the reaction of $(Me_2BH)_2$ described earlier.

$$\begin{array}{ll} RCN + Et_3B \longrightarrow (RCN + \tfrac{1}{2}(Et_2BH)_2 + H_2C{=}CH_2) & \\ R{=}{}^tBu,Ph \qquad\qquad\qquad \downarrow & \text{II.22} \\ \qquad\qquad \tfrac{1}{2}(RCH{=}NBEt_2)_2 + H_2C{=}CH_2 & \end{array}$$

Structural and spectroscopic features of the associated iminoboranes $(RCH=NBR'_2)_2$: The X-ray crystal structure of $(PhCH=NBMe_2)_2$

As noted in Chapter 1, methyleneamino ligands, RR'C=N-, having a lone pair of electrons on the nitrogen atom, can function as sources of three electrons when bonded to a coordinatively unsaturated metalloid such as boron. In cases where association of the resulting iminoborane is prevented, notably by the steric bulk of the groups R, dative N=B π bonding will occur and the molecule will assume a linear, or near linear, CNB skeleton (see Figure I.1(b)). A number of such compounds are discussed in Chapter 4. In cases where association is not prohibited it will be favoured by the energetically more desirable formation of two N-B σ bonds, rather than one σ and one π bond, the derivatives generally forming dimeric species.

Of the known monoalkyl-, and monoaryl-, methyleneaminoboranes $(R^1CH=NBR^2R^3)_n$ $(R^1=alkyl, aryl, R^2, R^3 = H, alkyl, aryl)$ only one, phenylmethyleneaminodimesitylborane, $PhCH=NB(mesityl)_2$, is known to exist in the monomeric state at room temperature (46). In this instance the degree of steric interaction between the carbon-,and boron-bonded aryl substituents can be shown to be too great to allow sufficient bending of the CNB unit to permit association. Of the remaining iminoborane species all are known to exist as dimers (n=2) at room temperature

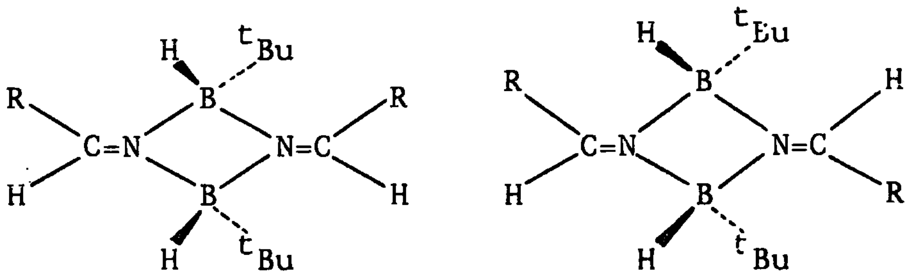
(9,25,35,37,46) although one, t-butylmethyleneaminodi-n-butylborane, $(^tBuCH{=}NB^nBu_2)_2$, is known to be monomeric in the vapour and solution phases above 70° (37). Dimeric structures have also been established for a number of halogen-substituted alkyl-, and aryl-, methyleneaminoboranes $RCH{=}NBX_2$ (R=alkyl, aryl; X=F,Cl,Br,I) (37,46,47) as well as in the analogous iminoalanes, $(RCH{=}NAlR'_2)_2$ (R=Me, ^{t}Bu, Ph; R'=Me,Et) (33,34).

In all the above dimeric compounds there exists the possibility of _syn_ and _anti_ isomerism, arising from the relative orientation of the carbon-bonded alkyl or aryl substituents (see Figure II.1). Earlier work, reinforced by the present study, has established that such isomerism is found in the compound $(MeCH{=}NBMe_2)_2$, where the _syn_ isomer, m.pt -5°, and the _anti_ isomer, m.pt. 76°, were separated and obtained in an approximately 2:5 molar ratio, as well as in the case of $(MeCH{=}NBEt_2)_2$ where the isomers could not be separated (25). During the course of the present study a further example of such _syn_/_anti_ isomerism was found in the compound $(EtCH{=}NBMe_2)_2$, which again could not be separated into its constituent isomeric forms, while solely _anti_ forms of the compounds $(RCH{=}NBR'_2)_2$ (R=^{t}Bu, Ph; R'=Me, Et) were isolated. Of the analogous iminoalanes, $(RCH{=}NAlR'_2)_2$ (33,34) only $(MeCh{=}NAlMe_2)_2$ has been shown to exist in both _syn_ and _anti_ forms (34), while the remaining compounds invesitigated (R=^{t}Bu, Ph; R'=Me,Et) exist as solely _anti_ isomers. The possibility of such syn/anti isomerism was also noted (35) in the case of the series of compounds (RCH=NBH^{t}Bu)$_2$ (R=alkyl, aryl), as well as the additional possibility of cis/trans isomerism arising from non-equivalent terminally-attached boron substituents (Figure II.4). In this instance however, the choice of bulky aryl and alkyl groups prevented separation of the various isomers, nor could the presence of any or all of the possible isomers be proved, although it was argued that the anti - trans isomer would be the thermodynamically most preferred. Other types of compound

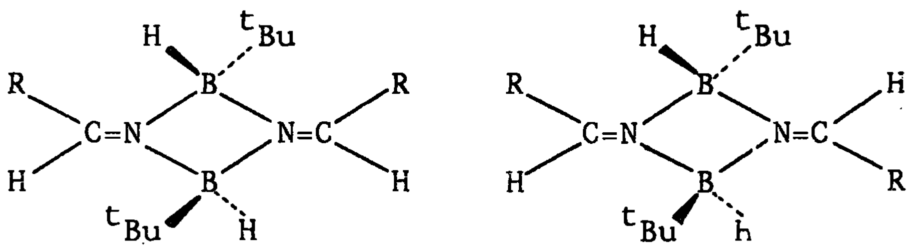
Figure II.4

Isomers of the structural form

(RCH=NBH^{t}Bu)$_2$



syn - cis   anti - cis



syn - trans   anti - trans

containing a $(BN)_2$ ring also have the possibility of such structural isomerism, as has been demonstrated in the case of a series of dimethylaminochloroboranes, $(Me_2NBClR)_2$ (48).

The principal factor dictating the adopted isomeric conformation in the iminoboranes $(RCH{=}NBR'_2)_2$ is likely to be the steric interaction between the imino-carbon-, and boron-, bonded substituents. In the cases of $(RCH{=}NBMe_2)_2$ (R=Me,Et) calculation suggests that the degree of such steric interaction is not severe, and in consequence both syn and anti isomeric forms may be accommodated, the anti isomer being the slightly less strained. Replacement of the methyl or ethyl groups by the more bulky phenyl or t-butyl groups however will introduce a considerably greater degree of interaction, and it is found that the compounds exclusively adopt the anti conformation. In this form the steric forces may be more easily accommodated than in the corresponding syn form, where the presence of both phenyl or t-butyl groups on the same side of the molecule would maximise the interaction and lead to considerable structural distortion of the molecule. A similar argument will account for the formation of solely anti isomers of the compounds $(RCH{=}NBEt_2)_2$ (R=^{t}Bu, Ph). None of the compounds synthesised in this study showed evidence of dissociation, and thus the possibility of isomeric rearrangement, in either the vapour or liquid phases, nor was the syn:anti isomeric ratio temperature dependent.

The anti isomer of $(MeCH{=}NBMe_2)_2$ was the subject of an earlier, and somewhat imprecise X-ray crystallographic study (8) as was the related anti isomer of the iminoalane $({}^tBuMeC{=}NAlMe_2)_2$ (8). During the course of the present work the desire for a more accurate structural determination of an iminoborane dimer, together with the interest in examining the effect of increasing the bulk of the carbon-bonded substituent, prompted a structural study of the compound $(PhCH{=}NBMe_2)_2$ (9). The results of this structural determination , performed by Dr. J. Halfpenny, are shown in Figure II.5 and Table II.2 while common features of the three related compounds are listed in Table II.3.

Crystals of $(PhCH{=}NBMe_2)_2$ were found to be orthorhombic, space group Pbca, with a = 9.15(1), b=18.26(2), C=10.37(1)Å. The molecule is centrosymmetric and has a planar, almost square, four membered $(BN)_2$ unit while the atoms C(3), C(3)', C(4), C(4)', H(1) and H(1)' also lie on the ring plane. With internal ring angles of $B\hat{N}B$=93.4(5)° and $N\hat{B}N$=86.7(4)° both boron and nitrogen show considerable distortion from the geometry of their formal sp^2 and sp^3 hybridisation states, the more acute ring angle at boron being consistent with both its formal sp^2 hybridisation, and its greater electropositivity. The two B-N distances of 1.592(5)Å and 1.585(6)Å do not differ significantly, and are of similar length to that of 1.591Å found in the aminoborane $(Me_2NBCl_2)_2$ (49) despite the fact that all

FIGURE II.5

Molecular structure of $(PhCH{=}NBMe_2)_2$

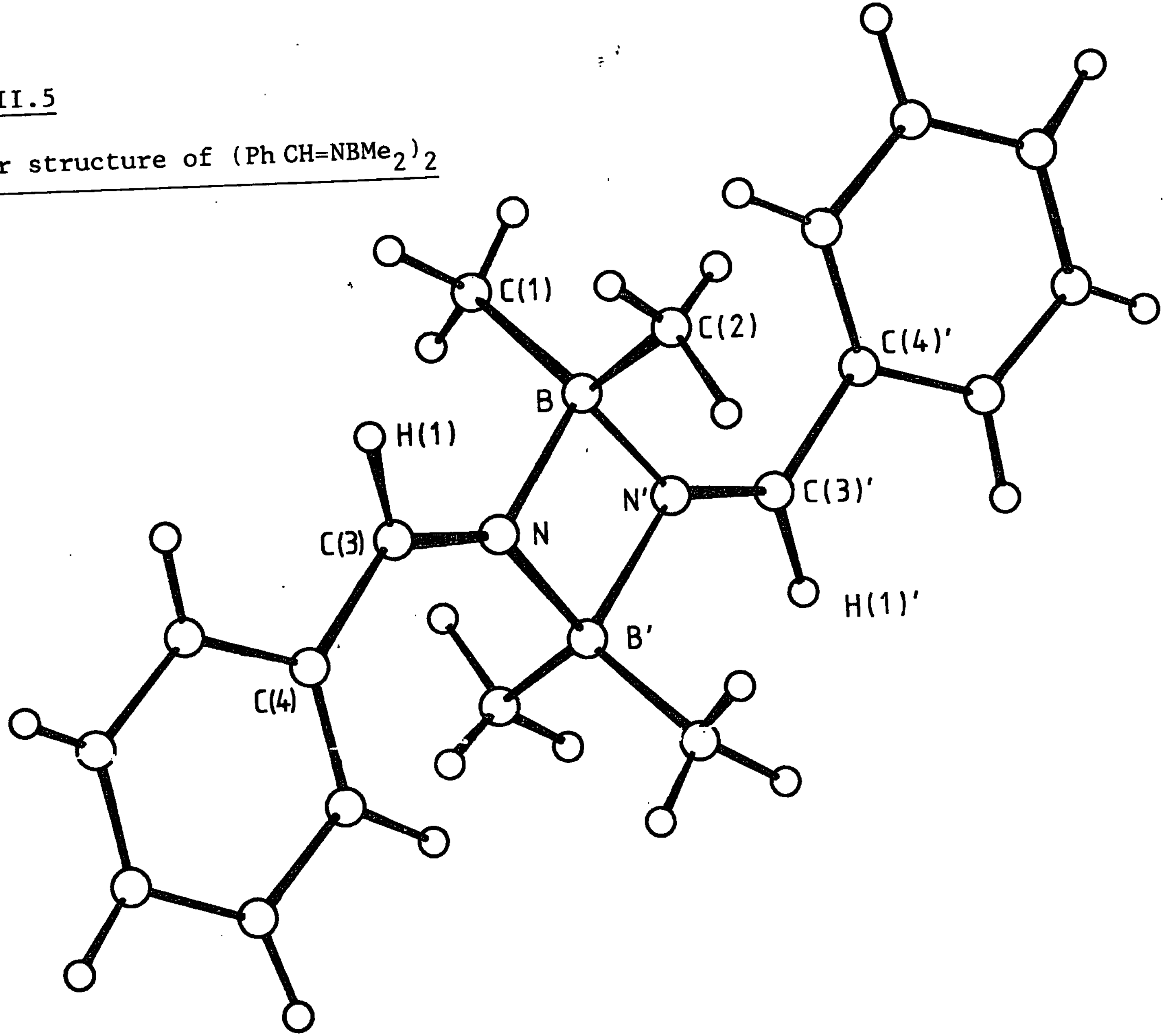


Table II.2

Selected bond lengths (Å) and angles (°) in $(PhCH=NBMe_2)_2$

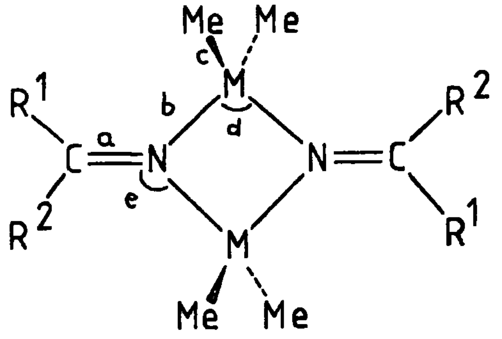
B - N	1.592(5)	B - N'	1.585(6)
B - C(1)	1.597(6)	B - C(2)	1.589(6)
N - C(3)	1.278(5)	C(3)-C(4)	1.462(5)

Intramolecular distances

B ... B'	2.305(9)	N ... N'	2.174(6)
B-N-B'	93.4(5)	N-B-N'	86.7(4)
C(1)-B-C(2)	117.9(4)	B-N-C(3)	125.7(3)
B'-N-C(3)	140.9(5)	N-C(3)-C(4)	127.8(4)

Table II.3

Comparison of selected bond lengths (Å) and angles (°) in $(PhCH=NBMe_2)_2$, $(MeCH=NBMe_2)_2$ and $(^tBuMeC=NAlMe_2)_2$(8,9).



R^1	R^2	M	a	b	c	d	e
Ph	H	B	1.28	1.59	1.59	87	126
Me	H	B	1.27	1.59	1.61	87	132
^{t}Bu	Me	Al	1.27	1.96	2.01	85	125

four ring atoms in the latter are of formally sp^3 character. Similar B-N distances have also been found in the compounds Me_3NBF_3 (50) and $(BH_2(NH_3)_2)^+Cl^-$ (51). The B-Me distances of 1.597(6) Å and 1.589(6) Å are comparable with those of $(Me_2BH)_2$ (52), while the $C(1)\hat{B}C(2)$ angle of 117.9(4)° showsan increase from the tetrahedral angle (109.5°) and parallels the decrease in the $N\hat{B}N$ internal ring angles. Both the $B\hat{N}C(3)$ and $B'\hat{N}C(3)$ bond angles in $(PhCH{=}NBMe_2)_2$, of 125.7(3)° and 140.9(5)° respectively, are considerably different from those of 131.7° and 134.5° observed in $(MeCH{=}NBMe_2)_2$, and demonstrate the increasing distortion of the molecular structure brought about as a consequence of the increasing steric interaction of boron and carbon substituents, as discussed earlier. Interestingly, the corresponding $Al\hat{N}C$ and $Al'\hat{N}C$ angles of 124.9° and 140.5° in $(^tBuMeC{=}NAlMe_2)_2$ (8) indicate a similar degree of distortion in this compound, while the $N\hat{C}(3)C(4)$ angle of 127.8(4)° in $(PhCH{=}NBMe_2)_2$ is, presumably, further evidence of this effect. The C=N bond distance of 1.278(5)Å is unexceptional, being similar to that observed in $(^tBuMeC{=}NAlMe_2)_2$, as well as a number of other compounds including the bridging C=N bond length of 1.279(14)Å in the compound $((^tBu_2C{=}N)_2Be)_2$ (16). A further interesting feature is the comparison of carbon-bonded imino-substituent bond lengths C(3) - C(4), in the three imino derivatives. The C(3) - C(4) bond lengths in $(PhCH\ NBMe_2)_2$ and $(MeCH{=}NBMe_2)_2$ were measured as 1.462(5)Å and 1.468(7)Å respectively, both values being significantly less than those of 1.54(3)Å (C-Me) and

1.55(2)Å (C-^{t}Bu) found in (^{t}BuMeC=NAlMe$_2$)$_2$, and 1.53Å found in dimethylglyoxime (HON=C(Me)C(Me))$_2$ (53). While the shortening of the C(3) - C(4) bond distance in (PhCH=NBMe$_2$)$_2$ can, in part, be explained in terms of interaction between the phenyl and C=N π systems, it is not clear why such a marked shortening is also observed in the case of (MeCH=NBMe$_2$)$_2$.

Infra red spectra

The infra red spectra of the iminoborane dimers were obtained from samples mounted as either KBr discs, or liquid films between KBr plates, as appropriate. All the samples displayed a characteristic olefinic stretch ν(C-H) between 2995 cm^{-1} and 3000 cm^{-1}, while the B-Me derivatives all possessed a strong δCH$_3$ deformation mode vibration at ca. 1280 cm^{-1}. Table II.4 lists the observed ν(C=N) stretching frequencies of these compounds together with those of a number of other iminoborane derivatives. All the compounds have ν(C=N) absorptions in the range 1640 cm^{-1} to 1700 cm^{-1} which is well within the region 1570 cm^{-1} to 1720 cm^{-1} established (33-35, 47, 54-58) as containing the ν(C=N) vibrations of imino ligands adopting a μ_2 bridging mode of bonding (Figure I.1(c)). By comparison, the ν(C=N) stretching frequencies displayed by a series of monomeric iminoboranes, R$_2$C=NBR'$_2$ (Figure I.2(i)), occur in the region 1730 cm^{-1} to 1850 cm^{-1}, and are discussed in chapter 4. Consideration of the observed trend in ν(C=N) frequencies shown in Table II.4 would indicate a decrease in absorption frequency associated

Table II.4

ν(C=N) infra red absorptions for some alkyl-, and aryl-, methyleneaminoborane dimers.

Compound	Isomer	Phase	ν(C=N)cm^{-1}	Ref.
$(MeCH{=}NBMe_2)_2$	syn	liq. film	1698	(a)
$(MeCH{=}NBMe_2)_2$	anti	KBr disc	1694	(a)
$(MeCH{=}NBEt_2)_2$	syn/anti	liq. film	1692	25
$(EtCH{=}NBMe_2)_2$	syn/anti	liq. film	1695	(a)
$(^tBuCH{=}NBMe_2)_2$	anti	KBr disc	1684	(a)
$(^tBuCH{=}NBEt_2)_2$	anti	KBr disc	1663	(a)
$(^tBuCH{=}NB^nBu_2)_2$	anti	nujol mull	1668	37
$(PhCH{=}NBMe_2)_2$	anti	KBr disc	1654	(a)
$(PhCH{=}NBEt_2)_2$	anti	KBr disc	1640	(a)
$(PhCH{=}NBPh_2)_2$	anti	nujol mull	1643	46

(a) This work.

with an increase in the mass of the carbon-bonded substituent, as might be expected from a consideration of the increased mechanical constraint imposed on the vibrating unit.

In the case of the phenymethyleneamino derivatives however, a second factor, the delocalisation of the phenyl and C=N π systems, would also have the effect of lowering the C=N bond order, and hence the associated frequency of vibration. Such an effect was also noted in the ν(C=N) frequencies of a series of phenyl(alkyl) methyleneaminoalanes, $(Ph(R)C{=}NAlR'_2)_2$ (33). The varying mass of the boron-bonded alkyl substituent would also seem to have a small effect on the ν (C=N) frequency, although, as might be expected, the effect is much less pronounced and barely significant.

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

The ^{1}H n.m.r. spectra were recorded from solutions in $CDCl_3$ and are summarised in table II.5. In most cases the samples were run with T.M.S. as an external reference to avoid the difficulty of overlap with signals due to the boron-bonded alkyl groups. For the compounds $(RCH{=}NBR_2')_2$ (R=alkyl) the olefinic proton was observed as a rather broad singlet in the region $\tau = 2.6$ to 2.8 p.p.m., while when R = phenyl the signal could not be completely distinguished from those due to the aromatic protons. The syn and anti isomers of the compounds $(MeCH{=}NBMe_2)_2$ and $(EtCH{=}NBMe_2)_2$ could each be distinguished on the basis of the signals due to the boron-bonded methyl groups, this technique being used to establish the exclusively anti isomerism of the remaining imino(dimethyl)boranes. In the case of the syn isomers, the methyl groups attached to the two boron atoms occupy magnetically non-equivalent environments, due to the relative positions of the carbon-bonded methyl or ethyl groups (Figure II.1), and consequently give rise to two equal signals of slightly differing shift, viz. $\tau = 9.98$ and 10.17 for syn $(MeCH{=}NBMe_2)_2$ and $\tau = 10.01$ and 10.15 for syn $(EtCH{=}NBMe_2)_2$. By contrast, the anti isomers, being centrosymmetric molecules, have B-Me groups in magnetically equivalent environments (Figure II.1), and thus give single methyl peaks in their n.m.r. spectra. In the case of $(EtCH{=}NBMe_2)_2$, whose syn and anti isomers could not be separated, integration of the

TABLE II.5 ^{1}H n.m.r. shifts for the imino boranes $(\mathrm{RCH{=}NBR'_2})_2$

Compound	Isomer	^{1}H n. m.r. shifts (τ,p.p.m.), T.M.S. Reference				
		$\mathrm{\diagdown C{=}}$ $\mathrm{H\diagup}$	$\mathrm{C{-}\underset{H}{C}}$	$\mathrm{C{-}C{-}\underset{H}{C}}$	$\mathrm{B{-}\underset{H}{C}}$	$\mathrm{B{-}C{-}\underset{H}{C}}$
$(\mathrm{MeCH{=}NBMe_2})_2$	syn	2.62(s)	8.06(d) J=5.5Hz	-	9.98(s) 10.17(s)	-
$(\mathrm{MeCH{=}NBMe_2})_2$	anti	2.62(s)	8.06(d) J=5.5Hz	-	10.08(s)	-
$(\mathrm{EtCH{=}NBMe_2})_2$	syn/anti	2.67(s)	7.95(i)	8.93(t) J=7.0Hz	10.01(s) 10.08(s) 10.15(s)	-
$(^t\mathrm{BuCH{=}NBMe_2})_2$	anti	2.79(s)	-	8.88(s)	10.00(s)	-
$(\mathrm{PhCH{=}NBMe_2})_2$	anti	(ii)	(iii)	(iii)	9.87(s)	-
$(^t\mathrm{BuCH{=}NBEt_2})_2$	anti	2.80(s)	-	8.86(s)	10.00(s,br)	8.32(t) J=7.0Hz
$(\mathrm{PhCH{=}NBEt_2})_2$	anti	(ii)	(iii)	(iii)	9.89(s,br)	8.34(t) J=7.0Hz

(i) Complex group due to splitting by adjacent methyl and olefinic protons.

(ii) Obscured by phenyl proton signals.

(iii) Aromatic protons at τ = 2.2 - 2.8 unresolved.

methyl signals of the syn and anti isomers suggested a relative molar ration of 2:5, being identical to the relative molar proportions of separable isomers of $(MeCH{=}NBMe_2)_2$. In each case considerable broadening of the signal due to the boron-bonded methyl group was observed, this being attributable to coupling effects between the protons and the quadrupolar boron nucleus. Similar broadening in the BEt Cα proton signals of the compounds $({}^tBuCH{=}NBEt_2)_2$ and $(PhCH{=}NBEt_2)_2$ was noted, and had the effect of preventing resolution of the signal splitting arising from coupling with the adjacent CH_3 protons. It was therefore not possible to unambiguously assign anti isomerism to these compounds on the basis of these signals, although the sharp triplets of the adjacent CH_3 protons, at τ =8.32, in $({}^tBuCH{=}NBEt_2)_2$ and τ =8.33, in $(PhCH{=}NBEt_2)_2$, would suggest magnetically equivalent environments, and hence exclusively anti isomerism. The non-equivalence of methyl environments, as demonstrated by 'H n.m.r., has also been cited as evidence for syn /anti isomerism in the compound $(MeCH{=}AlMe_2)_2$ (34), while the syn/anti isomerism of a series of associated dimethylaminochloroboranes $(Me_2NBClR)_2$, was also established by this method (48). In both the syn and anti isomers of $(MeCH{=}NBMe_2)_2$ and $(EtCH{=}NBMe_2)_2$, containing protons bonded to the carbon atom α to the C=N group, splitting of the respective CH_3 and CH_2 signals was observed due to coupling with the geminal proton. In the cases of the syn and anti isomers of $(MeCH{=}NBMe_2)_2$ this gave rise to doublet signals with a coupling constant of 5.5 Hz, this being typical of geminal-proton coupling constants in olefinic groups (59). The coupling in the syn/anti isomer mix of (EtCH=NBMe$_2$)$_2$ was further complicated by splitting of the CH$_2$ signal by the neighbouring CH$_3$ protons, and in this case the resultant signal could not be properly resolved.

^{13}C n.m.r. spectra

The proton decoupled ^{13}C n.m.r. spectra were obtained from approximately 20% solutions of compound dissolved in C$_6$D$_6$ and are summarised in table II.6, together with the carbon resonance frequencies of the corresponding parent nitriles. In no case was it possible to resolve the signals due to the α-bonded carbons of the B-Me and B-Et groups, the signals commonly appearing as broad and ill-defined peaks in the region δ = 0 to +10 p.p.m. downfield from T.M.S., and it was therefore not possible to further demonstrate syn and anti isomerism by this technique.

Similar broad and poorly defined α-carbon peaks have been observed elsewhere (60 - 62) in a number of organoboron compounds, the effect being due to the large B-C couplings which are incompletely relaxed by the quadrupolar mechanism (60). The imino-carbon resonances at 157 to 167 p.p.m. are consistent with those noted elsewhere (63,64) and as such fall in an intermediate shift position between those of nitrile carbons, at ca. 115 - 125 p.p.m., and those of carbonyl carbons at ca. 180 - 220 p.p.m. (63). Considering the series (RCH=NBMe$_2$)$_2$, (R=Me,Et,^{t}Bu), it can be seen that successively replacing alkyl substituents

TABLE II.6 ^{13}C n.m.r. resonances for the imino boranes $(RCH{=}NBR'_2)_2$ and parent nitriles, RCN

Compound	Isomer	^{13}C resonances (p.p.m.), T.M.S. Reference				
		$>C=$	Aromatic	α C-C=	β C-C-C=	RC≡N
$(MeCH{=}NBMe_2)_2$	syn	+157.1	-	+20.1	-	-
$(MeCH{=}NBMe_2)_2$	anti	+157.1	-	+20.1	-	-
$(EtCH{=}NBMe_2)_2$	syn/anti	+159.2	-	+23.2	+26.2	-
$(^tBuCH{=}NBMe_2)_2$	anti	+165.7	-	+27.0	+27.9	-
$(PhCH{=}NBMe_2)_2$	anti	+157.6	+133.9, +131.2, +130.6, +128.6	-		-
$(^tBuCH{=}NBEt_2)_2$	anti	+166.2		+27.0	+27.9	-
$(PhCH{=}NBEt_2)_2$	anti	+159.4	+134.0, +131.2 +130.7, +128.5	-	-	-
MeCN	-	-	-	-0.3	-	+117.7
EtCN	-	-	-	+9.7	+20.1	+120.8
^tBuCN	-	-	-	10.4	27.5	+125.1
PhCN	-	-	+109.4, +126.9, +129.8, +130.1	-	-	+118.7

of increasing size results in a gradual movement in the imino-carbon resonance to lower field. Moreover, the difference of 6.5 p.p.m. between the signals due to $(EtCH=NBMe_2)_2$ and $(^tBuCH=NBMe_2)_2$ is that which is predicted by the general observation that successive addition of alkyl groups to the ∝-carbon adjacent to a carbon-containing functional group will cause the resonance of the functional-group carbon to move downfield by c a. 3 p.p.m. (63). The intermediate position of the imino-carbon resonance in the phenyl derivative $(PhCH=NBMe_2)_2$ is, perhaps, surprising, ∝-bonded aryl substituents normally resulting in increased shielding, and hence higher field shifts, of the carbon nucleus (63). Such a trend is evident in the ^{13}C n.m.r. shifts of the carbonyl-carbon in the series of aldehydes EtCHO (202.7 p.p.m) MeCHO(200.5 p.p.m) PhCHO (190.7p.p.m) (65,66). However, the nitrile ^{13}C resonance of PhCN, at $\delta = 118.7$, falls between those of MeCN, $\delta = 117.7$, and EtCN, $\delta = 120.8$, and thus exactly parallels the trend observed in the iminoborane case.

<u>''B nm.r. spectra</u>

The ''B nm.r. spectra of the iminoboranes were recorded at 19.24 MHz and are summarised in Table II.7. together with those of some similar compounds. The compounds described in this chapter were run as concentrated toluene solutions, shifts being quoted relative to an external reference of $BF_3.OEt_2$. It should be noted however, that small variations in the shifts (± 0.4 p.p.m) were seen when some of the compounds were run as solutions in $CDCl_3$ or CCl_4

Table II.7

^{11}B n.m.r. signals of imino-borane dimers

$(RCH{=}NBX_2)_2$

Compound	Isomer	$^{11}B^+$	Ref
$(MeCH{=}NBMe_2)_2$	syn	+3.6	(a)
$(MeCH{=}NBMe_2)_2$	anti	+3.6	(a)
$(EtCH{=}NBMe_2)_2$	syn/anti	+3.7	(a)
$(^tBuCH{=}NBMe_2)_2$	anti	+5.4	(a)
$(PhCH{=}NBMe_2)_2$	anti	+6.1	(a)
$(^tBuCH{=}NBEt_2)_2$	anti	+6.6	(a)
$(PhCH{=}NBEt_2)_2$	anti	+7.6	(a)
$(^tBuCH{=}NB^nBu_2)_2$	anti	+7.4	37
$(^tBuCH{=}NBCl_2)_2$	anti	+4.3	37
$(^tBuCH{=}NBBr_2)_2$	anti	-2.3	37

\+ Shifts measured relative to an external reference of $Et_2O.BF_3$. Positive values are to lower field.

(a) This work.

The compounds have shifts in the region $\delta = +3.6$ to $+7.6$ and as such are closely grouped within a wider range of shifts associated with boron being in a four-coordinate environment (67, 68). By contrast, the observed shifts of the non-associated methyleneaminoboranes, $R_2C{=}NBR'_2$ (R,R' = alkyl, aryl), discussed in chapter 4, were found in the region $\delta = +26$ to $+39$. This marked difference in ^{11}B shift between monomeric and dimeric iminoborane derivatives was used to demonstrate the dissociation of $(^tBuCH{=}NB^nBu_2)_2$ above 70° (37), the associated molecule having a shift of + 7.4 p.p.m. while that of the monomer was measured as + 38.8 p.p.m. The technique should also, in principle, have allowed the syn and anti isomers of the compounds $(MeCH{=}NBMe_2)_2$ and $(EtCH{=}NBMe_2)_2$ to be distinguished, as was found to be the case with their ^{1}H n.m.r. spectra. Thus, the boron atoms of the syn isomer, being magnetically non-equivalent, would be expected to have slightly differing shifts while those of the anti isomer should be equivalent. In practice however this was not found to be the case as both syn and anti isomers of $(MeCH{=}NBMe_2)_2$ gave rise to single peaks of identical chemical shift and half-width, while a single peak was seen in the spectrum of $(EtCH{=}NBMe_2)_2$. The use of a higher field spectrometer, together with line narrowing techniques, may lead to observation of the expected splitting of the syn isomer shifts although such a study was not attempted during the course of the present work.

With an observed range of shift values of only 4 p.p.m. it is probably not possible to place too much emphasis on slight differences in chemical shift between the compounds prepared during the present study. It may be noted however that the replacement of methyl groups by ethyl on boron would seem to result in a slight decrease in the shielding of the boron nucleus, as is also seen in the case of the dimeric aminoboranes $(CH_3HNBMe_2)_2$ (- 1.0 p.p.m.) (69) and $(CH_3HNBEt_2)_2$ (+ 2.1 p.p.m) (70). A decrease in shielding is also observed in the carbon-bonded substituent sequence $Me > Et > {}^tBu > Ph$.

Mass spectra

The mass spectra of all seven iminoborane derivatives were obtained and the major features of each are summarised in Tables II 8-13. The spectra of the syn and anti isomers of $(MeCH{=}NBMe_2)_2$ were essentially identical, while all the spectra showed evidence of the dimeric species in the vapour phase. Owing to the similarity of alkyl substituents on both imino-carbon and boron it was not always possible to conclusively identify a particular ion peak in the spectrum, although comparison of all the spectra would suggest a common breakdown pattern. Molecular ions were not observed in the spectra of $(MeCH{=}NBMe_2)_2$ and $(EtCH{=}NBMe2)_2$, while all the spectra contained a large peak due to the loss of an alkyl substituent from a boron atom of the dimer. Peaks due to the monomeric species were also observed, the peak due to the loss of one boron-bonded alkyl group from the monomer representing the largest ion current in each case. A third break-down route, observed only in the B-Me derivative spectra, is suggested by the presence of signals due to species of the form $(RCH{=}N(BMe_2)_2)^+$, (Re=Me, Et, ^tBu, Ph).

Table II.8

Major peaks in the mass spectra of

syn-,and anti-, $(MeCH=NBMe_2)_2$

$^m/e$	Relative Intensity	Assignment
151	51	$(MeCH=NBMe_2)_2$ - Me
136	18	" - 2 Me
124	12	$MeCH=N(BMe_2)_2$
83	33	$MeCH=NBMe_2$
68	100	" - Me
53	8	" - 2Me
43	39	MeCH=NH
42	30	MeCH=N

Table II.9

Major peaks in the mass spectrum of

$(EtCH=NBMe_2)_2$

$^m/e$	Relative Intensity	Assignment
179	48	$(EtCH=NBMe_2)_2$ - Me
165	8	" - Et
164	12	" - 2 Me
138	13	$EtCH=N(BMe_2)_2$
123	7	" - Me
97	35	$EtCH=NBMe_2$
82	100	" - Me
57	22	EtCH=NH
56	17	EtCH=N
41	82	EtC

Table II.10

Major peaks in the mass spectrum of $({}^{t}BuCH{=}NBMe_2)_2$

$^{m}/e$	Relative Intensity	Assignment
250	15	$({}^{t}BuCH{=}NBMe_2)_2$
235	67	" - Me
220	7	" - 2Me
205	5	" - 3Me
166	23	${}^{t}BuCH{=}N(BMe_2)_2$
151	6	" - Me
125	44	${}^{t}BuCH{=}NBMe_2$
110	100	" - Me
95	15	" - 2Me
84	72	${}^{t}BuC{=}NH$
83	63	${}^{t}BuC{=}N$
57	49	${}^{t}Bu$

Table II.11

Major peaks in the mass spectrum of $(PhCH{=}NBMe_2)_2$

$^{m}/e$	Relative Intensity	Assignment
290	19	$(PhCH{=}NBMe_2)_2$
275	73	" - Me
260	8	" - 2Me
186	11	$PhCH{=}N(BMe_2)_2$
145	23	$PhCH{=}NBMe_2$
130	100	" - Me
104	96	$PhCH{=}NH$
103	87	$PhCH{=}N$
77	62	Ph

Table II.12

Major peaks in the mass spectrum of

$(^t\text{Bu CH=NBEt}_2)_2$

$^m/_e$	Relative Intensity	Assignment
306	12	$(^t\text{BuCH=NBEt}_2)_2$
291	5	" - Me
277	83	" - Et
276	12	" - 2 Me
153	29	$^t\text{BuCH=NBEt}_2$
138	8	" - Me
124	100	" - Et
123	12	" - 2Me
84	66	$^t\text{BuCH=NH}$
83	41	$^t\text{BuCH=N}$
57	69	^tBu

Table II.13

Major peaks in the mass spectrum of

$(\text{PhCH=NBEt}_2)_2$

$^m/_e$	Relative Intensity	Assignment
346	19	$(\text{PhCH=NBEt}_2)_2$
317	78	" - Et
288	14	" - 2Et
173	22	PhCH=NBEt_2
144	100	" - Et
104	69	PhCH=NH
103	52	PhCH=N
77	81	Ph

CHAPTER 3

REACTIONS OF LITHIUM TRIETHYLBOROHYDRIDE WITH SOME NITRILES; THE REACTIVITY OF LITHIUM t-BUTYL-, AND PHENYL-, METHYLENEAMINOTRIETHYLBORATE TOWARDS PHOSPHORUS TRICHLORIDE

INTRODUCTION

This chapter describes the reactions of lithium triethylborohydride, $LiBHEt_3$, with acetonitrile, benzonitrile and t-butyl cyanide in T.H.F. solution. Differences in the chemical and spectroscopic properties of the resulting species are interpreted in terms of differing reaction mechanisms. The reactivity of two of the products, the lithium t-butyl-, and phenyl-, methyleneaminotriethylborates $(RCH{=}N(BEt_3)Li)_n$, towards differing molar equivalents of phosphorus trichloride is described, together with the characterisation of the resulting four new methyleneaminophosphines; $(RCH{=}N)_3P$ and $RCH{=}NPCl_2$ ($R={}^{t}Bu$, Ph).

EXPERIMENTAL SECTION

(i) Starting materials

Lithium triethylborohydride ("Super Hydride") was purchased commercially as an approximately 1M solution in T.H.F. and was used as supplied. The solution was standardised by the volumetric determination of hydrogen evolution upon hydrolysis. Nitrile reagents were purified as described in Appendix 1. Reactions and subsequent manipulations were performed under an inert atmosphere of dry nitrogen.

(ii) Reaction of Lithium triethylborohydride and Acetonitrile (1:1).

Acetonitrile (0.83g, 20 mmol.) was added to Lithium triethylborohydride (20 mmol.) in 20 cm^3 T.H.F. and the solution stirred at room temperature for two hours.

Removal of solvent by pumping yielded a colourless, viscous oil which could not be crystallised. (Found : C67.2%, H13.4%, B 3.0%, Li 2.0%, N 3.7 %. A compound of the stoichiometric ratio CH_3CN : $LiBHEt_3$: 3 T.H.F. requires : C 66.1%, H11.9%, B 2.9%, Li 1.9%) ν_{max} (liquid film) 3370(w) 2980(s) 2935(s) 2890(s) 2855(s) 2796(s) 2698(w) 2224(m) 2179(m) 2147(w,sh) 2125(s) 1565(m) 1555(m) 1530(w,br) 1458(m) 1443(w,sh) 1430(w,br) 1267(w) 1340(w) 1313(w) 1293(w) 1257(w) 1195(w) 1178(w) 1103(w) 1042(s) 1015(w) 990(w) 954(w) 917(m) 888(s) 870(m,sh) 825(m) 800(w) 675(m) 533(w) 523(w) 510(w) cm^{-1}. The material decomposed upon exposure to air. Triethylborane is slowly lost over a number of days standing at room temperature, the process being accelerated at higher temperatures.

(iii) Reaction of Lithium triethylborohydride and Acetonitrile (2:1)

Acetonitrile (0.42g, 10.23 mmol.) was added to Lithium triethylborohydride (20.5 mmol.) in 20 cm^3 of T.H.F., the mixture stirred at room temperature for four hours, and the solvent removed by pumping. The infra red spectrum was essentially similar to that found in the 1:1 reaction with the addition of the following extra peaks; 2072(w,br) 2020(w,br) 1948(m,br) cm^{-1}, these being attributable to the ν(B-H) vibration in free $BHEt_3^-$(72).

In a further reaction the solution resulting from addition of 20.5 mmol. $LiBHEt_3$ to 10.25 mmol. CH_3CN was hydrolysed by addition of 5 cm^3 of water. The volume of hydrogen evolved was measured volumetrically (232.7 cm^3 at 290 K = 9.85 mmol.).

(iv) Reaction of Lithium triethylborohydride with t-Butylcyanide (1:1)

t-Butylcyanide (0.83 g, 10.00 mmol.) was added to Lithium triethylborohydride (10.0 mmol.) in 10 cm^3 T.H.F. and the mixture stirred for three hours at room temperature. Removal of solvent under vacuum yielded a colourless viscous oil which could not be crystallised. The oil was identified as Lithium t-butylmethyleneaminotriethylborate ^{t}BuCH=N(BEt$_3$)Li(3 T.H.F.). (Found : C 64.8%, H 14.5%, B 3.1%, Li 2.0%, N 3.6%, $C_{19}H_{49}BLiNO_3$ requires:C 63.9%, H 13.5%, B 3.0%, Li 1.9%, N 3.9%) ν_{max} (liquid film) 2980(s) 2924(s) 2895(s) 2830(s,br) 2800(m,sh) 2700(w) 1683(m,sh) 1658(s) 1658(m,sh) 1645(w,sh) 1473(m) 1458(s) 1430(m,sh) 1387(w) 1358(m) 1342(w,sh) 1293(w) 1250(m) 1211(w) 1202(w) 1178(w) 1095(w,sh) 1048(s) 1040(s) 958(w,sh) 938(m,sh) 916(s) 908(s) 887(s) 855(s) 840(s) 780(w) 673(m) 556(m) 517(m) cm^{-1}. The compound was found to be air sensitive, decomposing during a few seconds exposure.

A 20 mmol. sample of the product in 25 ml. of T.H.F. was hydrolysed by refluxing with 30% solution of sodium hydroxide over a period of four hours, the solution was then neutralised and fractionated. A fraction boiling in the range 75° - 80° was identified as comprising largely t-butylaldehyde, ^{t}BuCHO.

(v) Reaction of Lithium triethylborohydride, Pentamethyldiethylenetriamine (PMDETA) and t-Butylcyanide, (1:1:1).

t-Butyl cyanide (0.83g, 10.00 mmol.) was added to lithium triethylborohydride (10 mmol.) in 20 ml. of

T.H.F. and the mixture stirred for one hour at room temperature. Pentamethyldiethylenetriamine (1.73g, 10.00 mmol.) was then added, the mixture stirred for a further two hours, and the solvent removed by pumping to yield a colourless, viscous, oil which could not be crystallised. Analysis of the liquid gave : C 74.8%, H 15.2%, B 2.1%, Li 1.0%, N 5.0%. Li(PMDETA).^{t}BuCH=NBEt$_3$ would require : C 68.9%, H 13.9%, B 3.1%, Li 2.0%, N 12.1% ν_{max} (liquid film) 2970(s,br) 2860(s,br) 1664(s) 1460(s,br) 1392(w) 1362(m) 1300-1000 (strong, ill defined) 982(w) 938(m,sh) 831(s) 908(w) 880(s,vbr) 788(m) 772(m) cm^{-1}. Prolonged pumping at room temperature resulted in the recovery of further small amounts of triethylborane, T.H.F. and PMDETA, identified on the basis of their infra red spectra.

(vi) Attempted Reaction of Triethylborane with di-t-butylmethyleneaminolithium.

Triethylborane (0.83g, 8.47 mmol.) was condensed onto the surface of a frozen (-196°) solution of di-t-butylmethyleneaminolithium (1.24g, 8.42 mmol.) in 30 cm^3 T.H.F. The mixture was allowed to warm to room temperature and then refluxed for a period of two hours. Approximately half the solvent was removed by pumping and the remaining solution placed in a freezer, maintained at -30°, for a number of days. Pale yellow crystals were deposited which were subsequently identified as unreacted di-t-butylmethyleneamino lithium. Removal of the remaining solvent under vacuum yielded a further quantity of iminolithium together with almost quantitative recovery (0.83g, 8.27 mmol.) of triethylborane.

(vii) Reaction of Lithium triethylborohydride with Benzonitrile (1:1).

Benzonitrile (1.03g, 10.00 mmol.) was added to Lithium triethylborohydride (10 mmol.) in 20 cm^3 T.H.F. and the mixture stirred at room temperature for three hours. Removal of the solvent under vacuum yielded a brown viscous oil which could not be crystallised. The liquid was identified as Lithium phenylmethyleneaminotriethylborate $PhCH=N(BEt_3)Li(3.T.H.F.)$ (Found : C 71.2%, H 13.3%, B 2.6% Li 1.7%, N 3.5% $C_{25}H_{45}BLiN$ requires : C 70.6%, H 10.7%, B 2.5%, Li 1.6%, N 3.3%) ν_{max} (liquid film) 3075(w) 3058(w) 3018(w) 2978(s) 2930(s) 2882(s) 2854(s) 2790(m) 2702(w) 1644(w,sh) 1634(s) 1577(w) 1487(w) 1458(m) 1446(m) 1430(w,sh) 1368(w) 1360(w) 1341(w) 1302(w) 1290(w) 1049(w) 1203(w) 1177(w) 1072(m,sh) 1044(s) 1001(w) 957(w) 913(w) 888(s) 860(s) 852(m,sh) 849(m,sh) 755(s) 731(w) 697(s) 672(w) 572(w,br) cm^{-1}. The compound decomposed rapidly upon exposure to air. Slow decomposition also occurred after prolonged standing at room temperature, and more rapidly at elevated temperatures, the odour of triethylborane being detected above the liquid.

A further 20 mmol. sample of the product in 20 ml. T.H.F. was hydrolysed by refluxing with a 30% solution of sodium hydroxide over a period of 12 hours. The solution was then cooled, neutralised and fractionated to yield T.H.F., water, and a fraction which boiled at 176-178° and was identified as benzaldehyde (1.84g, 17.34 mmol.). The odour of triethylborane was detected in the T.H.F.

fraction but was not quantified. The remaining solids contained lithium, sodium and small amounts of carbon and hydrogen. No nitrogen-containing species was detected.

(viii) Formation of (bis(tetramethylethylenediamine)) Lithium triethylborohydride, Li(TMED)$_2$BHEt$_3$

Tetramethylethylenediamine (3.49g, 30.05 mmol.) was added to a solution of lithiumtriethylborohydride (15 mmol.) in 40 cm^3 of T.H.F. Removal of the solvent under vacuum yielded a white solid which was identified as (bis(tetramethylethylenediamine)) Lithium triethylborohydride Li(TMED)$_2$BHEt$_3$ m.pt. 120-125° (dec.). (Found : C 64.1% H 15.9%, B 3.1%, Li 2.1%, N 16.3%, $C_{18}H_{48}BLiN_4$ requires : C 63.9%, H 14.3%, B 3.2%, Li 2.1%, N 16.6%) ν_{max} (nujol mull) 2180(w) 2042(m) 1935(m,br) 1455(s,br) 1357(m) 1286(m) 1245(m) 1217(w) 1183(m) 1159(m) 1127(m) 1090(m,br) 1067(m) 1031(m) 1013(m) 943(s) 900(w) 951(w) 787(m) 773(w,sh) 586(w) cm^{-1}. The compound was exceedingly air sensitive, decomposing immediately upon exposure to air.

(ix) Reaction of Li(TMED)$_2$BHEt$_3$ and Benzonitrile (1:1).

Benzonitrile (0.75g, 7.24 mmol.) was added to a solution of Li(TMED)$_2$BHEt$_3$ (2.44g, 7.21 mmol.) in 30cm^3 of T.H.F. and the mixture stirred at room temperature for three hours. Removal of the solvent under vacuum yielded a brown viscous oil from which further small quantities of T.M.E.D. could be removed with prolonged pumping. Elemental analysis failed to give consistent results and could not be equated with any predicted molecular formulation. The infra red spectrum contained a large number of peaks, including an absorption at 1642 cm^{-1}, and further peaks attributable to both T.H.F. and T.M.E.D.

(x) Procedure for the chromatographic examination of reaction products.

The procedure adopted was similar to that described by Brown, Kim and Krishnamurthy (71). Samples of the reaction products obtained from the reaction of t-butylcyanide and benzonitrile with lithium triethylborohydride were prepared as 1M solutions in T.H.F. A 1M solution of triethylborane in T.H.F. was also prepared and a 1.0μdm^3 sample injected into a gas chromatography column (10% S.E., 8' x ⅛". Injection port 35°, column 50°) using nitrogen as the carrier gas. The column separated the components of the liquid into two distinct, symmetrical, peaks, triethylborane being retained longer on the column. 1μdm^3 samples of the reaction products were then syringed onto the column under similar conditions and the resulting spectra examined for evidence of triethylborane passing through the column. The experiment was subsequently repeated at higher temperature (port 80°, column 110°).

(xi) Reaction of Lithium t-butylmethyleneaminotriethylborate with Phosphorus trichloride (1:1).

t-Butyl cyanide (1.66g, 19.97 mmol.) was added to a solution of lithium triethylborohydride (20 mmol.) in 20 cm^3 of T.H.F., the solution stirred for half an hour and then frozen to -196°. Phosphorus trichloride (2.57g, 20.02 mmol.) was added to the frozen solution, the mixture stirred to room temperature, and the solvent then removed under vacuum to yield an orange, sticky , material. Extraction of the material, with 10cm^3 of toluene, and filtration of the resulting solution, gave a clear orange solution from which no solid material could be recovered. Subsequent removal of the toluene under vacuum yielded a viscous orange oil which decomposed upon attempts at its distillation, HCl being produced and an orange solid resulting. Elemental analysis of the viscous oil gave: C 38.3%, H 6.2%, B 2.2%, Cl 31.9%, N 6.8%, P 13.2% $^{t}BuCH=NPCl_2$ requires : C 32.3%, H 5.4%, Cl 38.2%, N 7.5%, P 16.7%. The infra red spectrum contained a strong absorption at 1666 cm^{-1}. Elemental analysis of the decomposition product failed to give consistent results (C 45-52%, H 7-10%, Cl 6-10%, N 14-16%, P 24-28%.

(xii) Reaction of Lithium phenylmethyleneaminotriethylborate and Phosphorus trichloride (1:1).

Phosphorus trichloride (2.06g, 19.98 mmol.) and lithium triethylborohydride (20 mmol.) were reacted in a manner similar to that described above. Extraction with toluene againyielded an orange viscous oil which decomposed upon attempts of its vacuum distillation. Elemental analysis of the oil gave C 48.7%, H 5.4%, B 1.9%, Cl 14.7%, N 3.7%, P 13.7%. $PhCH=NPCl_2$ requires: C 40.8%, H 2.9%, Cl 34.4%, N 6.8%, P 15.0%. The infra red spectra contained a strong absorption at 1629 cm^{-1}. Elemental analyses of the decomposition product failed to give consistent results (C 54-59%, H 8-11%, Bc.a.0.9%, Cl15-10%, N 6-7%, P 17-22%)

(xiii) Reactions of Lithium t-Butyl- and Phenyl- methyleneaminotriethylborate with Phosphorus trichloride, (2:1).

Two molar equivalents of Lithium t-butyl-, and phenylmethyleneaminotriethylborate in T.H.F. solution were reacted with single equivalents of phosphorus trichloride in a manner similar to that described above for the analogous 1:1 reactions. Both yielded, after extraction with toluene, sticky orange materials from which no solid material could be recovered. The infra red spectrum of the t-butyl derivative contained a broad absorption in the region 1625 - 1680 cm^{-1}, while that of the phenyl derivative absorbed in the region 1600 - 1645 cm^{-1}. Both compounds displayed two peaks in their ^{31}P n.m.r. spectra, which in both cases corresponded to those of the respective mono-, and tris-, methyleneaminophosphines.

(xiv) Reaction of Lithium t-Butylmethyleneaminotriethylborate and Phosphorus trichloride (3:1).

t-Butyl cyanide (1.66g, 19.97 mmol.) was added to a solution of lithium triethylborohydride (20 mmol.) in 20 cm^3 T.H.F., the mixture stirred at room temperature for half an hour, and then frozen to -196°. Phosphorus trichloride (0.91g, 6.63 mmol.) was added, the mixture stirred to room temperature, and the solvent then removed under vacuum to yield a sticky orange mass. The material was extracted with 20 cm^3 of hexane and filtered to yield a clear orange solution which slowly deposited a finely divided yellow material upon cooling in a freezer at

-30°. The solid was filtered, pumped dry, and identified as tris(t-butylmethyleneamino)phosphine, $({}^{t}BuCH=N)_3P$, m.pt.; decomposed slowly upon heating above 30°. (Found : C 63.8%, H 11.7%, N 14.8%, P 10.8%, B. absent, Cl absent, Li absent. $C_{15}H_{30}N_3P$ requires C 63.5%, H 10.7%, N 14.8%, P10.9%) ν_{max} (Nujol mull) 1662(m,sh) 1647(s) 1272(w) 1247(m) 1213(m) 1982(m) 1063(m) 1032(s) 1018(w,sh) 973(w) 962(w) 937(w,sh) 919(m) 888(w) 872(w) 815(w) 802(w) 797(m,sh) 760(m,sh) 752(m) 729(s) 692(m) 640(w) 580(m,br) 504(w) cm^{-1}. The compound became deliquescent upon exposure to moist air.

(xv) Reaction of Lithium phenylmethyleneaminotriethylborate and Phosphorus trichloride (3:1).

Benzonitrile (2.08g, 20.17g) was added to a solution of lithium triethylborohydride (20 mmol.) in 20 cm^3 T.H. F., the mixture stirred at room temperature for half an hour, and then frozen to -196°. Phosphorus trichloride (0.90g, 6.55 mmol.) was added, the mixture stirred to room temperature, and the solvent removed under vacuum. Extraction with 15 cm^3 of a 1:1 hexane/toluene mixture, followed by filtration, yielded a clear orange-coloured solution which slowly deposited a fine yellow powder after standing at room temperature for a number of days. The material was filtered, pumped dry, and identified as tris(phenylmethyleneamino) phosphine, $(PhCH=N)_3P$ m.pt. :- decomposed slowly upon heating above 28°. (Found : C 73.9%, H 6.2%, N 12.4%, P9.1%, B absent, Cl absent, Li absent. $C_{21}H_{18}N_3P$ requires; C 73.5%, H 5.3%, N 12.2%, P 9.0%) ν_{max} (Nujol mull) 1665(w,sh)

1639(m,sh) 1611(s) 1598(s) 1573(s) 1311(m) 1244(w) 1323(m,sh) 1218(s) 1200(m,sh) 1163(w) 1140(w) 1073(w) 1023(m) 1002(w) 942(w) 920(m) 905(w) 860(m) 842(m) 803(w) 790(m,sh) 780(m,br) 758(s) 735(w) 702(s) 694(s) 650(w) 617(w) 570(m,br) cm^{-1}.

DISCUSSION

Reactivity of alkali metal triethylborohydrides towards organic functional groups.

Alkali metal trialkylborohydrides, $MBHR_3$.(M=Li, Na, K, R=Me, Et, ^nBu, ^iBu) have been known for almost forty years (73-75), although it is only ir the last fifteen years that their potential as reagents in organic synthesis has been realised and exploited (71,73). The most widely studied of the compounds, Lithium triethylborohydride, $LiBHEt_3$, has a nucleophilicity approximately 10,000 times greater than the parent borohydride ion, BH_4^-, and as such is the most powerful, simple, nucleophile available for effecting S_N2 displacements (76). The compound, prepared and used as a T.H.F. solution, is made from the addition reaction of lithium hydride and triethylborane (Equation III.1) (73) and will react with

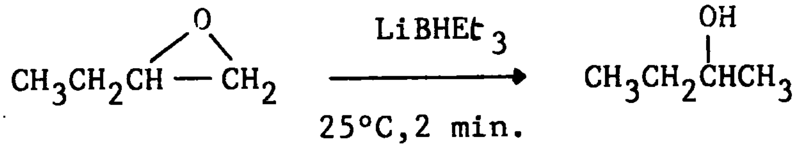
$$LiH + BEt_3 \xrightarrow{THF,\ 25°C} LiBHEt_3 \qquad III\ 1$$

an extensive range of organic functional groups to yield the corresponding reduction products. The reactions generally proceed at , or just above , room temperature and usually result in the formation of single products, in good yield and without the co-formation of unwanted bi-products. Examples include the reduction of hindered halides (Equation III.2) (13.76) epoxides (Equation III.3) (77), carboxylic acids (Equation III.4) (71) quarternary ammonium salts (Equation III.5) (78) as well as the reduction of cyclic and bicyclic ketones (Equation

III.6) (79-81).

$$ {}^{t}BuCH_2Br \xrightarrow[65^{\circ}C,3hrs.]{LiBHEt_3} {}^{t}BuCH_3 $$

III.2



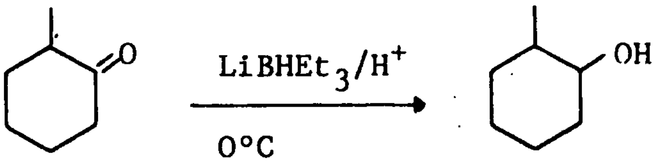
III.3

$$ RCO_2H \xrightarrow{LiBHEt_3} RCH_2OH $$

III.4

$$ CH_3(CH_2)_5\overset{+}{N}(CH_3)_3I^- \xrightarrow[65^{\circ}C,4\ hrs.]{LiBHEt_3} CH_3(CH_2)_5N(CH_3)_2 $$

III.5



III.6

Whereas most organic functional groups are susceptible to complete reduction upon reaction with $LiBHEt_3$, the nitrile function of capronitrile, $CH_3(CH_2)_4CN$, having a C-H unit bonded α to the nitrile function, will only consume one equivalent of hydride (71) rather than the two necessary for reduction to the corresponding amine (Equation III.7). Hydrolysis of the nitrile-hydride

$$\begin{tikzcd} CH_3(CH_2)_4CN + 2LiBHEt_3 \arrow[r, "\times" marking] & (CH_3(CH_2)_5N(BEt_3)_2)^{2-}Li_2^{2+} \arrow[d, "H_2O"] \\ & CH_3(CH_2)_5NH_2 \end{tikzcd}$$

III.7

reaction intermediate however does not yield the expected aldehyde, resulting from the addition of one B-H unit across the nitrile function, but an equimolar amount of unreacted nitrile and fully reduced amine (Equation III.8) (71). Such behaviour of an aliphatic nitrile

$$\mathrm{RCN} + \mathrm{LiBHEt_3} \xrightarrow{\mathrm{THF},\ 25^{\circ}\mathrm{C}} \xrightarrow{\mathrm{H_2O}} \qquad \mathrm{III.8}$$

$$\tfrac{1}{2}\mathrm{RCN} + \tfrac{1}{2}\mathrm{RCH_2NH_2} + \mathrm{BEt_3} + \mathrm{LiOH}$$

towards a trialkylborohydride is in marked contrast to that of nitriles towards lithium triethoxyaluminium hydride, $\mathrm{LiAlH(OEt)_3}$ (82). Reaction of equimolar amounts of RCN and $\mathrm{LiAlH(OEt)_3}$ will result in almost quantitative production of aldehyde, RCHO, upon hydrolysis, while reaction with two equivalents of $\mathrm{LiAlH(OEt)_3}$ will yield the amine, $\mathrm{RCH_2NH_2}$, upon hydrolysis (Equations III.9,10)

$$\mathrm{RCN} + \mathrm{LiAlH(OEt)_3} \xrightarrow{\mathrm{ether}} \xrightarrow{\mathrm{H_2O}} \mathrm{RCHO} +$$

$$\mathrm{LiOH} + \mathrm{Al(OEt)_3}$$

III.9

$$\mathrm{RCN} + 2\mathrm{LiAlH(OEt)_3} \xrightarrow{\mathrm{ether}} \xrightarrow{\mathrm{H_2O}} \mathrm{RCH_2NH_2} +$$

$$2\mathrm{LiOH} + 2\mathrm{Al(OEt)_3}$$

III.10

In contrast to the behaviour of capronitrile towards $\mathrm{LiBHEt_3}$, benzonitrile will react with one equivalent of the borohydride to yield the expected aldehyde, PhCHO (Equation III.11) (71), while reaction with an excess

$$PhCN + LiBHEt_3 \longrightarrow \xrightarrow{H_2O} PhCHO + LiOH + BEt_3 \qquad \text{III.11}$$

of $LiBHEt_3$ will proceed smoothly to the formation of the amine (Equation III.12). Elsewhere (83) the reactions

$$PhCN + X.S.LiBHEt_3 \longrightarrow \xrightarrow{H_2O} Ph_2CH_2NH_2 \qquad \text{III.12}$$

of both lithium, and sodium, triethylborohydride with the nitriles ^tBuCN, PhCN and cyclo-$C_6H_{11}CN$ have been investigated in toluene solution. In each case reaction of the nitrile with one equivalent of $LiBHEt_3$ resulted in the formation of the iminoborate species (Equation III .13), which could be isolated as a solid material

$$RCN + MBHEt_3 \xrightarrow{\text{toluene}} (RCH{=}N(BEt_3)M)_n \qquad \text{III.13}$$

$R = {}^tBu, Ph, cyclo\text{-}C_6H_{11};\ M = Li, Na$

in the case of the sodium derivatives, and as a viscous liquid in the case of the lithium species.

In the course of the present study the reaction between a T.H.F. solution of $LiBHEt_3$ and acetonitrile was investigated in order to establish whether a similar mode of reaction was displayed to that observed in the case of the longer chain aliphatic nitrile, capronitrile (71). Reactions between $LiBHEt_3$ and the nitriles ^tBuCN and PhCN in T.H.F. were also investigated, in an attempt to isolate crystalline lithium iminoborate derivatives and hence investigate the nature of the bonding mode adopted by the imino ligand, RCH=N-, in such systems.

The reactivity of the iminoborate derivatives, $RCH=N(BEt_3)Li$ ($R={}^tBu$, Ph), towards phosphorus trichloride was also studied.

Reaction of Lithium triethylborohydride and Acetonitrile in T.H.F.

One equivalent of acetonitrile underwent a mildly exothermic reaction with a T.H.F. solution of $LiBHEt_3$ at room temperature. No gas was evolved during the course of the reaction, which was apparently complete after a few minutes stirring. Subsequent removal of the T.H.F. solvent, by pumping at room temperature, yielded a colourless, air sensitive, and extremely viscous oil-like material; analysis suggested it comprised a mixture of reactant components corresponding to the stoichiometric ratio; CH_3CN : $LiBHEt_3$: 3 T.H.F. The material underwent slow decomposition at room temperature and under inert atmosphere, the odour of triethylborane above the oil becoming increasingly more noticeable after a few hours, while pumping on the oil under high vacuum for extended periods of time resulted in the loss of further quantities of BEt_3 in addition to some T.H.F. No solid material was recovered from the reaction, either during the course of attempts at crystallisation, or following pumping under vacuum for a total period of two weeks.

The hydrolysis of freshly prepared 10 mmol. samples of the oil was effected by the addition of 5 cm^3 aliquots of a 1:1, dilute acid : T.H.F., solution and shaking of the mixture, no evidence of gas formation being observed. The products were separated, following neutralisation, on a gas chromatography column. Successive 2μdm^3 samples of the mixture, standardised as 1M solutions in terms of the original reactants, were syringed onto the chromatography column (2½% S.E., 8' x ⅛", inlet port 30°, column 30°) and the separate fractions measured by a hot wire detector as they emerged from the column. Three components, in addition to the T.H.F. solvent, were separated and identified (in order of emission from the column) as ethylamine, $CH_3CH_2NH_2$, triethylborane, BEt_3, and acetonitrile, CH_3CN, by comparison with authentic samples. The intetgrated peak values determined from the chromatograph chart recorder trace, and corresponding to the three hydrolysis components, were measured in each of five separate runs and are listed in Table III.1. The corrected average molar ratio of $CH_3CH_2NH_2$: BEt_3 : CH_3CN, calculated as 0.46 : 0.98 : 0.51, would seem to parallel the results of an earlier study (71) of the hydrolysis products resulting from the reaction of capronitrile, where equimolar amounts of amide and nitrile were recovered. On the basis of this evidence a reaction mechanism was proposed (71) involving attack of two $BHEt_3^-$ units on the aliphatic nitrile (Equation III.13) to form an unstable species, A, which subsequently undergoes reaction with a second nitrile molecule to form the species B and C. Upon hydrolysis B will yield the amine (Equation III.15) while

TABLE III.1. Chromatograph peak integral values for hydrolysis solution aliquots.

Sample (2 dm^3)	Peak Integral (a)		
	$CH_3CH_2NH_2$	BEt_3	CH_3CN
Hydrolysis aliquot 1	274	684	362
" " 2	293	683	350
" " 3	269	659	351
" " 4	277	705	384
" " 5	301	695	388
Mean Values	282.8	681.2	367.0
1 molar $CH_3CH_2MH_2$	619	-	-
1 molar BEt_3	-	695	-
1 molar CH_3CN	-	-	720
Corrected average molar ratios	0.46	0.98	0.51

(a) Arbitrary units.

$$RCH_2CN + 2LiBHEt_3 \longrightarrow (RCH_2CH_2N(BEt_3)_2)^{2-}(Li)^{2+}$$

(A)

R=H,alkyl

$$\Big\downarrow RCH_2CN$$

$$(RCH_2CH_2NH(BEt_3))^{-}(Li)^{+} \qquad III.14$$

(B) +

$$(RCH{=}C{=}N(BEt_3))^{-}(Li)^{+}$$

(C)

$$(B) + H_3O \longrightarrow RCH_2CH_2NH_2 \qquad III.15$$

$$(C) + H_2O \longrightarrow RCH_2CN \qquad III.16$$

C will hydrolyse and rearrange to form the original nitrile (Equation III.16).

Further evidence supporting the proposed mechanism can be seen in the infra red spectrum of the viscous oil. A single, weak, absorption, at 3370 cm^{-1}, would be consistant with the ν(N-H) stretching frequency of a secondary amine (84) derivative such as species B, while there was no evidence of the ν(C=N) absorption of a linear, or bent $RCH{=}NMX_n$ type linkage. A second absorption in the infra red, at 2125 cm^{-1}, is somewhat lower than the ν(C≡N) stretching frequency of free acetonitrile, at 2256 cm^{-1}, and would be consistent with the asymmetric ν(C=C=N) vibration of species C, although of somewhat higher frequency than that observed for the compound $Ph_2C{=}C{=}NMe$, at 1998 cm^{-1}(85). An alternative assignment, in terms of the ν(C≡N) stretch of a coordinated nitrile function, $RC\equiv\overset{+}{N} \rightarrow \overset{-}{M}X_n$, would seem unlikely, as the coordination of nitriles to Lewis acids, MX_n, is almost invariably associated with an increase in the ν(C≡N) stretching frequency (86-89).

A satisfactory ^1H n.m.r. spectrum of the oil product could not be obtained, due both to the complexity of the system involved, and also the tendency of the material to form colloidal suspensions in non-reactive n.m.r. solvents. The ^{11}B n.m.r. spectrum of a neat sample displayed two fairly broad, and incompletely resolved, peaks at δ -13.1 and -14.8 upfield from the BF_3OEt_2 reference, which would be consistent with a boron coordination state of four (67). The observed values are listed in Table III.2 together with those of some analogous, or related compounds.

TABLE III.2 ^{11}B n.m.r. shifts of some N-bonded, four coordinate, boron compounds, and related species

Compound	$\delta\,^{11}B$(a)	Ref.
$(CH_3CH_2NHBEt_3)^-Li^+$	-13.1, -14.8	(b)
$(CH_2{=}C{=}NBEt_3)^-Li^+$		(b)
$^tBuCH{=}N(BEt_3)Li(3.T.H.F.)$	-6.1	(b)
$PhCH{=}N(BEt_3)Li(3.T.H.F.)$	-6.1	(b)
$LiBHEt_3$	-10.2	(b)
$(Et_3BNH_2)^-Na^+$	-9.8	67
$(Ph_3BNH_2)^-Li^+$	-6.0	67
$Et_3BN(H){=}C(NMe_2)Me$	-6.7	90
$(Et_3B{-}C\equiv CH)^-li^+$	-17.3	91

(a) Shifts measured relative to an external reference of $Et_2O.BF_3$. Higher field shifts are negative.

(b) This work.

A reaction between acetonitrile and two molar equivalents of $LiBHEt_3$ in T.H.F. resulted in uptake of only one equivalent of $LiBHEt_3$, as confirmed by measurement of the volume of hydrogen evolved upon hydrolysis of the reaction mixture. Removal of solvent from a repeat experiment yielded a colourless, viscous, oil of similar appearance to that resulting from the 1:1 reaction. The infra red spectrum of the oil was essentially similar to that obtained from the 1:1 reaction product, with the additional feature of a broad peak at c.a. 1948 cm^{-1}, attributable to the ν(B-H) stretching vibration of free $BHEt_3^-$ (72).

Reactions of Lithium triethylborohydride with t-Butyl cyanide and Benzonitrile in T.H.F.

The addition of equimolar amounts of either t-butylcyanide or benzonitrile to a T.H.F. solution of $LiBHEt_3$ at room temperature results in a mildly exothermic reaction which is apparently complete after a few minutes. Removal of T.H.F. solvent from the resulting solutions yielded viscous oil-like materials, colourless in the case of the t-butyl derivative and straw-coloured in the phenyl case. Neither material could be crystallised from a range of non-reactive organic solvents, the compounds either remaining in solution (ether solvents, toluene), or remaining largely immiscible (alkanes). (N.B. Addition of chloroform to either material results in a spontaneous and violent reaction which could be potentially dangerous). Elemental analysis of the oils suggested them to be the iminoborate derivatives $RCH{=}N(BEt_3)Li(3.T.H.F.)$, ($R={}^tBu,Ph$), which was further confirmed by the presence of ν(C=N) stretching vibrations in their infra red spectra, at 1658 cm^{-1} and 1634 cm^{-1} respectively. Base hydrolysis of the materials, followed by neutralisation and fractionation, yielded the corresponding aldehydes (Equation

III.17), the modes of formation and hydrolysis thus being

$$\begin{tikzcd} \mathrm{LiBHEt_3 + RCN} \arrow[r] & \mathrm{RCH{=}N(BEt_3)Li} \arrow[d, "\mathrm{OH^-}"] \\ & \mathrm{RCHO + BEt_3 + LiOH} \end{tikzcd} \qquad \text{III.17}$$

$R={}^{t}Bu$, Ph

markedly different from those of the aliphalic nitriles described earlier (Equation III.14).

An attempt to replace the coordinating T.H.F. ligands around lithium with a tridentate chelating ligand was unsuccessful, the addition of pentamethyldiethylenetriamine to the compound ${}^{t}BuCH{=}N(BEt_3)Li$, and subsequent removal of solvent, yielding an oily material which could not be crystallised and whose infra red spectrum still contained the ν (C-O) absorption of coordinated T.H.F., at 1048 cm^{-1}. A second reaction between the lithium-chelated triethylborohydride compound $Li(TMED)_2BHEt_3$, (TMED = tetramethylethyleneadiamine), and benzonitrile in T.H.F. yielded an oil-like product which again contained T.H.F., and from which quantities of TMED could be removed by pumping under vacuum.

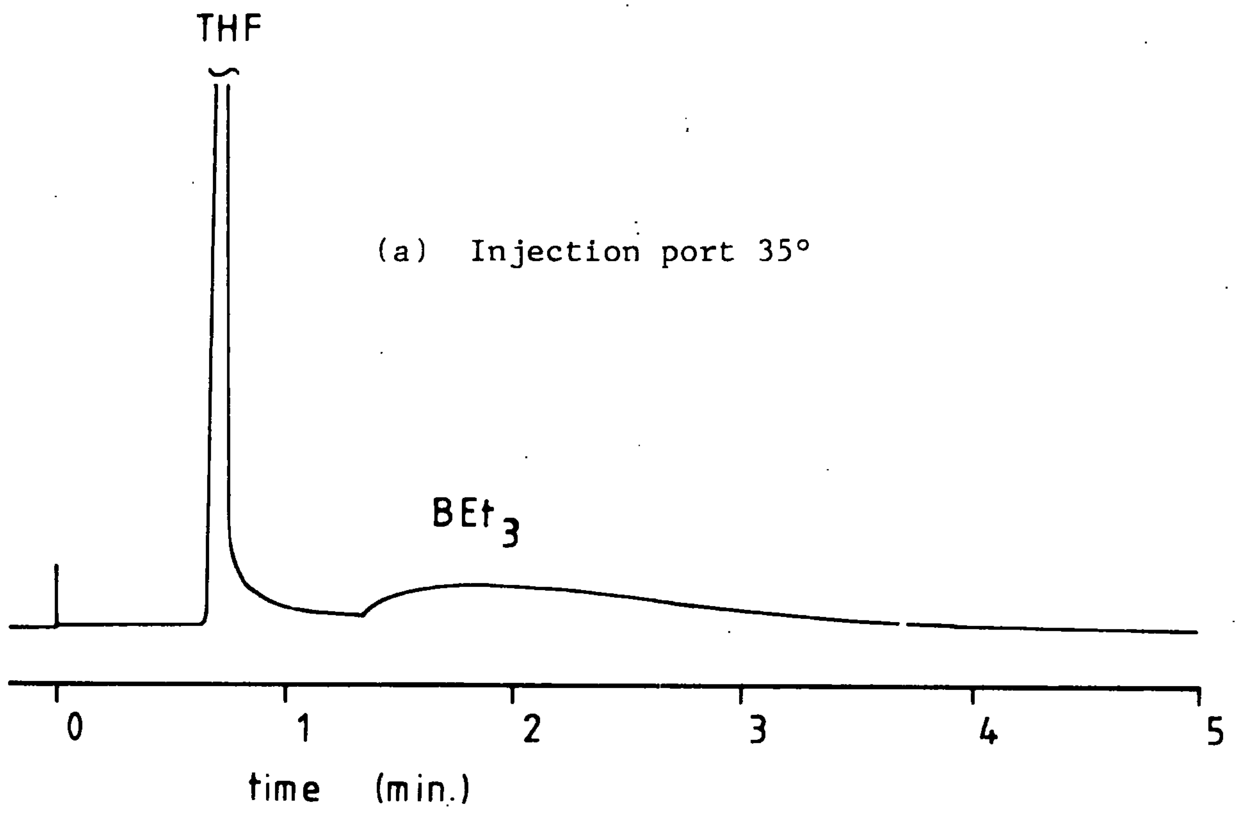
Both iminoborates suffered slow decomposition at room temperature under inert atmosphere, the odour of triethylborane over the materials becoming increasingly more pronounced with time. The decomposition was further investigated by a method similar to that described by

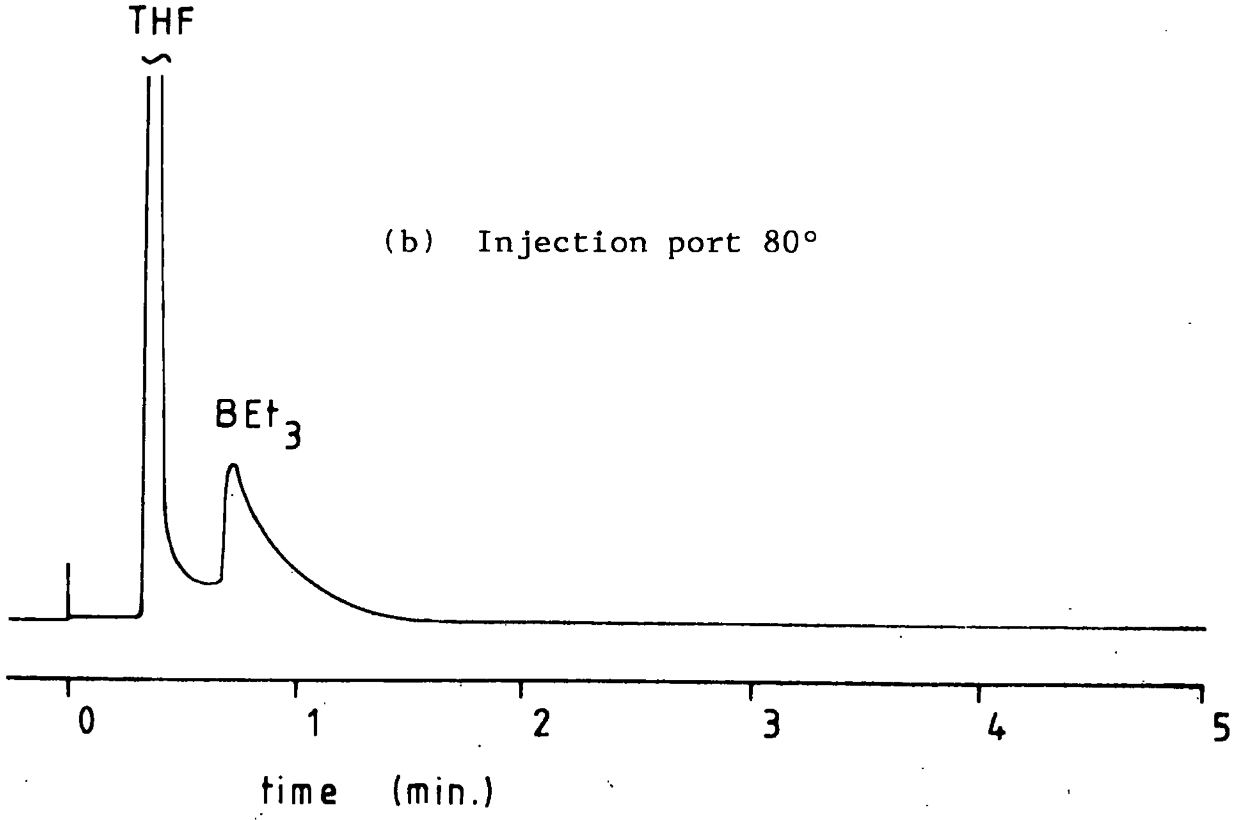
Brown and co-workers (71) and used to determine the extent of "borane-ate" complex formation in the products resulting from the reaction of a number of alcohols with $LiBHEt_3$ in T.H.F. (Equation III.18). The workers took freshly

$$\begin{tikzcd}
 & \mathrm{RCOLi + BEt_3 + H_2} & \\
\mathrm{ROH + LiBHEt_3} \arrow[ur] \arrow[dr] & & \mathrm{III.18} \\
 & \mathrm{(RCOBEt_3)^{-}Li^{+} + H_2} &
\end{tikzcd}$$

prepared samples of the reaction products, syringed them onto the inlet port of a gas chromatography column, and recorded the shape of the triethylborane peak on the chart print-out. A sharp symmetrical peak, similar to that obtained from a reference solution of BEt_3 in T.H.F., was taken as being indicative of essentially uncoordinated BEt_3 in the reaction mixture, while broadening and "tailing" of the peak was interpreted as being due to the formation of a borate-type complex in solution, and its subsequent slow decomposition, with loss of BEt_3, on the injection port of the column. The results obtained in the present study for the iminoborate species $RCH=N(BEt_3)Li$ ($R={}^tBu$, Ph) were essentially identical to each other and are illustrated, for the case of the t-butyl derivative, in Figure III.1. With an injection port temperature of 35°, the peak due to BEt_3 in the iminoborate solution appeared as a weak signal with extensive tailing when compared with that of the reference, this being indicative of a fairly strong borate complex undergoing slow decomposition. Raising of the injection

FIGURE III.1 Chromatograph traces from T.H.F. solutions of $^{t}BuCH=N(BEt_3)Li$





port temperature to 80°, however, resulted in a more intense BEt_3 peak, with less evidence of tailing, and indicated a more rapid rate of decomposition at the higher temperature.

The instability of the iminoborate derivatives, $RCH{=}N(BEt_3)Li$ ($R{=}{}^tBu$, Ph), with respect to loss of triethylborane, explains the failure to isolate these compounds as solid materials. Similar viscous oils $(RCH{=}N(BEt_3)Li)_n$ ($R{=}{}^tBu$, Ph, cyclo-C_6H_{11}), again unstable with respect to loss of BEt_3, were obtained from the reaction of lithium triethylborohydride and the corresponding nitrile in toluene (83), while the sodium salts $(RCH{=}N(BEt_3)Na)_n$, prepared from $NaBHEt_3$, were isolated as solids which only underwent loss of BEt_3 upon heating under vacuum.

A further series of compounds, the sodium iminoluminates, $(RCH{=}N(AlEt_3)Na)_n$ ($R{=}{}^tBu$, Ph, cyclo-C_6H_{11}) were also isolated as solids and did not lose Et_3Al upon heating (92), while it was noted, without explanation, that cryoscopic measurements on both these and also the sodium iminoborate derivatives suggested them to be dimeric in benzene solution. This latter observation could be accounted for in terms of the compounds adopting a structure such as that outlined in Figure II.2(a); the alkali metals involved in electron deficient bridging of the imino ligands, to which the trialkylborane, and -alane, groups are coordinated.

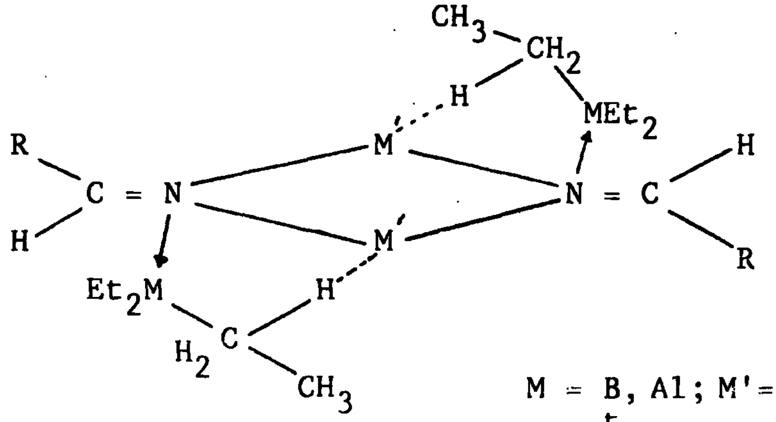
Such a conformation would, additionally, allow the possibility of M-bonded CH_2-hydrogen interactions with the formally valence-unstaturated alkali metal atoms, although no

FIGURE II.2

Proposed structures for the compounds

$(RCH{=}N(MEt_3)M')_2$ and $RCH{=}N(BEt_3)Li(3.T.H.F.)$

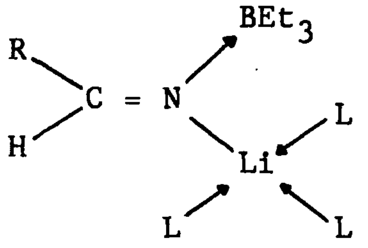
(a)



M = B, Al; M'=Li, Na

R = ^{t}Bu, Ph, cyclo-C_6H_{11}

(b)



L = T.H.F.

R = ^{t}Bu, Ph.

evidence for this is observed in the reported (83) ^{1}H n.m.r. spectra. The characterisation of the lithium iminoborates, prepared during the course of the present work,would suggest them to have structures such as outlined in Figure II.2(b), where the lithium atom, coordinated to three T.H.F. ligands, has a full valence shell and consequently no need to undergo dimerisation. A similar monomeric conformational form has been established crystallographically for the nickel iminoborate ^{t}Bu CH=N(BEt$_3$)NiEt(bipy) (93).

Bonding considerations will also explain the observed differences in stability of the iminoborate and iminoaluminate complexes towards loss of the corresponding Et_3M species. Triethylaluminium is a stronger Lewis acid than triethylborane, and it is therefore not surprising that the sodium iminoaluminates will not undergo loss of Et_3Al, even under forcing conditions. The relative stability of the sodium and lithium iminoborates, by comparison, may be explained in terms of the relative polarity of the alkali metal-nitrogen bond. A nitrogen-sodium bond will be considerably more ionic, and hence polar, in character than the more covalent nitrogen-lithium bond, with a resulting increase in the negative charge, δ -, associated with the nitrogen atom. This greater δ - charge on nitrogen will produce an enhancement of its ability to form a dative bond with the more electropositive boron atom, and thus result in the formation of a more stable donor-acceptor complex. By contrast, di-t-butylmethyleneamino lithium, $^tBu_2C{=}NLi$, known to exist as a hexameric species in some solvents (12), showed no inclination to form an analogous borate complex when reacted with one equivalent of triethylborane, although consideration of the conformation of such a hypothetical species suggests it would be a sterically very crowded molecule.

The stretching frequencies $\nu(C{=}N)$ of the two complexes $RCH{=}N(BEt_3)Li(3.T.H.F.)$ ($R{=}^tBu$, Ph) are listed in Table III.3. together with those of the corresponding dimeric sodium and lithium salts, prepared in toluene. Also listed, for comparison purposes, are the ν (C=N) frequencies of the iminosilane derivatives $RCH{=}NSiMe_3$ and iminoborane dimers $(RCH{=}NBEt_2)_2$. The observed ν (C=N) frequencies of the two presumed monomeric iminoborate derivatives discussed in this chapter are similar, although not identical, to both the corresponding iminoborates, $(RCH{=}N(BEt_3)Li)_2$ and iminoboranes, $(RCH{=}NBEt_2)_2$, as well as the monomeric iminosilanes $RCH{=}NSiMe_3$; the latter presumed to contain a bent CNSi unit in consequence of the coordinative saturation of the silicon atom (see chapter 1). In view of this

TABLE III.3

ν(C=N) stretching frequencies of some lithium-, and sodium-, iminoborates, and related compounds.

Compound	Phase	ν(C=N)cm^{-1}	Ref.
$^tBuCH{=}N(BEt_3)Li(3.T.H.F.)$	liq. film	1658	(a)
$PhCH{=}N(BEt_3)Li(3.T.H.F.)$	liq. film	1634	(a)
$(^tBuCH{=}N(BEt_3)Li)_2$	liq. film	1665	83
$(PhCH{=}N(BEt_3)Li)_2$	liq. film	1645	83
$(^tBuCH{=}N(BEt_3)Na)_2$	KBr disc	1660	83
$(PhCH{=}N(BEt_3)Na)_2$	KBr disc	1610	83
$(^tBuCH{=}NBEt_2)_2$	KBr disc	1663	(b)
$(PhCH{=}NBEt_2)_2$	KBr disc	1640	(b)
$^tBuCH{=}NSiMe_3$	liq. film	1676	94
$PhCH{=}NSiMe_3$	liq. film	1645	94

(a) This work

(b) This work, chapter 2.

it would not seem possible to draw any clear conclusions concerning the bonding mode of the imino ligands in the borate derivatives discussed in this chapter, beyond noting that the ν(C=N) frequencies would seem to be consistent with the proposed structures outlined in Figure II.2(b).

The ^{11}B n.m.r. chemical shifts of the two compounds $RCH=N(BEt_3)Li(3.T.H.F.)$ were measured against an external reference of BF_3OEt_2. Both occurred as identical, rather broad upfield peaks at δ = -6.1, and would seem to be compatible with a trialkylborane/nitrogen-ligand donor complex on the basis of a comparison with similar compounds (67). (See Table III.2).

Reactions of Lithium t-butyl-, and phenyl- methyleneaminoborates with Phosphorus trichloride.

With the exception of studies on their hydrolysis products (71), there have been only two reports concerning the reactive chemistry of the iminoborates $RCH=N(BEt_3)M$ (R=^{t}Bu, Ph, cyclo-C_6H_{11}; M=Li, Na). The reaction of an iminoborate and an equimolar amount of trimethylchlorosilane, Me_3SiCl, has been shown (94) to yield the iminotrimethylsilane derivative (Equation III.19) with consequent

$$RCH=N(BEt_3)M + Me_3SiCl \xrightarrow{T.H.F.} RCH=NSiMe_3 + MCl + BEt_3 \qquad III.19$$

R=^{t}Bu,Ph,cyclo-C_6H_{11}; M=Li, Na

elimination of MCl and BEt_3. By contrast, the analogous reaction between the sodium iminoaluminate derivatives and Me_3SiCl (94) did not yield the expected iminosilane but rather the associated iminoalane, $(RCH{=}NAlEt_2)_2$, together with trimethylethylsilane (Equation III.20),

$$\begin{aligned} RCH{=}N(AlEt_3)Na + Me_3SiCl \rightarrow \tfrac{1}{2}(RCH{=}NAlEt_2)_2 &+ NaCl \\ &+ Me_3EtSi \end{aligned} \qquad \text{III.20}$$

$R = {}^tBu$, Ph, cyclo-C_6H_{11}

and was accounted for in terms of the energetically more favourable formation of Al-N, rather than Si-N, σ bonds (93). A second, rather unusual, reaction has been reported (93) involving two equivalents of the sodium iminoborates, $RCH{=}N(BEt_3)Na$ ($R={}^tBu$,Ph) and either $NiBr_2$ or $Ni(acac)_2$,

$$\begin{tikzcd} & (RCH{=}N)_2Ni(bipy) + 2Et_3B + 2NaX_2 \\ 2RCH{=}N(BEt_3)Na + NiX_2 + bipy \arrow[ur, "+" marking] \arrow[dr] & \\ & RCH{=}N(BEt_3)Ni(Et)bipy + \tfrac{1}{2}(RCH{=}NBEt_2)_2 + 2NaX \end{tikzcd} \qquad \text{III.21}$$

$R={}^tBu$, Ph; X=Br,acac

in the presence of 2,2'bipyridine. When conducted in benzene solution the reactions yielded, not the expected bis(methyleneamino)nickel species, but bipyridine (methyleneaminoborate)nickel complexes (Equation III.21) as demonstrated crystallographically.

The present study involved an investigation of the reactions of phosphorus trichloride, PCl_3, with various stoichiometric ratios of the iminoborates $RCH{=}N(BEt_3)Li$ ($R{=}{}^tBu$, Ph) in T.H.F., with the aim of synthesising compounds of the form $(RCH{=}N)_nPCl_{3-n}$. Earlier work (3) has shown that the reaction of appropriate stoichiometric ratios of diaryl-, or dialkyl-, methyleneaminolithium reagents, $R_2C{=}NLi$ (R=aryl, ${}^tBu$), with PCl_3 yields compounds of the form $R_2C{=}NPCl_2$ (R=aryl, ${}^tBu$) and $(R_2C{=}N)_3P$ (R=aryl), while the synthesis of the compound $({}^tBu_2C{=}N)_3P$ is described elsewhere in this thesis (Equations III.22,23).

$$R_2C{=}NLi + PCl_3 \longrightarrow R_2C{=}NPCl_2 + LiCl \qquad III.22$$
($R{=}{}^tBu$, Ph, p-tolyl)

$$3R_2C{=}NLi + PCl_3 \longrightarrow (R_2C{=}N)_3P + 3LiCl \qquad III.23$$
($R{=}{}^tBu$, Ph, p-tolyl)

By contrast, attempts to synthesise bis(imino)phosphorus chlorides ($R_2C{=}N)_2PCl$, either by reaction of appropriate proportions of iminolithium and phosphorus trichloride, or the mixing of equimolar quantities of the tris- and mono- iminophosphines, were unsuccessful (3).

The reaction of three molar equivalents of iminoborate, $RCH{=}N(BEt_3)Li$ ($R{=}{}^tBu$,Ph), and PCl_3 in T.H.F. proceeds at below 0° to form the expected tris(methyleneamino) phosphines (Equation III.24), which were fully characterised.

$$3RCH{=}N(BEt_3)Li + PCl_3 \longrightarrow (RCH{=}N)_3P + 3BEt_3 + 3LiCl \qquad III.24$$

$R{=}{}^tBu$, Ph

Both compounds were yellow solids, apparently monomeric, on the basis of their mass spectra, and suffered decomposition on exposure to moist air. Both also showed evidence of gradual decomposition when heated, neither compound having a sharp melting point. The mild conditions required for the formation of the t-butyl derivative $(^{t}BuCH{=}N)_3P$, are in marked contrast to the considerably more forcing ones (reflux in 100° - 120° pet. ether for 24 hours) required for the preparation of the di-t-butyl analog, $(^{t}Bu_2C{=}N)_3B$, and indicate the lower steric requirements of the imino ligands in the former case.

Attempts to isolate iminophosphines from the reaction of 2:1 and 1:1 stoichiometric ratios of iminoborate and phosphorus trichloride were unsuccessful. The 1:1 reactions of $RCH{=}N(BEt_3)Li$, ($R{=}^{t}Bu$, Ph) and PCl_3 do, apparently, yield the desired iminophosphines in T.H.F. solution, removal of the solvent under vacuum yielding sticky orange masses whose infra red spectra contained absorptions at 1666 cm^{-1} ($R = ^{t}Bu$) and 1629 cm^{-1} (R = Ph). Extraction of the materials with toluene, and subsequent attempts of the vacuum distillation of the resulting oils, however, resulted in their decomposition, HCl being liberated in both cases. Elemental analysis of the oils suggested the presence of only small quantities of triethylborane, while the ^{31}P n.m.r. spectra were consistent with a three coordinate phosphorus environment. Analysis of the decomposition products failed to yield consistent results, although the samples again contained small quantities of boron, while a chlorine analysis of between 5% and 10% in each case is consistent with the observed loss of HCl during decomposition. The 2:1 reactions of iminoborate and phosphorus trichloride did not yield the bis(imino)phosphorus chloride species $(RCH{=}N)_2PCl$ ($R={}^tBu$, Ph), although it was again not possible to isolate characterisable products. The ^{31}P n.m.r. spectra of the reaction solutions however both contained two peaks, attributable to the mono- and tris- iminophosphines, and presumably resulting from the disproportionation of the bis(imino) species (Equation III.25). Elsewhere methyleneamino(chloro)-derivatives of boron (38,94), aluminium (94), silicon (96-98) and germanium (96) have also been found to be unstable with respect to similar disproportionation reactions.

$$2(RCH{=}N)_2PCl \longrightarrow (RCH{=}N)PCl_2 + (RCH{=}N)_3P \qquad (R = {}^tBu,\ Ph) \qquad \text{III.25}$$

The ν (C=N) infra red vibration frequencies of the four mono-t-butyl-, and monophenyl-, methyleneaminophosphines are listed in Table III.4 together with those of the analogous di-t-butyl and diphenyl derivatives. With the exception of $^tBuCH{=}NPCl_2$, all the mono-t-butyl-, and monophenyl-, derivatives have higher ν (C=N) frequencies than the corresponding di-t-butyl-, and diphenyl-, compounds, while in each case the phenyl derivative absorbs at a lower frequency than the analogous t-butyl compound. Similar lower ν (C=N) frequencies

TABLE III.4

ν(C=N) stretching frequencies of some methyleneamino derivatives of phosphorus (III)

Compound	Phase	R=Ph	R=^{t}Bu	Ref.
RCH=NPCl_2 (a)	liq. film	1629	1666	(b)
R_2C=NPCl_2	KBr disc	1620	1678	3
$(RCH=N)_3P$	nujol mull	1611	1647	(b)
$(R_2C=N)_3P$	nujol mull	1580	1623	(b),3

(a) Crude products

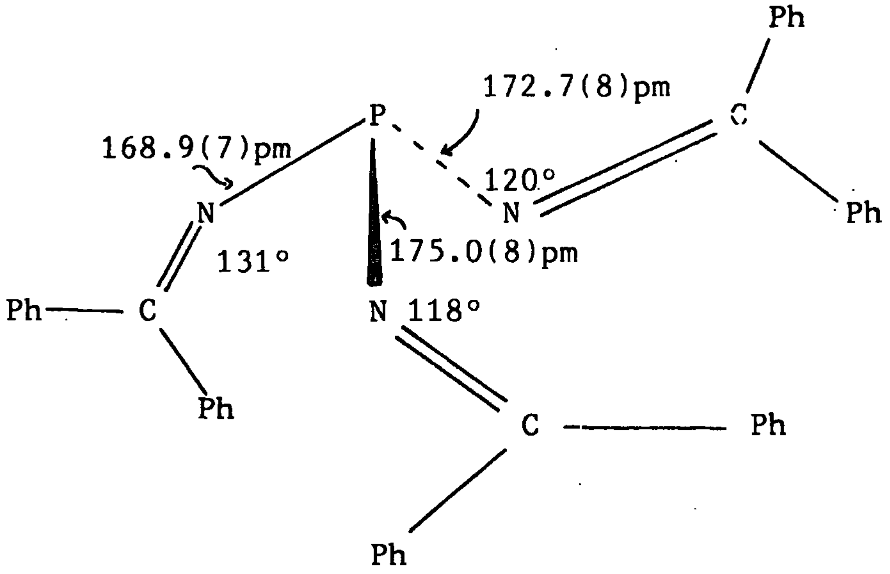
(b) This work

of phenyl derivatives have been observed in related methyleneamino- boron (38,95), aluminium (95), silicon (97), and germanium compounds (96), and have been attributed to conjugation of the phenyl and C=N π orbitals, resulting in a weakening of the C=N bond.

Earlier attempts to predict the $\widehat{PNC}$ bond angle, and its implication for the extent of P(d) - N(p) dative π bonding, were made on the basis of the ν(C=N) stretching frequencies of the di-t-butyl, and diphenyl, derivatives, R_2C=NPCl_2 and $(R_2C=N)_3P$ (3,99). Comparison with the corresponding ν(C=N) frequencies of some related iminosilanes, $(R_2C=N)_nSiR'_{3-n}$ (R=alkyl,aryl; R'=alkyl,aryl, halogen) (96-98) suggested the phosphorus compounds contain bent PNC linkages similar to those of the silanes, where an average $\widehat{CNSi}$ bond angle of 137.1° was measured for the compound $(Ph_2C=N)_4Si$(4). Such a bond angle, representing a significant increase over that of 120° associated with a pure sp^2 hybridisation of the orbitals around nitrogen, was taken as evidence for the existence of Si(d)-N(p)π bonding in these systems, the greater degree of linearity being more favourable for such interactions. A later structural determination of the compound $(Ph_2C=N)_3P$ (3), however, yielded values for the $C\hat{N}P$ bond angles, and PN bond lengths, as outlined in Figure III.3. This

FIGURE III.3

The molecular structure of $(Ph_2C=N)_3P$



confirmed the PNC linkages as being bent (average angle 123°) while the phosphorus occupies an almost pyramidal coordination environment in the molecule. Interestingly, one of the $C\hat{N}P$ angles (130.8°) is significantly larger than the other two (118.1° and 120.1°), and the ligand involved, is attached to phosphorus by a slightly shorter P-N bond length. Similar variations in the bond angles were observed in the case of $(Ph_2C=N)_4Si$ (4), although the average bond angle of 123°, and essentially pyramidal phosphorus environment, in $(Ph_2C{=}N)_3P$, would tend to suggest that the $P(d)$-$N(p)$ π interaction in this instance is only slight. It would therefore seem likely, on the basis of the infra red data, that the mono-t-butyl and monophenyl derivatives prepared during the course of the present study have molecular skeletons similar to those established for the dialkyl and diaryl derivatives, $(R_2C{=}N)PCl_2$ and $(R_2C{=}N)_3P$.

The ^1H n.m.r. spectra of the four iminophosphines were obtained from samples dissolved in C_6D_6 and are summarised in Table III.5. together with those of the analogous $(R_2C{=}N)_3P$ and $R_2C{=}NPCl_2$ compounds ($R{=}^tBu$, Ph) (3). Spectra of the monoiminophosphines $RCH{=}NPCl_2$ were obtained from crude reaction samples and their observed resonances may be slightly affected by the presence of by-product impurities. Particular attention was directed towards the signals due to the carbon-bonded groups R($R{=}^tBu$, Ph) in an attempt to find evidence for structural isomerism in such compounds. In principle a non-linear RCH=N-P linkage could display structural isomerism arising from two sources; (i) inversion about the nitrogen atom (Figure II.4(a) or (ii) the carbon-bonded group R occupying a position either syn or anti with respect to the lone pair on the phosphorus atom (Figure II.4(b)). In such cases the carbon-bonded substituents would occupy magnetically dissimilar environments from each other and, assuming the inversion process to be slow on the

TABLE III.5

^{1}H n.m.r. shifts for some Phosphorus (III) imino derivatives

Compound	$\underset{H}{\diagup}\overset{\diagdown}{C}=$(a)	^{t}Bu(a)	Aromatic	Ref.
^{t}BuCH=NP Cl_2	2.78(t)J=14Hz	8.72(s)	-	(b)
$^tBu_2$C=NP Cl_2	-	8.66(s)	-	3
PhCH=$NPCl_2$	(c)	-	2.62-2.89	(b)
Ph_2C=NP Cl_2	-	-	2.51-2.77	3
(^{t}Bu CH=N)$_3$P	2.68(t)J=14Hz	8.63(s)	-	(b)
($^tBu_2$C=N)$_3$P	-	8.57(s)	-	(b)
(Ph CH=N)$_3$P	(c)	-	2.40-2.81	(b)
(Ph_2C=N)$_3$P	-	-	2.37-2.79	3

(a) Chemical shifts, τ , expressed as p.p.m.; TMS=10.00.

(b) This work

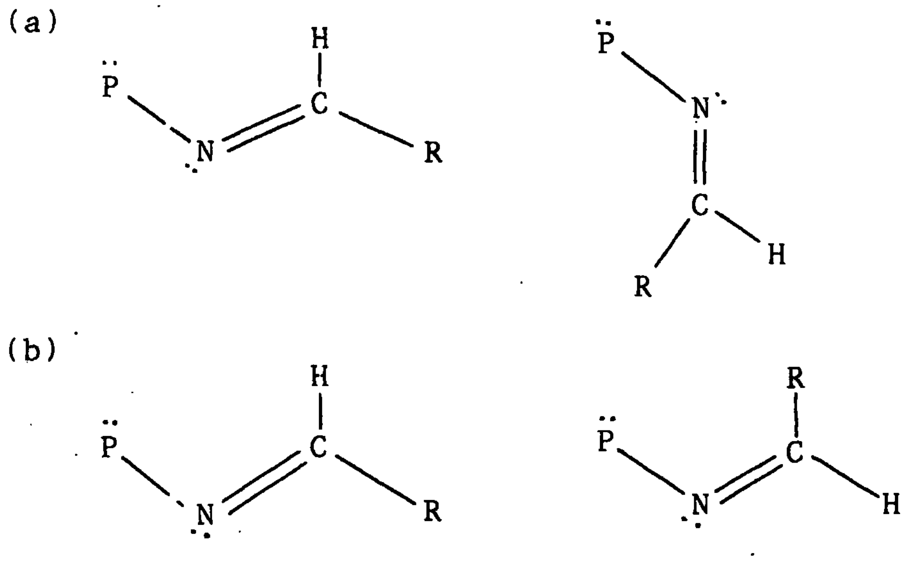
(c) Signal not located

(s) Singlet

(t) Triplet

FIGURE III.4

Possible structural isomerism in bent P-N=CHR linkages



n.m.r. timescale, it should be possible to distinguish these differing conformations by the resultant splitting of the substituent proton signals in their ^1H n.m.r. spectra. A number of studies have demonstrated that such nitrogen substituent inversion processes occur in solution (100 - 105), the compound $^tBu_2C=NH$, for example, displaying two separate ^tBu signals in the ^1H n.m.r. below -30° (105) attributable to the freezing out of the N-H inversion, while the changing of conformation about the C=N bond has been reviewed (106) and studies on the mechanism carried out (107). In practice however, no evidence for such structural isomerism was found in the n.m.r. spectra of any of the compounds described in this section, when run at 30°. Both mono-t-butyl derivatives, $^tBuCH=NPCl_2$ and $(^tBuCH=N)_3P$ displayed singlet signals due to the ^tBu protons, as was also found to be the case with the di-t-butyl derivatives $^tBu_2C=NPCl_2$ (3) and $(^tBu_2C=N)_3P$. The signals arising from the aromatic protons of the phenyl derivatives were, in each instance, too ill-defined to allow conclusions to be drawn as to their equivalence, or otherwise. Unfortunately technical problems have prevented a low temperature n.m.r. study of these compound being carried out. The resonance signals due to the N=CH protons were only positively located in the case of the two t-butyl derivatives, the coincidence of the aromatic proton signals of the phenyl derivatives preventing accurate determinations in these cases. In both cases where signals were observed they appeared as weak, broad, and rather ill-defined triplets, due to coupling with the neighbouring phosphorus nucleus. The coupling constants, $^3J_{PH}$, of ca. 14 Hz are, interestingly, almost identical to the trans phosphorus-proton coupling constant of 13.62 Hz obtained from the spectrum of $P(CH=CH_2)_3$ (108,109), although this cannot be regarded as evidence of a similar conformation in the present case.

The ^{31}P n.m.r. shifts of the four mono-t-butyl, and monophenyl, derivatives are listed in Table III.6 together with those of some related compounds. All the phosphorus (III) methyleneamino derivatives have shifts to lower field than that of the external reference, 85% H_3PO_4, consistent with the expected three-coordinate phosphorus environment. The lowest field shifts within the sequence of iminophosphines are those of the imino-phosphorus dichloride derivatives, $R^1R^2C=NPCl_2$ ($R^1R^2=H,{}^tBu,Ph$) reflecting the σ inductive withdrawal of electron density from the phosphorus atom by the more electronegative chlorine atoms. Considerable differences in shift are also seen which are dependent on the nature of the carbonbonded substituents. Comparison of the shielding of the phosphorus nucleus by otherwise similar mono-, and di-, substituted imino ligands, RCH=N- and $R_2C=N$- reveals that the former have the greater shielding effect, as is particularly apparent in the case of the tris derivatives $(RCH=N)_3P$ and $(R_2C=N)_3P$. The opposite effect

TABLE III.6

^{31}P n.m.r. chemical shifts of some iminophosphines, and related compounds.

Compound	Solvent	δ p.p.m.(a)	Ref.
$^tBuCH{=}NPCl_2$	Toluene	+138.7	(b)
$^tBu_2C{=}NPCl_2$	-	(c)	3
$(^tBuCH{=}N)_3P$	Toluene	+ 29.0	(b)
$(^tBu_2C{=}N)_3P$	Toluene	+ 62.9	(b)
$^tBu_2C{=}NPPh_2$	Pentane	+ 29.1	3
$PhCH{=}NPCl_2$	Toluene	+148.4	(b)
$Ph_2C{=}NPCl_2$	Benzene	+157.2	3
$(PhCH{=}N)_3P$	Toluene	+ 37.1	(b)
$(Ph_2C{=}N)_3P$	Toluene	+ 85.5	3
$Ph_2C{=}NPPh_2$	Benzene	+ 36.5	110
$Ph_2C{=}NPPhCl$	Benzene	+ 89.6	110
Me_2NPCl_2	liquid	+166.0	111,112
$(Me_2N)_3P$	liquid	+123.0	111,112
PCl_3	liquid	+220.0	113

(a) Measured relative to an external reference of 85% H_3PO_4. Positive shifts to lower field.

(b) This work.

(c) Satisfactory spectrum not obtained.

however is seen in the ^{11}B shifts of the iminoboranes $^tBuCH{=}NB^nBu_2$ (δ =+38.8) and $^tBu_2C{=}NB^nBu_2$ (δ =+35) (37,18) and was accounted for in terms of the differing electron releasing ability of the ligands. Further, phenyl-, and diphenyl-, methyleneamino ligands deshield the phosphorus nucleus to a greater extent than the analogous t-butyl and di-t-butyl ligands. This trend, by contrast, mirrors that seen in the ^{11}B shifts of a series of compounds,

$R_2C{=}NBR'_2$ ($R{=}{}^tBu,Ph; R'{=}$alkyl,aryl) (37,38,67).

Satisfactory mass spectra were only obtained for the two tris(imino)phosphines, $({}^tBuCH{=}N)_3P$ and $(PhCH{=}N)_3P$, some of the important features being listed in Tables III.7 and III.8. Neither of the spectra contained peaks with $^m/e$ values greater than those corresponding to the monomeric molecular ions. In both cases fragmentation in the mass spectrometer involved cleavage of the P-N, P-Cl and C-R bonds, together with migration of the groups, R, from imino-carbon to phosphorus.

TABLE III.7

Major peaks in the mass spectrum of $(^{t}BuCH{=}N)_3P$

$^m/_e$	Relative Intensity	Assignment
283	27	$(^{t}BuCH{=}N)_3P$
199	12	$(^{t}BuCH{=}N)_2P$
86	80	$^{t}BuC{=}NH_2$
85	92	$^{t}BuC{=}NH$
84	100	$^{t}BuC{=}N$
60	57	^{t}Bu
57	62	PNC

TABLE III.8

Major peaks in the mass spectrum of $(PhCH{=}N)_3P$

$^m/_e$	Relative Intensity	Assignment
343	33	$(PhCH{=}N)_3P$
239	14	$(Ph\ CH{=}N)_2P$
212	12	PhCH=NPPh
106	85	$Ph\ CH{=}NH_2$
105	100	PhCH=NH
104	92	PhCH=N
77	62	Ph
57	79	PN C

CHAPTER 4

SOME MONOMERIC DI-t-BUYTYLMETHYLENEAMINO DERIVATIVES OF BORON

INTRODUCTION

This chapter describes the preparation of six monomeric di-t-butylmethyleneaminoboranes of the general form $(^tBu_2C{=}N)_nBX_{3-n}$. The results of a recent X-ray crystallographic study on one of these compounds, $^tBu_2C{=}NBPh_2$, are presented and discussed in conjunction with other theoretical and structural studies on some similar compounds. Features of the infra red, ^{11}B n.m.r., ^{13}C n.m.r., ^1H n.m.r. and mass spectra of all six iminoboranes are presented and discussed in relation to the structural findings.

Appended to this chapter are the results of a second recent crystallographic study on a related methyleneammonium derivative, $^tBu_2C{=}NH_2{}^+BF_4^-$.

EXPERIMENTAL SECTION

(i) Starting materials

t-Butyl cyanide and the various organic solvents were dried as described in Appendix 1. Boron trichloride and boron trifluoride diethyletherate were distilled before use while diphenylboron chloride was prepared from appropriate quantities of boron trichloride and tetraphenyl tin, and again distilled before use. Tetramethyldiborane was prepared as described in Chapter 2. Solutions of di-t-butylmethyleneaminolithium were prepared in situ by the addition of t-butyl lithium to t-butyl cyanide. Di-t-butylmethyleneamine was prepared by methanolysis of the N-lithio reagent, $^{t}Bu_2C{=}NLi$, and subsequent distillation of the product (114).

(ii) Preparation of Di-t-butylmethyleneaminodichloroborane $^{t}Bu_2C{=}NBCl_2$(38).

Boron trichloride (4.64g, 39.60 mmol.) was condensed onto a frozen (-196°) solution of di-t-butylmethyleneaminolithium (5.83g, 39.54 mmol.) in 50 cm^3 pentane and the solution allowed to warm to room temperature with stirring. Lithium chloride was precipitated and the mixture filtered hot to yield a clear solution from which all solvent was removed by distillation at atmospheric pressure. Distillation of the remaining pale yellow liquid under vacuum (65°, 0.4 mm Hg) yielded a colourless liquid which was identified, by comparison with an earlier sample (38), as di-t-butylmethyleneaminodichloroborane, $tBu_2C{=}NBCl_2$ (Found : C 48.5%, H 9.2%, B 4.2%, Cl 30.8%, N 6.4%, $C_9H_{18}BCl_2N$ requires : C 48.7%, H 8.2%, B 4.9%, Cl 31.9%, N 6.31%) ν_{max} (liquid film) 2970(s) 2940(m,sh) 3879(m) 2011(w) 1947(w) 1843(vs) 1810(m,sh) 1765(w,sh) 1650(w,br) 1480(s) 1470(m,sh) 1458(m) 1445(w,sh) 1390(m) 1368(s) 1310(m,sh) 1305(m) 1287(s) 1198(m) 1150(w) 1049(m) 1028(w) 973(m) 910(s) 871(vs) 832(m) 650(m) 549(m) 459(w) cm^{-1}. The compound was air sensitive, fuming in moist air, and showed signs of discolouration upon prolonged standing at room temperature.

(iii) Preparation of Di-t-butylmethyleneaminodimethylborane $^{t}Bu_2C{=}NBMe_2$

Boron trichloride (4.40g, 37.55 mmol) was condensed onto the surface of a frozen (-196°) solution of di-t-butylmethyleneaminolithium (5.52g, 37.50 mmol.) in 50 ml. of a hexane/pentane solvent mixture and the solution allowed to warm to room temperature with stirring. After stirring for one hour at room temperature the mixture was filtered to remove the precipitated lithium chloride, the solution cooled to 0°, and 75.0 mmol. of a solution of methyllithium in diethylether slowly added. Refiltration of the mixture yielded a clear solution from which all solvent was removed by pumping under vacuum. The remaining liquid was fractionated through traps cooled to -63° and -196°, the liquid fraction collecting at -63° being identified as di-t-butylmethyleneaminodimethylborane, $^{t}Bu_2C{=}NBMe_2$. (Found : C 72.5%, H 14.8%, B 6.0%, N 7.8%, $C_{11}H_{24}BN$ requires : C 72.9%, H 13.4%, B 6.0%, N 7.7%). ν_{max} (liquid film) 2959(s) 2927(m) 2898(m,sh) 2870(m) 1817(s) 1804(m,sh) 1795(m,sh) 1840(w) 1480(m) 1473(m,sh) 1462(w) 1389(m) 1367(m) 1317(m,sh) 1297(s) 1276(m) 1255(w,sh) 1203(w) 1133(w) 1102(m) 1044(m) 1025(w,br) 973(m) 924(w,br) 894(m) 828(w) 714(w) 553(w) 477(w) cm^{-1}. The compound decomposed slowly upon exposure to air. Storage under nitrogen at room temperature, or heating above room temperature, resulted in the slow decomposition of the compound, the odour of trimethylborane being detected above the liquid.

(iv) Reaction of Di-t-butylmethyleneamine and Tetramethyldiborane (2:1).

Di-t-butylmethyleneamine (1.45g, 10.26 mmol.) and tetramethyldiborane (0.43g, 10.26 mmol.) were condensed into a 1000 cm^3 flask at -196°, the flask sealed and allowed to warm to room temperature. After two weeks the flask was opened to a vacuum line and the volatile components fractionated to yield trimethylborane (0.06g) and tetramethyldiborane (0.21g). The remaining fraction consisted of a clear liquid mixture which could not be separated into its constituent parts by trap to trap distillation. On the basis of its ^{11}B n.m.r. and infra red spectra the liquid was identified as a mixture of di-t-butylmethyleneamine and di-t-butylmethyleneaminodimethylborane, $^tBu_2C{=}NBMe_2$.

(v) Preparation of Di-t-butylmethyleneaminodiphenylborane, $^tBu_2C{=}NBPh_2$ (38).

Diphenylboronchloride (3.91g, 19.50 mmol.) in 25 ml. of hexane was added by syringe to a frozen (-196°) solution of di-t-butylmethyleneaminolithium (2.87g, 19.50 mmol.) in a hexane/pentane solvent mixture. The mixture was stirred to room temperature and filtered hot to remove the precipitated lithium chloride. Removal of the solvent by pumping yielded a white solid which was recrystallised from 10 ml. of pentane at -35° to yield colourless crystals of di-t-butylmethyleneaminodiphenylborane, $^tBu_2C{=}NBPh_2$(38) m.pt. 66°. (Found : C 82.2%, H 10.3%, B 3.7%, N 4.6%, Li absent. $C_{21}H_{28}BN$ requires : C 82.6%, H 9.3%, B 3.5%, N 4.6%). ν_{max} (KBr disc) 3070(w) 3050(w,sh) 3035(w,sh) 3025(w,sh) 2995(m,sh) 2969(s) 2930(m,sh) 2867(w) 1818(s) 1795(m,sh) 1476(m) 1458(w,sh) 1434(m) 1430(m) 1390(w) 1363(m) 1328(w,sh) 1320(w) 1294(w) 1260(w,sh) 1254(m,sh) 1230(s) 1179(w) 1151(w) 1100(w) 1063(w) 1045(m) 1029(w) 1021(w) 996(w) 972(m) 913(w) 898(w) 881(m) 853(w) 846(w) 762(s) 746(m) 707(w) 698(s) 723(w,sh) 609(m) 600(s) 541(w,br) cm^{-1}. The compound was stable to air.

(vi) Preparation of Biphenyl-2,2'-yleneboronfluoride, $C_{12}H_8BF$ (115).

A twice molar equivalent of n-butyllithium in hexane was added to a solution of 2,2'dibromobiphenyl in diethylether and the solution stirred at room temperature for one hour before being frozen to -196°. An equimolar amount of borontrifluoride diethyl etherate complex in diethylether was added by syringe, the mixture allowed to warm to room temperature, and stirred overnight. Solvent was removed by pumping, the residue extracted with hot 60° - 80° pet. ether and filtered to yield a clear solution which deposited yellow crystals of the desired product, biphenyl-2, 2'-yleneboronfluoride (115), upon cooling.

(vii) Preparation of Di-t-butylmethyleneaminobiphenyl-2, 2'-yleneborane, $^tBu_2C{=}NB(C_{12}H_8)$.

Biphenyl-2, 2'-yleneboronfluoride (0.60g, 3.30 mmol.) in 30 ml. of toluene was frozen to -196° and a solution of di-t-butylmethyleneaminolithium (0.49g, 3.32 mmol.) in toluene added by a syringe. The solution was allowed to warm to room temperature and stirred over night before being filtered to remove the precipitated lithium fluoride. Removal of the solvent by pumping yielded an orange oil which was dissolved in 10 ml. of hexane and placed in a freezer at -30°. Waxy yellow crystals were deposited over a number of days which were identified as di-t-butylmethyleneaminobiphenyl-2,2'-yleneborane. $^{t}Bu_2C{=}NB(C_{12}H_8)$ (Found : C 82.3%, H 10.2%, B 3.6%, N 4.8%, $C_{21}H_{26}BN$ requires : C 83.2%, H 8.6%, B 3.6%, N 4.6%) ν_{max} (Nujol mull) 3082(w,sh) 3050(m) 3024(m) 1820(w) 1742(s) 1732(m,sh) 1472(m) 1385(m) 1312(m) 1286(s) 1267(m,sh) 1258(m) 1245(w,sh) 1204(m) 1181(w) 1154(w) 1087(w) 1078(w) 1070(w) 1043(m) 1037(w) 1006(w) 967(m) 930(w) 912(w) 859(w) 832(m) 771(w,sh) 761(m,sh) 738(m,sh) 730(s) 700(m,sh) 696(s) 636(w) 633(w) 600(m) 535(w,br) 462(m) cm^{-1}. The compound was stable to air.

(viii) Preparation of Bis(di-t-butylmethyleneamino) fluoroborane, $(^{t}Bu_2C{=}N)_2BF$(1).

Borontrifluoride diethylether complex (1.42g, 10.0 mmol.) was added to a frozen (-196°) solution of di-t-butylmethyleneaminolithium (2.95g, 20.04 mmol.) in 40 ml. of pentane, the mixture allowed to warm to room temperature, and stirred over night. Removal of the solvent by pumping, and sublimation of the remaining material (90°, 0.005 mm Hg), yielded a white solid which was recrystallised from pentane (20 ml) at -30° to yield

colourless crystals. The recrystallised material was identified as bis(di-t-butylmethyleneamino)fluoroborane, $(^{t}Bu_2C{=}N)_2BF(1)$ m.pt. 73°.
(Found : C 69.4%, H 12.9%, B 3.5%, F 7.0%, N 9.1%, Li absent. $C_{18}H_{36}BFN$ requires : C 69.7%, H 11.7%, B 3.5%, F 6.1%, N 9.0%) ν_{max} (Nujol mull) 1850(w,sh) 1745(s,br) 1472(m) 1387(m) 1312(m) 1283(s) 1257(s) 1203(m) 1107(w) 1044(m) 1025(w) 968(s) 933(w) 867(w) 835(m) 795(w) 789(w) 721(w) 642(m) 618(m,sh) 601(s) 552(w) 530(m) cm^{-1}. The compound was moderately air sensitive, showing signs of decomposition after some minutes exposure.

(ix) Preparation of Tris(di-t-butylmethyleneamino)borane, $(^{t}Bu_2C{=}N)_3B(9)$.

Boron trifluoride diethyl ether complex (1.00g, 7.05 mmol.) was added to a frozen (-196°) solution of di-t-butylmethyleneaminolithium (3.12g, 21.20 mmol.) in 40 cm^3 of 100° - 120° petroleum ether. The mixture was allowed to warm to room temperature and then heated to reflux for a period of forty eight hours. After cooling the solution was filtered to remove the precipitated lithium fluoride and the solvent removed under vacuum to yield an off-white solid. Recrystallisation from boiling hexane yielded colourless crystals identified as tris(di-t-butylmethyleneamino)borane (9) $(^{t}Bu_2C{=}N)_3B$, m.pt. 184° (Found : C 75.0%, H 13.2%, B 2.5%, N 9.6%, F absent, Li absent $C_{27}H_{54}BN_3$ requires C 75.1%, H 12.6%, B 2.5%, N 9.2%) ν_{max} (KBr disc) 3019(w,sh) 2999(m) 2967(s)

2921(m) 2880(m) 1788(m,sh) 1765(m,sh) 1735(s) 1484(m) 1475(w,sh) 1458(w) 1390(w) 1369(m) 1364(m) 1257(s) 1205(w) 1172(m) 1049(m) 1028(w) 968(m) 935(w) 837(m) 639(m) 580(w) 552(w) cm^{-1}. The compound was stable to air.

(x) Reaction of Di-t-butylmethyleneaminolithium with Boron trifluoride diethylether complex, (4:1).

Borontrifluoride diethylether complex (0.50g, 3.52 mmol.) was added to a frozen solution of di-t-butylmethyleneaminolithium (2.07g, 14.06 mmol.) in 100° - 120° petroleum ether, the solution allowed to warm and then refluxed for forty eight hours. Upon cooling the solution was filtered to remove precipitated lithium chloride and the solvent removed under vacuum to yield a pale yellow solid. Recrystallisation from boiling hexane yielded colourless crystals identified as being tris(di-t-butylmethyleneamino)borane, $(^tBu_2C{=}N)_3B$.

(xi) Attempted reaction of Tris(di-t-butylmethyleneamino) borane and lithium triethylborohydride.

A T.H.F. solution of lithium triethylborohydride (1.04 mmol.) was added to tris(di-t-butylmethyleneamino) borane (0.45g, 1.04 mmol.) dissolved in 30 cm^3 of T.H.F. and the mixture refluxed for half an hour. Analysis of the liquid by ^{11}B n.m.r. showed the presence of peaks due to the unreacted starting materials, no other boron-containing species being indicated. Subsequent hydrolysis and work-up of the reactants permitted quantitative recovery of the tris(imino)borane.

(xii) Attempted reaction of Tris(di-t-butylmethyleneamino) borane with Methyl Lithium

Tris(di-t-butylmethyleneamino)borane (0.40g, 0.93 mmol.) was dissolved in 10 cm^3 of T.H.F. and 0.93 mmol. of a diethylether solution of methyl lithium added. The mixture was refluxed for a period of three hours and a sample of the solution analysed by ^{11}B n.m.r., the spectrum of which showed a single peak due to the unreacted iminoborane. Hydrolysis and subsequent work-up afforded quantitative recovery of the iminoborane starting material.

(xiii) Attempted reaction of Tris(di-t-butylmethyleneamino) borane and Acetonitrile.

A saturated solution of tris(di-t-butylmethyleneamino) borane in acetonitrile was prepared and a sample examined by infra red spectroscopy. The resulting spectrum showed evidence of an unchanged nitrile absorption at 2256 cm^{-1} and an unchanged ν(C=N)absorption at 1735 cm^{-1}. Subsequent removal of the solvent under vacuum afforded quantitative recovery of the iminoborane starting material.

(xiv) Preparation of Di-t-butylmethyleneammonium tetrafluoroborate.

Di-t-butylmethyleneamine (1,41g, 10 mmol.) was added to a 10 mmol. aliquot of fluoroboric acid in water. After stirring for two minutes the water was removed by pumping to yield a white solid which could be recrystallised from hot toluene in the form of colourless, plate-like, crystals. The crystals were identified as di-t-butylmethyleneammonium tetrafluoroborate, $^{t}Bu_2C{=}NH_2^+\ BF^-_4$

(Found : C 46.8%, H 9.7%, B 4.7%, F 35.1%, N 6.3%, $C_9H_{18}BF_4N$ requires : C 47.6%, H 8.0%, B 4.8%, F 33.5%, N 6.2%) m.pt. 153(dec)° ν_{max} (nujol mull) 3320(w,br) 1670(s,br) 1402(m) 1383(w) 1236(w,sh) 1215(m) 1187(m) 1070(s,br) 1040(s,br) 943(w) 907(m,br) 863(m) 846(w) 763(w) 724(w) 643(w) 519(w) 446(w) cm^{-1}. The compound was stable to air.

DISCUSSION

Of the six monomeric di-t-butylmethyleneaminoboranes described in this chapter two, di-t-butylmethyleneaminodimethylborane, $^{t}Bu_2C{=}NBMe_2$, and di-t-butylmethyleneaminobiphenyl-2,2'-yleneborane, $^{t}Bu_2C{=}NB(C_{12}H_8)$, are described here for the first time. The syntheses, and some spectroscopic features, of the remaining four compounds, $^{t}Bu_2C{=}NBCl_2$(28), $^{t}Bu_2C{=}NBPh_2$(38), $(^{t}Bu_2C{=}N)_2BF$(1) and $(^{t}Bu_2C{=}N)_3B$(19) have previously been described elsewhere, although this study amends some details concerning two of these, $^{t}Bu_2C{=}NBPh_2$ and $(^{t}Bu_2C{=}N)_3B$. The purpose of the present study was therefore to supplement earlier work performed in these laboratories and, in particular, to provide further structural and spectroscopic information on these compounds.

Preparation of dialkyl-, and diaryl-, methyleneaminoboranes.

Five general preparative routes have been established for the synthesis of dialkyl-, or diaryl-, methyleneamino derivatives of boron. Each of the routes is summarised below, together with a list of iminoboranes prepared by that method.

Route 1 : Reaction of an iminolithium derivative and a haloborane.

The reaction of an iminolithium reagent, $R_2C{=}NLi$, (usually prepared in situ) and a haloborane, BX_nY_{3-n} (Equation IV.1) has been used to prepare a large number

$$n\ R_2C{=}NLi + BX_nY_{3-n} \longrightarrow \tfrac{1}{z}((R_2C{=}N)_nBY_{3-n})_z + nLiX$$

X = halogen, Y = halogen, alkyl, aryl.

IV.1

of methyleneaminoboranes (Table IV.1) including the compounds $^tBu_2C{=}NBCl_2$(38), $^tBu_2C{=}NBPh_2$(38), $^tBu_2C{=}NB(C_{12}H_8)$, $(^tBu_2C{=}N)_2$ BF(1) and $(^tBu_2C{=}N)_3B$(1,9), prepared during the course of the present study. The reactions are generally performed in either diethyl ether or an alkane solvent and proceed below 0°. An exception is the preparation

TABLE IV.1

Iminoborane derivatives prepared by the reaction of an iminolithium reagent and a haloborane.

Compound	Ref.	Compound	Ref.
$(Ph_2C{=}NBX_2)$		$^tBu_2C{=}NBCl_2$	(a),38
X=Cl,Br,I;n=2	39,116	$^tBu_2C{=}NB^nBu_2$	38
X=F, polymeric	39,116	$^tBu_2C{=}NB(O_2C_6H_4)$	1
$(Ph_2C{=}NB(O_2C_6H_4))_2$	46	$^tBu_2C{=}NB(O_2C_2H_2)$	1
$Ph_2C{=}NBPh_2$	46,117	$^tBu_2C{=}NB((NH)_2C_6H_4)$	1
$Ph_2C{=}NB(mesityl)_2$	46,117	$^tBu_2C{=}NB((NMe)_2C_2H_4)$	1
$(p\text{-}tolyl)_2\,C{=}NBPh_2$	46	$^tBu_2C{=}NB(O_2(Me_2C_2))$	1
$(Ph_2C{=}N)_2BPh$	118	$^tBu_2C{=}NB(C_{12}H_8)$	(a)
$(Ph_2C{=}N)_3B$	46,117	$(^tBu_2C{=}N)_2BF$	(a)3
$(Me_2N)_2C{=}NBPh_2$	119	$(^tBu_2C{=}N)_2BCl$	120
$^tBu_2C{=}NBPh_2$	(a),38	$(^tBu_2C{=}N)_3B$	(a)9
$^tBu_2C{=}NBPh\,Cl$	120		

(a) This work

of $(^tBu_2C{=}N)_3B$, which requires the considerably more forcing conditions of refluxing in 100° - 120° pet. ether for 48 hours (9), apparently due to the high degree of steric crowding experienced by the $(^tBu_2C{=}N)_2BF$ intermediate upon approach of the third imino ligand. Steric factors are also thought to account for the failure to prepare a further compound, $^tBu_2C{=}NB(mesityl)_2$ (mesityl = 2,4,6 trimethylphenyl), by this route (120).

Route 2 : Reaction of a methyleneaminosilane and a haloborane.

A number of methyleneaminoboranes have been prepared (Table IV.2) by the reaction of a haloborane with the corresponding methyleneaminotrimethylsilane (Equation IV.2), in a manner analogous to that used to prepare aminoboranes from haloboranes and aminosilanes (121, 122).

$$nR_2C{=}NSiMe_3 + BX_nY_{3-n} \longrightarrow \tfrac{1}{z}((R_2C{=}N)_nBY_{3-n})_z + nMe_3SiX \qquad \text{IV.2}$$

X = halogen, Y = halogen, aryl

The reaction generally requires more forcing conditions (reflux in toluene) to ensure completion than that of route 1, although it has the advantage that the bi-product, $Me_3Si\,Cl$, is volatile and therefore easily separated from the iminoborane. An impure sample of one of the compounds discussed in this chapter, $^tBu_2C{=}NBPh_2$, has previously been prepared by this route (120) as have a number of monophenylmethyleneaminoboranes, $PhCH{=}NBR'_2$ (46), also

TABLE IV.2

Iminoborane derivatives prepared by the reaction of an iminosilane reagent and a haloborane

Compound	Ref.	Compound	Ref.
$(Ph_2C=NBX_2)_n$	118	$(C_{12}H_8)C=NBPh_2$	46
X= Cl,Br,n=2;X=F,n $=\infty$		$(PhCH=NBPh_2)_2$	46
$Ph_2C=NBPh_2$	118	$(PhCH=NBPhCl)_2$	46
$Ph_2C=NBPhCl$	118	$PhCH=NB(mesityl)_2$	46
$Ph_2C=NB(mesityl)_2$	118	$(Ph_2C=N)_2BPh$	118
$Ph_2C=NB(C_{12}H_8)$	46	$(Ph_2C=N)_3B$	118
$(Ph_2C=NB(O_2C_6H_4))_n$	118	$^tBu_2C=NBPh_2$	120

listed in Table IV.2.

Route 3 : Alkylation of a methyleneaminoboron halide.

The addition of an alkyllithium reagent to an iminoboron halide generally results in elimination of LiX and formation of the corresponding imino(alkyl)borane (Equations IV.3,4). The compound $^tBu_2C=NBMe_2$ was prepared,

$$(R_2C=NBX_2)_n + 2R'Li \longrightarrow n\ R_2C=NBR'_2 + 2LiX \qquad IV.3$$

$$(R_2C=N)_2BX + R'Li \longrightarrow (R_2C=N)_2BR' + LiX \qquad IV.4$$

during the course of the present study, by the reaction of $^tBu_2C=NBCl_2$ and two equivalents of MeLi, similar reactions having been used to prepare $Ph_2C=NBPh_2$ (46)

${}^tBu_2C{=}NB^nBu_2$(38), ${}^tBu_2C{=}NB^tBu_2$(1) and $({}^tBu_2C{=}N)_2BMe$ (1). Additionally, $({}^tBu_2C{=}N)_2BF$ will react with $LiAlH_4$ to yield $({}^tBu_2C{=}N)_2BH$ (1). The reaction of ${}^tBu_2C{=}NBCl_2$ with one equivalent of ${}^tBuLi$, however, is reported (120) to yield ${}^tBu_2C{=}BHCl$, rather than ${}^tBu_2C{=}NB^tBuCl$, and in marked contrast to the 1:2 reaction which yields the expected ${}^tBu_2C{=}NB^tBu_2$ (1). A radical mechanism has been proposed to account for this reaction (120) although an alternative explanation would involve initial decomposition of ${}^tBuLi$ to give isobutene, C_4H_8, and LiH, a process known to occur under certain conditions (123). Subsequent reaction of LiH with ${}^tBu_2C{=}NBCl_2$ would account for the observed product.

Route 4 : Reaction between a methyleneamine and a borane.

The reaction of Ph_2BCl with two equivalents of the appropriate methyleneamine in boiling 80° - 100° pet. ether (Equation IV.5) has been used to prepare the

$$2\ R_2C{=}NH + Ph_2BCl \longrightarrow R_2C{=}NBPh_2 + R_2C{=}NBH_2^+Cl^- \qquad \text{IV.5}$$

compounds $R(Ph)C{=}NBPh_2$ (R=Ph, p-Cl-C_6H_4, p-Br-C_6H_4) and $(p\text{-tolyl})_2C{=}NBPh_2$ (46). A similar reaction was used to prepare $(Ph_2C{=}N)_3B$, from $Ph_2C{=}NH$ and BCl_3 (46), while the reaction of $Ph_2C{=}NH$ with $B(NMe_2)_3$ (Equation IV.6) yielded a mixture of products (124, 125). The reaction

$$\text{X.S. } Ph_2C{=}NH + B(NMe_2)_3 \rightarrow (Ph_2C{=}N)_nB(NMe_2)_{3-n} + n\ Me_2NH \qquad \text{IV.6}$$

of a methyleneamine and an organoborane to yield an iminoborane derivative (Equation IV.7) has been found to be

$$R_2C{=}NH + BR_3 \longrightarrow {}^1/n(R_2C{=}NBR_2)_n + RH \qquad IV.7$$

limited to a few specific cases. Thus, $(Ph_2C{=}NBMe_2)_2$ (124) and ${}^tBu_2C{=}NBEt_2$ (120) have been prepared by this method, while the reaction of $Ph_2C{=}NH$ and BEt_3 resulted in reduction of the methyleneamine to $Ph_2C{=}NCHPh_2$, ethylene also being produced (124). During the course of the present study a further sample of ${}^tBu_2C{=}NBMe_2$ was prepared by reaction of tetramethyldiborane with two equivalents of ${}^tBu_2C{=}NH$ (Equation IV.8) in the absence of solvent.

$${}^tBu_2C{=}NH + \tfrac{1}{2}(Me_2BH)_2 \longrightarrow {}^tBu_2C{=}NBMe_2 + H_2 \qquad IV.8$$

By contrast, the reaction of diborane, B_2H_6, with $Ph_2C{=}NH$ will not stop at the iminoborane (125), but proceeds further, via migration of a hydrogen across the C=N bond, to yield the borazine (Equation IV.9).

$$Ph_2C{=}NH + \tfrac{1}{2}(B_2H_6) \longrightarrow \tfrac{1}{3}(Ph_2CHNBH)_3 + H_2 \qquad IV.9$$

Route 5 : Pyrolysis of an immonium salt.

The iminoboranes $Ph_2C{=}NBPh_2$ and p-tolyl$_2C{=}NBPh_2$ have been prepared by pyrolysis of the corresponding methyleneammonium tetraphenylborate salt (Equation IV.10), benzene being the bi-product from the reaction (46).

$$R_2C{=}NH_2^+BPh_4^- \xrightarrow{\Delta} R_2C{=}NBPh_2 + 2PhH \qquad \text{IV.10}$$

R = Ph,p-tolyl

Of the six iminoboranes discussed in this chapter two, $^tBu_2C{=}NBMe_2$ and $^tBu_2C{=}NBCl_2$ (38), were colourless liquids which could be distilled under vacuum, and which decomposed upon exposure to air. The remaining four were all solids, $^tBu_2C{=}NBPh_2$ (38), $(^tBu_2C{=}N)_2BF$ (1) and $(^tBu_2C{=}N)_3B$ (9) being colourless crystalline solids while the fourth, $^tBu_2C{=}NB(C_{12}H_8)$, was a yellow waxy compound. Two of the four solids, $^tBu_2C{=}NBPh_2$ and $(^tBu_2C{=}N)_3B$, were unaffected by exposure to air while the others showed signs of decomposition after a few minutes. Such stability is unusual amongst non-associated iminoboranes (1,9,38,46, 120,126,127) and probably reflects the shielding of the C=N=B skeleton by the surrounding bulky t-butyl groups.

Structures of methyleneaminoboranes; the X-ray crystal structure of di-t-butylmethyleneaminodiphenylborane, $^{t}Bu_2C=NBPh_2$

All the known di-t-butylmethyleneamino derivatives of boron, $(^{t}Bu_2C=N)_nBX_{3-n}$(X=H, alkyl, aryl, halogen) have been assigned monomeric structures, in the condensed and vapour phases, on the basis of their high ν($C=N\doteq B$) stretching frequencies (1735 cm^{-1} to 1845 cm^{-1}) and mass spectra (1,9,38,120). Monomeric structures have also been assigned to a number of diarylmethyleneaminoboranes; $R^1_2C=NBR^2_2$ (R^1=Ph; R^2=Et(117), ^{n}Bu(128), Ph (46), mesityl (46) and R^2=Ph; R^1=p-tolyl (46), p-$Cl-C_6H_4$(46), p-$Br-C_6H_4$ (46)), $(Ph_2C=N)_2BPh$ (125), $(Ph_2C=N)_2BNEt_2$ (128), $(Ph_2C=N)_3B$ (116,118), $C_{12}H_8C=NBPh_2$ (46) and also the guanidino derivative $(Me_2N)_2C=NBPh_2$ (118). Other iminoborane derivatives with apparently monomeric structures include some halogenated derivatives, $Cl_3C(X)C=NBR^1R^2$(X,R^1=Cl,Br; R^2=Cl,Br, Me,Ph) (47,129), and some compounds with carbon-bonded sulphur-containing substituents , $X(R^1S)C=NBR^2R^3$(X=Me, ^{i}Pr,^{n}Bu, Cl_3C;R^2,R^3=S-alkyl,Ph,Br) (56,130,131), although in some instances the solution phase contains equilibrium mixtures of both monomeric and associated species.

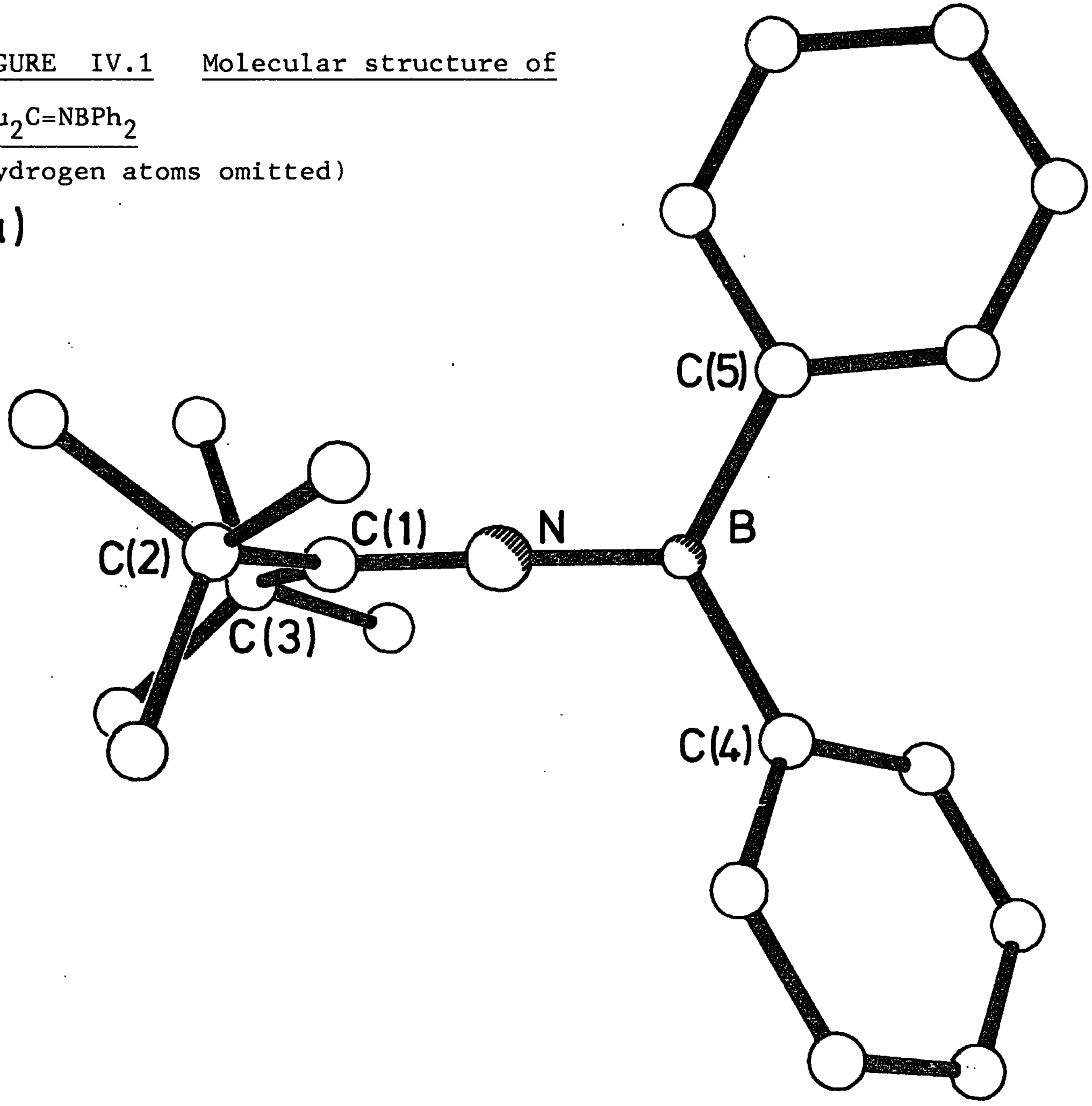
In all monomeric iminoboranes it would appear that the non-association of the molecule is dictated by the steric bulk of the carbon-, and boron-, bonded substituents, preventing the adoption of a four-coordinate, formally valence saturated,configuration about the boron atom. In the case of the di-t-butyl derivatives, the bulk of the t-butyl groups is, of itself, sufficient to prevent association, although the same is not true for other types of methyleneamino ligand. Thus, while $^{t}Bu_2C{=}NBPh_2$, $^{t}Bu_2C{=}NB(C_{12}H_8)$, $Ph_2C{=}NBPh_2$ and $C_{12}H_8C{=}NBPh_2$ are all monomeric, $(Ph_2C{=}NBPhCl)_n$ (n probably equals 2(38)) and $Ph_2C{=}NB(C_{12}H_8)$ (38) adopt associated structures similar to that of the monophenyliminoborane $(PhCH{=}NBMe_2)_2$ discussed in Chapter 2. Similarly, although some of the compounds of the general type $X(R^1S)C{=}NBR^3R^4$, listed above, are monomeric, the case where X is the comparatively small substituent, CF_3, has a dimeric structure, as do the compounds $(X^1H_2C(X^2)C{=}NBX_2{}^2)_2$ (X^1=F, Cl,Br,I, X^2= Cl,Br) (47,54,55). Aminoboranes, $R_2NBR'_2$, are more commonly monomeric, mainly in consequence of the reduction in the intramolecular separation of nitrogen and boron substituents, and consequently more demanding steric criteria for association (132-134).

Crystals of one of the compounds described in this study, di-t-butylmethyleneaminodiphenylborane, $^{t}Bu_2C{=}NBPh_2$, have been the subject of a recent X-ray crystallographic study conducted by Dr. W. Clegg (Göttingen University), the results of which are presented in Figure IV.1 (a and b) and Table IV.3. Two other monomeric iminoboranes, the related diphenylmethyleneaminodimesitylborane, $Ph_2C{=}NB(mesityl)_2$ (14,15), and tris(di-t-butylmethyleneamino) borane, $(^{t}Bu_2C{=}N)_3B$ (9), were the subject of earlier, less precise, crystallographic studies, their structures being illustrated in Figures IV.2 and IV.3. Common features of all three compounds are contrasted in Table IV.4.

FIGURE IV.1 Molecular structure of $^{t}Bu_2C{=}NBPh_2$

(hydrogen atoms omitted)

(a)



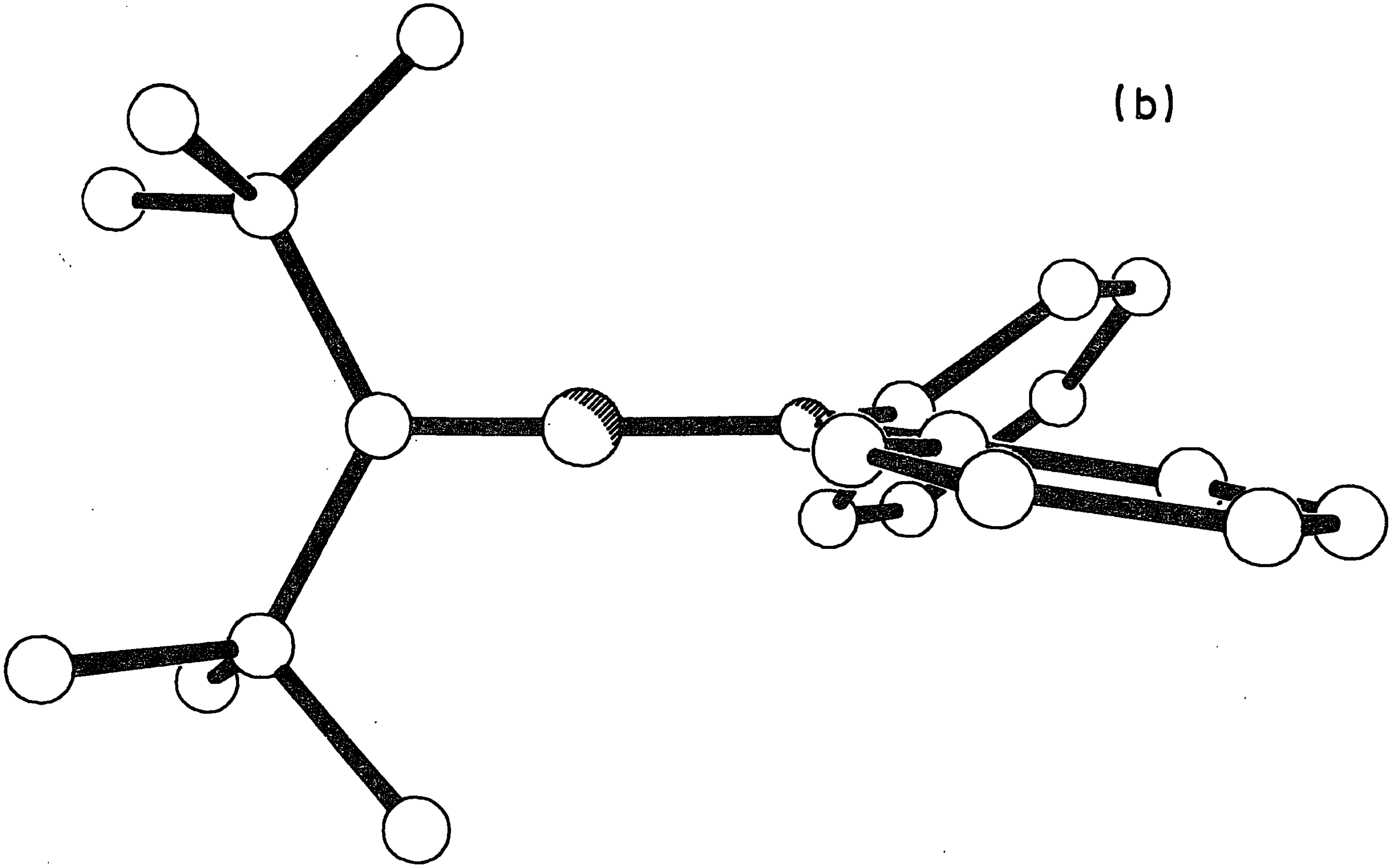

(b)

TABLE IV.3

Selected bond lengths (Å) and angles (°) for $^{t}Bu_2C{=}NBPh_2$

B - N	1.367(6)	B - C(4)	1.583(6)
B - C(5)	1.574(6)	N - C(1)	1.243(5)
C(1) - C(2)	1.529(6)	C(1) - C(3)	1.546(6)

N - B - C(4)	118.5(4)	N - B - C(S)	118.5(4)
C(4) - B - C(5)	123.0(4)	B - N - C(1)	178.2(4)
N - C(1) - C(2)	118.0(4)	N-C(1)-C(3)	117.5(4)
C(2) - C(1) - C(3)	124.5(3)		

FIGURE IV.2 Molecular structure of $Ph_2C{=}NB(mesityl)_2$ (15)

(hydrogen atoms omitted)

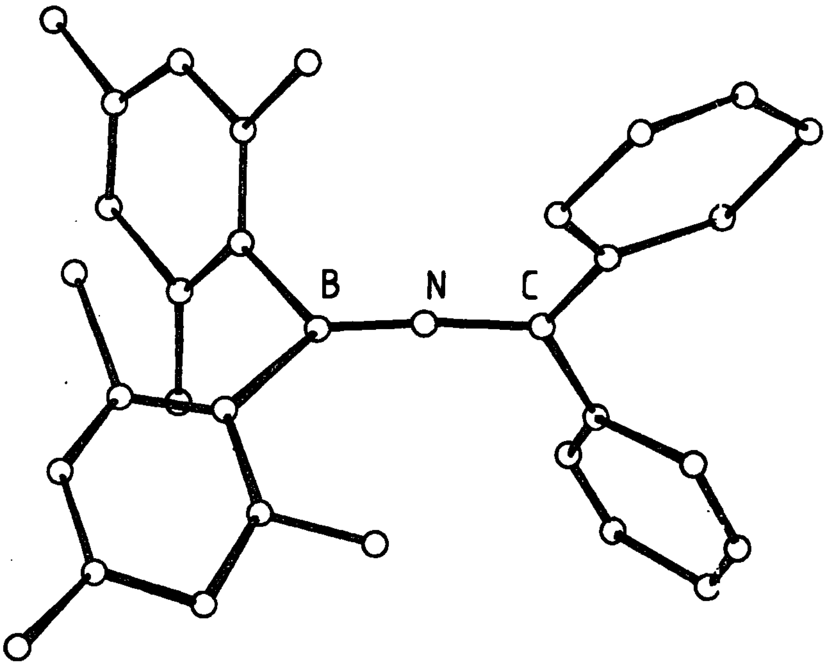


FIGURE IV.3 Molecular structure of $(^tBu_2C{=}N)_3B$ (9)

(hydrogen atoms omitted)

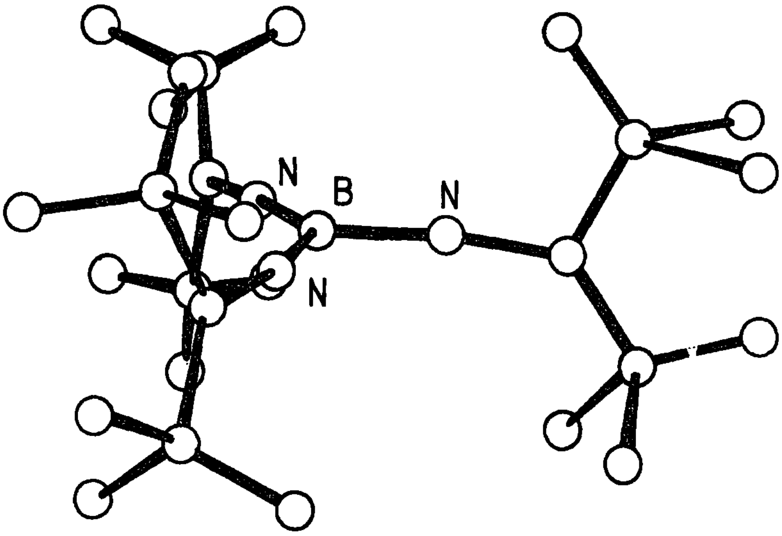


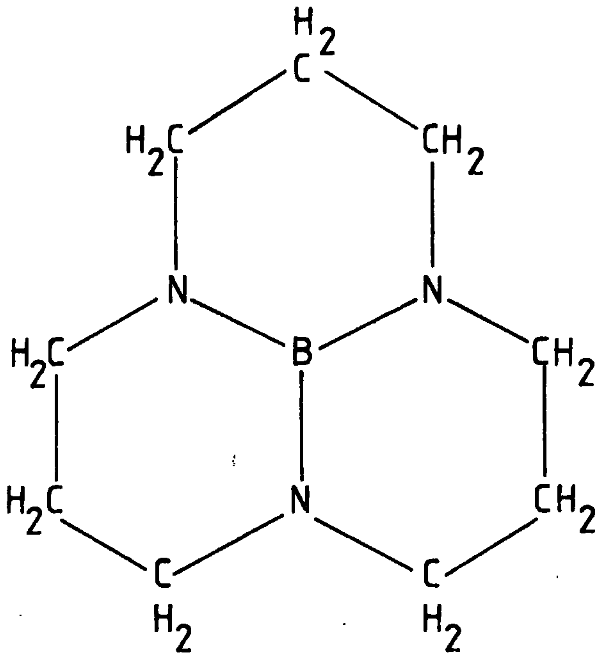
TABLE IV.4

Comparison of selected common features of the compounds $^tBu_2C{=}NBPh_2$, $Ph_2C{=}NB(mesityl)_2$ and $(^tBu_2C{=}N)_3B$

	$^tBu_2C{=}NBPh_2$	$Ph_2C{=}NB(mesityl)_2$	$(^tBu_2C{=}N)_3B$
C=N(Å)	1.24	1.29	1.23
B-N(Å)	1.37	1.38	1.39
$C\hat{N}B$(°)	178	173	166

FIGURE IV.4

1,5,9-Triaza-13-boratricyclotridecane



Crystals of $^{t}Bu_2C{=}NBPh_2$ are orthorhombic, space group Pbca, with a = 11.354(1)Å, b = 13.875(1)Å, c = 22.909(3)Å, Z = 8. The C(1)$\hat{N}$B angle of 178.2(4)° is more nearly linear than those of $Ph_2C{=}NB(mesityl)_2$, 172(2)°, and $(^{t}Bu_2C{=}N)_3B$, 166(1)°, and is the most nearly linear $CNMX_n$-type linkage yet structurally characterised (cf. the unique C$\hat{N}$Al angle of 175.2(2)° in $((Ph_2C{=}N)_3Al)_2$: see Chapter 5). Such an angle is consistent with there being a high degree of N(p) - B(p) dative bonding between the lone pair occupied p orbital of an essentially sp-hybridised nitrogen and the vacant p orbital of boron, the bonding interaction being maximised by the adoption of a linear $C{=}N{\doteq}B$ linkage. Further evidence of such bonding is seen in the extremely short B-N bond length of 1.367(6)Å (cf. 1.38(2)Å in $Ph_2C{=}NB$ $(mesityl)_2$ and 1.385(6)Å in $(^{t}Bu_2C{=}N)_3B$) which is near the length of 1.35Å predicted, by Pauling, for a full B=N double bond (135). Elsewhere, B-N bond lengths of 1.40Å and 1.43Å, in Me_2NBMe_2 (136), 1.37Å and 1.41Å, in $(Me_2NBCH_2)_3$ (137), 1.41Å, in $(HNBH)_3$(138), and 1.431Å (average), in 1,5,9 Triaza-13-boratricyclotridecane (139), have been determined for some aminoborane and borazine compounds where similar N(p)-B(p) dative bonding is postulated. The latter compound (Figure IV. 4) is interesting as a tris(amino)borane containing an almost planar BN_3 ring and is therefore analogous to the tris(imino)borane,

$(^tBu_2C{=}N)_3B$. The six N-bonded carbon atoms in this compound are displaced from the mean BN_3 plane by distances of less than 0.21Å, and confirm the nitrogen atoms as being of essentially sp^2 character with a large degree of N(p)-B(p) dative π bonding. The B-N bond lengths are larger than those of $(^tBu_2C{=}N)_3B$, as might be expected on the basis of the greater p-orbital character of the hybridised nitrogen atomic orbitals (sp^2 as opposed to sp), although the configuration of the tricyclic ring will also be of influence. By comparison, typical bond lengths for a B-N single bond between tetravalent boron and nitrogen atoms occur in the region 1.56 Å to 1.65Å (140).

A surprising feature of the structure of $^tBu_2C{=}NBPh_2$ is the C=N bond length of 1.243(5)Å which is considerably shorter than that of 1.29(2)Å, in $Ph_2C{=}NB(mesityl)_2$(15), and nearer to that of 1.229(8)Å in $(^tBu_2C{=}N)_3B$. By comparison, the terminal-ligand C=N bond length in $((^tBu_2C{=}N)_2Be)_2$ was measured as 1.269(12)Å (16), while the average terminal-ligand bond length in $((Ph_2C{=}N)_3Al)_2$ is 1.257Å (see chapter 5). A further major difference between the structures of $^tBu_2C{=}NBPh_2$ and $Ph_2C{=}NB(mesityl)_2$ is the relative orientation of the boron-bonded aromatic rings with respect to the molecular skeleton. In $^tBu_2C{=}NBPh_2$ the phenyl rings are inclined at angles of 8.0° and 43.6° from the mean plane C(1)NBC(4)C(5) (i.e. one of the rings is almost co-planar with the C=N$\rightleftharpoons$B skeleton), while the mesityl rings of $Ph_2C{=}NB(mesityl)_2$ orientate themselves well away from co-planarity with the corresponding plane (Figure IV.2). In the latter case such a conformation is dictated by the steric bulk of the mesityl groups, while the near co-planarity of one of the phenyl rings in $^tBu_2C{=}NBPh_2$ allows the delocalisation of π electronic charge between the N(pπ) - B(pπ) and phenyl π systems.

Consideration of the remaining features of the structure show it to be essentially as expected. The geometry around C(1) is almost trigonal planar, although the slightly greater angle $C(2)\hat{C}(1)C(3)$, 124.5(3)°, probably reflects some slight steric repulsion between the methyl protons of the two t-butyl groups, as has been noted in other similar systems (e.g. the corresponding angles in $((^tBu_2C{=}N)_2Be)_2$ are 123.4(9)° and 122.2(8)° (16)). The angle between the mean planes C(4)C(5)BN and C(1)C(2)C(3)N is 85.7°, and reflects the orthogonal nature of the C=N and N$\rightleftharpoons$B π systems about the nitrogen atom. The geometries of the phenyl and t-butyl groups are unremarkable.

The structural data obtained for $Ph_2C{=}NB(mesityl)_2$ has been used as the basis for an LCAO-MO calculation of the B-N bond order (15) and forms part of a wider theoretical and structural study of compounds containing B-N bonds (15,136,139,141,142). The results of this theoretical study suggested a total B-N bond order ($\sigma + \pi$) of 1.59, this being greater than those of 1.57, in dimethylaminodimethylborane (136), and 1.48 in tris (1,3,2 benzodioxaborol-2-yl) (141), which were calculated by a similar method. In view of the even shorter B-N bond length in $^tBu_2C{=}NBPh_2$ an even higher bond order would be predicted in this case, probably similar to that of benzene (1.67), although still somewhat less than those of ethylene and allene.

More recently, Dr. R. Snaith and co-workers of Strathclyde University have used the molecular skeleton geometries of both $Ph_2C{=}N(mesityl)_2$ and $(^tBu_2C{=}N)_3B$ to calculate values for the bond indices of the interatomic interactions within these molecules. The concept of bond indices, first introduced by Salem (143) and Wiberg (144), and extended by Armstrong, Perkins and Stewart (145), involves the interpretation of the density matrix results obtained from CNDO calculations to assign a bond index value to each specific atomic interaction within the molecule in question . In the case of what is formally recognised as a bonding interaction between two atoms, the corresponding bond index can be equated with the classical concept o the bond order of that bond, while the sum of all the bond index terms involving a specific atom can be equated with the classical concept of that atom's valency. The application of this method yielded bond index values for the B-N bonds of $Ph_2C{=}NB(mesityl)_2$ and $(^tBu_2C{=}N)_3B$ of 1.541 and 1.158 respectively. It is interesting to note that the former value agrees fairly well with that of 1.59, the B-N bond order derived from the LCAO-MO method described above. Further, if it is assumed that the σ bond contribution to the bond index value is equal to one, the corresponding dative π bond contributions in $Ph_2C{=}NB(mesityl)_2$ and $(^tBu_2C{=}N)_3B$ are 0.541 and 0.158 respectively. The fact that the latter value is roughly one third of the former is not surprising if one considers the nature of the dative bonding in the two cases. In the tris(imino) derivative three separate imino ligands are competing for dative $p\pi$- $p\pi$ bonding with the central boron atom, and consequently the degree of π bonding to each individual ligand is likely to be only a third of that in the monoimino derivative, where the boron atom is only involved in one dative π bond. It should be noted however, that this argument is only valid if one assumes (as their orientations would tend to suggest) that there is little delocalisation of electronic charge from the mesityl ring π system into the vacant p orbital of boron. Such reasoning would, however, explain the less linear C=N=B skeleton of $(^tBu_2C{=}N)_3B$, where a decrease in the B-N bond order, compared with $Ph_2C{=}NB(mesityl)_2$, might result in the nitrogen atom adopting a more sp^2-like character than in the latter case. No calculations have, as yet, been performed on the molecule $^tBu_2C{=}NBPh_2$, where it might be expected that the shorter B-N bond length, and the greater possibility of π bond interaction between the phenyl ring π system and the boron atom, may yield results significantly different to those of $Ph_2C{=}NB(mesityl)_2$.

A further interesting contrast of ligand π-bonding effects would involve a comparison of the B-N bond index of $(^tBu_2C{=}N)_3B$ with that calculated for $(^tBu_2C{=}N)_2BF$, crystals of which are currently the subject of an X-ray crystallographic study. Fluorine, being more electronegative than nitrogen, will tend to remove σ charge from the boron environment, although it also has lone pair occupied π orbitals of a suitable energy to partake in dative $p\pi$ - $p\pi$ bonding to the vacant boron p orbital. Such dative π bonding is a significant feature of fluoroborane chemistry and explains the fact that BF_3 is a weaker Lewis acid than BCl_3; in the latter case the relative energies of the boron and chlorine valence p orbitals make such π bonding less favourable, and the boron atom consequently more electrophilic. The implication of such bonding in $(^tBu_2C{=}N)_2BF$ might be a lowering of the B-N bond index value from the intermediate position, between those of $Ph_2C{=}NB(mesityl)_2$ and $(^tBu_2C{=}N)_3B$, which might otherwise have been predicted for a bis(imino)borane derivative. In this context it is interesting to note that the ^{11}B n.m.r. shifts of $(^tBu_2C{=}N)_2BF$ and $(^tBu_2C{=}N)_3B$, which are indicative of the electronic density and symmetry around boron, are almost identical, thus suggesting that B-F π bonding is a significant feature in these compounds.

The ability to prepare the air stable tris(imino) borane, $(^tBu_2C{=}N)_3B$, is in marked contrast to the failure of various attempts to prepare the analogous aluminium derivative, $(^tBu_2C{=}N)_3Al$ (see chapter 5). As is noted in Chapter 5, the maximisation of dative N(p) - Al(p) π bonding would require the carbon-bonded t-butyl substituents to adopt positions directly above and below the AlN_3 plane in a "paddle wheel" type conformation (see Figure V.2). An analogous situation exists in the tris(imino)borane, $(^tBu_2C{=}N)_3B$ (9) (Figure IV.3) where consideration of a molecular model would suggest the t-butyl ligands exert a substantial shielding effect on the boron atom. This effect will explain the moisture stability of the compound and may also, in part, explain the failure of attempts made in this study to isolate a borane-nitrile adduct of the form $(^tBu_2C{=}N)_3BNCCH_3$, and analogous to similar tris(imino)alane-nitrile adducts, $(^tBu_2C{=}N)_3AlNCR$, reported elsewhere (1). A further reason however, is likely to be the extremely weak Lewis acid-acceptor strength of the iminoborane, as demonstrated by its failure to react with either MeLi or $LiBHEt_3$. In addition, attempts to form a tetrakis(imino)borate derivative analogous to $LiAl(N{=}C^tBu_2)_4$ (17) from the reaction of BF_3OEt_2 with four equivalents of $^tBu_2C{=}NLi$ also failed; $(^tBu_2C{=}N)_3B$

was the only product recovered from the reaction.

Infra red spectra

The infra red spectra of all six di-t-butylmethyleneaminoboranes contained strong absorptions in the 1850 cm^{-1} to 1730 cm^{-1} region of the spectrum, established as being characteristic of the ν (C=N$\hat{=}$B) asymmetric stretching vibration of monomeric iminoboranes with linear, or near linear, CNB skeletons (9,38,46,47,56,116-120,127-131). The values are listed in Table IV.5 together with those of some other di-t-butylmethyleneaminoboranes which have been the subject of earlier studies (1,9,38,120). By contrast with these ν (C=N$\hat{=}$B) frequencies, the corresponding asymmetric ν(C=C=C) vibrations of some isoelectronic allene derivatives, $R_2C=C=CR_2$, have been observed between 2000 cm^{-1} and 1920 cm^{-1} (146-148).

Of the monoiminoboranes, $^tBu_2C=NBX_2$, the two highest, and almost identical frequencies, are those of $^tBu_2C=NBHCl$, 1845 cm^{-1}, and $^tBu_2C=NBCl_2$, 1843 cm^{-1}. The similarity of these two values is, perhaps surprising, as the considerable difference in the total masses of the boron-bonded substituents might have been expected to have a more significant effect on ν (C=N$\hat{=}$B). A similar insensitivity to the boron substituent is apparent in the absorption frequencies of the imino(dialkyl)boranes $^tBu_2C=NBMe_2$ (1817 cm^{-1}), $^tBu_2C=NBEt_2$ (1821 cm^{-1} (120)), $^tBu_2C=NB^nBu_2$ (1821 cm^{-1} (18)) and $^tBu_2C=NB^tBu_2$ (1821 cm^{-1} (38)) while the same is generally true of alkyl-substituted allenes (146-148).

TABLE IV.5

ν(C=N$\doteq$B) stretching frequencies in a series of monomeric di-t-butylmethyleneaminoboranes.

Compound	Phase	ν(C=N$\doteq$B),cm^{-1}	Ref.
$^{t}Bu_2C{=}NBCl_2$	liq. film	1843	(a)
$^{t}Bu_2C{=}NBHCl$	liq. film	1845	120
$^{t}Bu_2C{=}NBMe_2$	liq. film	1817	(a)
$^{t}Bu_2C{=}NBEt_2$	liq. film	1818	120
$^{t}Bu_2C{=}NB^{n}Bu_2$	liq. film	1821	38
$^{t}Bu_2C{=}NB^{t}Bu_2$	liq. film	1812	1
$^{t}Bu_2C{=}NBPhCl$	liq. film	1838	38
$^{t}Bu_2C{=}NBPh_2$	KBr disc	1818	(b)
$^{t}Bu_2C{=}NB(C_{12}H_8)$	nujol mull	1742	(a)
$(^{t}Bu_2C{=}N)_2BF$	KBr disc	1745	(c)
$(^{t}Bu_2C{=}N)_2BCl$	nujol mull	1777	120
$(^{t}Bu_2C{=}N)_2BH$	nujol mull	1760	1
$(^{t}Bu_2C{=}N)_2BPh$	nujol mull	1774	120
$(^{t}Bu_2C{=}N)_3B$	KBr disc	1735	(d)

(a) This work.

(b) This work,Lit. (38) 1820 cm^{-1}(nujol mull).

(c) This work,Lit. (1) 1750 cm^{-1}.

(d) This work,Lit. (1) 1740 cm^{-1}.

A sizeable difference is, however, observed between the ν(C=N$\doteq$B) stretching frequencies of $^{t}Bu_2C{=}NBPh_2$ (1818 cm^{-1}) and $^{t}Bu_2C{=}NB(C_{12}H_8)$ (1742 cm^{-1}). In the latter case the aromatic rings are constrained into a co-planar orientation with the CNB unit which would allow maximisation of any interaction between the phenyl rings and the boron atom. As has been noted earlier, any such competition for π bonding to boron would be expected to result in a weakening of the N≐B bond and a corresponding decrease in ν(C=N≐B), as is indeed observed. A second feature which may also be significant however, is the fact that the boron-bonded aryl unit in $^{t}Bu_2C{=}NB(C_{12}H_8)$ will be constrained in its vibrating modes by the coupling of the aromatic rings. This may also result in a lowering of the asymmetric stretching frequency, independently of any π interaction.

The ν(C=N≐B) stretching frequencies of the bis(methyleneamino)-, and tris(methyleneamino)-, boranes are found in the region 1777 cm^{-1} to 1735 cm^{-1}, some 60 to 110 cm^{-1} below those of the monomethyleneamino compounds. The lower values are considered to reflect the lowering of the B≐N bond order as discussed earlier.

^{11}B n.m.r. spectra

As has been noted in connection with the series of monoalkyl-, and monoaryl-, methyleneaminoboranes, $(RCH{=}NBR'_2)_2$ (see chapter 2), the use of ^{11}B n.m.r. to determine the coordination state of boron is well established (67). Thus, the ^{11}B n.m.r. shifts of a series of monomeric di-t-butyl and diphenyl-, methyleneaminoboranes containing three-coordinate boron lie in the range δ = + 23 p.p.m. to + 38 p.p.m. downfield from BF_3OEt_2 (Table IV.6) while those of the associated derivatives $(RCH{=}NBR'_2)_2$, containing four-coordinate boron, were found to have shifts in the region δ = + 3 p.p.m. to + 8 p.p.m.

In consequence of the formally non-hybridised vacant p orbital in a three coordinate, sp^2, boron compound,

TABLE IV.6

^{11}B n.m.r. shifts of some monomeric methyleneamino and dialkylamino derivatives of boron containing 3-coordinate boron atoms.

Compound	δ ^{11}B(a)	Ref.	Compound	δ ^{11}B(a)	Ref.
$^{t}Bu_2C{=}NBMe_2$	+ 32.0	(b)	$(^{t}Bu_2C{=}N)_2BH$	+ 13.9	1
$^{t}Bu_2C{=}NB^{n}Bu_2$	+ 35	38	$(^{t}Bu_2C{=}N)_2BMe$	+ 26.9	1
$^{t}Bu_2C{=}NB^{t}Bu_2$	+ 32.5	1	$(^{t}Bu_2C{=}N)_2BF$	+ 24.1	(b)
$^{t}Bu_2C{=}NBPh_2$	+ 29.3	(b)	$(Ph_2C{=}N)_2BPh$	+ 32.2	128
$^{t}Bu_2C{=}NB(C_{12}H_8)$	+ 26.4	(b)	$(Ph_2C{=}N)_2BNEt_2$	+ 30.2	128
$^{t}BuCH{=}NB^{n}Bu_2$	+ 38.8	149	$(^{t}Bu_2C{=}N)_3B$	+ 23.3	(b)
$^{t}Bu_2C{=}NBCl_2$	+ 28.8	(b)	$(Ph_2C{=}N)_3B$	+ 27.9	(b)
$Ph_2C{=}NBEt_2$	+ 36.5	67	$(Me_2N)_2BH$	+ 28.6	151
$Ph_2C{=}NB^{n}Pr_2$	+ 37.3	128	$(Me_2N)_2BMe$	+ 33.5	151
$Ph_2C{=}N^{n}Bu_2$	+ 37.4	128	$(Me_2N)_2BPh$	+ 32.5	153
$Ph_2C{=}NBPh_2$	+ 34.0	128	$(Me_2N)_3B$	+ 27.3	154
Me_2NBMe_2	+ 44.6	150			
$Me_2NB^{n}Bu_2$	+ 44.9	151			
Me_2NBPh_2	+ 49.6	152			

(a) Shifts measured relative to an external reference of BF_3OEt_2. Positive shifts are to low field.

(b) This work.

the ^{11}B n.m.r. shift reflects the nature and extent of both σ and π bonding between the boron atom and its substituent groups (6). Because of this, the technique has particular relevance to the present study where the relative extent of dative π bonding between the boron atom and the attached groups is being considered. The ^{11}B shifts of the series of amino-, and imino-, di-n-butylborane derivatives listed in Table IV.6 would suggest that the degree of shielding increases in the sequence $Me_2N < {}^tBuCH{=}N < Ph_2C{=}N < {}^tBu_2C{=}N$ (rather than that suggested in reference 67), while a more distinct pattern emerges in the shift sequence ${}^tBu_2C{=}NBMe_2$ (+32.0 p.p.m.) < ${}^tBu_2C{=}NBPh_2$ (+ 29.3 p.p.m.) < ${}^tBu_2C{=}NB(C_{12}H_8)$ (+ 26.4 p.p.m.) In this case it would seem that the increasing ability of the non-imino ligands to π bond to boron is reflected in an increase in the electron symmetry around boron, and hence an increase in the electromagnetic shielding of the nucleus. A similar effect would account for the greater shielding of the boron nucleus in Me_2NBPh_2, compared with that of Me_2NBMe_2.

The ^{11}B n.m.r. shifts of the bis(imino)-, and tris(imino)-, boranes are at higher field than those of the monoiminoboranes and reflect the increase, and greater symmetry, of the π electron density around boron. The similarity of the shifts of $({}^tBu_2C{=}N)_3B$ and $({}^tBu_2C{=}N)_2BF$ has already been remarked upon as evidence of a substantial amount of π bonding between the boron and fluorine atoms, a factor which also explains the considerably higher field shift of Me_2BF (δ = + 59.0) (155), compared with that of Me_3B (δ = + 86.6) (156). As was noted for the monoiminoboranes, the ligand ${}^tBu_2C{=}N-$ would seem to have a greater shielding effect on boron than $Ph_2C{=}N-$, even to the extent that $({}^tBu_2C{=}N)_2BMe$ has a higher field shift than $(Ph_2C{=}N)_2BPh$, while the greater shielding in $(Ph_2C{=}N)_2BPh$ compared with that in $Ph_2C{=}NBPh_2$ is not unexpected, and reflects the relative shielding of imino and phenyl ligands.

The shielding of the boron nucleus in the tris(imino) boranes, $(R_2C{=}N)_3B$, is generally slightly greater than in some analogous tris(amino)boranes, $(R_2N)_3B$ (67), this having been cited (1) as evidence of lesser N(p) - B(p) dative π bonding in the latter compounds, as steric requirements force the nitrogen-attached groups, R, out of the BN_3 plane. While such a deformation is found in such sterically crowded amino derivatives, the fact that there is a greater difference between the shifts of the monoiminoboranes and monoaminoboranes, than between the tris(imino)boranes and tris(amino)boranes, would tend to suggest that other factors are associated with these shift differences.

^{13}C n.m.r. spectra

The imino-ligand ^{13}C n.m.r. shifts of the six di-t-butylmethyleneaminoboranes discussed in this chapter, together with those of the parent imine, are listed in Table IV.7. The samples were run as solutions in deuterated benzene and the proton-decoupled shifts measured with respect to an external reference of T.M.S.

All the spectra contained singlet imino-carbon resonances with the exception of that of $({}^tBu_2C{=}N)_2BF$ where a doublet, J = 5 Hz, was observed. In this instance the magnitude of the coupling constant is consistent with the splitting being due to coupling with the fluorine nucleus, similar $^3J_{CF}$ coupling constants have been observed in other conjugated fluorocarbons (157) although not, apparently, in the borazine derivative $(FBNCH_3)_3$ (158). The greater

TABLE IV.7

^{13}C n.m.r. shifts of some monomeric di-t-butylmethyleneaminoboranes

Compound	δ (p.p.m.) (a)		
	$>C=$	H_3C	$-\!\!>C-$
$^tBu_2C{=}NBMe_2$	+ 174.2	+ 30.4	+ 42.9
$^tBu_2C{=}NBPh_2$	+ 170.7	+ 30.2	+ 43.4
$^tBu_2C{=}NB(C_{12}H_8)$	+ 168.2	+ 30.5	+ 43.2
$^tBu_2C{=}NBCl_2$	+ 182.6	+ 29.4	+ 42.9
$(^tBu_2C{=}N)_2BF$	+ 181.9(b)	+ 30.4	+ 43.8
$(^tBu_2C{=}N)_3B$	+ 173.7	+ 30.9	+ 43.7
$^tBu_2C{=}NH$	+ 191.7	+ 30.6	+ 41.6

(a) Compounds run as solutions or liquid mixes in C_6D_6 with an external reference of T.M.S. Positive shifts are to low field.

(b) Doublet $^3J_{CF}$ = 5 Hz.

shielding of these carbons with respect to that of the free imine is, perhaps, surprising in view of the fact that N$\rightleftharpoons$B dative π bonding will tend to remove charge from the adjacent nitrogen, and might therefore have been expected to decrease the magnetic shielding around the carbon atom. As this is obviously not the case it would seem that the observed shifts reflect changes in the local magnetic anisotropy of the C=N bond, dependent on the hybridisation state of nitrogen. Differences in shift due to the nature of the boron-bonded substituent are also apparent, although in view of the fact that the shifts do not correlate in any meaningful way with the infra red ν(C=N) , and ^{11}B n.m.r. data it would seem difficult to rationalise the relative ^{13}C shifts in terms of the predicted extent of N(p) - B(p) dative π bonding. Thus, while the difference in shifts between $(^tBu_2C{=}N)_2BF$ (+ 181.9 p.p.m.) and $(^tBu_2C{=}N)_3B$ (173.7 p.p.m.), together with the low field shift of $^tBu_2C{=}NBCl_2$ (182.6 p.p.m), would suggest a correlation between imino-^{13}C shift and the inductive effect of the electronegative boron substituent, it is not obvious why the ^{13}C imino shift of $(^tBu_2C{=}N)_3B$ should occur at an intermediate value between those of $^tBu_2C{=}NBMe_2$ and $^tBu_2C{=}NBPh_2$.

^1H n.m.r.

The ^1H n.m.r. spectra of the four previously prepared compounds discussed in this chapter have been reported elsewhere (1,9,38,120) but are presented here (Table IV.8) together with those of the two new iminoboranes, $^tBu_2C{=}NBMe_2$ and $^tBu_2C{=}NB(C_{12}H_8)$. The compounds were run as solutions in d_8 toluene and the shifts quoted relative to T.M.S. The shifts of a number of other monomeric iminoboranes are also listed in the table. The t-butyl proton resonances of all the compounds were seen as sharp singlets at room temperature, while earlier studies (1,120) have established that they remain so at temperatures as low as -60°. As has been noted elsewhere in this thesis, the ^1H n.m.r. spectrum of $^tBu_2C{=}NH$ shows a single t-butyl proton resonance at room temperature, whereas upon cooling to -30° the signal splits into two resonances of equal intensity (105). This has been interpreted as arising from the slowing

TABLE IV.8

^{1}H n.m.r. shifts of some di-t-butylmethyleneaminoborane derivatives

Compound	τ values (a)		Ref.
	^{t}Bu	others	
$^tBu_2C=NBMe_2$	8.90(s)	9.84(s)	(b)
$^tBu_2C=NBEt_2$	8.89(s)	9.78(q),9.04(t)	120
$^tBu_2C=NB^nBu_2$	8.85(s)	8.4 - 9.2(c)	38
$^tBu_2C=NBPh_2$	8.86(s)	2.31(c),2.75(c)	(b),38
$^tBu_2C=NB(C_{12}H_8)$	8.85(s)	2.42(c)	(b)
$^tBu_2C=NBCl_2$	8.92(s)		(b),38
$(^tBu_2C=N)_2BF$	9.12(s)#		(b),1
$(^tBu_2C=N)_2BMe$	8.91(s)		1
$(^tBu_2C=N)_2BPh$	8.73(s)	2.69(c)	120
$(^tBu_2C=N)_3B$	9.18(s)		(b),1

(a) Values in p.p.m., Me_4Si = 10.00

(b) This work (c) Complex signal (q) quartet

(s) singlet (t) triplet

Lit. (1) 9.38

of the proton inversion process about nitrogen, to the extent that the magnetically non-equivalent syn and anti conformations of the t-butyl groups are seen on the n.m.r. timescale. For a linear $CNMX_n$ skeleton, such as has been established for the crystal phase of $^tBu_2C=NBPh_2$ and postulated for the remaining compounds, no such syn and anti isomerism exists and the t-butyl groups remain magnetically equivalent at all temperatures. The fact that no splitting in the signals of these compounds has been observed is thus consistent with the persistence of a linear CNB skeleton in the solution phase although not, in itself, proof, as it does not exclude the possibility of a rapid inversion process existing at low temperature. Such a process would seem unlikely however, as it would require an extremely low inversion energy barrier to persist at such temperatures.

Mass spectra

The mass spectra of all six iminoboranes discussed in this chapter were recorded during the course of the present study. Those of the four previously known compounds did not differ significantly from the data already published and are consequently not recorded here. Prominent features of the remaining two spectra are summarised in Tables IV.9 and IV.10. Both contained weak peaks attributable to the parent molecular ions, subsequent fragmentation involving successive loss of methyl and t-butyl groups.

TABLE IV.9

Prominent features in the mass spectrum of ${}^{t}Bu_2C{=}NBMe_2$

$^{m}/e$	Relative Intensity	Assignment	
181	4	${}^{t}Bu_2C{=}NBMe_2$	
166	12	"	-Me
151	32	"	-2 Me
136	7	"	-3 Me
124	39	${}^{t}BuC{=}NBMe_2$	
109	21	"	-Me
94	7	"	-2 Me
84	24	${}^{t}BuC{=}NH$	
83	29	${}^{t}BuC{=}N$	
69	100	${}^{t}BuC$	
57	62	${}^{t}Bu$	
41	36	Me_2B	

TABLE IV.10

Prominent features in the mass spectrum of ${}^{t}Bu_2C{=}NB(C_{12}H_8)$

$^{m}/e$	Relative Intensity	Assignment	
303	9	${}^{t}Bu_2C{=}NB(C_{12}H_8)$	
288	14	"	-Me
273	16	"	-2 Me
258	5	"	-3 Me
246	48	${}^{t}BuC{=}NB(C_{12}H_8)$	
231	57	"	-Me
216	20	"	-2 Me
163	14	$B(C_{12}H_8)$	
152	87	$C_{12}H_8$	
102	33	C_8H_6	
84	12	${}^{t}BuC{=}NH$	
83	10	${}^{t}BuC{=}N$	
77	35	C_6H_5	
76	100	C_6H_6	

APPENDIX TO CHAPTER 4

The X-ray crystal structure of di-t-butylmethylene ammonium tetrafluoroborate, $^{t}Bu_2C=NH_2^+BF_4^-$

During attempts at the low temperature re-crystallisation of the compound bis(di-t-butylmethyleneamino)fluoroborane, $(^{t}Bu_2C=N)_2BF$, a number of small, colourless, plate-like crystals were deposited which were subsequently identified as di-t-butylmethyleneammonium tetrafluoroborate, $^{t}Bu_2C=NH_2^+BF_4^-$. The formation of this compound would appear to have been the result of the partial hydrolysis of the iminoborane (Equation IV.11), in a manner analogous to

$$4(^{t}Bu_2C=N)_2BF + 9H_2O \longrightarrow {}^{t}Bu_2C=NH_2^+BF_4^- + 7^{t}Bu_2C=NH + 3B(OH)_3 \qquad IV.11$$

the preparation of fluoroboric acid by the addition of boron trifluoride to water (Equation IV.12) (159). Subsequent investigation revealed that the compound could

$$4BF_3 + 6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3 \qquad IV.12$$

be prepared directly by the addition of $^{t}Bu_2C=NH$ to an aqueous solution of fluoroboric acid (Equation IV.13),

$$^{t}Bu_2C=NH + HBF_4 \longrightarrow {}^{t}Bu_2C=NH_2^+BF_4^- \qquad IV.13$$

the immonium salt displaying a surprising resistance to subsequent hydrolysis. A single crystal of the salt has been the subject of a recent X-ray crystallographic study by Dr. W. Clegg (Göttingen University), the results of which are summarised in Figures IV.5 and IV.6 and Table IV.11. This represents only the second structural characterisation of a protonated methyleneammonium derivative, the other (160) being that of bis(diphenylmethyleneammonium) hexachlorostannate,

FIGURE IV.5 Structures of the ions (a) ${}^{t}Bu_2C{=}NH_2{}^{+}$ and (b) BF_4^- of the compound ${}^{t}Bu_2C{=}NH_2{}^{+}BF_4^-$

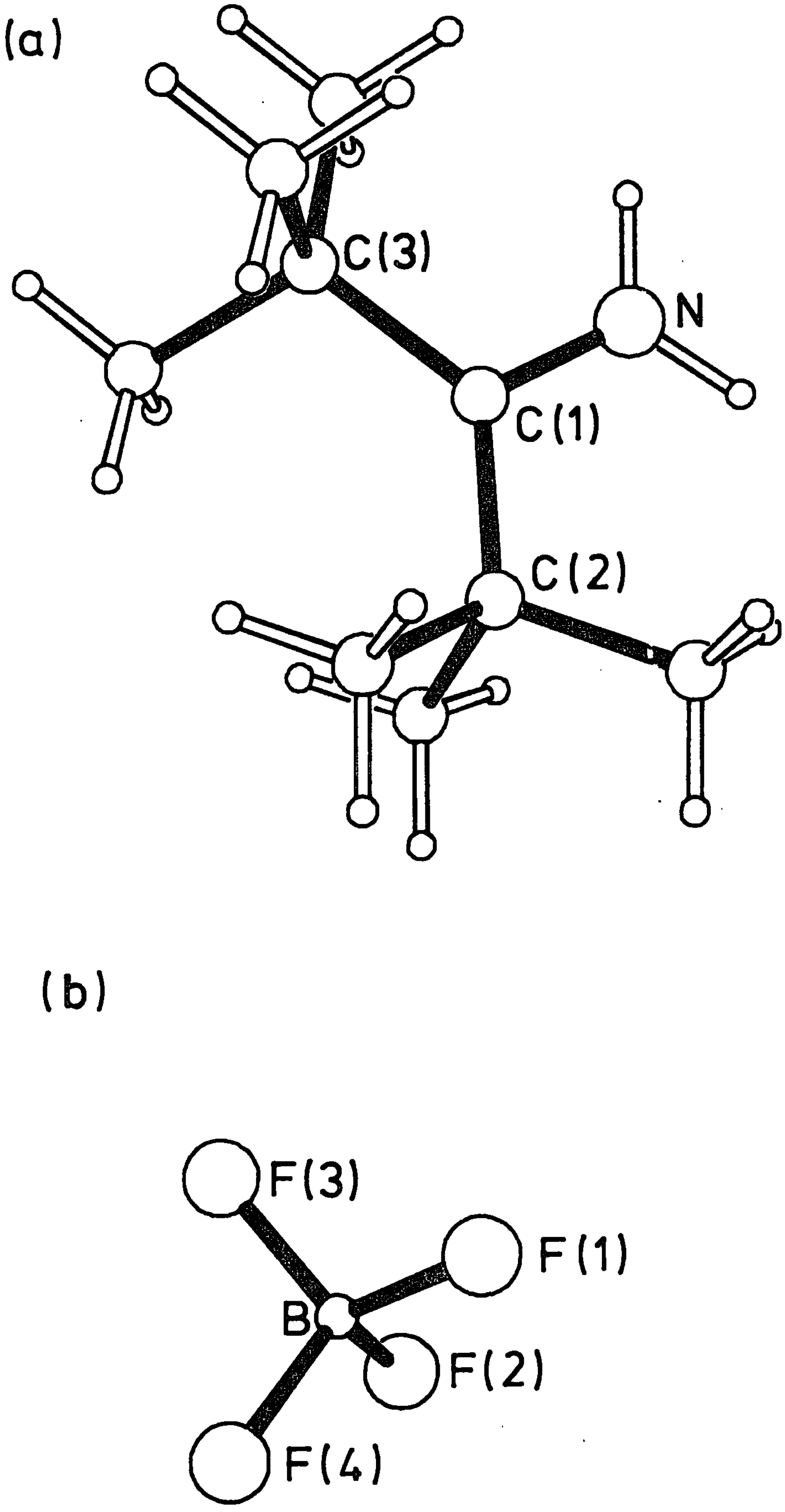


FIGURE IV.6 Crystal lattice structure of the compound $^{t}Bu_2C{=}NH_2^{+}BF_4^{-}$

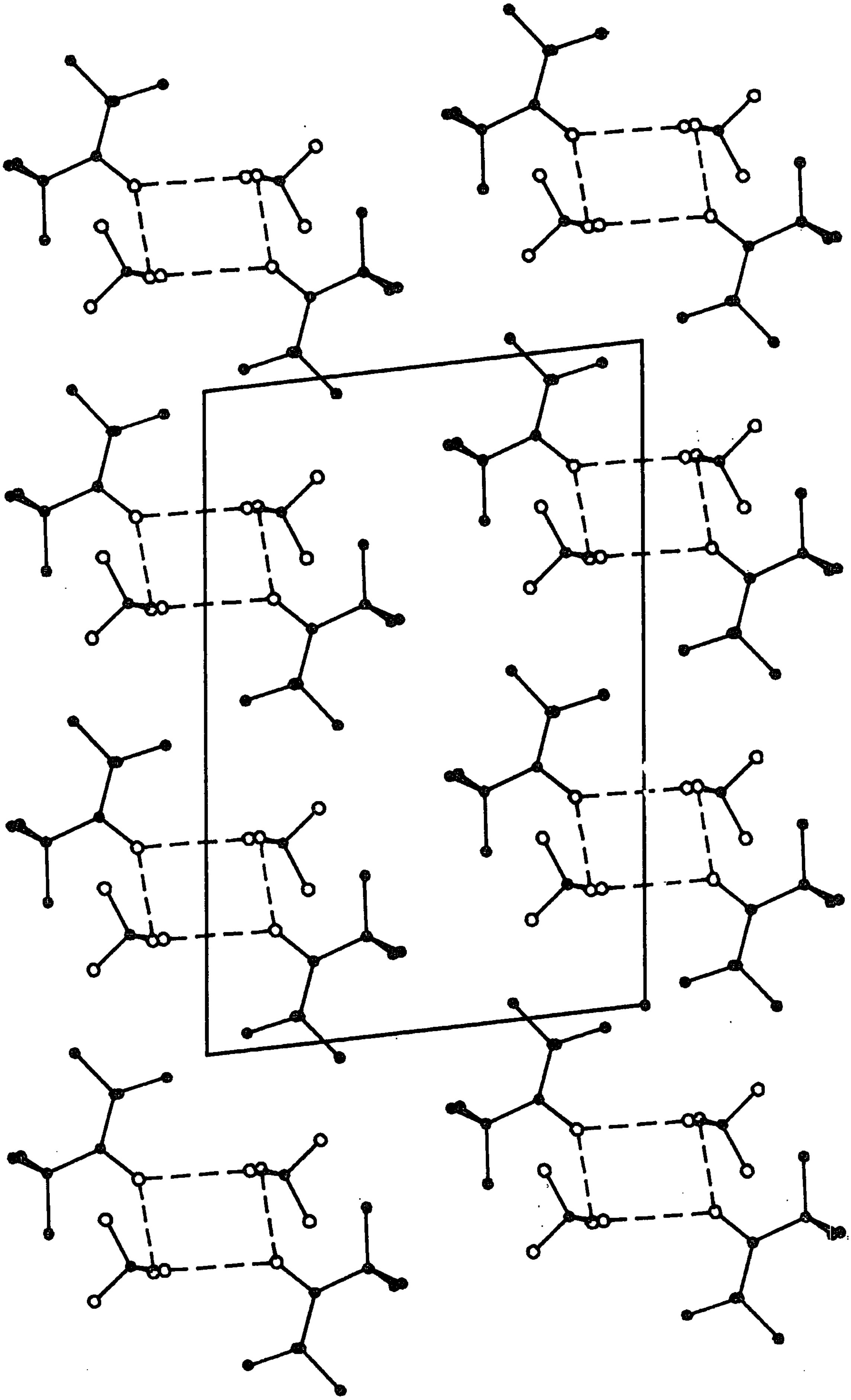


TABLE IV.11

Selected bond lengths (Å) and angles (°)
for ${}^{t}Bu_2C{=}NH_2^{+}BF_4^{-}$

C(1) - N	1.29	C(1) - C(2)	1.49
C(1) - C(3)	1.51	B - F(1)	1.35
B - F(2)	1.33	B - F(3)	1.29
B - F(4)	1.34		

N-C(1)-C(2)	116.6	N-C(1)-C(3)	115.1
C(2)-C(1)-C(3)	128.3	F(1)-B-F(2)	111.6
F(1)-B-F(3)	109.4	F(1)-B-F(4)	111.0
F(2)-B-F(3)	109.8	F(2)-B-F(4)	110.1
F(3)-B-F(4)	104.6		

Intraionic distances

N ..... F(2)	2.9	N ..... F(1)	3.02

esd's in range 0.01 - 0.02Å, 0.4 - 0.9°

$(Ph_2C{=}NH_2)_2^{2+}SnCl_6^{2-}$.

The compound $^tBu_2C{=}NH_2^+BF_4^-$ crystallises as colourless plates, space group $P2_1/C$, a = 11.341Å, b = 6.679Å, c = 16.874Å, β = 96.11°, Z = 4. Final refinement of the structure was rather poor (R = 0.102), due mainly to the high thermal motion of the fluorine and methyl groups within the crystal lattice. The C=N bond length of 1.29 Å is identical, within experimental error, to those of 1.296(7) Å, in $(Ph_2C{=}NH_2)_2^{2+}SnCl_6^{2-}$(160), and 1.302 Å in the related cation $Me_2C{=}NMe_2^+$(161) while barely being significantly longer than the μ_2-ligand C=N bond lengths of 1.262Å, in $(^tBuMeC{=}NAlMe_2)_2$ (8) and 1.278(5) Å, in $(PhCH{=}NBMe_2)_2$ (9). The bond is considerably longer, however, than that of 1.243(5)Å in $^tBu_2C{=}NBPh_2$, discussed earlier in this chapter. Both the $N\hat{C}(1)C(2)$ and $N\hat{C}(1)C(3)$ bond angles, of 116.6° and 115.1° respectively, are unexceptional, being only marginally less than those of 118.0(4)° and 117.5(4)° in $^tBu_2C{=}NBPh_2$, while the geometry around atoms C(2) and C(3) is essentially tetrahedral. Similarly, the BF_4^- anions show no significant distortion from a tetrahedral environment although an average B- F bond length of 1.328Å is somewhat less than that of 1.43Å in $NH_4^+BF_4^-$ (162), and more nearly that of 1.30Å in BF_3 (163). Such shortening in the B-F bond lengths of a BF_4^- anion would seem to be of little significance however, values as low as 1.23Å having been noted elsewhere (164).

Although the nitrogen-bonded protons were not located in this instance, (those shown in Figure V.5 are the assumed locations), it would appear that both are involved in hydrogen bonding with fluorine atoms of separate, adjacent, BF_4^- anions (see Figure IV.6). The measured N ..... F_1 and N ..... F_2 interionic distances, of 3.02Å and 2.97Å respectively, are both less than 3.58Å (calculated as being the sum of the hydrogen and fluorine Van de Waals radii, plus an assumed N-H bond length of 1.03Å (164)), although the differences between this value and the observed lengths (0.56Å and 0.61Å), would suggest the degree of hydrogen bonding to be weak. Evidence of a single, weak, hydrogen bond interaction was found in $(Ph_2C{=}NH_2)_2^{2+}SnCl_6^{2-}$ (160).

The infra red spectrum of ${}^{t}Bu_2C{=}NH_2^+BF_4^-$ contained a strong stretching frequency, ν(C=N), at 1670 cm^{-1}, identical to that of the related methyleneammonium chloride derivative ${}^{t}Bu_2C{=}NH_2^+Cl^-$ (114) and representing an increase, Δ , of 60 cm^{-1} over that of the parent methyleneamine, ${}^{t}Bu_2C{=}NH$ (114). Similar increases in the frequency ν(C=N) were noted in a wide range of methyleneammonium chloride, $R^1R^2C{=}NR^2H^+Cl^-$, and methyleneamine-boron trifluoride coordination complexes, $R^1R^2C{=}N(R^2)BF_3$, (114) Δ varying from 5 cm^{-1} to 64 cm^{-1}. The increases may be attributed to the higher mechanical constraint imposed of the ν(C=N) vibration by the coordination of the Lewis acid to the nitrogen atom, although similar increases in the nitrile frequency, ν(C≡N), upon formation of σ-donor complexes, $R\text{-}C{\equiv}N\overset{+}{\rightarrow}MX_n^-$ (165-167), have been attributed, in part, to fractional increases in the C≡N bond order upon complex formation.

CHAPTER 5

SOME METHYLENEAMINO DERIVATIVES OF ALUMINIUM

INTRODUCTION

This chapter describes the synthesis of three new methyleneamino derivatives of aluminium, tris(diphenylmethyleneamino)alane $((Ph_2C=N)_3Al)_2$, lithium tetrakis (diphenylmethyleneamino)aluminate, $LiAl(N=CPh_2)_4$, and fluorenonemethyleneaminoaluminiumdichloride $((C_{12}H_8)C=NAlCl_2)_2$. Attempts to synthesise two further derivatives, $(^tBu_2C=N)_3Al$ and $LiAl(N=CPh_2)_2Me_2$ are also described. The results of a recent X-ray crystallographic study on one of these compounds, $((Ph_2C=N)_3Al)_2$ are presented and discussed, together with features of the infra red, mass, and ^1H n.m.r. spectra of all three compounds.

EXPERIMENTAL SECTION

(i) Starting Materials

Aluminium trichloride was purified by sublimation before use. Dimethylaluminium chloride was prepared by stirring a 2:1 molar ratio of trimethylaluminium and aluminium trichloride at room temperature, the resulting liquid being freshly distilled before use. Diphenylmethyleneamine, $Ph_2C=NH$, was prepared by the methanolysis of the product of the reaction between phenylmagnesium bromide and benzonitrile (168). The N-lithio reagent, $Ph_2C=NLi$, was prepared by adding the appropriate amount of ^nBuLi in hexane to the methyleneamine at 0°. The iminotrimethylsilyl species, $R_2C=NSiMe_3$ ($R={}^tBu$, Ph), were prepared by the reaction of the N-lithio imine with trimethylchlorosilane. Fluorenonemethyleneaminotrimethylsilane was prepared from the reaction of fluorenone and sodium bis(trimethylsilyl)amide (98)

(ii) Reaction of Diphenylmethyleneaminolithium with Aluminium trichloride (1:1).

A solution of aluminium trichloride (1.57g, 11.77 mmol.) in 20 cm^3 of diethyl ether was added to a frozen (-196°) solution of diphenylmethyleneaminolithium (2.20g, 11.75 mmol.) in 40 cm^3 of diethylether and the solution allowed to warm to room temperature. After two hours the solvent was removed by pumping under vacuum, the resultant pale yellow solid extracted with 60 cm^3 of boiling toluene, and the mixture filtered hot to yield a pale yellow solution. Upon cooling a white solid was precipitated which was filtered, pumped dry, and identified as <u>diphenylmethyleneaminoaluminiumdichloride,</u> $(Ph_2C{=}NAlCl_2)_2$, by comparison with an authentic sample (105) m.pt. 199 - 200°. (Found : C 56.7%, H 4.3%, Al 9.8%, Cl 26.2%, N 5.1%, $C_{26}H_{20}Al_2Cl_4N_2$ requires : C 56.1%, H 3.6%, Al Al 9.7%, Cl 2.5%, N 5.0%) ν_{max}(Nujol mull) 1640(w,sh) 1587(s) 1569(s) 1561(s) 1542(m,sh) 1326(m) 1293(m) 1272(m) 1189(m) 1162(w) 1076(2) 1030(w) 1001(w) 958(m) 833(w,sh) 922(m) 803(s) 729(s) 720(s) 702(s) 690(m,sh) 641(m) 585(m) 552(s) 496(s) 457(w) 432(m) cm^{-1}.

(iii) Reaction of Diphenylmethyleneaminolithium and Aluminium trichloride (2:1).

(Reaction performed by Mr. B. Hall).

Aluminium trichloride (13.16 g, 98.69 mmol.) was added to a frozen solution of diphenylmethyleneaminolithium 35.65g, 196.70 mmol.) in 100 cm^3 of toluene. The mixture was allowed to warm to room temperature, refluxed for a total period of six hours and then filtered to remove the precipitated lithium chloride. Upon standing at room temperature for a number of days a quantity of pale yellow material was deposited, filtered, and subsequently identified as diphenylmethyleneaminoaluminium dichloride, $(Ph_2C{=}NAlCl_2)_2$, by comparison with the authentic sample. The remaining solution was allowed to stand at room temperature for a period of six months during which time a further quantity of orange crystalline material was deposited and identified as tris(diphenylmethyleneamino)alane $((Ph_2C{=}N)_3Al)_2$, m.pt. 205 - 206° (Found : C 80.4% H 5.9%, Al 4.7%, N 7.5%, Cl Absent, Li Absent, $C_{78}H_{60}Al_2N_6$ requires C 82.5%, H 5.3%, Al 4.8%, N 7.4%) ν_{max}(Nujol mull) 1695(m,sh) 1683(m,sh) 1668(s) 1650(m,sh) 1610(s) 1594(m,sh) 1572(w,sh) 1302(w) 1283(w) 1265(w) 1240(m) 1187(w) 1171(w) 1155(w) 1068(w) 1034(w) 978(w) 968(w) 950(w) 927(w) 911(w,sh) 901(m) 985(w,sh) 824(m) 818(m) 790(s) 773 (w,sh) 709(s,sh) 698(s) 670(m,sh) 618(m) 564(w) 525(w) 487(m) 430(w) cm^{-1}. The compound was exceedingly air sensitive, suffering immediate hydrolysis upon exposure to air.

(iv) Reaction of Diphenylmethyleneaminotrimethylsilane and Aluminium trichloride (3:1),

Aluminium trichloride (0.66g, 4.95 mmol.) in 20 ml of di-n-butyl ether was added to diphenylmethyleneaminotrimethylsilane, $Ph_2C{=}N\,SiMe_3$ (3.77g, 14.88 mmol) in $20cm^3$ di-n-butylether and the mixture refluxed for a total period of 48 hours. After cooling the ether solvent was removed under vacuum, 30 cm^3 of hexane added to the resulting viscous liquid, and the mixture shaken. A quantity of pale cream solid (1.32g) was deposited, filtered and identified as diphenylmethyleneaminoaluminium dichloride $(Ph_2C{=}NAlCl_2)_2$, on the basis of its infra red spectrum (105).

(v) Reaction of Di-t-butylmethyleneaminotrimethylsilane with Aluminium trichloride (3:1).

In a reaction similar to that described above aluminium trichloride (0.63g, 4.72 mmol.) and di-t-butylmethyleneaminotrimethylsilane, $^tBu_2C{=}NSiMe_3$ (3.03g, 14.20 mmol) were refluxed together for a period of sixty hours. A work-up proceedure identical to that described above yielded a white solid (1.07g) identified as di-t-butylmethyleneaminoaluminium dichloride $(^tBu_2C{=}NAlCl_2)_2$ on the basis of its infra red spectrum (105).

(vi) Reactions of Diphenyl- and Di-t-butyl- methyleneaminotrimethylsilane with Aluminium trichloride (3:1) in the absence of solvent.

1:1 molar ratios of the iminotrimethylsilane species $R_2C{=}NSiMe_3$ (R = ^tBu, Ph) and aluminium trichloride were sealed in Carius tubes under vacuum. The tubes were heated to a temperature of 170° for a period of 48 hours before being cooled and opened. In both cases the only identifiable aluminium-containing species were the corresponding methyleneaminoaluminium dichlorides $(R_2C{=}NAlCl_2)_2$, (R = ^tBu, Ph), identified on the basis of their infra red spectra (105).

(vii) Reaction of Diphenylmethyleneaminolithium and Aluminium trichloride (4:1).

Aluminium trichloride (0.62g, 4.65 mmol.) in 10 cm^3 diethylether was added to a frozen (-196°) solution of diphenylmethyleneaminolithium (3.48g, 18.59 mmol.) in 25 cm^3 diethylether, the solution allowed to warm to room temperature, and then refluxed for a period of three hours. Removal of the solvent under vacuum yielded a yellow solid which was extracted with 20 cm^3 of boiling toluene, the solution filtered hot, and allowed to cool. A quantity of yellow solid was deposited which was filtered, washed with a small quantity of cold pentane, pumped dry, and identified as Lithium tetrakis(diphenylmethyleneamino)-aluminate, $LiAl(N{=}CPh_2)_4$ m.pt.244° (Found C 82.3%, H H 5.6%, Al 3.6%, Li 0.9%, N 7.5%, Cl absent. $C_{52}H_{40}AlLiN_4$ requires : C 82.7%, H 5.3%, Al 3.6%, Li 0.9%, N 7.4%) ν_{max} (Nujol mull) 1656(m,sh) 1651(s) 1622(s) 1600(m,sh) 1571(w) 1441(m) 1308(w) 1280(w) 1272(w,sh) 1247(m) 1239(m) 1190(w) 1175(w) 1152(w) 1117(w) 1107(w) 1077(s) 1030(w) 985(w) 967(w) 941(m) 935(w,sh) 915(w) 900(m) 890(w,sh) 877(m) 847(w) 799(s) 787(s) 739(w) 705(s) 684(m,sh) 677(s) 667(m,sh) 630(m) 526(m) 443(w,br) 441(w) cm^{-1}. The compound was extremely sensitive to air, suffering immediate hydrolysis.

(viii) Reaction of Diphenylmethyleneaminolithium and Dimethylaluminium chloride (2:1).

Dimethylaluminium chloride (1.06g, 11.46 mmol.) in 20 cm^3 of diethyl ether was added to a frozen solution of diphenylmethyleneaminolithium (4.30g, 22.97 mmol.) in 40 cm^3 of diethylether, the solution allowed to warm to room temperature, and refluxed for a total period of thirty hours. Removal of the solvent under vacuum yielded a sticky orange material which was extracted with 20 cm^3 of toluene, the solution filtered to remove a small amount of insoluble material, and placed in a freezer at -35°. Over a period of several weeks orange crystals were deposited in the bottom of the flask which were filtered, washed with a small amount of cold pentane and identified as diphenylmethyleneaminolithium, $Ph_2C{=}NLi$, on the basis of its infra red spectrum (116). No further aluminium containing species could be recovered from this reaction.

(ix) Reaction of Fluorenonemethyleneaminotrimethylsilane with Aluminium trichloride (1:1).

Aluminium trichloride (1.1g, 8.35 mmol.) was added to a frozen (-196°) solution of fluorenonemethyleneaminotrimethylsilane (2.10g, 8.35 mmol.) in 30 cm^3 of toluene, the solution stirred to room temperature, and then refluxed for a period of sixty hours. An orange solid was deposited in the flask and, after cooling, was filtered, washed with a small amount of pentane and pumped dry. The solid was identified as fluorenonemethyleneaminoaluminium dichloride, $(C_{12}H_8CNAlCl_2)_2$, m.pt. 220° (dec.) (Found : C 56.1%, H 3.0%, Al 9.6%, Cl 25.4%, N 5.0%, Si absent. $C_{26}H_{16}Al_2Cl_4N_2$ requires : C 56.6%, H 2.9%, Al 9.8%, Cl 25.7%, N 5.1%) ν_{max} (Nujol mull) 1602(m,sh) 1572(s) 1557(m,sh) 1304(m) 1187(m) 1150(w) 1106(m) 1008(w,br) 933(m) 908(w) 868(w)

829(m) 806(m) 794(m,sh) 762(w,sh) 734(m,sh) 721(s) 665(w) 648(m) 579(m) 543(s) 526(w,sh) 506(w) 480(w,br) 413(w,br) cm^{-1}. The compound decomposed slowly upon exposure to to moist air.

TABLE V.1 SUMMARY OF REACTIONS

Reactants	Conditions	Products
$Ph_2C{=}NLi + AlCl_3$	Diethylether, room temp.	$(Ph_2C{=}NAlCl_2)_2 + LiCl$
$2\ Ph_2C{=}NLi + AlCl_3$	Refluxing toluene	$(Ph_2C{=}NAlCl_2)_2 + ((Ph_2C{=}N)_3Al)_2 + LiCl$
$3\ Ph_2C{=}NSiMe_3 + AlCl_3$	i. Refluxing di-n-butylether ii. 170°, no solvent	i. $(Ph_2C{=}NAlCl_2)_2 + Me_3SiCl$ ii. $(Ph_2C{=}NAlCl_2)_2 + Me_3SiCl$
$3\ {}^tBu_2C{=}NSiMe_3 + AlCl_3$	i. Refluxing di-n-butylether ii. 170°, no solvent	i. $({}^tBu_2C{=}NAlCl_2)_2 + Me_3SiCl$ ii. $({}^tBu_2C{=}NAlCl_2)_2 + Me_3SiCl$
$4\ Ph_2C{=}NLi + Al\,Cl_3$	Refluxing diethylether	$LiAl(N{=}CPh_2)_4 + 3\ LiCl$
$2\ Ph_2C{=}NLi + Me_2AlCl$	Refluxing toluene	$Ph_2C{=}NLi$ + ?
$(C_{12}H_8)C{=}NSiMe_3 + AlCl_3$	Refluxing toluene	$((C_{12}H_8)C{=}NAlCl_2)_2 + Me_3SiCl$

DISCUSSION

The reactions described in the experimental section, and discussed in this chpater, are summarised in Table V.1.

Four differing preparative routes have been established for the synthesis of methyleneamino derivatives of aluminium, $(R^1R^2C{=}NAlR^3R^4)_n$, (R^1 = alkyl,aryl; R^2 = H,alkyl,aryl; R^3,R^4 = alkyl,aryl,halogen). The most widely studied route involves the addition of an Al-C or Al-N unit across the C≡N triple bond of a nitrile to form the corresponding iminoalane (Equation V.1), although there are

$$\begin{tikzcd} R^1C\equiv N + R^2R^3R^4Al \arrow[r] & R^1C\equiv NAlR^2R^3R^4 \arrow[d, "\Delta"] \\ & {}^1/n(R^1R^2C{=}NA(R^3R^4)_n \end{tikzcd} \tag{V.1}$$

a number of limitations to the generality of this reaction, imposed by the nature of the alkyl or aryl groups R^1 and R^2. When R^2 = alkyl (other than ethyl), aryl or R_2N, and R^1 is a group with no α-carbon bonded hydrogens, then the reaction will proceed as indicated in Equation V.1, initially forming the stable nitrile-alane complex which will react further upon heating to form the imino product (33,34,169-172). Dialkylaluminium hydrides, R^3R^4AlH, however, will react with nitriles below 0° to yield the correspondong monoalkyl-, or monoaryl-, methyleneaminoalanes, $(R^1CH{=}NAlR^3R^4)_n$, without isolation of the intermediate adduct (33,34,173,174), and in a manner analogous to tetraalkyldiboranes (See Chapter 2).

By contrast, aluminium hydride has been reported to yield polymeric compounds upon reaction with acetonitrile (175). In cases where R^1CN does contain α-carbon bonded hydrogen, and where R^3, R^4, R^5 = alkyl (other than ethyl) or aryl, thermolysis of the adduct forms a mixture of polymeric materials as the major products, rather than the imino aluminium compounds (33,34,176-180) (Equation V.2),

$$R^1CH_2C{\equiv}N + R^2R^3R^4Al \longrightarrow \underset{(I)}{R^1CH_2C{\equiv}NAlR^2R^3R^4} \qquad V.2$$

$$\begin{tikzcd}[column sep=large] & {}^1/n(R^1CH{=}C{=}NAlR^3R^4)_n + R^2H \\ (I) \arrow[ur, "\Delta"] \arrow[dr] & \\ & {}^1/n(R^1CH(AlR^3R^4)CN)_n + R^2H \end{tikzcd}$$

In cases where R^2 is an ethyl group, reaction with a nitrile R^1CN (R^1 = Me, Et, ^tBu) does not yield $(R^1EtC{=}NAlR^3R^4)_n$ as the major product, but the monoalkyliminoalane, $(R^1CH{=}NAlR^3R^4)_n$ together with ethylene (Equation V.3); R^3R^4AlMe thus apparently functioning as a source of R^3R^4AlH

$$R^1CN + R^3R^4EtAl \longrightarrow R^1CNAlEtR^3R^4 \qquad V.3$$

$$\longrightarrow {}^1/n(R^1CH{=}NAlR^3R^4)_n + CH_2{=\!=}CH_2$$

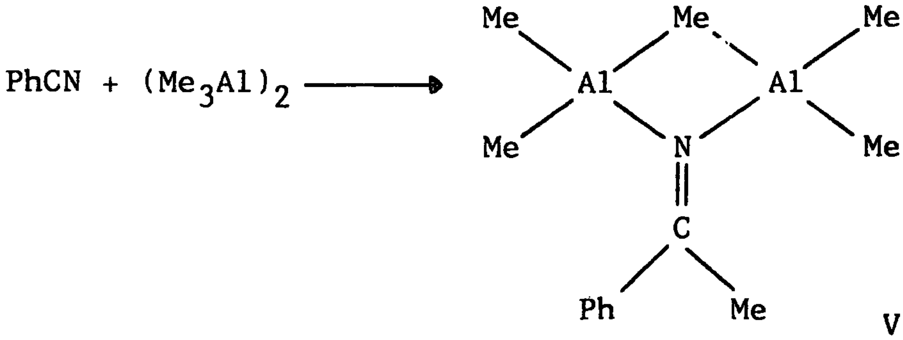
in such reactions. If benzonitrile is reacted with triethyl aluminium however, a mixture of $(PhCH{=}NAlEt_2)_n$ and $(PhCEt{=}NAlEt_2)_n$ is obtained (Equation V.4) (44), the ratio of products depending on the relative amounts of reactants. Thus, if benzonitrile is in excess the

$$\begin{tikzcd}
PhCN + Et_3Al \arrow[r] & PhCNAlEt_3 \arrow[dl, "reduction"'] \arrow[d, "addition"] \\
{}^1/n(PhCH{=}N\,AlEt_2)_n + CH_2 = CH_2 & {}^1/n(PhCEt{=}NAl\,Et_2)_n
\end{tikzcd}$$

V.4

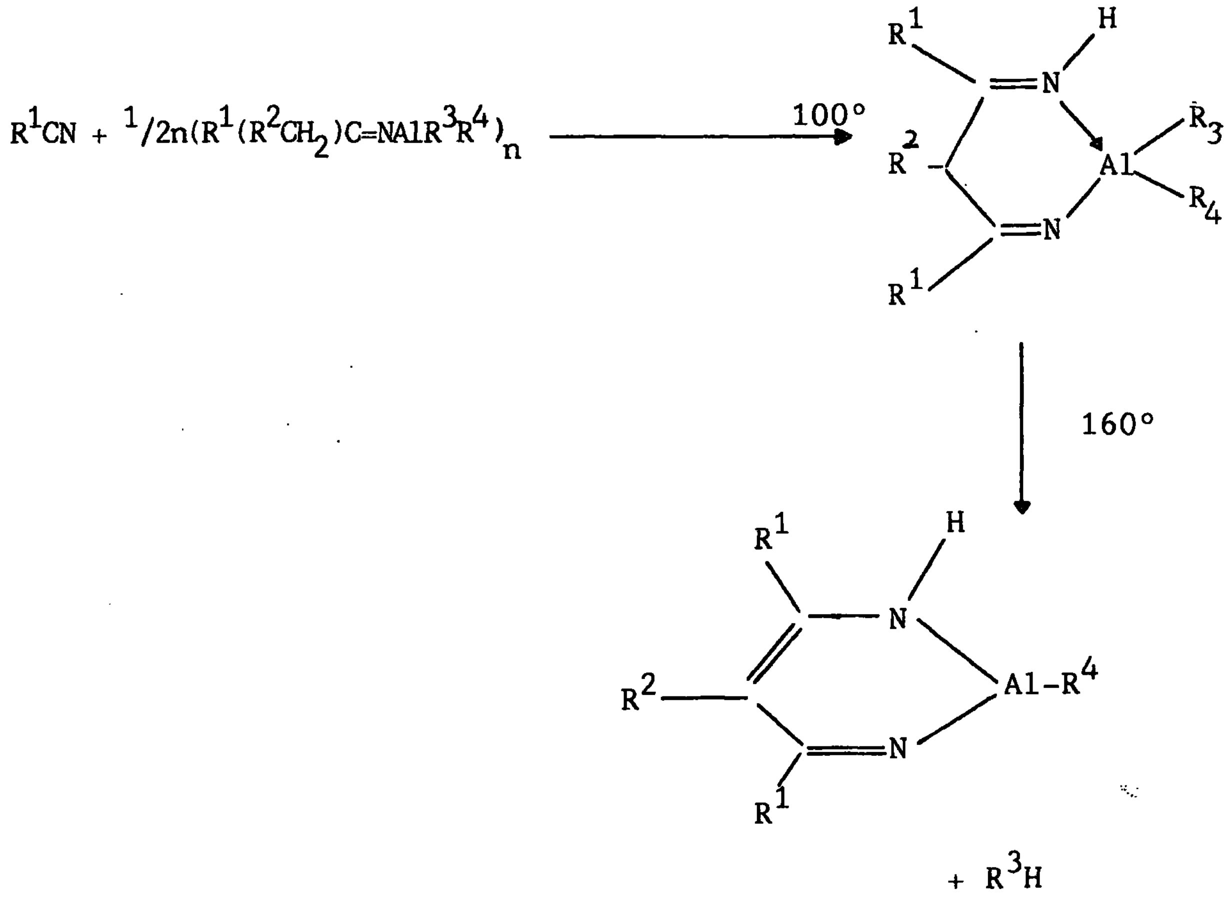
reduction mechanism is favoured, while an excess of triethyl aluminium favours formation of the addition product.

By comparison, the reaction of benzonitrile with two equivalents of trimethyl aluminium yields, not $(PhMeC{=}NAlMe_2)_2$ but the compound $Me_2AlN{=}CMePh.Me.AlMe_2$ (181) (Equation V.5) in a manner analogous to the formation of "hemialkoxides" from reaction of trialkyl aluminium compounds with aldehydes



V.5

and ketones (181-183). Elsewhere (184,185), the reaction of iminoalanes, $(R^1(R^2CH_2)C{=}NAlR^3R^4)_n$ (R^1 = alkyl, aryl; R^2 = alkyl; R^3R^4 = Et, Cl) with further quantities of nitrile, R^1CN, has been shown to yield cyclic derivatives which will themselves rearrange on further heating (Equation V.6).



V.6

The second preparative route to imino alanes involves the thermolysis of the adduct species resulting from the reaction of methyleneamines, $R_2C{=}NH$, ($R = {}^tBu$, Ph, R_2N), with trialkyl alanes R'_3Al, ($R' = Me$, Et, ${}^iBu$, Ph) (186,187) (Equation V.7). In the case of $Ph_2C{=}NH$ the thermolysis reaction will proceed at less than 100° (187), in marked contrast to the analogous reactions of $Ph_2C{=}NH$

$$\begin{tikzcd}
R_2C{=}NH + R'_3Al \arrow[r] & R_2C{=}NHAlR'_3 \arrow[d] \\
R = {}^tBu,Ph,R_2N & {}^1/n(R_2C{=}NAlR'_2)_n + R'H
\end{tikzcd} \qquad V.7$$

with trialkylboranes (124), although $^tBu_2C=NH$ will react with tetramethyldiborane, $(Me_2BH)_2$, to form $^tBu_2C=NBMe_2$ at room temperature (see Chapter 4).

Two further preparative methods have been established, examples of which are discussed in this chapter. Aluminium triahlides, $Al X_3$, (X = Cl,Br) will react with one equivalent of diphenyl-, or di-t-butyl-, methyleneaminolithium to form the corresponding methyleneaminolaluminium dichlorides (Equation V.8) (105), while reaction with four equivalents

$$R_2C=NLi \quad + \quad Al X_3 \longrightarrow \tfrac{1}{2}(R_2C=NAlX_2)_2 \quad + \quad LiX$$
$$R = {}^tBu,Ph \qquad\qquad V.8$$

of the iminolithium species yields the lithium tetrakis(methyleneamino)aluminates $Li Al(N=CR_2)_4$ (Equation V.9)

$$4\ R_2C=NLi \quad + \quad Al Cl_3 \longrightarrow Li Al(N=CR_2)_4 \quad + \quad 3\ LiCl \qquad V.9$$

(17,120). A further reaction between $AlCl_3$ and three equivalents of $Ph_2C=NLi$, yielded the tris(diphenylmethyleneamino)alane, $((Ph_2C=N)_3Al)_2$. (Equation V.10), which is discussed further in this chapter.

$$3Ph_2C=NLi \quad + \quad AlCl_3 \longrightarrow \tfrac{1}{2}((Ph_2C=N)_3Al)_2 \quad + \quad 3LiCl \qquad V.10$$

The diphenylmethyleneaminoaluminium dihalides have also been prepared via the reaction of the iminosilane derivative with the appropriate aluminium halide (105) (Equation V.11), a reaction similar to that used to prepare

$$Ph_2C=NSiMe_3 \quad + \quad AlX_3 \longrightarrow \tfrac{1}{3}(Ph_2C=NAlX_2)_2 \quad + \quad Me_3SiX \qquad V.11$$

some methyleneamino derivatives of boron (46,118,120).

(See discussion in Chapter 4). The preparation of $((C_{12}H_8)C{=}NAlCl_2)_2$, by reaction of $(C_{12}H_8)C{=}NSiMe_3$ with $AlCl_3$, is further example of this type of reaction and is described in this chapter.

Tris(diphenylmethyleneamino)alane, $((Ph_2C{=}N)_3Al)_2$

The reaction of aluminium trichloride and two molar equivalents of diphenylmethyleneaminolithium in toluene yielded, not bis(diphenylmethyleneamino)aluminium chloride, but a mixture of diphenylmethyleneaminoaluminium dichloride and tris(diphenylmethyleneamino)alane (Equation V.12). The latter compound, an orange crystalline solid, was

$$2Ph_2C{=}NLi + AlCl_3 \longrightarrow \tfrac{1}{4}(Ph_2C{=}NAlCl_2)_2 + \tfrac{1}{4}((Ph_2C{=}N)_3Al)_2 + 2LiCl \qquad \text{V.12}$$

first reported (105) as being obtained from the reaction of three equivalents of $Ph_2C{=}NLi$ with $AlCl_3$ in diethyl ether, the workers concluding it to be monomeric on the basis of cryoscopic measurements, its mass and infra red spectra, as well as its extreme moisture sensitivity. Mass spectral evidence obtained during the course of the present study (see Table V.5), together with a re-evaluation of its infra red spectrum, however, suggested the compound might be associated in the crystal phase, as has now been confirmed by a recent X-ray crystallographic study performed by Dr. W. Clegg (Göttingen University). This represents the first structural determination of a tris(methyleneamino)alane derivative and, after $LiAl(N{=}C^tBu_2)_4$ (105), only the second example of a group III element bonded to both terminal and bridging methyleneamino ligands in the same molecule.

The structure of $((Ph_2C{=}N)_3Al)_2$, with protons omitted, is shown in Figure V.1 with selected bond lengths and angles listed in Table V.2. In addition to $LiAl(N{=}C^tBu_2)_4$, two other methyleneaminoalanes, $(^tBuMeC{=}NAlMe_2)_2$ (8) and $(p\text{-}Br\text{-}C_6H_4(Ph)C = NAlPh_2)_2 . C_6H_6$ (188), have been the subject of crystallographic studies, both compounds containing imino ligands bridging the aluminium atoms. Both the above compounds, together with $((Ph_2C{=}N)_3Al)_2$, contain planar $(AlN)_2$ rings although, unlike the other two, $((Ph_2C{=}N)_3Al)_2$ is not a centrosymmetric molecule, the orientation and geometry of all six imino ligands being different. Similar cyclic $(MN)_2$ ring structures have also been proposed for the dimeric aminoalanes $(^iPr_2NAlH_2)_2$, $(Me_2NAlCl_2)_2$, $((Me_2N)_2AlCl)_2$ and $((Me_2N)_3Al)_2$ (189,190) as well as for a number of aminogallanes (191,192)

The $(AlN)_2$ ring of $((Ph_2C{=}N)_3Al)_2$ is almost square, the average internal ring angles of $N\hat{Al}N$, 84.2°, and $Al\hat{N}Al$, 95.4°, falling at intermediate values to those of $(^tBuMeC{=}NAlMe_2)_2$ (85.4° and 94.6°) and $(p\text{-}Br\text{-}C_6H_4(Ph)C{=}NAlPh_2)_2 . 2.C_6H_6$ (82.9° and 97.1°). In each case the larger internal ring angle occurs at the bridging nitrogen, as was also found in the case of the iminoboranes $(RCH{=}NBMe_2)_2$(R=Me(8), Ph(9)), and again reflects the greater electronegativity of the nitrogen atom compared with the group III element. In consequence of this decrease in $N\hat{Al}N$ ring angle, from that of 109.5° required for a tetrahedral conformation around aluminium, a corresponding increase in the external ring angles $N(3)\hat{Al}(1)N(4)$ (120.1(1)°) and $N(5)\hat{Al}(2)N(6)$ (126.5(1)°) is observed, again mirroring

FIGURE V.1 Molecular structure of $[(Ph_2C{=}N)_3Al]_2$

(hydrogen atoms omitted)

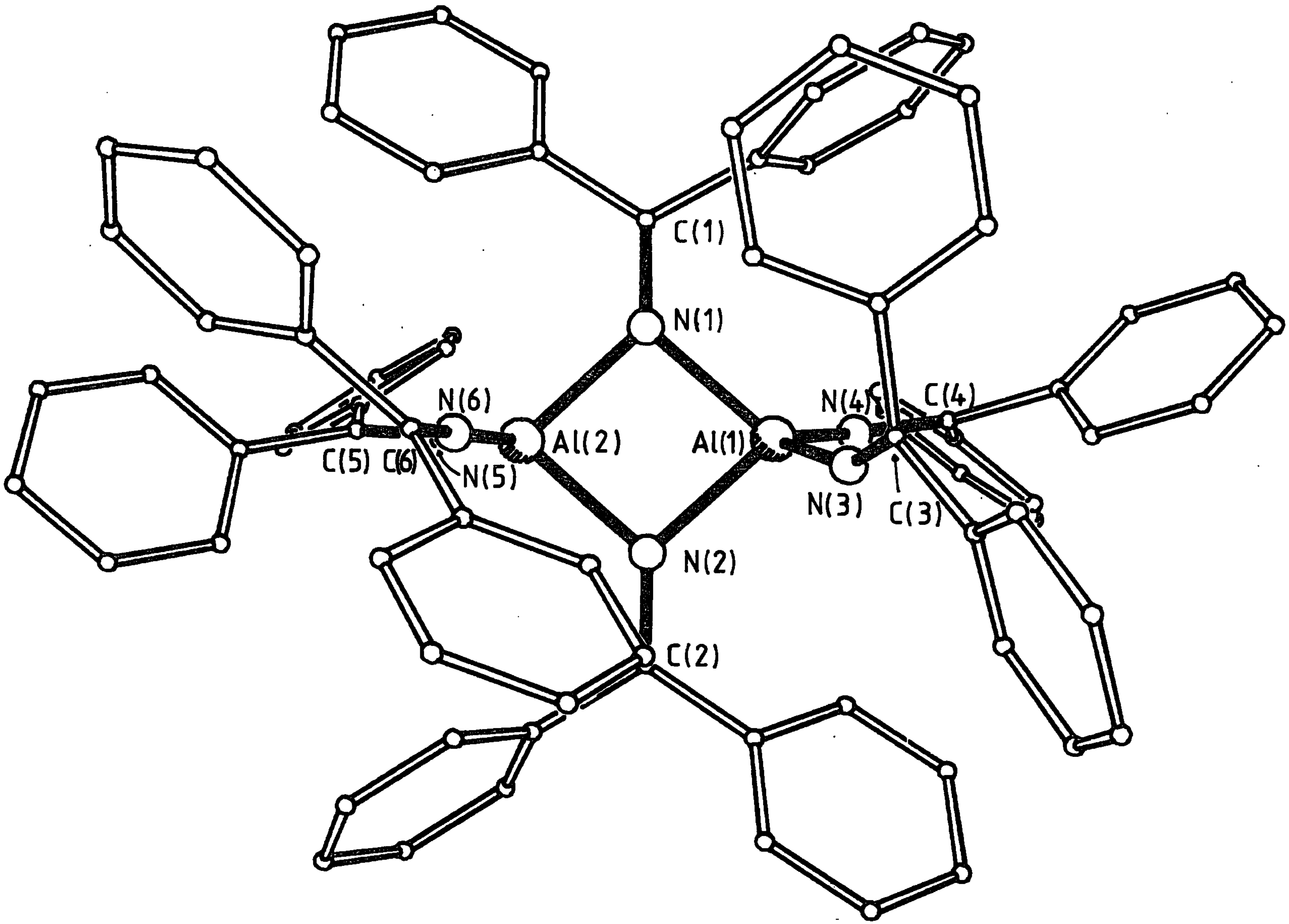


TABLE V.2

Selected bond lengths (Å) and angles (°) in $((Ph_2C{=}N)_3Al)_2$

Al(1)-N(1)	1.930(3)	Al(1)-N(2)	1.933(3)
Al(2)-N(1)	1.926(3)	Al(2)-N(2)	1.920(3)
Al(1)-N(3)	1.781(3)	Al(1)-N(4)	1.797(3)
Al(2)-N(5)	1.786(3)	Al(2)-N(6)	1.775(3)
N(1)-C(1)	1.290(4)	N(2)-C(2)	1.278(5)
N(3)-C(3)	1.257(4)	N(4)-C(4)	1.260(4)
N(5)-C(5)	1.257(4)	N(6)-C(6)	1.254(4)
N(1)-Al(1)-N(2)	84.0(1)	N(1)-Al(1)-N(3)	118.7(1)
N(2)-Al(1)-N(3)	104.8(1)	N(1)-Al(1)-N(4)	110.0(1)
N(2)-Al(1)-N(4)	113.2(1)	N(3)-Al(1)-N(4)	120.1(1)
N(1)-Al(2)-N(2)	84.4(1)	N(1)-Al(2)-N(5)	107.6(1)
N(2)-Al(2)-N(5)	110.6(1)	N(1)-Al(2)-N(6)	107.7(1)
N(2)-Al(2)-N(6)	111.7(1)	N(5)-Al(2)-N(6)	126.5(1)
Al(1)-N(1)-Al(2)	95.3(1)	Al(1)-N(1)-C(1)	131.0(2)
Al(2)-N(1)-C(1)	132.6(2)	Al(1)-N(2)-Al(2)	95.4(1)
Al(1)-N(2)-C(2)	133.3(2)	Al(2)-N(2)-C(2)	130.5(2)
Al(1)-N(3)-C(3)	155.4(3)	Al(1)-N(4)-C(4)	148.2(3)
Al(2)-N(5)-C(5)	148.2(3)	Al(2)-N(6)-C(6)	175.2(2)

the increase in the $C\hat{B}C$ angle of the iminoborane. The average $(AlN)_2$ ring bond length of 1.927Å falls between those of 1.916(10)Å in $(p\text{-}Br\text{-}C_6H_4(Ph)C{=}N\,AlPh_2)_2 2.C_6H_6$ (188), and 1.942Å, in $(^tBuMeC{=}NAlMe_2)_2$ (8), while all are shorter than the corresponding $Al(sp^3)\text{-}N(sp^3)$ bond length of 1.96Å in the dimeric aminoalane $(Me_2NAlMe_2)_2$ (193). Differences in the observed Al-N bond lengths in the present compound are significant, and probably reflect the strain imposed on the $(AlN)_2$ ring by the packing of the imino ligands within the crystal lattice. The average terminal Al-N bond length of 1.785Å is essentially identical to that of 1.78Å found for the terminally-attached $^tBu_2C{=}N\text{-}$ ligands in the compound $LiAl(N{=}C^tBu_2)_4$ (17), while being substantially shorter than that of c a. 1.94Å expected for a single Al-N bond (193-197). Such shortening is consistent with the existence of a significant degree of dative π bonding between a lone-pair occupied p orbital of nitrogen, and a vacant d orbital of aluminium, the $N \rightharpoonup Al$ bond lengths of 1.78Å, in $((Me_3Si)_2N)_3Al$ (198), and 1.79Å, in $Al_4Cl_4(NMe_2)_4(NMe)_2$ (195) having been attributed to a similar effect.

Further evidence of $N \rightharpoonup Al$ pπ - dπ bonding should also be seen in the $C\hat{N}Al$ bond angles of the four terminally attached ligands, arising from the distortion, from sp^2 to nearly sp, of the hybridisation state of the nitrogen atom. The two terminal ligands of the compound $LiAl(N{=}C^tBu_2)_4$ (17) show evidence of this effect, both having a $C\hat{N}Al$ angle of 167°. A similar distortion is indeed displayed by the terminal ligands of $((Ph_2C{=}N)_3Al)_2$, although the observed differences in the magnitude of the distortion are striking. Three of the four ligands have $C\hat{N}Al$ angles of c a. 150° while the fourth terminal ligand has an angle at nitrogen of 175.2(2)°, almost as large as that of 178.2(4)° in $^tBu_2C{=}NBPh_2$ (see chapter 4), where the linearity of the ligand arises through the coordinative unsaturation of the metalloid. Consideration of the $((Ph_2C{=}N)_3Al)_2$ molecule as a whole would suggest that the unique, near linear, CNAl unit arises in consequence of the steric constraint imposed upon the ligand by the extremely crowded ligand coordination sphere, while the magnitude of the angle difference would imply that such deformations are energetically relatively soft. Similar, although less marked, differences in the $C\hat{N}MX_n$ angles have been noted in the crystal structures of the compounds $(Ph_2C{=}N)_4Si$ (4) and $(Ph_2C{=}N)_3P$ (3), where the effect is again explicable in terms of inter-, and intra-, molecular steric repulsions. The terminal-ligand average C=N bond length of 1.257Å is similar to that of 1.27Å in $LiAl(N{=}C^tBu_2)_4$ (17) and falls at an intermediate value to those of 1.29(2)Å, in $Ph_2C{=}NB(mesityl)_2$ (15), and 1.243(5)Å in $^tBu_2C{=}NBPh_2$ (see chapter 4). The bridging C=N bond lengths of 1.290(4)Å and 1.278(5)Å are somewhat longer than the terminal C=N bonds, while being similar to that of 1.282(15)Å in $(p\text{-}Br\text{-}C_6H_4(Ph)C{=}NAlPh_2)_2\ 2.C_6H_6$ (188) and only slightly longer than those of 1.27Å, in $LiAl(N{=}C^tBu_2)_4$, and 1.272Å in $(^tBuMeC{=}NAlMe_2)_2$ (8).

Consideration of the orientations adopted by the phenyl rings in the molecule reveals that all show some displacement from co-planarity with the CN Al imino unit to which they are bonded. Such a configuration, preventing the possibility of significant π-electron delocalisation between the C=N and phenyl π systems, has been observed in all the structurally-characterised associated diphenylmethyleneamino compounds (6-9, 188), and in this case reflects not only the steric interaction between the phenyl rings of an imino ligand, but also the extreme steric crowding between all twelve phenyl rings in the molecule. Of further interest is the observation that all four phenyl rings bonded to bridging imino ligands orientate themselves out of the $(AlN)_2$ plane, and thus remove the possibility of interaction between the aluminium atoms and the ortho-bonded protons of the rings. Any such interaction would be maximised by one of the phenyl rings aligning itself co-planar with the $(AlN)_2$ unit where, calculation would suggest, the ortho-proton would be approximately 2.0 Å distant from the aluminium nucleus.

The compounds infra red spectrum contained two absorptions, at 1610 cm^{-1} and 1668 cm^{-1}, attributable to the ν (C=N) and ν (C=N⇌Al) stretching modes of the imino ligands. The values are listed in Table V.3 together with those of a number of other methyleneamino derivatives of aluminium and the parent methyleneamines. The lower frequency absorption, 1610 cm^{-1}, is assigned to the ν (C=N) stretching vibration of the bridging methyleneamino

TABLE V.3

ν(C=N) and ν(C=N$\overset{\rightharpoonup}{=}$Al) stretching frequencies of the methyleneamino-aluminium derivatives and related methyleneamines

Compound	Phase	ν(C=N)	ν(C=N$\overset{\rightharpoonup}{=}$Al)	Ref.
$(Ph_2C{=}NAlCl_2)_2$	nujol mull	1573	-	(a)
$(Ph_2C{=}NAlPh_2)_2$	nujol mull	1604	-	187
$((Ph_2C{=}N)_3Al)_2$	nujol mull	1610	1668	(a)
$LiAl(N{=}CPh_2)_4$	nujol mull	1622	1651	(a)
$((C_{12}H_8)C{=}NAlCl_2)_2$	nujol mull	1572	-	(a)
$Ph_2C{=}NH$	liq. film	1603	-	187
$(^tBu_2C{=}NAlCl_2)_2$	nujol mull	1664	-	105
$LiAl(N{=}C^tBu_2)_4$	nujol mull	1642	1700	120
$^tBu_2C{=}NH$	liq. film	1608	-	114

(a) This work

TABLE V.4

^1H n.m.r. spectra of the methyleneamino-aluminium derivatives

Compound	Solvent	τ	Ref.
$(Ph_2C{=}NAlCl_2)_2$	Toluene	2.6 - 2.9	105
$((Ph_2C{=}N)_3Al)_2$	$CDCl_3$	2.58 - 2.95 (m)	(a)
$LiAl(N{=}CPh_2)_4$	$CDCl_3$	2.7(m),3.02(m)	(a)
$((C_{12}H_8)C{=}NAlCl_2)_2$	(b)	(b)	(a)

(a) This work

(b) Compound insufficiently soluble

(m) Multiplet

ligand and compares with those of 1622 cm^{-1}, for the bridging ligands in $LiAl(N{=}CPh_2)_4$, and 1604 cm^{-1}, in $(Ph_2C{=}NAlPh_2)_2$ (187). All these values are above that of the ν(C=N) stretching frequency of the parent imine, $Ph_2C{=}NH$, (1603 cm^{-1} (187)) although the bridging ligand of $(Ph_2C{=}NAlCl_2)_2$ (105) absorbs at the lower value of 1573 cm^{-1} (Lit.(105), 1593 cm^{-1}). Interestingly, the ν(C=N) stretching frequency of $(^tBu_2C{=}NAlCl_2)_2$ (1664 cm^{-1} (105)) is considerably higher than that of the free imine, $^tBu_2C{=}NH$ (1608 cm^{-1} (114)). The higher absorption frequency of 1668 cm^{-1} is attributable to the asymmetric vibration ν(C=N$\doteq$Al) of the terminal ligands, and compares with that of 1651cm^{-1} for the analogous vibrational mode of $LiAl(N{=}CPh_2)_4$. Both values are towards the lower end of the region, 1640 cm^{-1} to 1780 cm^{-1}, in which the ν(C=N$\doteq$Si) absorptions of the iminosilane derivatives $R_2C{=}NSiR_nCl_{3-n}$ and $(R_2C{=}N)_nSiX_{4-n}$ (R = alkyl, aryl; X = alkyl, halogen) (98,118,199,200) are found. In all these cases the marked increase in the frequency of ν(C=N), above that of the free imine, arises through coupling with the metal or metalloid, and reflects the existence of $p\pi - d\pi$ dative bonding in the N-Al, and N-Si, linkages.

The ^1H n.m.r. spectrum of $((Ph_2C{=}N)_3Al)_2$ was recorded from a $CDCl_3$ solution and contained a complex series of aromatic proton resonances in the range $\tau = 2.58$ to 2.95 (Table V.4). The complexity of the spectrum is not surprising in view of the lack of symmetry in the associated molecule although it should not, of itself, be regarded as evidence of a dimeric state of association in the solution phase.

Features of the compunds mass spectrum are listed in Table V.5. The highest observed $^{m}/e$ value of 774 would correspond to the ion $((Ph_2C{=}N)_4Al_2)^+$, resulting from the loss of two imino units from the parent molecule, and is evidence of some degree of association persisiting in the vapour phase.

TABLE V.5

Major peaks in the mass spectrum of $((Ph_2C{=}N)_3Al)_2$

$^{m}/e$	Relative Intensity	Assignment
774	2	$Ph_8(CN)_4Al_2$
567	10	$Ph_6(CN)_3Al$
490	3	$Ph_5(CN)_3Al$
387	15	$Ph_4(CN)_2Al$
310	9	$Ph_3(CN)_2Al$
233	6	$Ph_2(CN)_2Al$
181	67	Ph_2CNH
180	85	Ph_2CN
104	63	PhCNH
103	100	PhCN
78	54	PhH
77	93	Ph

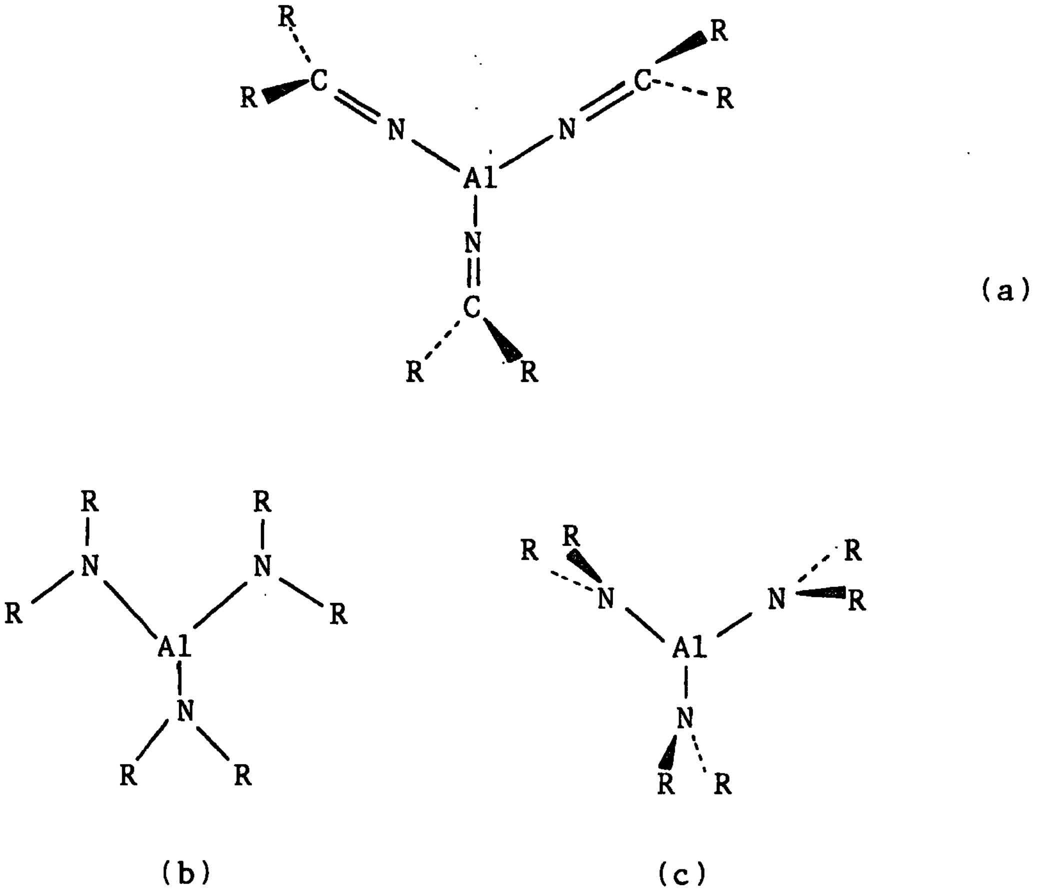
The preparation of $((Ph_2C{=}N)_3Al)_2$, by reaction of $AlCl_3$ with two equivalents of $Ph_2C{=}NLi$, illustrates a general feature of the imino-derivative chemistry of aluminium, namely, a failure to prepare bis(methyleneamino) derivatives of the form $((R_2C{=}N)_2AlX)_n$ (R=^{t}Bu, aryl; X=alkyl,aryl,halogen) (105). A similar feature has also characterised the imino-derivative chemistry of phosphorus III (see Chapter 3) as well as some boron (38), silicon (96,97,105) and germanium (96) systems. Further, the dimeric state of association of $((Ph_2C{=}N)_3Al)_2$, was, initially, surprising in view of earlier reports (105) that it was monomeric in the solution and vapour phases, although kinetic studies (201,202) on a number of nitrile/R_3Al reactions have indicated that the dimeric state of association of methyleneaminolalane derivatives is the thermodynamically most preferred. The present study was prompted, in part, by continuing uncertainty as to the existence of such tris(methyleneamino)alanes, $(R_2C{=}N)_3Al$ (R=^{t}Bu,Ph) following contradictory reports (1,105) of their preparation and spectroscopic properties.

Interest in these systems initially arose through the realisation that the compounds may have monomeric structures, dictated by the steric bulk of the phenyl, and particularly t-butyl substituents, and as such should display evidence of N(2p)-Al(3p) dative π bonding. Such bonding, between the lone-pair occupied p orbital of a formally sp-hybridised nitrogen atom, and the appropriate p orbital of an sp^2-hybridised aluminium, would be maximised by the adoption of a linear C=N$\Rightarrow$Al unit, thus permitting the greatest degree of overlap between the orbitals concerned. A consequence of this conformation would be the adoption of a "paddle wheel" configuration by the carbon-bonded substituents; the groups positioned directly above and below the plane defined by the aluminium and nitrogen atoms (Figure V.2(a)). Similar pπ- pπ dative bonding should, in principle, also occur in the monomeric aminoalanes, $(R_2N)_3Al$, where the bulk of the substituent, R, is such as to prevent association (Figure V.2(b)). In these cases however, sp^2 hybridisation of the nitrogen valence orbitals would require the groups, R, to be co-planar with the AlN_3 unit, and it is found in practice that the bulk of the groups required to prevent association also prevents the adoption of a co-planar orientation. In such cases the molecule is forced to adopt a non-planar structure (Figure V.2(c)), such as has been established for the compound $((Me_3Si)_2N)_3Al$ (198), with consequent reduction in the extent of dative π interaction.

Earlier attempts to synthesise $(^tBu_2C{=}N)_3Al$, which is expected to be monomeric in consequence of the steric demands of the t-butyl substituents, were made by the reaction of aluminium trichloride with three molar equivalents of t-butylmethyleneaminolithium. The material isolated from the reaction was initially suggested (105) to be the desired product, monomeric tris(di-t-butylmethyleneamino) alane, although subsequent work (1) has suggested it to be a mixture of $(^tBu_2C{=}NAlCl_2)_2$, $LiAl(N{=}C^tBu_2)_4$,

FIGURE V.2

Possible structures of the monomeric tris(imino)-, and tris(amino)-, alanes, $(R_2C{=}N)_3Al$ and $(R_2N)_3Al$



and possibly other species, arising from a disproportionation reaction (Equation V.13). Another report (1) of its

$$3\,{}^t\mathrm{Bu_2C{=}NLi} + \mathrm{Al\,Cl_3} \longrightarrow \mathrm{Li\,Cl} + ({}^t\mathrm{Bu_2C{=}NAl\,Cl_2})_2 + \mathrm{LiAl(N{=}C^tBu_2)_4} + \text{others?} \qquad \text{V.13}$$

synthesis via the reaction of an ethereal solution of aluminium hydride with di-t-butylmethyleneamine (Equation V.14) must be questioned in the absence of wholly satisfactory physical data. This thesis also describes attempts

$$3{}^{t}Bu_2C{=}NH + AlH_3 \xrightarrow{Et_2O} ({}^{t}Bu_2C{=}N)_3Al + {}^{3}/_{2}\,H_2 \qquad V.14$$

to synthesise both the phenyl- and t-butyl-, derivatives, $((R_2C{=}N)_3Al)_n$, via the reaction of appropriate stoichiometric quantities of aluminium trichloride and the corresponding methyleneaminotrimethylsilane, $R_2C{=}NSiMe_3$. In both cases reaction resulted in the substitution of only one chlorine to form the corresponding methyleneaminoaluminium dichloride derivative (Equation V.15) which would not undergo further

$$R_2C{=}NSiMe_3 + AlCl_3 \longrightarrow \tfrac{1}{2}(R_2C{=}NAlCl_2)_2 + Me_3SiCl \qquad V.15$$

$$R = {}^{t}Bu, Ph$$

reaction. In view of the successful preparation of $((Ph_2C{=}N)_3Al)_2$ by another route (Equation V.12), this observation would therefore suggest that the reaction of more than one Al-Cl unit with a methyleneaminosilane derivative is a non-viable process, while not, of itself, implying anything concerning the relative stability of diphenyl-, and di-t-butyl-, methyleneaminoaluminium derivatives. Conclusions may be drawn, however, from the observation that $((Ph_2C{=}N)_3Al)_2$ adopts an associated structure, whereas $({}^{t}Bu_2C{=}N)_3Al$ is likely to be monomeric.

In the former case, association of the molecule will alow aluminium to assume a four-coordinate, valence-saturated, conformation, thus assigning a considerable degree of stability to the dimeric species. In the t-butyl derivative however, such association is unlikely to be possible, and the resulting instability of the three-coordinate aluminium species renders it susceptible to further reaction with a donor molecule. Such a proposal would account for the formation of mixtures of $({}^{t}Bu_2C{=}NAlCl_2)_2$ and $LiAl(N{=}C{}^{t}Bu_2)_4$, from the reaction of $AlCl_3$ with three equivalents of ${}^{t}Bu_2C{=}NLi$ (Equation V.13), as well as the observation that nitrile-donor complexes of the form $({}^{t}Bu_2C{=}N)_3AlNCR$ can be prepared (1,13).

Lithium tetrakis(diphenylmethyleneamino)aluminate $LiAl(N=CPh_2)_4$

The reaction of aluminium trichloride with four molar equivalents of diphenylmethyleneaminolithium in diethyl ether yielded, after removal of the ether and extraction with toluene, a yellow, crystalline, air sensitive solid which was identified as lithium tetrakis (diphenylmethyleneamino)aluminate, $Li\,Al(N=CPh_2)_4$ (Equation V.16). The analogous t-butyl derivative $LiAl(N=C^tBu_2)_4$

$$4Ph_2C=NLi + AlCl_3 \longrightarrow Li\,Al(N=CPh_2)_4 + 3Li\,Cl \qquad V.16$$

was prepared during an earlier study of di-t-butylmethyleneamino derivatives of aluminium (105,120) and has been the subject of an earlier crystallographic study (17) (see Figure V.3), while the iminogallate $LiGa(N=C^tBu_2)_4$ has also been prepared (203). More recent claims (1) concerning the synthesis of the compounds $Li\,AlMe_2(N=C^tBu_2)_2$ and $LiAlMe_3(N=C^tBu_2)$ must be regarded as uncertain in the absence of satisfactory analytical and spectroscopic data. Unsuccessful attempts were made, during the course of the present study, to prepare the compound $LiAlMe_2(N=CPh_2)_2$ from the reaction of Me_2AlCl and two equivalents of $Ph_2C=NLi$, $(Ph_2C=NLi)_n$ being the only solid material recovered from the reaction, while reaction of $AlCl_3$ with two equivalents of $Ph_2C=NLi$ yielded a mixture of $(Ph_2C=NAlCl_2)_2$ and $((Ph_2C=N)_3Al)_2$ rather than $Li\,Al\,Cl_2(N=CPh_2)_2$.

The infra red spectrum of $LiAl(N=CPh_2)_4$ contained two bands, at 1651 cm^{-1} and 1622 cm^{-1}, attributable to the ν(C=N$\rightharpoonup$Al) and ν(C=N) stretching modes. By analogy with Li Al(N=$C^tBu_2)_4$ (17,120) the higher frequency vibration is assigned to the ν(C=N$\rightharpoonup$Al) stretch in the terminally-bonded imino ligand (c f. 1668 cm^{-1} for the terminal ligand stretching frequency in $((Ph_2C=N)_3Al)_2$) and again demonstrates the increase in ν(C=N) stretching frequency associated with N(p) - Al(d) dative π bonding. The lower frequency at 1632 cm^{-1} is assigned to the ν(C=N) vibration of the two imino ligands bridging the aluminium and lithium atoms, and compares with that of 1610 cm^{-1} for the bridging ν (C=N) vibration in $((Ph_2C=N)_3Al)_2$.

The ^{1}H n.m.r. spectrum of the compound was obtained from a solution in $CDCl_3$ and contained two unresolved multiplet resonances, centred at τ values of 2.71 and 3.02, the integration of which gave respective peak intensities of approximately 2:3 which were not readily interpretable. Similar complex multiplet signals were observed in the spectrum of $LiAl(N=C^tBu_2)_4$, between τ values of 8.55 and 9.44 (120).

The results obtained from the earlier X-ray structure determination of the compound Li Al(N=$C^tBu_2)_4$ are summarised in Figure V.3 Table V.6. On the basis of the available spectroscopic evidence a similar structure is proposed for the compound $LiAl(N=CPh_2)_4$, in which two of the imino ligands bridge the Li and Al atoms while the remaining two, termianlly bonded, ligands display a significant degree of N(p) - Al(d) dative π bonding. The most

FIGURE V.3

Molecular structure of Li Al(N=C^{t}Bu$_2$)$_4$(17).

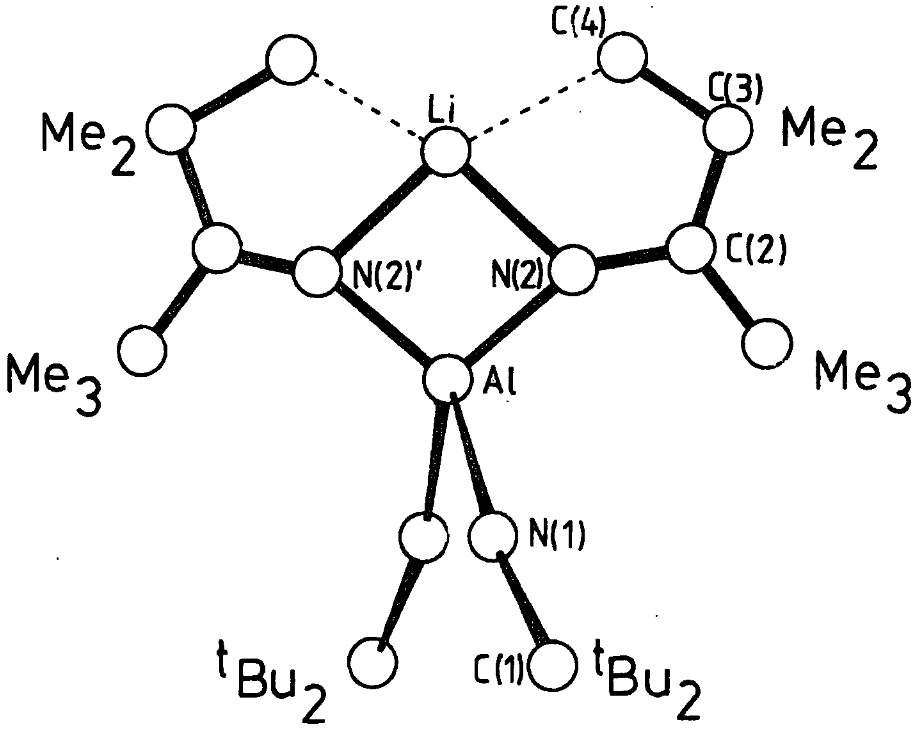


TABLE V.6

Selected lengths (Å) and angles (°) for

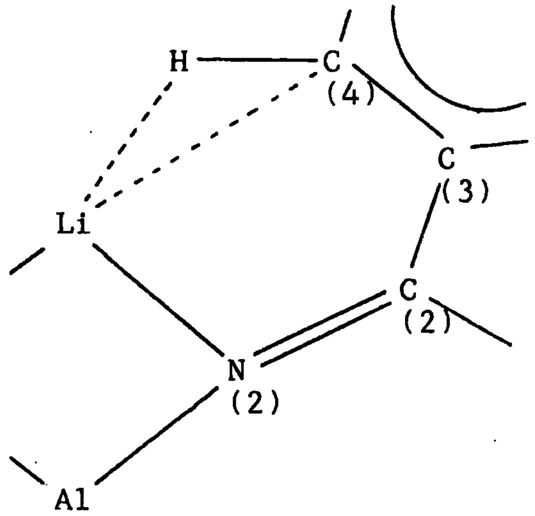
LiAl(N=C^{t}Bu$_2$)$_4$(17)

Al-N(1)	1.78(1)	Al-N(2)	1.87(1)
N(2)-Li	1.95(2)	N(2)-C(2)	1.27(1)
C(2)-C(3)	1.56(1)	C(3)-C(4)	1.54(2)
Al ... Li	2.55(1)	Li ... C(4)	2.37(2)
Al(1)-N(1)-C(1)	167.2	N(2)-Al-N(2)'	98.5
Al-N(2)-Li	83.9	Al-N(2)-C(2)	148.6
N(2)-C(2)-C(3)	117.7	C(2)-C(3)-C(4)	110.3

notable feature of the $LiAl(N=C^{t}Bu_2)_4$ structure, however, was the observation that the large $C\hat{N}Al$ bridging angle of 148.6° has the effect of moving one of the bridging-ligand t-butyl groups towards the Li ... Al axis. In each of the t-butyl groups in question, and despite the fact that, in principle, free rotation about the $C-{}^{t}Bu$ bonds can occur, one of the methyl carbon atoms aligns itself as close as possible to the lithium atom, within the constraint of a normal C-C bond length. The resulting C(4) ... Li distance of 2.37Å is only slightly longer than that of 2.31Å in $(MeLi)_4$ (204) although somewhat longer than a formally single C-Li bond of ca. 2.18Å (205,206,207). Of greater significance however, is the observation that a Li ... H ... C(4) angle of ca. 107.6° would enable one of the methyl protons of the tetrahedrally coordinate carbon to align itself almost directly between the lithium and carbon atoms, and thus give rise to the possibility of a three-centre bonding interaction. Unfortunately however, the protons were not located in this instance and the fact that the tetrahedral conformation of C(4) would enable the protons to avoid the Li ... C(4) axis meant that the existence of a three-centre interaction could not be conclusively established on the basis of this structural determination. The synthesis of $LiAl(N=CPh_2)_4$ was therefore undertaken in an attempt to conclusively demonstrate this point. In this instance location of the two phenyl rings adjacent to the lithium atom would define the plane containing the ortho phenyl proton, structurally analogous to the methyl proton of the t-butyl derivative, and hence establish its position relative to the lithium atom (Figure V.4). Unfortunately however, it has not proved possible to produce single crystals of Li Al(N=CPh$_2$)$_4$ suitable for use in a crystallographic study, and hence the question of such Li ... H ... C interactions in this compound as yet remain unproven. Calculation would suggest that the Li ... C(4) distance to the ortho carbon of a phenyl ring, co-

FIGURE V.4

Detail of proposed structural conformation in LiAl(N=CPh$_2$)$_4$



planar with C(2), N(2), Al and Li (Figure V.4), would be approximately 2.59Å (c f. 2.39Å in LiAl(N=C^{t}Bu$_2$)$_4$) while the ortho H atom, in a normal phenyl conformation, would be placed approximately 0.36 Å from the direct line of the Li ... C(4) axis. It is therefore possible that such a three-centre interaction exists in this compound, although no direct spectroscopic evidence has been found for this.

Fluorenonemethyleneaminoaluminium dichloride, $((C_{12}H_8)C{=}NAlCl_2)_2$

The reaction of aluminium trichloride with an equimolar amount of fluorenonemethyleneaminotrimethylsilane, $(C_{12}H_8)C{=}N\,SiMe_3$, in refluxing toluene resulted in formation of fluorenonemethyleneaminoaluminium dichloride, $((C_{12}H_8)C{=}NAlCl_2)_2$ (Equation V.17). The compound, an

$$(C_{12}H_8)C{=}NSiMe_3 \quad + \quad AlCl_3 \longrightarrow \tfrac{1}{2}((C_{12}H_8)C{=}NAl\,Cl_2)_2 \quad + \; Me_3SiCl \qquad V.17$$

amorphous orange solid, proved to be effectively insoluble in a wide range of non-reactive organic solvents, while exposure to moist air resulted in its slow decomposition. The mass spectrum (Table V.7), contained, as the highest mass peaks observed, a series of peaks with a maximum $^m/e$ value of 558, assigned to the molecular ion $((C_{12}H_8)CNAlCl_2)_2$, and confirmed as such by comparison with a computed isotope peak pattern. The compound would thus appear to exist as a dimeric species in the vapour phase, similar to the related methyleneaminoalanes $(Ph_2C{=}NAlCl_2)_2$ and $(^tBu_2C{=}NAlCl_2)_2$ (105), where cryoscopic measurements established the dimeric state to persist in solution. One further significant feature of the mass spectrum was the existence of a large peak due to the monomeric species $(C_{12}H_8)C{=}NAlCl_2^+$; this feature was notably absent from the mass spectrum of the analogous diphenyl derivative $(Ph_2C{=}NAlCl_2)_2$ (105).

TABLE V.7

Major peaks in the mass spectrum of

$((C_{12}H_8)CNAlCl_2)_2$

$^m/e$	Relative Intensity	Assignment
550	22	$((C_{12}H_8)CNAlCl_2)_2$
515	5	" -Cl
275	63	$(C_{12}H_8)CNAlCl_2$
240	13	$(C_{12}H_8)CNAlCl$
205	10	$(C_{12}H_8)CNAl$
179	92	$(C_{12}H_8)CNH$
178	100	$(C_{12}H_8)CN$
164	15	$(C_{12}H_8)C$
154	19	$(C_6H_5)_2$
153	27	$C_{12}H_9$
152	47	$C_{12}H_8$
129	23	C_6H_4CNAl
103	27	C_6H_5CN
102	74	C_6H_4CN
77	67	C_6H_5
76	86	C_6H_4

Note: $^m/e$ values refer to ^{35}Cl isotope

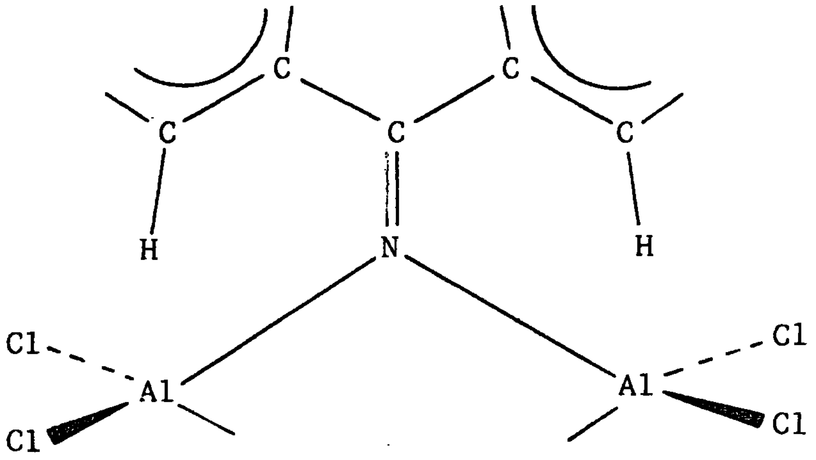
The infra red spectrum (Table V.3) contained a strong absorption at 1572cm^{-1}, attributable to the ν(C=N) stretching mode of the bridging methyleneamino ligand and essentially identical to that of 1573cm^{-1} noted for $(Ph_2C{=}N\,Al\,Cl_2)_2$. A second band, at 543cm^{-1}, may be due to the ν(Al-N) bridge vibration, similar absorptions at 553cm^{-1}, $(Ph_2C{=}NAlCl_2)_2$ (105), 516cm^{-1}, $(^tBu_2C{=}NAlCl_2)_2$ (105) and 509cm^{-1} $(Me_2NAlMe_2)_2$ (208), having also been assigned to this mode by comparison with published data (208, 209).

The very low solubility of the compound, noted above, originally prevented the production of a single crystal sample of the compound, suitable for structural determination. More recently however, suitable single crystals have been obtained via a temperature cycle technique. A small quantity (c a. 300 mg) of the amorphous sample, together with 5 cm^3 of toluene, was placed in a small Carius tube and the tube sealed under vacuum. The tube was then slowly heated and cooled, between 20° and 100°, for a period of five months. At the end of this time small crystals began to appear in the bottom of the flask while a significant amount of the material appeared to have dissolved into solution. Standing at room temperature for a further period of several weeks resulted in the gradual increase in size of the crystals, one of which is currently the subject of an X-ray crystallographic study.

A feature of particular interest in the structure of this compound is the orientation of the aromatic substituent of the bridging ligand with respect to the plane containing the $(AlN)_2$ ring. As has been noted in the case of $((Ph_2C{=}N)_3Al)_2$, the phenyl rings of a bridging ligand would appear to preferentially orientate themselves out of the plane of the $(AlN)_2$ ring, and thus remove any possibility of interaction between the ortho-bonded protons of the phenyl ring and the metal atom. In the present case however, (Figure V.5) the rigidity imposed upon the aromatic group would prevent such an orientation of the phenyl rings, and thus raise the possibility of such interaction. However, a calculated minimum Al .... H distance of ca. 2.5Å, assuming co-planearity of the aromatic and $(AlN)_2$ rings, would imply any such interaction is likely to be weak. A decrease in the Al ... H distance, and corresponding increase in the interaction, could, however, be effected by a distortion of this conformation involving an in-plane rock of the ligand, thus bringing one ortho proton of each ligand nearer the aluminium centre. Any rotation about the C=N ligand axis, by contrast, would remove the proton further from the aluminium atom while also, presumably, weakening the bridging Al-N bond. Calculation would suggest however that any such deformation would be limited by steric interaction between the ortho proton and a terminally attached chlorine atom.

FIGURE V.5

Detail of possible conformation of the compound $((C_{12}H_8)CNAlCl_2)_2$



CHAPTER 6

^{15}N n.m.r. SPECTRA OF SOME METHYLENEAMINES AND METHYLENEAMINO DERIVATIVES

INTRODUCTION

This chapter describes the ^{15}N n.m.r. spectra of some methyleneamines and methyleneamino derivatives. Differences in the imino-nitrogen shifts of these compounds are discussed in terms of changes in the paramagnetic shielding of the nitrogen atom. During the course of the study the previously unknown compound $(^tBu_2C=N)_3P$ was prepared, details of which are included.

EXPERIMENTAL SECTION

(i) Preparation of previously reported compounds

The following methyleneamines and methyleneamino derivatives were prepared by the author unless specifically indicated otherwise.

Di-t-butylmethyleneamine, $^tBu_2C=NH$ (114), was prepared from the reaction of t-butylcyanide and t-butyllithium in hexane followed by methanolysis of the resulting imino-lithium compound. The product was purified by distillation (158°, 1 atm). Diphenylmethyleneamine, $Ph_2C=NH$ (114) was prepared (by Mr. B. Hall) from the reaction of phenylmagnesiumbromide and benzonitrile followed by methanolysis of the resulting iminomagnesium bromide and distillation of the product under vacuum (120°C, 0.29 mm Hg). The preparations of tris(di-t-butylmethyleneamino)borane, $(^tBu_2C=N)_3B$ (9), bis(di-t-butylmethyleneamino)fluoroborane, $(^tBu_2C=N)_2BF$ (1), di-t-butylmethyleneaminodichloroborane, $^tBu_2C=NBCl_2$ (38) and di-t-butylmethyleneaminodimethylborane, $^tBu_2C=NBMe_2$ are described in Chapter 4. Tris(diphenylmethyleneamino)borane, $(Ph_2C{=}N)_3B$ (118) was prepared from the reaction of three molar equivalents of diphenylmethyleneaminotrimethylsilane, $Ph_2C{=}N\,SiMe_3$ and boron trichloride in toluene, and recrystallised from hexane. Trans t-butylmethyleneaminodimethylborane, $({}^tBuCH{=}NBMe_2)_2$ was prepared as described in Chapter 2, while diphenylmethyleneaminodichloroborane, $(Ph_2C{=}NBCl_2)_2$ (39), was prepared from the reaction of diphenylmethyleneaminolithium and boron trichloride in diethyl ether. Diphenylmethyleneaminotrimethylsilane, $Ph_2C{=}N\,SiMe_3$ (118), and tetrakis(diphenylmethyleneamino) silane, $(Ph_2C{=}N)_4Si$ (118), were prepared from the reaction of appropriate amounts of diphenylmethyleneaminolithium and either trimethylchlorosilane or silicon tetrachloride in toluene; the former purified by distillation under vacuum (110° 0.50 mm Hg) and the latter by recrystallisation from hexane. A purified commercial sample of bis(dimethylamino)methyleneamine, $(Me_2N)_2C{=}NH$, together with samples of bis(dimethylamino)methyleneaminolithium $((Me_2N)_2C{=}NLi)_6$ (186), and Lithium tetrakis(di-t-butylmethyleneamino) aluminate, $LiAl(N{=}C{}^tBu_2)_4$ (17,120) were supplied by Dr. R. Snaith of Strathclyde University. The synthesis of tris(di-t-butylmethyleneamino)phosphine, $({}^tBu_2C{=}N)_3P$, is reported here for the first time and described in detail below.

(ii) <u>Preparation of Tris(di-t-butylmethyleneamino)phosphine, $({}^tBu_2C{=}N)_3P$</u>

Phosphorus trichloride (1.37g, 10 mmol.) was added to a frozen (-196°) solution of di-t-butylmethyleneaminolithium (4.42g, 30 mmol.) in 40 cm^3 of 100 - 120° petroleum ether, the solution stirred to room temperature, and then refluxed for a period of 24 hours. After cooling the solution was filtered to remove the precipitated lithium chloride and the solvent removed under vacuum to yield a viscous red material. Distillation under vacuum (165°, 0.005 mm Hg) yielded a clear red liquid which solidified upon cooling to room temperature and was identified as <u>tris(di-t-butylmethyleneamino)phosphine</u>, $(^tBu_2C=N)_3P$, m.pt. 59-60° (Found : C 72.0%, H 12.9%, N 9.4%, P 6.9%, $C_{27}H_{54}N_3P$ requires : C 71.8%, H 12.1%, N 9.3%, P 6.9%) ν_{max}(Nujol mull) 1675(w,sh) 1656(m,sh) 1623(s,br) 1485(s) 1218(s) 1201(m,sh) 1175(w,sh) 1042(s) 1010(w) 963(s) 930(m) 873(w) 844(w) 796(m) 745(s) 687(w) 621(m) 588(m) 540(w) 518(w,sh) 502(s) cm^{-1}. The compound was deliquescent.

(iii) <u>Procedure for obtaining ^{15}N n.m.r. spectra</u>

The ^{15}n n.m.r. spectra described in this study were run by Dr. M.W. Cooper at PCMU, Harwell. With the exception of $(Ph_2C=NBCl_2)_2$ and $(^tBuCH=NBMe_2)_2$, which were run as $CDCl_3$ solutions, all the samples were run as concentrated solutions or liquid mixes (ca. 20-30% by weight) in either toluene or benzene. The use of an aromatic solvent was dictated by the need to ensure that sufficiently concentrated solutions of each of the imino derivatives could be prepared, while avoiding large and irregular shift variations associated with strongly polar solvents

(210-212). Chromium III acetylacetonate was added to each of the solutions, with the exception of those of $^{t}Bu_2C{=}NH$ and $Ph_2C{=}NH$, in order to enhance the nuclear relaxation process. The solutions were sealed in ampoules of approximately 8-10 cm^3 capacity which were designed to fit into a 25 mm n.m.r. tube; a small coaxial tube containing d_8-toluene was also placed in the ampoule in order to provide a locking signal for the spectrometer.

DISCUSSION

In recent years both ^{15}N and ^{14}N n.m.r. spectroscopy have been used as tools for structural investigations in organic and inorganic chemistry. A majority of the earlier studies in this field made use of the ^{14}N technique, where the high natural abundance, and comparatively high receptivity, of the nucleus made the detection of resonance signals fairly easy. However, ^{14}N n.m.r. suffers from the disadvantage that the ^{14}N nucleus is quadrupolar, $I = 1$, and the consequent broadening of the observed resonance signal severely limits its use as a high resolution tool. By contrast, ^{15}N n.mr. spectroscopy, where the observed nucleus has a spin value $I = \frac{1}{2}$, does not suffer from this effect although the ^{15}N isotope, with a low natural abundance (0.36%) and low receptivity, originally limited its use to the study of isotopically enriched samples. More recently the availability of wide-bore spectrometers, and consequent increase in the permitted sample volume, have enabled studies to be performed with samples containing naturally abundant amounts of nitrogen-15, and has established it as a superior structural tool to that of ^{14}N n.m.r. Both techniques have recently been comprehensively reviewed by Mason (213).

Nuclear magnetic shielding of nitrogen nuclei

The observed n.m.r. shift of a particular nucleus is dependent on the magnetic shielding of the nucleus by the electrons surrounding it. The approximate "local term" nuclear magnetic shielding theory (214 - 216) expresses the shielding of a particular nucleus, A, as the algebraic sum of a diamagnetic shielding term, σ_d^A, a paramagnetic term, σ_p^A, plus a third term $\sum \sigma^{AB}$ summing the shielding contributions of electrons on adjacent nuclei. For a particular nucleus it is found that variations in the σ_d^A and $\sum \sigma^{AB}$ terms are generally small and the paramagnetic term, σ_p^A, therefore becomes the main contributor to the observed chemical shift. For an element such as nitrogen the term σ_p^A is given by equation VI.1, where

$$\sigma_p^A = \frac{-\mu_0\mu_B^2\langle r^{-3}\rangle_{2p}\sum Q}{2\pi\Delta E} \qquad \text{VI.1}$$

μ_0 is the permeability of free space and $\mu_B = e\hbar/2m$ is the Bohr magnetron. The three variables in the expression, which therefore influence the resultant chemical shift, are the terms $\langle r^{-3}\rangle_{2p}$, $\sum Q$ and ΔE. The term $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube of the 2p electron radius, while the Q terms (derived from the charge density - bond order matrix) express the inbalance of charge around the nucleus. The third term, ΔE, expresses the virtual excitation energy of the HOMO→LUMO electronic transition in the molecule, and is a measure of the deshielding of the nucleus by the rotation of charge in the magnetic field. In the case of the majority of nitrogen compounds this transition has $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ character, where charge rotates between the nitrogen lone pair orbital and an anti-bonding π or σ orbital. Other possibilities for nitrogen include a $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ transition, as long as a rotation of charge around the nucleus is involved. Considering the three shielding terms together it is found that the deshielding of a nitrogen nucleus is the greater the closer the paramagnetic circulation is to the nucleus (the larger is $\langle r^{-3} \rangle_{2p}$), the greater the assymetry of the valence electrons (the larger is ΣQ) and the easier the HOMO→LUMO excitation (the smaller is ΔE). Thus, NH_4^+ has a high-field nitrogen shift because of the high local symmetry (and hence low ΣQ) of the valence electrons and the large ΔE value of the $\sigma \rightarrow \sigma^*$ HOMO→LUMO transition. By contrast, azo and nitroso derivatives have low field shifts because of the high local asymetry (high ΣQ) of the valence electrons and the low ΔE value of the $n \rightarrow \pi^*$ transition in the N=N and N=O groups.

^{15}N shifts of methyleneamines and methyleneamino derivatives

Prior to the present study the only nitrogen n.m.r. studies on imino compounds had concerned the methyleneamines $(Me_2N)_2C{=}NR$ (R=H,Me,Ph) (212,217), $Ph_2C{=}NH$ (218,219) and PhCH=NMe (220,221). By contrast, the ^{14}N and ^{15}N shifts of a large number of amino derivatives of main group metals and metalloids have been reported, notably those of boron (154,222), silicon (223) and phosphorus (234,225). The present study however, was prompted by the results of an ^{15}N n.m.r. study on a series of transition metal mononitrosyl derivatives $ONMX_n$ (226). By comparing a series of such compounds a clear correlation was established between the ^{15}N shift of the ligand nitrogen atom and the metal ligand bond angle $M\hat{N}O$, the shift progressively moving to higher field as the linkage becomes more nearly linear. In view of the fact that similar variations in the $C\hat{N}M$ bond angle are found in methyleneamino derivatives, $R_2C{=}NMX_n$, the ^{15}N n.m.r. spectra of a representative range of these compounds were obtained in order to investigate whether the same effect is observed. The spectra were run by Dr. M.W. Cooper at PCMU, Harwell; details of preparation and handling of the samples are given in the experimental section.

The ^{15}N n.m.r. shifts of thirteen methyleneamines and methyleneamino derivatives determined during the course of the present study are listed in Table VI.1 together with those of a number of other derivatives which have been the subject of earlier ^{15}N or ^{14}N n.m.r. studies. No sign of resonance signals were observed in the spectra of three further compounds, $^tBu_2C{=}NBCl_2$, $(Ph_2C{=}NBCl_2)_2$, and $LiAl(N{=}C^tBu_2)_4$, for reasons that are not apparent. Also listed in the table are the predicted ligand bond angles, $C\hat{N}M$, the values being those derived from structural studies on either the compound concerned or a similar derivative.

The observed imino-nitrogen shift values fall within

TABLE VI.1

Nitrogen n.m.r. shifts and $C\hat{N}M$ bond angles of some methyleneamines and methyleneamino derivatives.

Compound	solv.	$C\hat{N}M$(°)	δ (^{15}N)#		$^{1}J_{NM}$(Hz)	Ref. (n.m.r.)
			=N-	Other		
$^{t}Bu_{2}C=NH$	tol.	120	- 90.3	-	50.6	a
$Ph_{2}C=NH$	bz.	120	- 77.2	-	s	a
"	pn.	120	-	-	(51)	218,219
$PhCH=NMe$	$CHCl_{3}$	120	- 62.3	-	s	220
"	liq.	120	- 56.9	-	s	221
$(Me_{2}N)_{2}C=NH$	tol.	120	-209.8	-334.3	s	a
"	liq.	120	(-207.8)	(-333.4)	s	219
$(Me_{2}N)_{2}C=NMe$	liq.	120	(-187.0)	(-334.0)	s	219
$(Me_{2}N)_{2}C=NPh$		120	-176.5	-325.2	s	212
$((Me_{2}N)_{2}C=NLi)_{6}$	tol.	*	-391.7	-327.0	s	a
$^{t}Bu_{2}C=NBMe_{2}$	tol.	180	- 84.4	-	s	a
$(^{t}Bu_{2}C=N)_{2}BF$	bz.	165-175	- 64.6	-	s	a
$(^{t}Bu_{2}C=N)_{3}B$	tol.	166	- 56.1	-	s	a
$(Ph_{2}C=N)_{3}B$	bz.	166	- 44.7	-	s	a
$(^{t}BuCH=NBMe_{2})_{2}$	$CDCl_{3}$	137	-	- 91.4	s	a
$Ph_{2}C=NSiMe_{3}$	bz.	130-140	- 35.6	-	s	a
$(Ph_{2}C=N)_{4}Si$	tol.	130-140	- 39.0	-	s	a
$^{t}Bu_{2}C=NPCl_{2}$	tol.	120-125	- 67.1	-	71.5	a
$(^{t}Bu_{2}C=N)_{3}P$	tol.	120-125	- 45.8	-	56.6	a

\# Values are in p.p.m., relative to an external reference of $Me^{15}NO_{2}$, and are uncorrected for differences in susceptibility.
Negative values are to higher field.
Figures in parentheses refer to ^{14}N n.m.r. studies.

* μ_{3} bridging of Li_{3} face. See Chapter 1.

(a) This work (s) singlet.

a range of over 360 p.p.m., the highest field shift being that of -391.7 p.p.m., in the case of $((Me_2N)_2C{=}NLi)_6$, and the lowest, -35.6 p.p.m., for $Ph_2C{=}NSiMe_3$. By comparison, metal-nitrile complexes, $RC{\equiv}N{\rightarrow}MX_n$, generally have shifts within a narrower range of values from δ = -245 to -325 (213) while isonitriles, $R{-}N{\equiv}C$, are found in the range δ = -180 to -220 (212,227,228) and the α-nitrogen resonances of azides, RNNN, between δ = -245 and -325 (212,227,228). The amino-nitrogen shifts of the four guanidine derivatives $(Me_2N)_2C{=}NR$ (R=H,Me,Ph) and $((Me_2N)_2C{=}NLi)_6$ are typical of those of tertiary amines. When considered as a whole, however, the shift values and predicted ligand bond angles of these methyleneamines and methyleneamino derivatives do not show a general correlation similar to that observed in the case of the metal-nitrosyl derivatives (26). Thus, the free methyleneamines $R_2C{=}NR'$, where a $C\hat{N}R$ angle of ca. 120° would be expected, have shifts at the high field end of the range, while the phosphorus and silicon derivatives, which have similar angular-ligand geometries, are at the low field end. Further, the monomeric iminoborane derivatives have ^{15}N shifts at intermediate values, despite having more nearly linear ligand-metalloid linkages, although the expected increase of the $C\hat{N}B$ angle in the sequence $(^tBu_2C{=}N)_3B < (^tBu_2C{=}N)_2BF < {}^tBu_2C{=}NBMe_2$ would appear to be associated with an increase in the shielding of the nitrogen nucleus. It therefore remains possible that a ^{15}N shift/ligand bond angle correlation does exist for methyleneamino derivatives of a specific metal or metalloid, although there is insufficient evidence available at present to conclusively establish this point.

Despite the failure to establish a general shift/angle correlation for methyleneamino derivatives it is possible to rationalise the major differences in the ^{15}N shifts of these compounds by considering the factors associated with the paramagnetic shielding of the nucleus. The methyleneamines, $R_2C=NR'$, have lower field shifts than amines, R_3N, which generally have shifts in the region $\delta = -280$ to -360 (154,222), largely reflecting the change in the ΔE term between the two classes of compound. In the case of amines the HOMO→LUMO electronic transition will have $n \longrightarrow \sigma^*$ character (213) involving transition of the lone pair of electrons on nitrogen into a high energy σ^* antibonding orbital. In methyleneamines however, the transition will be of an $n \rightarrow \pi^*$ type, involving promotion of the lone pair of electrons into the π^* antibonding orbital of the C=N double bond, and will have a considerably lower ΔE energy of excitation.

As noted earlier, a reduction in the ΔE value is associated with a deshielding of the nucleus and will therefore account for the lower field shifts of methyleneamines. The resonance signal of one of the methyleneamines, $^tBu_2C=NH$, was observed as a well defined doublet, J = 50.6 Hz, when the sample was run at 22°, the splitting being due to coupling between the nitrogen and adjacent proton. An earlier study (219) has shown that similar splitting of the ^{15}N signal of $Ph_2C=NH$ is observed when the sample is cooled to -40°, although when run at 22°, during the course of the present study, both $Ph_2C=NH$ and $(Me_2N)_2C=NH$ gave rise to sharp singlets. The differences in the signals observed at 22° would thus seem to arise through differing rates of proton exchange between methyleneamines. The iminophosphine derivatives, $(^tBu_2C=N)_3P$ and $^tBu_2C=NPCl_2$, also displayed splitting of the nitrogen signals, due to coupling with the phosphorus nucleus; the respective coupling constants of 56.6 Hz and 71.5 Hz are consistent with other $^1J_{NP}$ values (225, 229). Both compounds have ^{15}N shifts to lower field than that of the parent methyleneamine, $^tBu_2C=NH$, which may again be explained in terms of the relative HOMO-LUMO transition energies ΔE. Interaction of the vacant d orbitals of the phosphorus atom with the orbitals of the imino ligand will tend to stabilize both the n and π^* orbitals of the ligand (230). The π^* orbital however, being energetically more compatible with the phosphorus d orbitals, will be stabilized to a greater extent than the nitrogen lone pair orbital, thus lowering ΔE for the $n \rightarrow \pi^*$ transition, and deshielding the nitrogen nucleus, relative to that of the free imine. A surprising feature of the ^{15}N shifts of these two compounds however is their relative position, the nitrogen atom of $Ph_2C=NPCl_2$ being more shielded than those of $(Ph_2C=N)_3P$. This trend runs contrary to both that of the ^{31}P n.m.r. shifts (see Chapter 3) and also the observed deshielding of the nitrogen nucleus upon increasing halogen substitution in a series of aminohalophosphines, $(Me_2N)_nPX_{3-n}$ (224,225).

Perturbation of the ligand n and π^* orbitals in the manner described above, will also account for the lower field shifts of $(Ph_2C{=}N)_4Si$ and $Ph_2C{=}NSiMe_3$ relative to $Ph_2C{=}NH$. The spectrum of $Ph_2C{=}NSiMe_3$ contained a single symmetrical resonance signal at $\delta = -35.6$ while that of $(Ph_2C{=}N)_4Si$ contained the additional feature of a weakly defined shoulder to the main peak ($\delta = -39.0$), apparently due to the partial splitting of the signal by coupling between ^{15}N and ^{29}Si nuclei (^{29}Si has a natural abundance of 4.70%, $I = \frac{1}{2}$, ^{28}Si and ^{30}Si both have $I = 0$). The estimated $^1J_{NSi}$ coupling constant of 5Hz is comparable with that of 6Hz for $^{15}N(^{29}SiH_3)_4$ (225).

All three monomeric iminoboranes, $^tBu_2C{=}NBMe_2$, $(^tBu_2C{=}N)_2BF$ and $(^tBu_2C{=}N)_3B$ have ^{15}N shifts to lower field than the parent methyleneamine, $^tBu_2C{=}NH$, in the same way that the aminoboranes $R_2NBR'_2$, have lower field shifts than the amines R_2NH (e.g. Me_2NBMe_2, $\delta = -302$ has a lower field shift than that of Me_2NH, $\delta = -373$ (154)). However, the decrease in the shielding of the nitrogen nucleus in the sequence $BN > BN_2 > BN_3$, from $^tBu_2C{=}NBMe_2$ to $(^tBu_2C{=}N)_3B$, is the opposite to that observed in the sequence of fully-methylated aminoboranes $(Me_2N)BMe_{3-n}$ (154). In the case of the iminoborane derivatives it would again seem that changes in one or more of the paramagnetic shielding terms is responsible for the observed sequence of shifts. The conjugative effect of the N=B bond will reduce the value of ΔE compared with the free imine and therefore accounts for the general deshielding of the iminoboranes with respect to $^tBu_2C=NH$. Against this however, the increasing linearity of the CNB linkage will reduce the local electronic asymmetry around nitrogen (lower ΣQ), providing greater shielding of the nucleus. This effect will become increasingly significant as the ligand bond angle approaches 180° and would account for the higher field shift of $^tBu_2C = NBMe_2$ compared with $(^tBu_2C=N)_3B$. The ^{15}N shift of $(^tBuCH=NBMe_2)_2$ ($\delta = -91.4$) is considerably higher than the shifts of the monomeric iminoboranes and reflects both an increase in ΔE, and a decrease in $\langle r^{-3} \rangle_{2p}$, as the nitrogen lone pair of electrons are stabilized by forming a σ bond to boron. This effect also accounts for the higher field shifts of amine-borane adducts, $R_3NBR'_3$, compared with aminoboranes, $R_2NBR'_2$ (225).

The imino-nitrogen resonance of lithioguanidine, $((Me_2N)_2C=NLi)_6$, is the highest field shift ($\delta = -391.7$) measured during the course of the present study. As described in Chapter 1 each imino ligand adopts a μ_3 bonding mode, bridging a triangular face of the Li_6 core by means of a pair of resonating two-centre and three-centre bonds. Such a bonding mode will tend to reduce the radial factor $\langle r^{-3} \rangle_{2p}$ relative to the free imine ($\delta = -209.8$) and may, in part, account for the high magnetic shielding of the nucleus. In the absence of further ^{15}N data on similar imino-metal compounds however, it is not possible to provide a detailed rationale of the shielding effects in such compounds.

PART 2

STUDIES IN THE METAL-DERIVATIVE CHEMISTRY OF SOME BORANES AND CARBORANES

CHAPTER 7

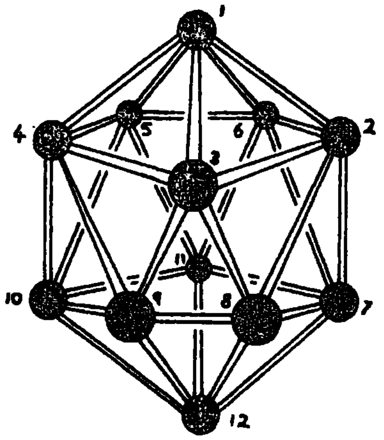
SOME METAL DERIVATIVES OF ICOSAHEDRAL CARBORANES CONTAINING METAL - CARBON σ BONDS

INTRODUCTION

Dicarba-closo-dodecaborane, $C_2B_{10}H_{12}$, is the highest member of the closo-carborane series $C_2B_{n-2}H_n$ (n = 5-12). The structure of each of these compounds is based on a triangular-faced polyhedron having n vertices, each of the vertices being occupied by a carbon or boron atom (closo = closed). The relationship which links the number of carbon and boron atoms with the polyhedral shape of the cluster is discussed more fully in the following chapter. The structure of dicarba-closo-dodecaborane, $C_2B_{10}H_{12}$, aspects of whose derivative chemistry this chapter is concerned with, is based on an icosahedron (Figure VII.1) in which ten of the twelve vertices are occupied by boron atoms and the remaining two by the carbon atoms. Consideration of the molecular skeleton

FIGURE VII.1

Icosahedral skeleton of $C_2B_{10}H_{12}$

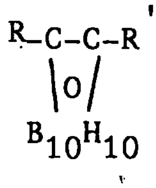


of carbon and boron atoms reveals the possibility of three isomeric forms of $C_2B_{10}H_{12}$, all of which are known. By analogy with benzene, the isomer having the carbon atoms in positions 1 and 2 (Figure VII.1) is known as *ortho*-carborane, that with carbons in positions 1 and 7, *meta*-carborane, and that with carbons in positions 1 and 12, *para*-carborane. Each of the n hydrogen atoms of a *closo* (n vertex) carborane is bonded to a single boron or carbon atom by a localised two-electron bond, the bonds being orientated radially outwards from the surface of the cage. Numerous derivatives of *ortho*- *meta*- and *para*- $C_2B_{10}H_{12}$ are known in which one or more of these *exo*-bonded hydrogens is replaced by an organic residue (as in the methyl carboranes $C_2B_{10}H_{11}Me$) or by a metal or metalloid species.

Despite the wealth of structural information now available on polyhedral boranes and carboranes and their metalla derivatives (231-234), no carborane with a main group I or II metal atom covalently bonded in an *exo* position appears to have been structurally characterised, despite the extensive use of such substances as intermediates in the synthesis of other carboranyl derivatives (235). During the course of the present study two compounds, the pentamethyldiethylenetriamine (PMDETA) adduct of 1-lithio-2-methyl-1,2-dicarba-*closo*-dodecaborane, $Li(C_2B_{10}H_{10}Me)(PMDETA)$, and the bis(1,4 dioxan) adduct of magnesium bis(2-methyl-1,2-dicarba-*closo*-dodecaborane), $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2.C_7H_8$, have been prepared and structurally characterised. The crystallographic studies were performed by Dr. W. Clegg (Göttingen University); at the time of writing prelimiary results only are available on the magnesium derivative. Unsuccessful attempts were also made to prepare carboranyl derivatives of aluminium. In describing the two characterised compounds features of their structures are compared with related features of other organolithium and organomagnesium compounds, while the structural data are used to calculate the cone angles and steric requirements of icosahedral carboranyl, and methylcarboranyl, ligands attached to metal atoms of various sizes.

Note on Nomenclature

In the following text the formal nomenclature for the isomers of $C_2B_{10}H_{12}$ and their derivatives has been used in title headings and in other places where it is considered warranted. Thus, the formal name for ortho-$C_2B_{10}H_{12}$ is 1,2-dicarba-closo-dodecaborane while its carbon-substituted methyl derivative, $MeC_2B_{10}H_{11}$ (methyl-ortho-carborane), becomes 1-methyl-1,2-dicarba-closo-dodecaborane. In the same way the meta and para derivatives are known as the 1,7-, and 1,12-, dicarba-closo-dodecaboranes. In other places the more convenient terms ortho-, meta-, and para-, $C_2B_{10}H_{12}$ have been used. Additionally, the generally recognised symbolic representation of ortho-carboranyl compounds,



$$\begin{array}{c} R{-}C{-}C{-}R' \\ \backslash O / \\ B_{10}H_{10} \end{array}$$

(R, R$'$=H,organyl, metal etc.) has been used in certain places.

EXPERIMENTAL SECTION

(i) Starting materials

1,2-Dicarba-*closo*-dodecaborane (*ortho*-carborane) was prepared, via the bis(acetonitrile)decaborane derivative, from decaborane and 2-butyne-1,4-diacetate (236) 1-Methyl-1,2-dicarba-*closo*-dodecaborane (methyl-*ortho*-carborane) was prepared, via the bromomethyl derivative, from bis(acetonitrile)decaborane and 3-bromopropyne (237). All reactions and subsequent manipulations were carried out under an inert atmosphere of dry nitrogen using standard techniques.

(ii) Preparation of 1-Lithio-2-methyl-1,2-dicarba-closo-dodecaborane, $LiC_2B_{10}H_{10}Me$

A solution of n-butyl lithium (10 mmol.) in hexane was added to a solution of 1 methyl-*ortho*-carborane (1.58g, 10.00 mmol.) in 15 cm^3 of toluene. The mixture was stirred at room temperature for three hours during which time the lithio-carborane precipitated from solution. The solvent volume was reduced by pumping, the remaining solution filtered, and the solid material washed with 5 cm^3 of cold pentane. The resultant white solid was identified as *1-lithio-2-methyl-1,2-dicarba-closo-dodecaborane*, $LiC_2B_{10}H_{10}Me$ (Found : C 20.5%, H 9.2%, Li 4.5%, $C_4H_{13}B_{10}Li$ requires: C 21.9%, H 8.0%,Li 4.2%) ν_{max}(Nujol mull) 2580(s) 1253(w) 1225(w) 1130(w) 1093(m) 1080(w,sh) 1032(m)

1016(m) 994(m) 872(w) 834(w) 815(w) 786(m) 767(w) 723(s) 652(w) 492(w) cm^{-1}. The compound was air and moisture sensitive, decomposing immediately upon exposure to air. Attempts to recrystallise the compound failed, decomposition usually resulting.

(iii) Preparation of 1-(PMDETA)lithio-2-methyl-1,2-dicarba-closo-dodecaborane.

A solution of n-butyl lithium (10 mmol.) in hexane was added to a solution of 1-methyl-ortho-carborane (1.58g, 10.00 mmol.) in 30 cm^3 of toluene. The mixture was stirred at room temperature for three hours during which time the lithiated carborane, 1-Li-2-$MeC_2B_{10}H_{10}$, precipitated from solution. Pentamethyldiethylenetriamine, PMDETA, (1.73g, 10.00 mmol.) was added, the solution warmed to dissolve the remaining precipitate and placed in a freezer maintained at -30°. Crystals were deposited which were filtered, washed with a small amount of cold pentane, and pumped dry. Recrystallisation from toluene afforded colourless crystals identified as 1-(PMDETA)-lithium-2- methyl-1,2-dicarba-closo-dodecaborane. $Li(MeN(CH_2CH_2NMe_2)_2)(MeC_2B_{10}H_{10})$, m.pt. 195-197° (Found : C 42.5%, H 10.2%, Li 2.0%, N 12.1%, $C_{12}H_{36}B_{10}LiN_3$ requires: C 42.7%, H 10.8%, Li 2.1%, N 12.5%) ν_{max}(Nujol mull) 2595(m,sh) 2580(s) 2550(m,sh) 2512(m,sh) 1358(m) 1318(w) 1297(m,sh) 1289(m) 1252(w) 1172(w) 1158(w) 1119(w) 1102(w) 1060(m) 1041(s) 1024(m) 992(w) 947(m,sh) 943(s) 937(m,sh) 905(w) 799(m) 783(m) 770(w) 758(w) 737(m) 730(m,sh) 695(w) 671(w) 660(w) 603(m) 577(w) 548(w) 508(w) cm^{-1}. The compound was air and moisture-sensitive, decomposing immediately upon exposure to air. Attempts to record its mass spectrum afforded evidence of the ligand PMDETA ($^{m}/e$=173) and fragments thereof, and of the carboranyl residue $C_2B_{10}H_{10}Me$ (a characteristic group of peaks showing the appropriate isotope pattern, with that at $^{m}/e$=159 of highest mass) and its breakdown fragments.

(iv) Addition of Pentamethyldiethylenetriamine to 1-Lithio-1,2-dicarba-closo-dodecaborane.

A solution of n-butyl lithium (8.28 mmol.) in hexane was added to a solution of ortho-carborane, $C_2B_{10}H_{12}$ (1.19g, 8.25 mmol) in 30 cm^3 of toluene and the mixture stirred for three hours at room temperature. Pentamethyldiethylenetriamine (1.43g, 8.25 mmol.) was added, the solvent volume reduced by pumping, and the solution placed in a freezer at -30° for a number of days. No solid material was deposited so the remaining solvent was removed under vacuum to yield a yellow viscous oil. (Found : C 52.9%, H 15.1%, Li 1.1%, N 10.1% : Li(PMDETA)$C_2B_{10}H_{12}$ requires : C 40.9%, H 10.6%, Li 2.2%, N 13.0%). Prolonged pumping under vacuum yielded small quantities of PMDETA and toluene, identified on the basis of their infra red spectra.

(v) Addition of Tetramethylethylenediamine to 1-Lithio-1,2-dicarba-closo-dodecaborane

In an experiment similar to that described above, tetramethylethylenediamine, TMEDA (1.10g, 9.47 mmol.) was added to a solution of Lithio-ortho-carborane (1.42g, 9.46 mmol.) in 20 cm^3 of toluene. Cooling to -30° for a number of days failed to yield any solid material so the solvent was removed under vacuum to yield a pale yellow oil. (Found : C 47.0%, H 12.6%, Li 1.2%, N 8.5% (TMEDA)Li$C_2B_{10}H_{11}$ requires : C 36.1%, H 10.2%, Li 2.6%, N 10.5%). Further pumping under vacuum resulted in recovery of additional small quantities of TMEDA.

(vi) Preparation of 1-Bromo-2-methyl-1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{10}$MeBr

A diethyl ether/hexane solution of 1-Lithio-2-methyl-*ortho*-carborane, Li$C_2B_{10}H_{10}$Me, was slowly added to a stirred solution of bromine in diethyl ether at 0°. The resulting solution was shaken with an equal volume of dilute aqueous sodium thiosulphate, the ether layer separated, and dried over anhydrous magnesium sulphate. Removal of the ether by pumping yielded a white solid which was purified by sublimation (80°, 0.004 mm Hg) and identified as 1-Bromo-2-methyl-1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{10}$BrMe, m.pt. 222° (Lit. (238) 220-1°) (Found : C 15.3%, H 5.7%, B 45.5%, Br 34.5%, $C_3H_{13}B_{10}Br$ requires : C 15.2%, H 5.5%, B 45.6%, Br 33.7%) ν_{max}(nujol mull) 2568(s,br) 1195(w) 1158(w,br) 1097(w) 1039(w) 1020(w) 987(m) 937(w,sh) 932(m) 921(w,sh) 905(w) 872(m) 854(m) 791(m) 772(w) 728(s) 673(w) 658(w) cm^{-1}.

(vii) Preparation of bis(dioxan)Magnesium-bis(2-methyl-1,2-dicarba-closo-dodecaborane)

A solution of 1-bromo-2-methyl-*ortho*-carborane, $C_2B_{10}H_{10}$MeBr (1.81g, 7.63 mmol.) in 20 cm^3 of diethyl ether was slowly added to magnesium turnings (0.35g, 10.29 mmol.) in 10 cm^3 of refluxing diethyl ether. A small crystal of iodine was added to initiate the Grignard reaction. At the end of the addition the reaction was refluxed for a further period of three hours and then filtered to remove unreacted magnesium.5 cm^3 of 1,4 dioxan was then added to the clear solution which resulted in the precipitation of a white solid. After stirring overnight the solvent was removed by pumping, the resulting solid extracted with 15 cm^3 of hot toluene, and filtered to yield a colourless solution which deposited colourless crystals upon cooling. The crystals were identified as bis (1,4 dioxan)magnesium bis(2-methyl-1,2-dicarba-closo-dodecaborane), $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 .C_7H_8$m.pt. 180-185°(dec.). (Found : C 40.0%, H 10.3%, B 33.2%, Mg 3.8%, $C_{21}H_{50}B_{20}MgO_4$ requires : C 41.5%, H 8.3%, B B 35.6%, Mg 4.0%) ν_{max}(Nujol mull) 2565(s,br) 1299(m) 1264(m) 1223(w) 1131(s) 1096(w) 1047(s) 1017(w,sh) 972(w) 937(w,br) 895(m) 878(s) 846(w) 823(m) 793(w) 773(w) 763(s) 697(w) 670(w) 654(w) 621(m) 573(w) 503(w) 467(w) 458(w) cm^{-1}. The compound was extremely air sensitive. Its mass spectrum showed evidence of peaks due to the fragmentation of dioxan as well as the characteristic isotope peak pattern of $MeC_2B_{10}H_{10}$ (high mass $^m/e$ = 159).

(viii) Reaction of 1-Lithio-2-methyl-1,2-dicarba-closo-dodecaborane and Methylaluminiumdichloride (2:1)

n-Butyl lithium (11.35 mmol.) in hexane was added to a toluene solution of methyl-ortho-carborane (1.78g, 11.25 mmol.), the solution stirred at room temperature for three hours and then frozen to -196°. Methylaluminium dichloride (0.64g, 5.66 mmol.) in 20 cm^3 of toluene was added and the solution stirred to room temperature. Evidence of a reaction below 0° was observed and a quantity of white solid, subsequently confirmed as Li Cl, was deposited. The reaction was refluxed for one hour and filtered hot to yield a clear solution. Cooling to -30° failed to yield any solid material so the solvent was removed by pumping to yield a colourless, viscous, oil. Elemental analysis of the oil failed to give consistent results; its infra red spectrum was poorly resolved but showed no evidence for an exo C-H stretching absorption above 3000 cm^{-1}. Further attempts at the recovery of crystalline materials from this reaction were unsuccessful .

(ix) Reaction of 1-Lithio-2-methyl-1,2-dicarba-closo-dodecaborane and Dimethylaluminium chloride (1:1)

In a reaction similar to that described above dimethylaluminium chloride (0.88g, 9.51 mmol.) and 1-lithio-2-methyl-1,2-dicarba-closo-dodecaborane (1.56g, 9.50 mmol.) were reacted in toluene solution. Removal of the Li Cl precipitate and solvent again yielded a colourless, and very viscous, oil which could not be characterised.

DISCUSSION

Preparation of carboranyl derivatives of metals and metalloids

A very extensive organic chemistry has been developed for the icosahedral carboranes ortho-, meta-, and para-$C_2B_{10}H_{12}$, and their carbon-bonded derivatives, based largely on the metallation of one (or both) of the carbon atoms of the carborane cage. In addition, a considerable number of compounds having carboranyl groups bonded to metals or metalloids through C-metal or C-metalloid exo σ bonds have been prepared and characterised.

The preparation of such σ-bonded metalla derivatives of ortho-, meta, and para-, $C_2B_{10}H_{12}$, and their carbon-substituted derivatives, has recently been comprehensively reviewed by Bresadola (235), and it is not intended to provide a similar survey in the present work. This discussion is therefore limited to a brief description of the various preparative routes which have been employed in the synthesis of such compounds; the reader is referred to the above review for a more detailed coverage of the literature.

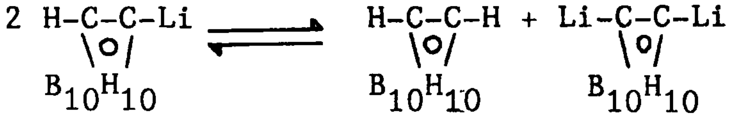
The carbon-hydrogens of the $C_2B_{10}H_{12}$ isomers and their C-alkyl and C-aryl derivatives, $RC_2B_{10}H_{11}$, are mildly acidic in nature and can be easily replaced by the metals of certain active metallating agents such as butyl—lithium and phenyl—lithium (239 - 246) (Equations VII 1,2). In the case of the mono-lithium derivative

$$RLi + R'C_2B_{10}H_{11} \longrightarrow R'C_2B_{10}H_{10}Li + RH \qquad VII.1$$

$R = {}^{n}Bu, Ph;\ R' = H, alkyl, aryl.$

$$2RLi + C_2B_{10}H_{12} \longrightarrow C_2B_{10}H_{10}Li_2 + 2RH \qquad VII.2$$

of ortho-carborane, $C_2B_{10}H_{11}Li$, the reaction is complicated by a disproportionation equilibrium, existing in either ether or ether/benzene solvents, (Equation VII.3) between the C-monolithium and C,C' dilithium species (246). In



$$2\ \underset{B_{10}H_{10}}{H\text{-}C\text{-}C\text{-}Li} \rightleftharpoons \underset{B_{10}H_{10}}{H\text{-}C\text{-}C\text{-}H} + \underset{B_{10}H_{10}}{Li\text{-}C\text{-}C\text{-}Li} \qquad VII.3$$

aryl solvents the equilibrium is well over to the left hand side, in favour of the monolithium derivative (244), while the problem may otherwise be avoided, as was the case with the synthesis of $Li(C_2B_{10}H_{10}Me)(PMDETA)$, by the use of a C-alkylated carborane where the alkyl group prevents formation of the dilithio species. Alkali metal derivatives of ortho-, meta-, and para-, $C_2B_{10}H_{12}$ have also been prepared by treating the carborane with the corresponding alkali-metal amide in liquid ammonia (247-249) (Equation VII.4). In this manner both mono-,

$$C_2B_{10}H_{12} + MNH_2 \xrightarrow{\text{liq. } NH_3} C_2B_{10}H_{11}M + NH_3 \qquad VII.4$$

$M = Li, Na, K$

and di-, metal derivatives have been prepared, while unsubstituted and C-monosubstituted carboranes have also been metallated by sodium amide in boiling toluene (250). In contrast to the reactions in liquid ammonia, the latter reactions, between $NaNH_2$ and one equivalent of the unsubstituted carborane, yield solely monosodium derivatives. In a similar manner calcium derivatives of unsubstituted and C-monoalkyl carboranes have been obtained by reaction of the appropriate carborane with calcium amide in liquid ammonia (247, 248).

The reaction of a lithio-carborane with a halide compound of a metal or metalloid has been by far the most extensively used route for the synthesis of σ-bonded derivatives of $C_2B_{10}H_{12}$ and $C_2B_{10}H_{11}R$ (Equation VII .5). Thus, an extensive range of derivatives of

$$n\ RC_2B_{10}H_{10}Li + X_nMY_{z-n} \longrightarrow (C_2B_{10}H_{10}R)_n\ MY_{z-n} + n\ LiX$$

R=H, alkyl, aryl; X = halogen. VII.5

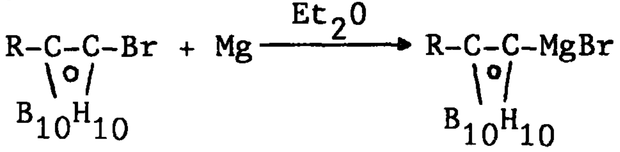
the main-group elements boron (251), gallium (252) silicon (239,240,253-259), germanium (253,260,261), tin (253,262-269), phosphorus (253,264,270-272), arsenic (253,273) and antimony (253) have been synthesised by this method, together with derivatives of mercury (253, 263,264,274-276), zinc (277) and a large number of transition metals (233,235).

The mildly acidic activity of the carbon-bonded hydrogens of $C_2B_{10}H_{12}$ allows facile preparation of carborane Grignard reagents through reaction with alkylmagnesium halides (Equation VII.6), although the reaction

$$RMg\,X + R'C_2B_{10}H_{11} \longrightarrow R'C_2B_{10}H_{10}MgBr + RH \qquad \text{VII.6}$$

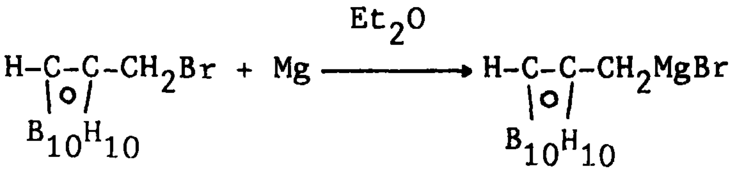
R=Et,Ph R' = alkyl,aryl,H

may be dependent on the ether solvent used. Thus, ethylmagnesium bromide will react smoothly with ortho-, and meta-, $C_2B_{10}H_{12}$ in tetrahydrofuran (but not diethyl ether) to give carboranylmagnesium bromide (278,279) although the para compound will not undergo this reaction. Carboranylmagnesium bromides can also be obtained by reacting 1-Br-,2-R-$C_2B_{10}H_{10}$ with magnesium turnings in refluxing diethyl ether (239) (Equation VII.7), this being the



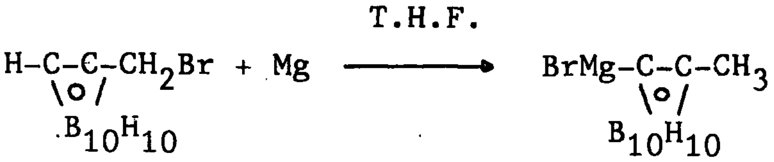
$$\underset{B_{10}H_{10}}{R\text{-}C\text{-}C\text{-}Br} + Mg \xrightarrow{Et_2O} \underset{B_{10}H_{10}}{R\text{-}C\text{-}C\text{-}MgBr} \qquad VII.7$$

method used in this study during the synthesis of $Mg(C_2B_{10}H_{10}Me)$ $(O_2C_4H_8)_2$. A further example of ether-solvent dependency in the formation of carboranyl Grignard reagents is the reaction of 1-$BrCH_2$-ortho-$C_2B_{10}H_{11}$ and magnesium. In diethyl ether the reaction proceeds to form the expected product (271) (Equation VII.8), whereas in T.H.F.



$$\underset{B_{10}H_{10}}{H\text{-}C\text{-}C\text{-}CH_2Br} + Mg \xrightarrow{Et_2O} \underset{B_{10}H_{10}}{H\text{-}C\text{-}C\text{-}CH_2MgBr} \qquad VII.8$$

solution (240,280) the species apparently undergoes isomerisation to yield the 1-methyl-2-carboranylmagnesium bromide derivative (Equation VII.9).



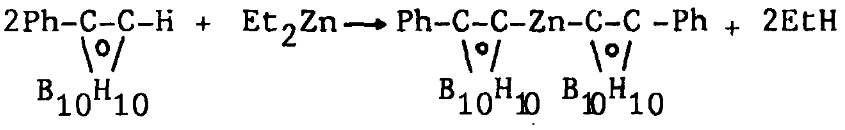
$$\underset{B_{10}H_{10}}{H\text{-}C\text{-}C\text{-}CH_2Br} + Mg \xrightarrow{T.H.F.} \underset{B_{10}H_{10}}{BrMg\text{-}C\text{-}C\text{-}CH_3} \qquad VII.9$$

In a manner analogous to the lithio reagents, carboranylmagnesium bromide derivatives will react with halide derivatives of metals and metalloids (Equation VII.10). Although used less extensively than the former

$$n\,RC_2B_{10}H_{10}MgBr + X_nMY_{z-n} \longrightarrow n\,(RC_2B_{10}H_{10})_nMY_{z-n} + MgBrX \qquad \text{VII.10}$$

method, a considerable number of exo σ-bonded derivatives have been synthesised by this route, notably some derivatives of mercury, tin, silicon and phosphorus (281).

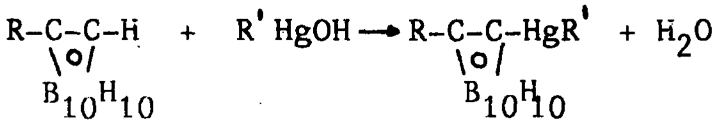
Finally, two further reactions have been reported, resulting in the formation carborane-metal σ bonds. Reaction of phenyl-ortho-carborane, $C_2B_{10}H_{11}Ph$, with diethyl zinc in hexamethyltriamidophosphate at elevated temperatures (Equation VII.11) yields a bis(carboranyl)zinc



$$2\,\underset{B_{10}H_{10}}{\underset{\backslash\circ/}{\text{Ph-C-C-H}}} + Et_2Zn \longrightarrow \text{Ph-}\underset{B_{10}H_{10}}{\underset{\backslash\circ/}{\text{C-C}}}\text{-Zn-}\underset{B_{10}H_{10}}{\underset{\backslash\circ/}{\text{C-C}}}\text{-Ph} + 2EtH$$

VII.11

derivative (277), while a reaction between an ortho-carborane derivative and an organomercury hydroxide will yield a C-substituted mercury derivative (Equation VII.12) (282).



$$\underset{B_{10}H_{10}}{\underset{\backslash\circ/}{\text{R-C-C-H}}} + R'HgOH \longrightarrow \underset{B_{10}H_{10}}{\underset{\backslash\circ/}{\text{R-C-C-HgR}'}} + H_2O$$

VII.12

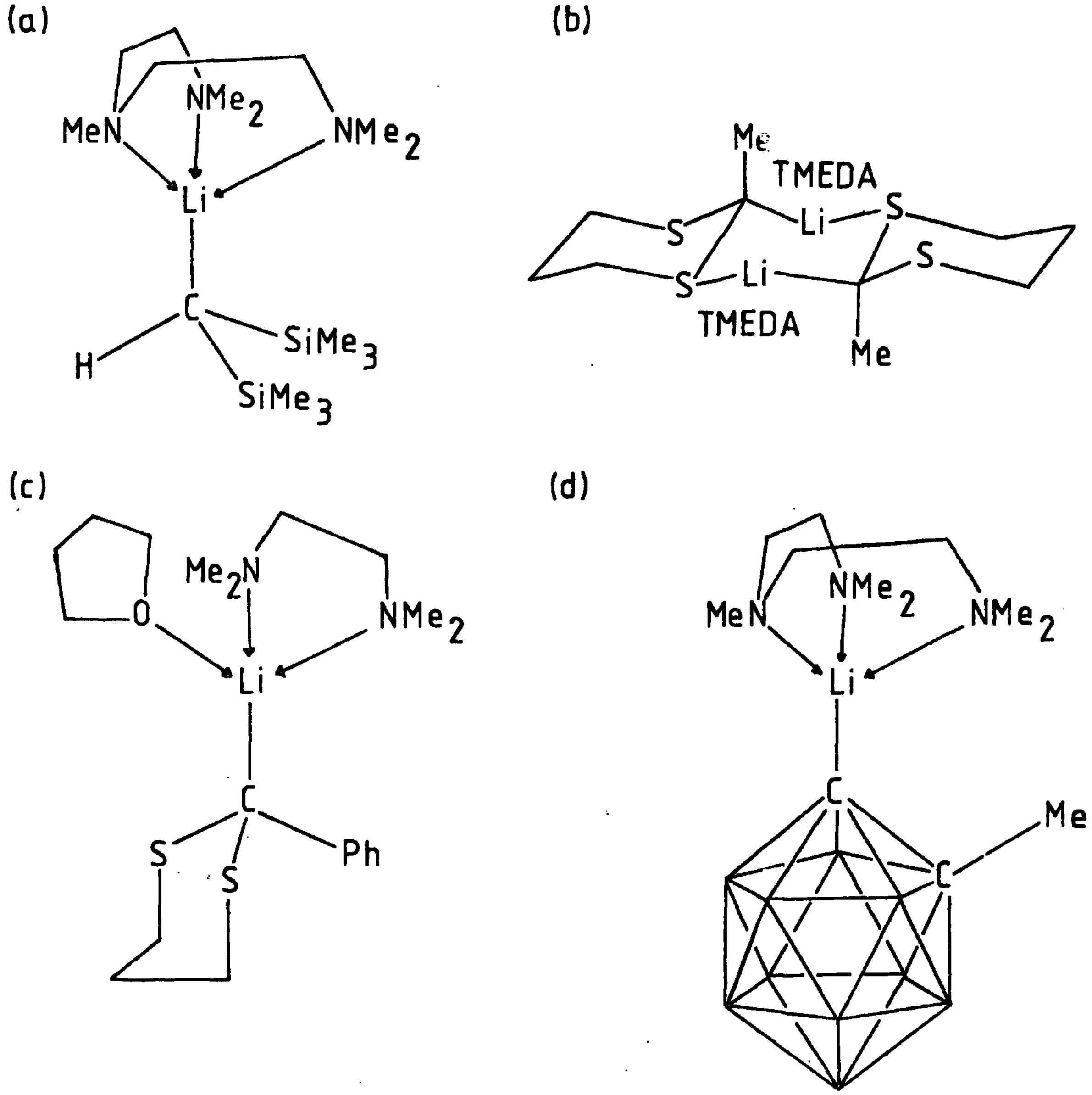
R = H, Me, Ph; R' = Me, Ph.

The crystal structure of the pentamethyldiethylenetriamine adduct of 1-lithio-2-methyl-1,2-dicarba-closo-dodecaborane: $Li(C_2B_{10}H_{10}Me)(MeN(CH_2CH_2NMe_2)_2)$

A familiar feature of organolithium chemistry is the multicentre bonding which normally occurs between the metal atoms and the ligand carbon atoms (231,283,284). Lithio derivatives of unsaturated hydrocarbons have structures in which the metal atoms are within bonding distance of at least two (and more commonly three or four) ligand carbon atoms (285). Lithium alkyls normally have strongly associated structures which persist even in solution in donor solvents, being held together by four-centre two-electron bonds, as in tetrahedral tetrameric molecules like $(LiMe)_4$ (204) or chair-shaped hexameric molecules like $(Li\text{-cyclohexyl})_6$ (286). The number of ligand carbon atoms to which each lithium atom bonds (and the number of lithium atoms to which each ligand bonds) can be reduced by the presence of a chelating base. Thus, phenyl lithium, for example, crystallises in the presence of tetramethylethylenediamine (TMEDA) as the dimer $(LiPhTMEDA)_2$, held together by three-centre Li ... C ... Li bonds (287). The steric bulk of certain organic ligands can also be sufficient to prevent association and it is significant that one of the only two organolithium compounds known prior to the present study to have unassociated structures, $(PMDETA)LiCH(SiMe_3)_2$ (206), contains the very bulky ligand $CH(SiMe_3)_2$ (Fig. VII.2(a)). The Li-C bond in this compound was described in terms of a two-centre two-electron covalent interaction on account of the similarity in its length (2.13(5)Å) to that of the associated organolithium compound 2-lithio-2-methyldithiane (205) (Figure VII.2(b)) where the Li-C bond, of length 2.186(5)Å was shown to be essentially covalent by electron density plots.

FIGURE VII. 2

Compounds containing two-centre carbon-lithium bonds.



By contrast, the longer Li-C bond (2.280(5)Å) of the only other organolithium compound known to be unassociated, 2-lithio-2-phenyldithiane (Figure VII.2(c)) (205), was shown to have considerably more ionic character, again on the basis of an electron density plot.

The compound described in the present study, $Li(C_2B_{10}H_{10}Me)(PMDETA)$ (FigureVII.2(d)), was synthesised in the expectation (now realised) that for a combination of electronic and steric reasons it would have a monomeric structure, so providing an unprecedented example of lithium terminally attached to a six-coordinate carbon atom. The compound is, additionally, the first structurally characterised example of a carboranyl unit bonded exo-skeletally to a group I metal. The tridentate base, PMDETA, was therefore used to block the three spare valencies of the lithium atom.

The results of the crystallographic study are illustrated in Figure VII.3 while selected bond lengths and angles are given in Table VII.1. Crystals of $Li(C_2B_{10}H_{10}Me)(PMDETA)$ are monoclinic, space group P21/m,with a = 8.242(1), b=13.522(1) c=10.799(1)Å, β=108.75(1)°, Z=2. The molecule possesses a plane of symmetry which passes through the atoms C(1), N(1), Li, C(6), C(7) and C(8). The four-coordinate lithium atom is terminally attached to the six-coordinate carbon atom of the carborane cage by a bond of length 2.176(8)Å which is similar to those of 2.186(5)Å, in 2-lithio-2-methyldithiane (205) (Figure VII.2(b)), and 2.13(5)Å, in $(PMDETA)LiCH(SiMe_3)_2$ (206) (Figure

FIGURE VII.3 Molecular structure of $Li(C_2B_{10}H_{10}Me)(PMDETA)$

(hydrogen atoms omitted)

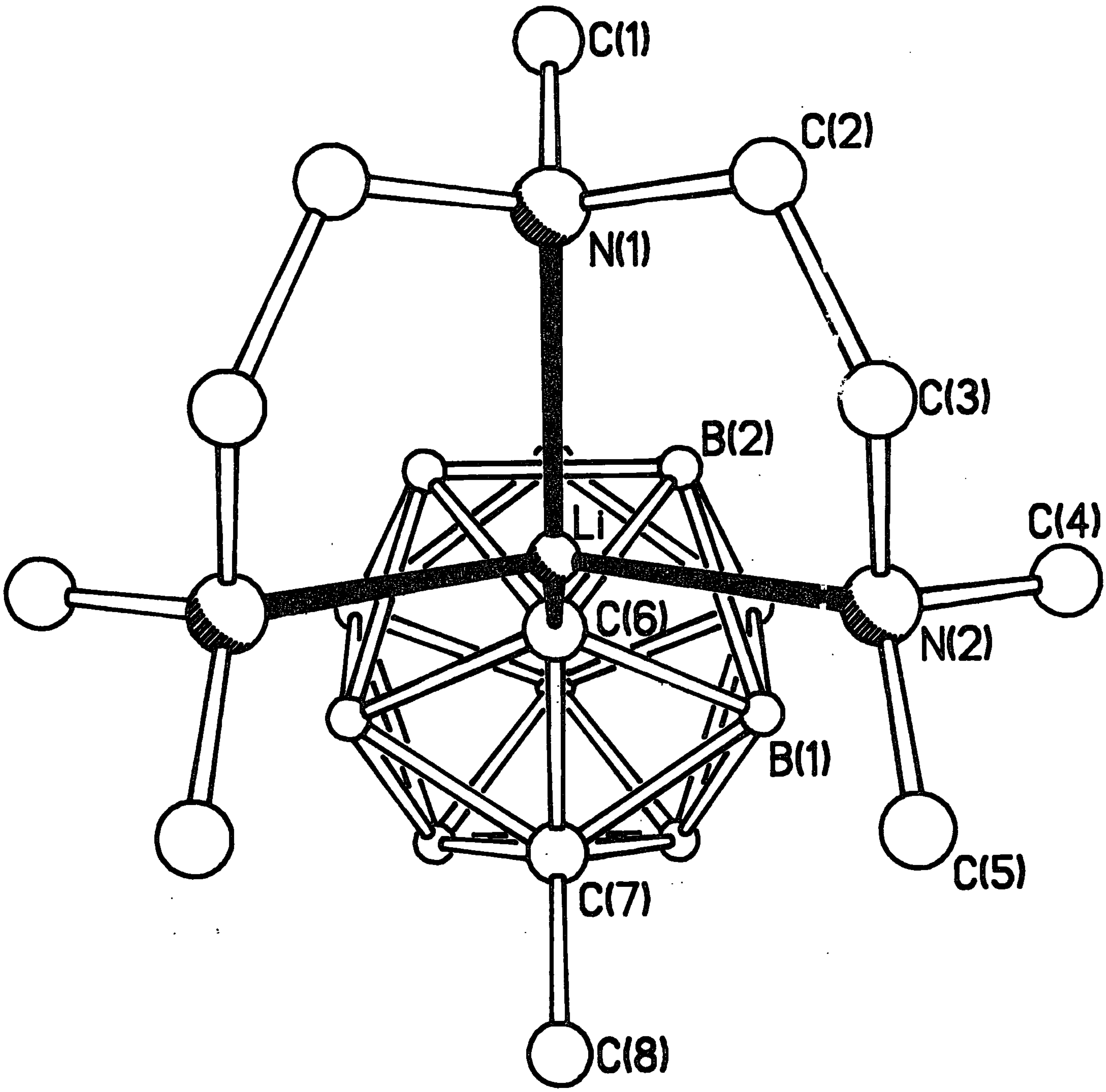


TABLE VII.1

Selected bond lengths (Å) and angles (°)

for Li($C_2B_{10}H_{10}$Me)(PMDETA)

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

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

VII.2(a)), though somewhat shorter than that of 2.280(5)Å, in 2-lithio-2-phenyldithiane (205) (Figure VII.2(c)). The bond length in the present case might have been expected to be somewhat longer, in view of the higher coordination number of the carbon atom concerned, although the sp hybridisation commonly assumed for the skeletal atoms of icosahedral carboranes would require a relatively short exo bond. All the terminal Li-C bonds are shorter than the fractional order Li-C bond in unsolvated $(MeLi)_4$ (2.36Å) (204) although they are actually longer than some of the bonds formally of order < 1 in some other associated lithium alkyls or aryls, where bond lengths in the range 2.11 to 2.47Å have been reported (284). By contrast, the fractional order Al-C bonds in aluminium alkyls and aryls are usually 0.20Å or more longer than the corresponding terminal Al-C bonds (231,288), as might be expected. The correlation between bond length and bond order in the organolithium derivatives is thus less clear cut and indeed these bonds must be regarded as being at, or beyond, the limit of what can be regarded as a covalent interaction (283,289-291).

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

From the structure of $(PMDETA)LiC_2B_{10}H_{10}Me$ it is possible to calculate the effective cone angle subtended by the 2-methyl-ortho-carboranyl group at a metal atom such as lithium. The concept of cone angles, first introduced by Tolman (292) to facilitate the discussion of steric effects in crowded transition-metal coordination complexes, is particularly helpful in assessing how many bulky, pseudo-spherical, ligands such as icosahedral carboranyl groups can be attached to a particular metal atom. Table VII.2 lists the cone angles for (a) unsubstituted carboranyl units $C_2B_{10}H_{11}$ and (c) 2-methyl-ortho-carboranyl ligands $MeC_2B_{10}H_{10}$ for a representative range of metal-carbon bond lengths. The approximate cone angles were determined, as outlined in Figure VII.4, by summing the calculated angles, θ and γ, between the exo C-M bond and the surface of the nearest hydrogen atoms. These were either of a C-H or B-H group or of a C-Me group in the ortho position relative to the metallated

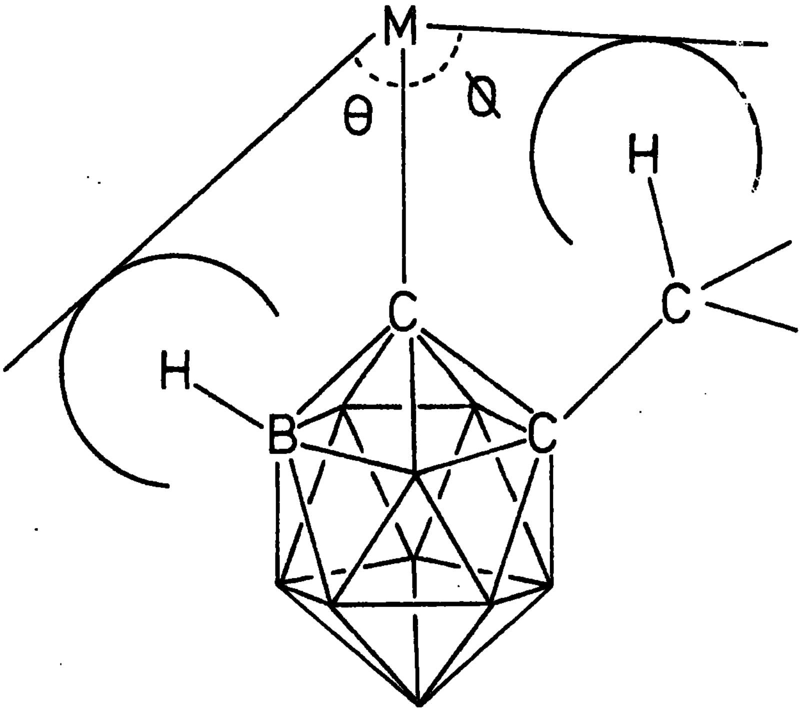
TABLE VII.2

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

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

FIGURE VII.4

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



carbon atom. A hydrogen Van de Waals radius of 1.2Å was assumed. Also included in Table VII.2, for comparison, are the cone angles for (b) phenyl and (d) ortho-tolyl groups, calculated in a similar manner. The cone angles for the latter, when calculated in the plane of the aromatic ring, are seen to be slightly greater than those of 1-Me-1,2-$C_2B_{10}H_{10}$.

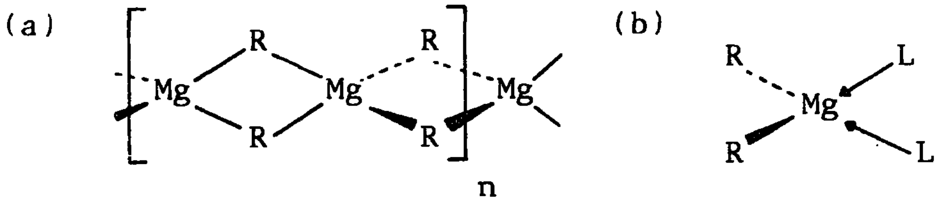
The cone angles of Table VII.2 indicate that there is room for uncoordinated 1-lithio-2-methyl-ortho-carborane to adopt a dimeric structure, $(LiC_2B_{10}H_{10}Me)_2$, in which the carboranyl groups, like the phenyl groups of $(LiPh.TMEDA)_2$ (287), perform a bridging role between the metal atoms. Such a conformation would seem unlikely on electronic grounds, however, as the electron-withdrawing properties of the carborane group would be expected to reduce the capacity of the carbon atoms to participate in multicentre bonding outside the cage. The lack of success in attempts to isolate such an associated compound, during the course of the present study, is therefore not surprising. A further implication of the data in Table VII.2 is that it is not realistic to expect more than two $C_2B_{10}H_{11}$ units, let alone ortho-methylated carboranyl units, to be linked to a single boron, carbon or nitrogen atom, where an exo bond length of ca. 1.52 to 1.62 Å would be expected. A larger second-row element such as aluminium, silicon or phosphorus might just be big enough to accommodate three $C_2B_{10}H_{11}$ icosahedra, though not when they are orthomethylated.

The X-Ray crystal structure of the bis(1,4 dioxan) adduct at Magnesium bis(2-methyl-1,2-dicarba-closo-dodecaborane): $Mg(C_2B_{10}H_{10}Me)(O_2C_4H_8)_2C_7H_8$

The X-ray determined crystal structures of the solids MgR_2(R=Me,Et) (293,294) show these to be linear polymeric molecules with symmetrically bridging alkyl groups (Figure VII.5(a)). The bonding may be formalised in terms of electron-deficient three-centre two-electron covalent (but polar) links, each metal atom having an approximately tetrahedral coordination of four ligands. By contrast

FIGURE VII.5

Structures of the polymeric dialkylmagnesium compounds $(MgR_2)_n$ and monomeric adduct derivatives MgR_2L_2



X-ray determinations of the crystal structures of adducts $MgR_2(L_2)$ (R=Me, L=quinuclidine (295) or L_2 = TMEDA (296); R=Ph, L_2=TMEDA (297); R=$(Me)_2C_5H_3$, L_2=TMEDA (298)) have established monomeric structures (Figure VII.5(b)) with distorted tetrahedral geometry around magnesium, while the metal-carbon bonding may be described in terms of two-centre two-electron covalent interactions. The Mg-C bond lengths in these compounds (ca. 2.16Å) are similar to those of some ether-coordinated alkyl- and aryl-, magnesium halides, $RMgX(L_2)$ (299), which possess similar two-centre linkages, while being somewhat shorter than the formally half-order Mg-C bonds in $(MgMe_2)_n$ and $(MgEt_2)_n$, which have lengths of 2.24Å and 2.26Å respectively (293, 294).

During the course of the present study a further example of a monomeric ether-adduct species, $Mg(C_2B_{10}H_{10}Me)_2(O_2C_4H_8)_2.C_7H_8$ has been synthesised and structurally characterised. The compound contains a unique example of magnesium bonded to a six-coordinate carbon atom by means of a two-centre two-electron bond, and is the first structurally characterised example of an exo-bonded group II carboranyl derivative. The compound was synthesised by the addition of 1,4-dioxan to a diethyl ether solution of the corresponding carboranylmagnesium bromide (Equation VII.13), this method being well established as a route

$$2\ MeC_2B_{10}H_{10}MgBr + 4\ C_4H_8O_2 \longrightarrow (MeC_{10}B_{10}H_{10})_2Mg(C_4H_8O_2)_2 + MgBr_2(C_4H_8O_2)_2 \qquad \text{VII.13}$$

to ether-coordinated diorganylmagnesium compounds (299). Separation of the carboranylmagnesium compound from $MgBr_2(C_4H_8O_2)_2$ was effected by subsequent removal of the ether solvent and extraction with hot toluene. It is interesting to note that, whereas the disproportionation reaction outlined in Equation VII.13 readily occurs upon addition of a base such as dioxan, addition of ortho-phenanthroline to carboranylmercury halides does not yield the corresponding bis(carboranyl)mercury derivative

(300) (Equation VII.14), despite the fact that such

$$2\ (RC_2B_{10}H_{10})HgX + 2o\text{-phen} \begin{array}{l} \not\nearrow\ (RC_2B_{10}H_{10})_2Hg + HgX_2(o\text{-phen}) \\ \searrow\ 2\ (RC_2B_{10}H_{10})HgX(o\text{-phen}) \end{array} \qquad \text{VII.14.}$$

R=H, alkyl

reactions are well known in the chemistry of organomercury halides (301).

The preliminary results of an X-ray crystallographic study on $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2.C_7H_8$ are presented in Figures VII.6 and VII.7 and Table VII.3. As shown in Figure VII.7 the crystal lattice contains one molecule of toluene per magnesium unit. The unit $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2$ (Figure VII.6) contains a two-fold axis of symmetry passing through the magnesium atom while the geometry around magnesium is very similar to that in the bis(carboranyl)dimethylgermanium compound $(C_2B_{10}H_{11})_2GeMe_2$ (302) which was the subject of an earlier crystallographic study. The Mg-C bond length of 2.16(2)Å is essentially identical to those of 2.167Å, in $Ph_2Mg(TMEDA)$, and 2.165Å, in $Me_2Mg(TMEDA)$, and similar to that of ca. 2.2Å, in $PhMgBr(OEt_2)_2$ (299), confirming the bonding to be of a similar covalent nature. The large e.s.d. value associated with the bond length prevents any conclusions being drawn as to the effect on the Mg-C linkage of an increase in the coordination number of carbon from four (in $Me_2Mg(TMEDA)$

FIGURE VII.6 Molecular structure of the unit $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2$

(hydrogen atoms omitted)

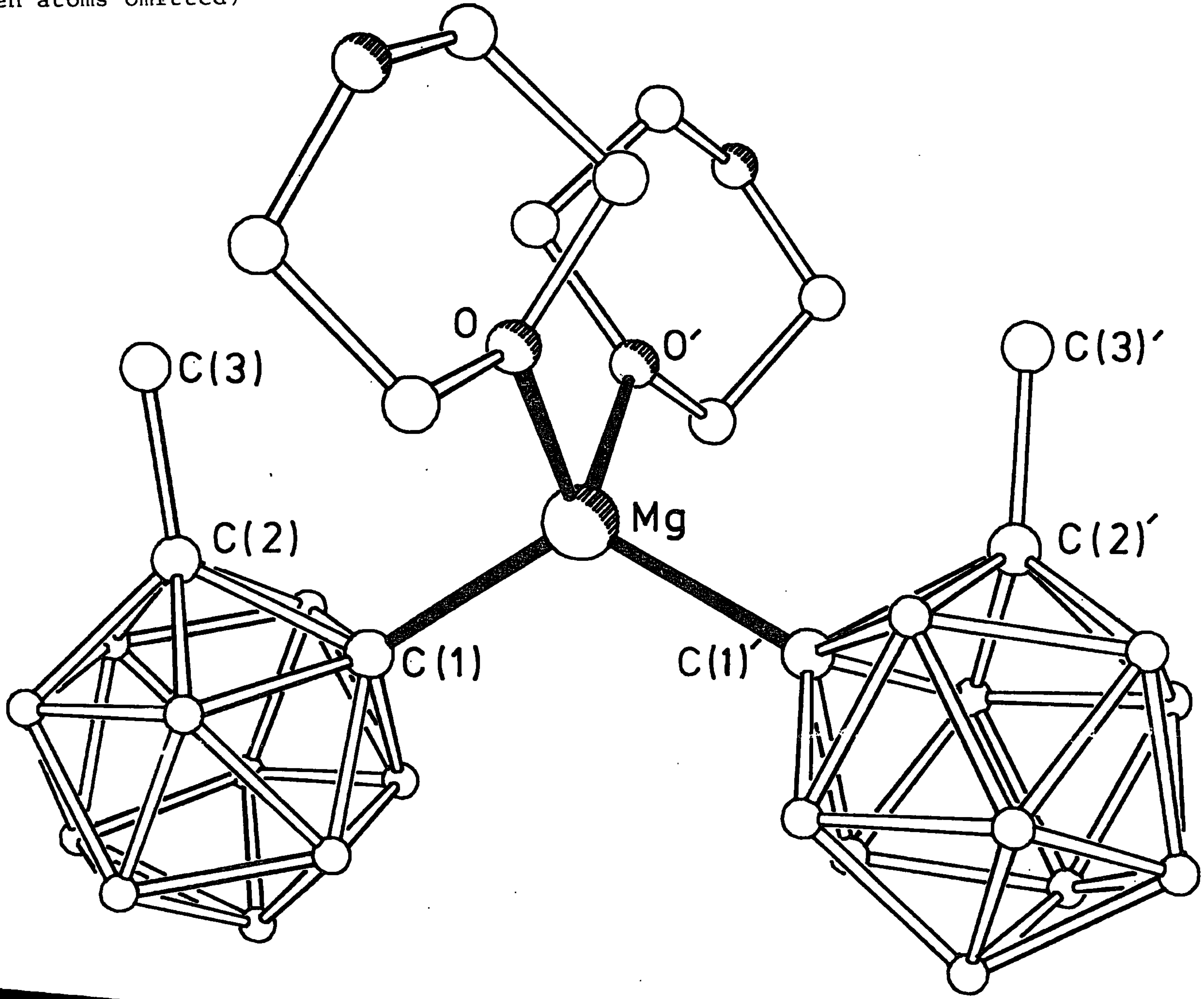


FIGURE VII.7 Crystal lattice structure of $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 \cdot C_7H_8$

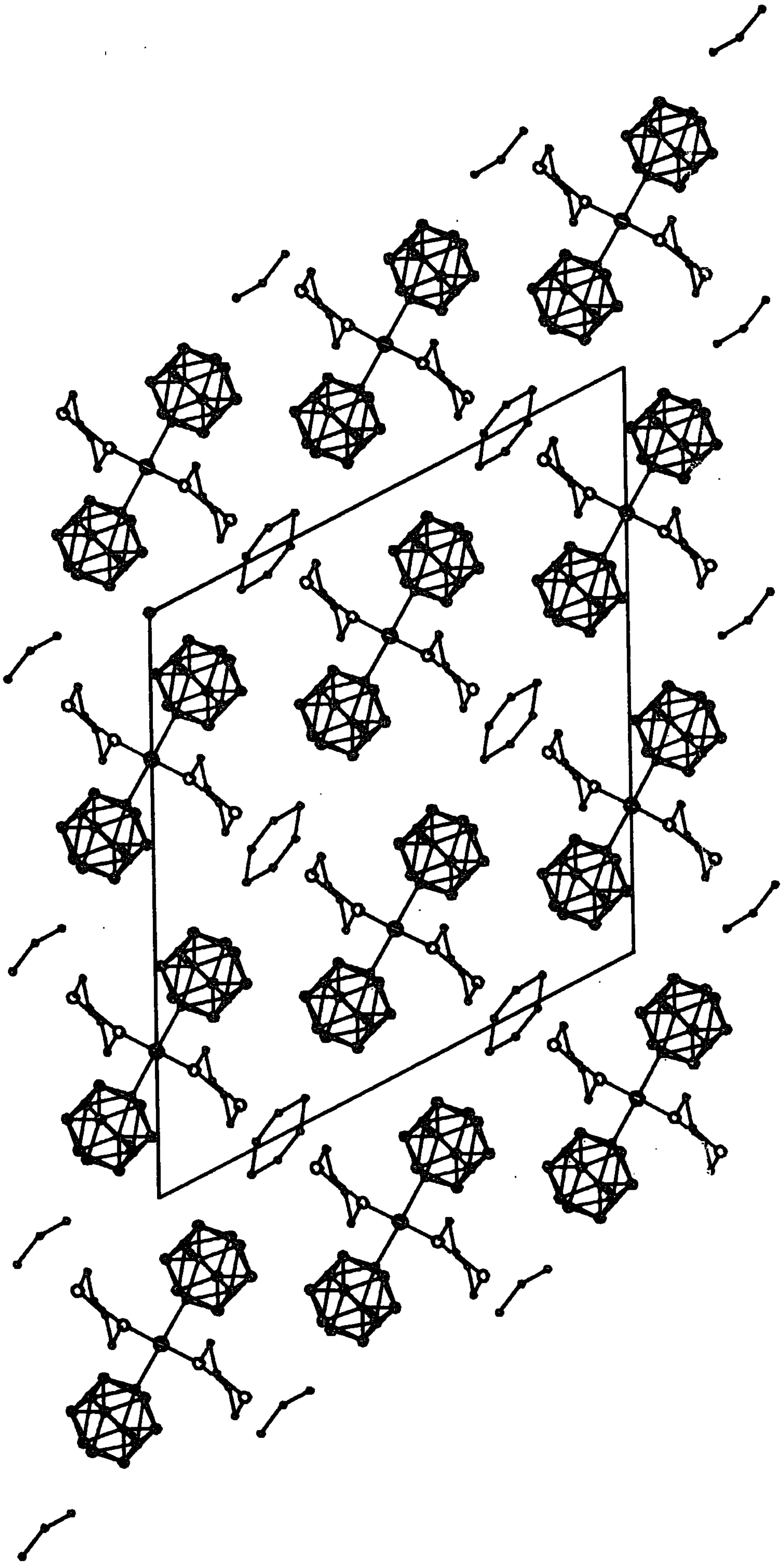


TABLE VII.3

Preliminary structural data for the compound $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2.C_7H_8$

Bond lengths (Å)

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

Bond angles (°)

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

to six. It has already been noted that little, if any, such effect is seen in $Li(C_2B_{10}H_{10}Me)(PMDETA)$, while the Ge-C bond lengths of 2.01(1)Å and 2.04(1)Å in $(C_2B_{10}H_{11})_2GeMe_2$ (302) are only slightly longer than those of ca. 1.95Å associated with a bond from germanium to four-coordinate carbon (231). The Mg-O bond lengths of 2.03(1)Å do not differ significantly from those found in a series of ether-coordinated alkyl-, and aryl-, magnesium bromides, $RMgBr(OR'_2)_2$ (299), while the $O\hat{Mg}O'$ angle of 100.5(6)° reflects the distortion of the magnesium environment arising from the steric interaction of the two carboranyl ligands.

In connection with the distortion of the tetrahedral environment around magnesium, it is interesting to compare the observed $C(1)\hat{Mg}C(1)'$ angle of 121.2(9)° with that which might have been predicted on the basis of the carboranyl cone angles discussed earlier. For a metal-carbon bond length of 2.16Å, the angle θ (Figure VII.4) between the M-C axis and the surface of the boron-bonded hydrogen <u>ortho</u> to the metallated carbon, is calculated to be 66°. Thus, if one set of <u>ortho</u> B-H units, on each of the two carboranyl ligands in a compound such as $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2$, were aligned co-planar with the atoms C(1), Mg and C(1)', the minimum possible angle $C(1)\hat{Mg}C(1)$ would be expected to be 132° (i.e. 2 x 66°), somewhat greater than the observed value. However, the carboranyl ligands of $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2$ adopt a conformation such that the methyl-carbon atoms C(3) and C(3)' are twisted out of the plane C(1)MgC(1)' (Figure VII.6), allowing the *ortho* B-H units of the two carboranyl ligands to "mesh" together to a certain extent. This allows the carboranyl units to approach each other more closely (reducing the distortion around Mg) and accounts for the observed $C(1)\hat{M}gC(1)'$ angle of 121.2(9)°. The remaining features of the structure, so far established, are unexceptional.

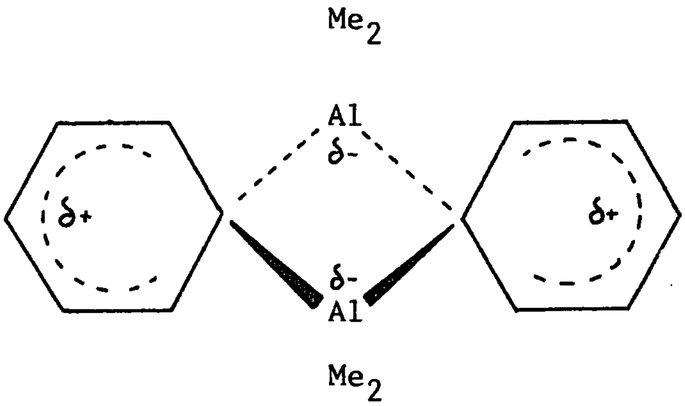
Attempted preparation of carboranylaluminium derivatives.

During the course of the present study unsuccessful attempts were made to isolate carboranylaluminium derivatives of the type $((C_2B_{10}H_{10}Me)AlMe_2)_n$ and $((C_2B_{10}H_{10}Me)_2AlMe)_n$ from the reactions of appropriate amounts of lithio-carborane and alkylaluminium halide in toluene solution. Besides being the first examples of exo-bonded carboranylaluminium compounds, the major feature of interest in these derivatives would concern their structural conformation. Cone angle calculations, similar to those described earlier, would suggest that $((C_2B_{10}H_{10}Me)AlMe_2)_n$ (and possibly also $((C_2B_{10}H_{10}Me)_2AlMe)_n$) could adopt a dimeric structure, involving electron-deficient bridging of the aluminium atoms, in a manner similar to that found elsewhere in organoaluminium chemistry (288). The question would therefore arise as to the nature of the bridging group in these compounds.

The crystal structure of $(Me_2PhAl)_2$ (303) shows the phenyl, rather than methyl, groups to be involved in the three-centre bridging of the metal atoms, and it has been suggested (10) that there is a significant degree of π-electronic charge delocalisation from the rings into the Al-C bonds (Figure VII.8). As the carboranyl ligands of $((C_2B_{10}H_{10}Me)AlMe_2)_2$ could potentially function as a similar means of charge delocalisation it could be argued that the preferred conformation of this molecule would involve metal bridging by the carboranyl,

FIGURE VII.8

Charge delocalisation in $(Me_2PhAl)_2$



rather than methyl groups. However, such a structure would require the metallated carboranyl carbon atoms to adopt a coordination number of seven, and a compound of this form would be unprecedented in carborane chemistry.

As it was not possible to isolate homogeneous materials from attempts at the preparation of these compounds, the possibility of such a bonding mode, involving hypercoordinate carbon, must remain as speculation; the infra red and ^1H n.m.r. spectra of the oils produced were uninformative in this respect.

CHAPTER 8

ATTEMPTS AT THE PREPARATION OF SOME ICOSAHEDRAL closo-DICOBALTABORANES

INTRODUCTION

Icosahedral carboranes, $R_2C_2B_{10}H_{10}$, are normally prepared from acetylenes, RC≡CR, and decaborane adducts $B_{10}H_{12}.2L$ (L=R'CN,$R_2'S$). Since recent work has shown that compounds containing metal-metal triple bonds react in many respects like acetylenes, it was thought that metallaboranes of the form $(X_nM)_2B_{10}H_{10}$ might be accessible through reactions between such compounds and $B_{10}H_{12}.2L$ or $B_{10}H_{14}$. Accordingly, a number of attempts at the insertion of pseudo-acetylenic units of the form Co_2L_6 (L=CO, phosphine: derived from the parent compounds Co_2L_8 by partial degradation) into the boranes $B_{10}H_{12}.2CH_3CN$ and $B_{10}H_{14}$ were made. The attempts however, proved unsuccessful, the cobalt species generally suffering further degradation without reacting with the borane.

EXPERIMENTAL SECTION

Dicobalt octacarbonyl, bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane were obtained commercially and used as supplied. Decaborane was obtained commercially and sublimed before use (70°, 0.005 mm Hg). Bis(acetonitrile) decaborane was prepared by refluxing decaborane in an approximately 1:1 mixture of acetonitrile and benzene. Di-μ-carbonyldicarbonylbis(diphenylphosphinoethane)dicobalt, $((Ph_2P(C_2H_4)PPh_2)Co(CO)_2)_2$ (304), and di-μ-carbonyltetracarbonyl(diphenylphosphinomethane)dicobalt, $Co_2(CO)_6(Ph_2PCH_2PPh_2)$ (305) were prepared by methods described in the literature. Nitriles and organic solvents were dried as described in Appendix 1. Reactions were performed under an atmosphere of dry nitrogen.

A summary of the reactions performed during the course of this study is given in Table VIII.1.

TABLE VIII.1 Summary of Experiments

Reactants	Conditions	Isolated Products
$B_{10}H_{12}(NCCH_3)_2$+$Co_2(CO)_8$	Solutions in (a) Toluene (b) Acetonitrile 24 hrs., 20°	No reaction
$B_{10}H_{14}$+$Co_2(CO)_8$	Solutions in (a) Toluene (b) Acetonitrile 24 hrs., 20°	No reaction
$B_{10}H_{12}(NCCH_3)_2$+$Co_2(CO)_8$	Solutions in (a) Toluene (b) Acetonitrile 48 hrs., Reflux	$B_{10}H_{12}(NCCH_3)_2$+Co + $Co_4(CO)_{12}$ (?)
$B_{10}H_{14}$+$Co_2(CO)_8$	Solutions in (a) Toluene (b) Acetonitrile 48 hrs., Reflux	$B_{10}H_{14}$+Co+$Co_4(CO)_{12}$(?)
$B_{10}H_{12}(NCCH_3)_2$+$Co_2(CO)_8$	200°, No solvent, 24 hrs.	$B_{10}H_{12}(NCCH_3)_2$+Carbonyls
$B_{10}H_{14}$+$Co_2(CO)_8$	200°, No solvent, 24 hrs.	$B_{10}H_{14}$+Carbonyls
$B_{10}H_{12}(NCCH_3)_2$+$Co_2(CO)_8$	Toluene solution, u.v. irradiation, 24 hrs.	$B_{10}H_{12}(NCCH_3)_2$+Co
$B_{10}H_{14}$+$Co_2(CO)_8$	Toluene solution, u.v. irradiation, 24 hrs.	$B_{10}H_{14}$+Co
$B_{10}H_{12}(NCCH_3)_2$ + $(Co(CO)_2Ph_2P(C_2H_4)PPh_2)_2$	Reflux in Toluene, 24 hrs.	$B_{10}H_{12}(NCCH_3)_2$+$Ph_2P(C_2H_4)PPh_2$ + carbonyls
$B_{10}H_{12}(NCCH_3)_2$ + $Co_2(CO)_6Ph_2PCH_2PPh_2$	Reflux in Toluene, 24 hrs.	$B_{10}H_{12}(NCCH_3)_2$+$Ph_2PCH_2PPh_2$ + carbonyls

DISCUSSION

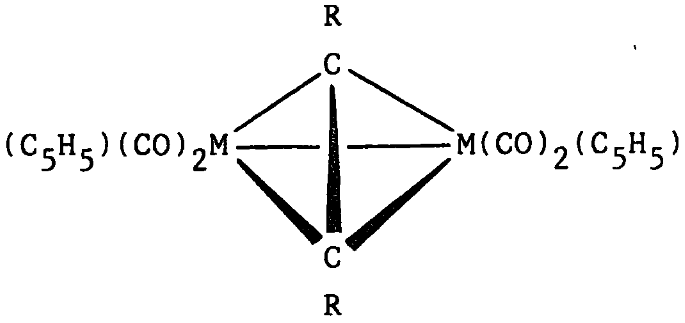
As noted in the introductory remarks the synthesis of a carborane is commonly achieved by the reaction of an acetylene and a borane fragment (232). Thus, the synthesis of the ortho-carborane $C_2B_{10}H_{12}$, and its C-organyl derivatives, involves the insertion of an acetylene into the neutrally-charged borane species $B_{10}H_{12}.2L$ ($L=R'_2S, R'CN$) (Equation VIII.1) with consequent elimination of the Lewis

$$RC{\equiv}CR + B_{10}H_{12}.2L \longrightarrow C_2B_{10}H_{10}RR' + 2L + H_2 \qquad VIII.1$$

base and hydrogen (236,237). In terms of the skeletal electron counting formalism (306,307) the resulting carborane can be regarded as comprising ten B-H units each contributing two electrons for cage bonding, and two R-C units, each contributing three electrons. The compound therefore has a total of thirteen pairs of electrons available for cluster bonding and, as predicted by the formalism,the structure is based on a twelve-vertex triangular-faced polyhedron, each of the vertices being occupied by a carbon or boron atom.

A recent extension in the use of triply-bonded species for the synthesis of clusters has been the use of metal analogues of acetylenes in the preparation of four-vertex metal, and metal-carbon, cages (308-317). The compounds $(M_2(CO)_4(\eta-C_5H_5)_2)$ (M=Cr,Mo,W), formally containing metal-metal triple bonds, will readily add to acetylenes, $RC{\equiv}CR$, to yield compounds of the form $(M_2(\mu-RC_2R)(CO)_4(\eta-C_5H_5)_2)$ (Equation VIII.2) in which the two metal atoms and the

$M_2(CO)_4(n-C_5H_5)_2$ + R-C≡C-R ⟶ VIII.2



M=Cr,Mo, W

two acetylenic carbons occupy the vertices of a tetrahedron (309-313). In a similar manner reactions between $(W(\equiv CR)(CO)_2(n-C_5H_5))$(R=p-tolyl), which contains a metal-carbon triple bond, and the species $(M_2(CO)_4(n-C_5H_5)_2)$ (M=Cr,Mo,W) yield the four-vertex metal-carbon clusters $(MW_2(\mu_3-CR)(CO)_6(n-C_5H_5)_3)$ (314), while the analogy between acetylenes and $(W(\equiv CR)(CO)_2(n-C_5H_5))$ is further demonstrated by their behaviour towards $Co_2(CO)_8$. Thus, reactions between $Co_2(CO)_8$ and acetylenes, RC≡CR (318,319), yield species of the form $Co_2(CO)_6(\mu-RC_2R)$ (Equation VIII.3), analogous to the four-vertex cluster resulting from the

$$Co_2(CO)_8 + RC\equiv CR \longrightarrow Co_2(CO)_6(\mu-RC_2R) + 2CO \qquad VIII.3$$

reaction of $Co_2(CO)_8$ and $(W(\equiv CR)(CO)_2(n-C_5H_5))$ (Equation VIII.4) (316).

$$Co_2(CO)_8 + W(\equiv CR)(CO)_2(n-C_5H_5) \longrightarrow Co_2W(\mu_3-CR)(CO)_8(n-C_5H_5) + 2CO$$

R = p-tolyl VIII.4.

The successful use of metal analogues of acetylene in the synthesis of cluster units prompted attempts, described in the present chapter, to directly insert a metal analogue of acetylene into the open face of a B_{10} cluster unit and so form a neutrally charged *closo*-metallaborane, in a manner similar to the preparation of $C_2B_{10}H_{12}$ described above. The formation of an icosahedral cluster by this method would be a novel feature in metallaborane chemistry and would, in principle, permit a considerable extension of the existing chemistry of such compounds.

The synthesis of metallaboranes and metallacarboranes has been reviewed by a number of authors (244, 320-325), most recently by Grimes (326). In general metallacarboranes have received considerably more attention than metallaboranes, although the syntheses of a number of twelve-vertex *closo*-metallaboranes, containing one or more metal atoms, have been reported. Most of the reactions, examples of which are listed in equations VIII.5 to VIII.7 (326), involve the insertion of a metal fragment into a *nido* 11-vertex borane or heteroborane substrate, although the *closo* anions

$$\underline{\text{nido}} - B_{11}H_{13}^{2-} + Cp_2Ni \xrightarrow[\text{MeCN}]{\text{Na/Hg}} \underline{\text{closo}} - CpNiB_{11}H_{11}^{-} \qquad \text{VIII.5}$$

$$\underline{\text{nido}} - CpNiB_{10}H_{12} + Cp_2Co \longrightarrow \underline{\text{closo}} - Cp_2CoNiB_{10}H_{10}^{-} \qquad \text{VIII.6}$$

$$\underline{\text{nido}} - B_{11}H_{14}^{-} \xrightarrow[\text{or } TeO_2]{NaHSeO_3} M\ B_{11}H_{11} \qquad \text{VIII.7}$$

$$(M = Se,\ Te)$$

$B_{11}H_{11}^{2-}$ and $B_{10}H_{10}^{2-}$ have been used in the synthesis of some nickelaboranes (Equations VIII.8,9) (327). In a similar manner, 12-vertex closo metallaheteroboranes,

$$\underline{closo} - B_{11}H_{11}^{2-} + CpNi(CO)_2 \longrightarrow \underline{closo} - CpNiB_{11}H_{11}^{-} \qquad \text{VIII.8}$$

$$\underline{closo} - B_{10}H_{10}^{2-} + Cp_2Ni \longrightarrow \underline{closo} - CpNi_2B_{10}H_{10} \qquad \text{VIII.9}$$

containing a main group heteroatom, have been prepared by the insertion of transition metals into neutral or anionic heteroboranes (236). Examples of such compounds include the products obtained from the reaction of a transition metal species and the thiaborane anion $SB_{10}H_{10}^{2-}$ (Equations VIII.10-14) (238), the clusters $(SB_{10}H_{10})_2Fe^{2-}$ and

$$SB_{10}H_{10}^{2-} \xrightarrow{FeCl_3} (SB_{10}H_{10})_2Fe^{2-} \qquad \text{VIII.10}$$

$$\xrightarrow{Co\,Cl_3} (SB_{10}H_{10})_2Co^{-} \qquad \text{VIII.11}$$

$$\xrightarrow{Co\,Cl_2,\ C_5H_5^{-}} Cp\ Co\,SB_{10}H_{10} \qquad \text{VIII.12}$$

$$\xrightarrow{(Et_3P)_2PtCl} (Et_3P)_2PtSB_{10}H_{10} \qquad \text{VIII.13}$$

$$\xrightarrow{(CO)_5ReCl} (CO)_3\,ReSB_{10}H_{10}^{-} \qquad \text{VIII.14}$$

$(SB_{10}H_{10})_2Co^{-}$ prepared in this way being interesting in that they have metal-sandwich type structures in which the metal atom sits between the two cages, forming a common vertex.

A neutrally-charged icosahedral closo-metallaborane, $(X_nM)_2B_{10}H_{10}$, such as might be prepared from the reaction of a B_{10} borane and the metal analogue of an acetylene, would require the MX_n fragments to be isolobal with the C-H fragment of the corresponding carborane $C_2B_{10}H_{12}$. The concept of isolobality, as developed by Hoffmann (329), dictates that two fragments may be considered as isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons they contain are similar. The skeletal electron counting formalism (306) considers the C-H fragment to contribute three electrons and three orbitals for cluster bonding and an isolobal metal fragment, MX_n, would therefore be required to fulfill the same criteria. The cobalt tricarbonyl fragment, $Co(CO)_3$, is such a species (329,330), and this chapter describes a number of attempts to promote the insertion of two $Co(CO)_3$ units into the B_{10} cage of bis(acetonitrile)decaborane, $B_{10}H_{12}.2CH_3CN$. The source of the cobalt-carbonyl fragments selected was dicobalt octacarbonyl, $Co_2(CO)_8$, and it was hoped that the loss of two carbonyl ligands to form a pseudo-acetylenic intermediate, $Co_2(CO)_6$, followed by reaction with $B_{10}H_{12}.2CH_3CN$ (Equation VIII.15) would result in the

$$B_{10}H_{12}.2CH_3CN + Co_2(CO)_8 \longrightarrow (CO)_6Co_2B_{10}H_{10} + 2CO + H_2 + 2\,CH_3CN \qquad \text{VIII.15}$$

formation of closo-metallaboranes in a manner similar to these reactions described earlier. Such a reaction would, however, require the unstable $Co_2(CO)_6$ intermediate to preferentially react with the borane, rather than undergo further degradation to form the tetranuclear carbonyl cluster $Co_4(CO)_{12}$, known to result from the thermal decomposition of $Co_2(CO)_8$ (331-333).

The reactions performed during the course of this study are summarised in the experimental section. Parallel reactions, between $Co_2(CO)_8$ and $B_{10}H_{14}$, were also performed.

Neither $B_{10}H_{12}(NCCH_3)_2$ nor $B_{10}H_{14}$ showed any sign of reaction with $Co_2(CO)_8$ in either toluene or acetonitrile at room temperature. When solutions of these reactants were heated to reflux temperature the solutions slowly darkened from red to black, over varying periods of time. Removal of the solvent and subsequent work-up of the tar-like products invariably afforded quantitative recovery of the borane plus varying quantities of black solids. Elemental analysis of these solids yielded varying results, although all were consistent with the solids comprising mixtures of cobalt metal and a higher carbonyl, possibly $Co_4(CO)_{12}$. Further reactions, conducted at 200° and in the absence of solvent, yielded similar black solids in addition to unreacted borane. Additionally, attempts at promoting insertion reactions by irradiating toluene solutions of borane and $Co_2(CO)_8$ resulted in complete degradation of the carbonyl unit without further reaction, cobalt metal being recovered from these reactions.

It was apparent from the above reactions that the facile loss of carbonyl ligands from $Co_2(CO)_8$ was proceeding beyond the formation of the $Co_2(CO)_6$ species, formally required for insertion into the borane cage. Attempts were therefore made to stabilise intermediate carbonyl species of this type by the replacement of some of the carbonyl ligands of $Co_2(CO)_8$ with coordinated phosphines. The compounds di-μ-carbonyldicarbonylbis-(diphenylphosphinoethane)dicobalt, $((Ph_2P(C_2H_4)PPh_2)Co(CO)_2)_2$ (Figure VIII.1(a)) (304), and di-μ-carbonyltetracarbonyl-(diphenylphosphinomethane)dicobalt, $Co_2(CO)_6(Ph_2PCH_2PPh_2)$ (Figure VIII.1(b)) (305), were therefore synthesised for this purpose. Insertion of the fragment $Co_2(CO)_4(Ph_2PCH_2PPh_2)$ (derived from the latter compound by the loss of two carbonyl ligands) into the borane cage would yield a compound of the form $CH_2(Ph_2P)_2(CO)_4Co_2B_{10}H_{10}$ (Figure VIII.2), the coordinated phosphine ligand being of suitable geometry to form a five-membered exocyclic ring sharing a common Co- Co linkage with the cage. However, reactions of both phosphine-coordinated cobalt carbonyl derivatives with $B_{10}H_{12}(NCCH_3)_2$ in toluene again yielded black tar-like products from which free phosphine ligand and unreacted borane were recovered. The remaining black solids were apparently of similar composition to those described earlier.

The study was not taken beyond this point as it was apparent that the degradation of the cobalt carbonyl

FIGURE VIII.1

The compounds (a) di-μ-carbonyldicarbonylbis(diphenylphosphinoethane)dicobalt and (b) di-μ-carbonyltetracarbonyl(diphenylphosphinomethane)dicobalt

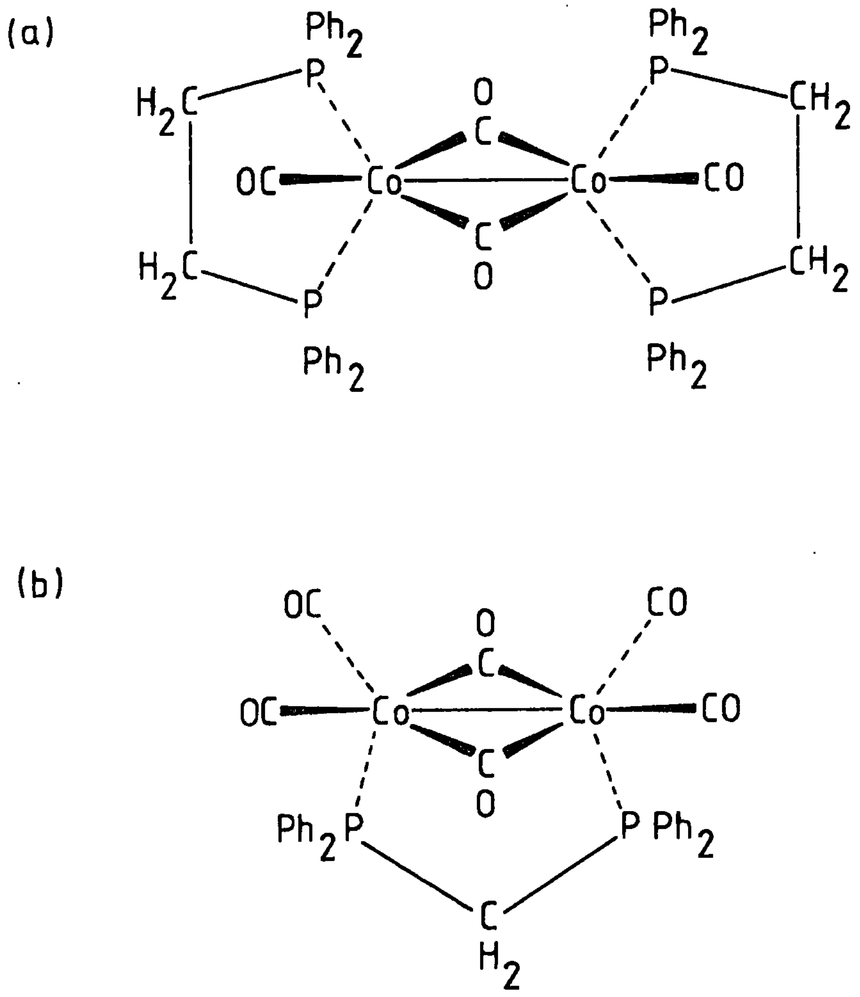
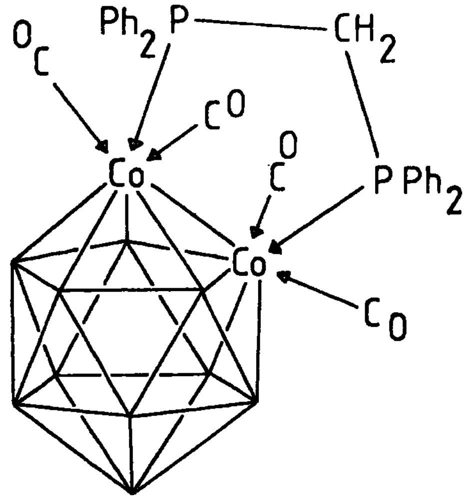


FIGURE VIII.2

Proposed structure of the metallaborane $CH_2(Ph_2P)_2(CO)_4Co_2B_{10}H_{10}$



species could not be controlled sufficiently to allow the possibility of insertion into the borane cage. A possibly more promising route to metallaboranes, from the use of metal-metal triply bonded species, would involve use of the compounds $(M_2(CO)_4(n\text{-}C_5H_5)_2)$ (M=Cr, Mo, W), described earlier, in conjunction with more reactive <u>nido</u>-borane species such as B_5H_9 or B_6H_{10}.

APPENDIX 1

GENERAL EXPERIMENTAL TECHNIQUES

1. General

The majority of compounds synthesised during the course of this study, and many of the starting materials used, are sensitive to atmospheric exposure, either through hydrolysis or oxidation. All operations were therefore performed under vacuum, or an atmosphere of dry nitrogen, as appropriate. Solvents and liquid reagents of low volatility were transferred by syringe against a counter-current of dry nitrogen, gases and volatile liquid reagents were generally handled in a vacuum line, using standard techniques. Filtrations made use of standard filter stick techniques; apparatus manipulations were minimised and, when necessary, made against a counter-current of nitrogen. Air sensitive solids were handled in a glove box.

2. Nitrogen

Nitrogen gas was supplied to the laboratory as the boil-off from a tank containing liquid nitrogen, the gas having subsequently been passed through a de-oxygenating plant. The gas was dried by passage through columns packed with phosphorus pentoxide.

3. Glove Boxes

Compounds of limited air sensitivity were handled in a glove box of simple design, the dry nitrogen atmosphere of which was maintained by continuous recycling through columns packed with phosphorus pentoxide. The box was periodically purged with fresh dry nitrogen to avoid the build-up of oxygen and volatiles. Compounds of more extreme air-sensitivity were handled in glove boxes designed to maintain levels of oxygen and moisture below one part per million. Oxygen was removed from the atmosphere of these boxes by recylcing through columns of catalytically activitated copper, moisture was removed by passage over activated molecular sieve.

4. Solvents

Hydrocarbon solvents and diethyl ether were dried and stored over freshly extruded sodium wire. Other ether solvents were dried by refluxing with potassium metal until the addition of a single crystal of benzophenone yielded a permanent blue colouration. The liquids were then distilled onto extruded sodium wire and stored under nitrogen. Deuterated n.m.r. solvents were obtained commercially and used as supplied.

5. Starting Materials

As described in the various experimental sections, solids were generally either freshly sublimed or recrystallised from an appropriate solvent prior to use. Liquid reagents were generally distilled, either under an atmosphere of dry nitrogen or under vacuum, as appropriate. Nitriles were dried by successive distillation from calcium hydride and phosphorus pentoxide (twice). TMEDA and PMDETA were distilled from calcium hydride and stored over molecular sieve. Solutions of alkyl-lithium reagents were standardised by titration against a 0.1M solution of sec-butanol in xylene (334), 1,10-phenanthroline being used as an indicator.

6. Instrumentation

(a) Infra red spectra

Infra red spectra in the range 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 or 577 grating spectrometer. Samples were mounted as either nujol mulls or liquid films between KBr plates, or as pressed KBr discs.

(b) ^{1}H n.m.r. spectra

Spectra were recorded on a Varian EM360L spectrometer operating at 60 MHz, or a Brucker HX90E Fourier-transform spectrometer operating at 90 MHz.

(c) ^{11}B n.m.r. spectra

Spectra were recorded on a purpose-built Fourier-transform spectrometer, designed by Dr. A. Royston of these laboratories, and operating at 19.24 MHz. The spectrometer magnet was formerly that of a Perkin- Elmer R10 machine, while computing was performed on a PDP 11/34 computer.

(d) ^{13}C n.m.r. spectra

Spectra were recorded on a Brucker HX90E Fourier-Transform spectrometer operating at 22.63 MHz.

(e) ^{13}P n.m.r. spectra

Spectra were recorded on a purpose-built Fourier-Transform spectrometer operating at 24.29 MHz. The machine was designed around a former Perkin- Elmer R10 spectrometer, computing was performed on a Varian computer.

(f) Mass spectra

Mass spectra were recorded on an A.E.I. MS9 spectrometer at 70 eV and an accelerating potential of 8K V, with a source temperature of 150-250°. The spectrum was scanned electromagnetically. Samples were introduced into the ion source by direct insertion.

7. Analytical methods

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Air sensitive samples were sealed in preweighed aluminium capsules in a glove box. Halogens were determined by oxygen flask combustion followed by potentiometric titration. Metals were determined using a Perkin- Elmer 403 Atomic Absorption Spectrometer. The boron content of methyleneaminoboranes was determined as boric acid after ignition of a weighed sample. Boron analyses on boranes and carboranes were made on boric acid solutions prepared by careful degradation of the compounds with concentrated nitric acid.

APPENDIX 2

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES, 1980 - 83.

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an Appendix listing;

(a) all research colloquia, research seminars, and lectures arranged by the Department of Chemistry and the Durham University Chemical Society during the period of the writer's residence as a postgraduate student;

(b) details of the first-year postgraduate induction course; and

(c) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out.

A. RESEARCH COLLOQUIA, SEMINARS, AND LECTURES

1. Durham University Chemistry Department Colloquia.

Academic Year 1980-81.

7 October	Prof. T. Fehlner (Notre Dame University, Indiana), "Metallaboranes - cages or co-ordination compounds".
15 October	Dr. R. Alder (University of Bristol), "Doing chemistry inside cages - medium ring bicyclic molecules".
12 November	Dr. M. Gerloch (University of Cambridge), "Magnetochemistry is about chemistry".
19 November	Dr. T. Gilchrist (University of Liveprool), "Nitroso-olefines as synthetic intermediates".
3 December	Dr. J.A. Conner (University of Manchester), "Thermochemistry of Transition metal compounds".

18 December	Dr. R.F. Evans (University of Brisbane), "Some recent communications to the Australian Journal of Failed Chemistry".
18 February	Prof. S.F.A. Kettle (University of East Anglia), "Variations in the molecular dance at the crystal ball".
25 February	Dr. K. Bowden (University of Essex), "The transmission of polar substituent effects".
4 March	Dr. S. Cradock (University of Edinburgh), "Pseudolinear pseudohalides".
18 March	Dr. P.J. Smith (Int. Tin Research Institute), "Organotin compounds-a versatile class of organometallic derivatives".
6 May	Prof. M. Szwarc, F.R.S., "Ions and ion Pairs".
8 May	Prof. H.F. Koch (Bathaca College, U.S.A.), "Proton transfer during elimination reactions".
13 May	Prof. H. Fritzer (University of Graz), "Simple methods to construct representations for discrete symmetry groups".
14 May	Prof. H. Fritzer (University of Graz), "The interplay of permutational and geometrical symmetry of certain electronic systems".
10 June	Dr. J. Rose (I.C.I. Plastics Division), "New engineering plastics".
17 June	Dr. P. Moreau (University of Montpellier), "Recent results in perfluoro-organometallic chemistry".

24 June	Dr. S.A.R. Knox (University of Bristol), "Coordination and reactivity of organic species at dinuclear metal centres".
26 June	Prof. A.P. Schaap (U.S. Office of Naval Research, London) "Mechanism of chemiluminescence and photooxygenation".

Academic Year 1981-82

14 October	Prof. E. Kluk (University of Katowice), "Chemoluminescence and photo-oxidation".
28 October	Dr. R.J.H. Clark (University College, London), "Resonance Raman spectroscopy".
6 November	Dr. W. Moddeman (Monsanto Research Labs., St. Louis, Missouri), "High energy materials".
18 November	Prof. M.J. Perkins (Chelsea College, London), "Spin trapping and nitroxide radicals".
25 November	Dr. M. Baird (University of Newcastle), " Intramolecular reactions of carbenes and carbinoids".
30 November	Dr. B.T. Heaton (University of Kent), "N.M.R. studies of carbonyl clusters".
2 December	Dr. G. Beamson (University of Durham), "Photoelectron spectroscopy in a strong magnetic field".
20 January	Dr. M.R. Bryce (University of Durham), "Organic metals".
27 January	Dr. D.L.H. Williams (University of Durham), "Nitrosation and nitrosoamines".

3 February	Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".
10 February	Prof. R.D. Chambers (University of Durham), "Recent reactions of fluorinated internal olefins".
24 February	Dr. L. Field (University of Oxford), "Applications of M.M.R. to biosynthetic studies on penicillin".
3 March	Dr. P. Bamfield (I.C.I. Organics Division), "Computer aided design in synthetic organic chemistry".
17 March	Prof. R.J. Haines (University of Natal) "Clustering around Ruthenium, Iron, and Rhodium".
7 April	Dr. A. Pensak (DuPont, U.S.A.), "Computer aided synthesis".
5 May	Dr. G. Tennant (University of Edinburgh), "Exploitation of the aromatic nitro-group in the design of new heterocyclisation reactions".
7 May	Dr. C.D. Garner (University of Manchester), "The structure and function of Molybdenum centres in enzymes".
26 May	Dr. A. Welch (University of Edinburgh), "Conformation patterns and distortion in carbonmetalloboranes".
14 June	Prof. C.M.J. Stirling (University College of Wales, Bangor), "How much does strain affect reactivity?".

28 June	Prof. D.J. Burton (University of Iowa), "Some aspects of the chemistry of fluorinated phosphonium salts and their phosphonates".
2 July	Prof. H.F. Koch (Ithaca College, U.S.A.), "Proton transfer to and elimination reactions from localized and delocalized carbanions".

Academic Year 1982-83

13 September	Prof. R. Neidlein (University of Heidelberg), "New aspects and results of bridged annulene chemistry".
27 September	Dr. W.K. Ford (Zerox research centre, Webster, New York), "The dependence of the electronic structure of polymers on their molecular architecture".
14 October	Prof. H. Suhr (University of Tubingen) "Preparative chemistry in non-equilibrium plasmas".
27 October	Dr. C.E. Housecroft (University of Notre Dame), "Bonding capabilities of butterfly-shaped Fe_4 units. Implications for C-H bond activation in hydrocarbon complexes".
28 October	Prof. M.F. Lappert F.R.S. (University of Sussex), "Approaches to assymetric synthesis and catalysis using electron-rich olefins and some of their metal complexes".
15 November	Dr. G. Bertrand (Universite Paul Salatier, Toulouse), "Curtius rearrangement in organometallic series : a route for a new hybridised species".

24 November	Prof. F.R. Hartley (R.M. C.S., Shrivenham) "Supported metal complex hydroformylation catalysts : a novel approach using γ radiation".
24 November	Prof. G.G. Roberts (University of Durham), "Langmuir-Blodgett films".
8 December	Dr. G. Wooley (Trent Polytechnic) "Bonds in transition metal cluster compounds".
12 January	Dr. D.C. Sherrington (University of Strathclyde), "Polymer supported plane-transfer catalysts".
9 February	Dr. P. Moore (University of Warwick) "Mechanistic studies in solution by stopped flow F.T.N.M.R. and high pressure N.M.R. line broadening".
21 February	Dr. R. Lynden-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCl".
2 March	Dr. D. Bloor (Queen Mary College), "The solid state chemistry of diacetylene monomers and polymers".
8 March	Prof. D.C. Bradley F.R.S. (Queen Mary College), "Recent developments in organo-imido-transition metal chemistry ".
9 March	Dr. D.M.J. Lilley (University of Dundee) "DNA, sequence, symmetry, structure and supercooling".
11 March	Prof. H.G. Viehe (University of Louvain) "Oxidations on sulphur"
11 March	Prof. H.G. Viehe (University of Louvain) "Fluorine substitution in radical and bi-radical addition reactions".

16 March	Dr. I. Gosney (University of Edinburgh), "New extrusion reactions : Organic synthesis in a hot tube".
25 March	Prof. F.G. Baglin (University of Nevada) "Interaction induced raman spectroscopy in supercritical ethane".
21 April	Prof. J. Passmore (University of New Brunswick), "Novel selenium-iodine cations".
4 May	Prof. P.H. Plesch (University of Keele) "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of ".
10 May	Prof. K. Berger (University of Munich) "New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds".
11 May	Dr. N. Isaacs (University of Reading) "The application of high pressures to the theory and practice of organic chemistry".
13 May	Dr. R. de Kock (Calvin College, Grand Rapids, Michigan) "Electronic structural calculations on organometallic cobalt cluster molecules : Implications for metal surfaces".
13 May	Dr. T.D. Marder (University of California in Los Angeles) "The chemistry of metal-carbon and metal-metal multiple bonds".
16 May	Prof. R.J. Lagow (University of Texas) "The chemistry of polylithium organic compounds: an unusual class of matter".

18 May	Dr. D.M. Adams (University of Leicester) "Spectroscopy at very high pressures".
25 May	Dr. J.M. Vernon (University of York) "New heterocyclic chemistry involving lead tetra-acetate"
15 June	Dr. A. Pietrzykowski (Technical University of Warsaw) "Synthesis, structure and properties of aluminoxanes".
22 June	Dr. D.W.H. Rankin (University of Edinburgh) "Floppy molecules - the influence of phase on structure".
5 July	Prof. J. Miller (University of Campinas) "Reactivity in nucleophilic substitution reactions".

2. Durham University Chemical Society Lectures

Academic Year 1980-81

16 October	Dr. D. Maas (University of Salford), "Reactions a go-go ".
23 October	Prof. T.M. Sugden (University of Cambridge), " Some reactions of metals in high temperature flames ".
30 October	Prof. N. Grassie (University of Glasgow), "Inflammability hazards in commercial polymers".
6 November	Prof. A.G. Sykes (University of Newcastle), "Metalloproteins: an inorganic chemists approach".
13 November	Prof. N.N. Greenwood (University of Leeds), "Metalloborane chemistry".

4 December	Rev. R. Lancaster (Kimbolton School, Cambridgeshire), "Fireworks".
22 January	Prof. E.A. Dawes (University of Hull), "Magic and mystery through the ages".
29 January	Mr. H.J.F. MacLean (I. C.I. Agricultural Division), "Managing in the chemical industry in the 1980's".
5 February	Prof. F.G.A. Stone (University of Bristol), "Chemistry of carbon to metal triple bonds".
12 February	Dr. I. Fleming (University of Cambridge), "Some uses of silicon compounds in organic synthesis".
17 March	Prof. W.P. Jencks (Brandeis University, Massachusetts), "When is an intermediate not an intermediate".
7 May	Prof. M. Gordon (University of Essex), "Do scientists have to count?".

Academic Year 1981-82

22 October	Dr. P.J. Corish (Dunlop Ltd.), "What would life be like without rubber?".
29 October	Miss J.M. Cronyn (University of Durham), "Chemistry in archaeology".
12 November	Prof. A.I. Scott (University of Edinburgh), "An organic chemist's view of life in the N.M.R. tube".
19 November	Prof. B.L. Shaw (University of Leeds), "Big rings and metal-carbon bond formation".

26 November	Dr. W.O. Ord (Northumbrian Water Authority), "The role of the scientist in a regional water authority".
3 December	Dr. R.E. Hester (University of York), "Spectroscopy with lasers ".
28 January	Prof. I. Fells (University of Newcastle), "Balancing the energy equation".
11 February	Dr. D.W. Turner (University of Oxford), "Photoelectrons in a strong magnetic field ".
18 February	Prof. R.K. Harris (University of East Anglia) "N.M.R. in the 1980's".
25 February	Prof. R.O.C. Norman (University of York), "Turning points and challenges for the organic chemist".
4 March	Dr. R. Whyman (I.C.I. Runcorn), "Making metal clusters work ".

Academic Year 1982-83

The following lectures were organised by the author while President of the Society for the year 1982-83.

14 October	Mr. F. Shenton (Durham County Analyst), "There is death in the pot".
28 October	Prof. M.F. Lappert F.R.S. (University of Sussex) "The Chemistry of some unusual subvalent compounds of the main group IV and V elements".

4 November	Dr. D.H. Williams (University of Cambridge) "Studies on the structures and modes of action of antibiotics".
11 November	Dr. J. Cramp (I.C.I. Ltd.) "Lasers in Industry".
25 November	Dr. D.H. Richards (P.E.R.M.E., M.O.D.) "Terminally functional polymers - their synthesis and uses".
27 January	Prof. D.W.A. Sharp (University of Glasgow), "Some redox reactions in fluorine chemistry".
3 February	Dr. R. Manning (University of Durham), "Molecular mechanisms of hormone action".
10 February	Sir G. Allen F.R.S. (Unilever Ltd.), "U.K. Research Ltd. ".
17 February	Prof. A.G. Mac Diarmid (University of Pennsylvania), "Metallic covalent polymers : $(SN)_x$ and $(CH)_x$ and their derivatives".
3 March	Prof. A.C.T. North (University of Leeds) "The use of a computer display system in studying molecular structures and interactions".

B. POSTGRADUATE INDUCTION COURSE

In each part of the course, the uses and limitations of the various services available were explained by those responsible for them.

Departmental organisation - Dr. E.J.F. Ross

Electrical appliances and infra red spectroscopy - Mr. R.N. Brown

Chromatography and microanalysis - Mr. T.F. Holmes

Atomic absorption spectrometry and inorganic analysis - Mr. R. Coult

Mass spectrometry - Dr. M. Jones

N.M.R. spectrometry - Dr. R.S. Matthews

Glassblowing techniques - Mr. W.H. Fettis and Mr. R. Hart

Safety matters - Dr. M.R. Crampton

C. RESEARCH CONFERENCES

"Interboron III", University of Leeds, 14th - 16th September 1982.

Graduate Symposium, Durham, 21st April, 1982.

REFERENCES

1. E.A. Petch, Ph. D. Thesis, Univ. of Durham, 1974.

2. K. Manning, Ph.D. Thesis, Univ. of Durham, 1980.

3. B. Hall, J. Keable, R. Snaith, and K. Wade, J. Chem. Soc. Dalton Trans., 1978, 986.

4. N.W. Alcock, M. Pierce-Butler, G.R. Willey and K. Wade, J. Chem. Soc. Chem. Commun., 1975, 183.

5. N.W. Alcock and M. Pierce-Butler, J. Chem. Soc. Dalton Trans., 1975, 2469.

6. M.M. Mahmoud, Ph. D. thesis, Univ. of Nottingham, 1976.

7. K. Manning, E.A. Petch, H.M.M. Shearer and K. Wade, J. Chem. Soc. Chem. Commun., 1976, 107.

8. J. Willis, Ph.D. Thesis, Univ. of Durham, 1966.

9. J.R. Jennings, R. Snaith, M.M. Mahmoud, S.C. Wallwork, S.J. Bryan, J. Halfpenny, E.A. Petch and K. Wade, J. Organomet. Chem., 1983, <u>249</u>, C1.

10. K. Wade, "Electron deficient compounds", Nelson, 1971.

11. R. Mason and D.M.P. Mingos, J. Organomet. Chem., 1973, <u>50</u>, 53.

12. W. Clegg, R. Snaith, H.M.M. Shearer, K. Wade and G. Whitehead, J. Chem. Soc. Dalton Trans., 1983, 1309.

13. R. Snaith and K. Wade, Personal communication.

14. G.J. Bullen and K. Wade, Chem. Commun., 1971, 1122.

15. G.J. Bullen, J. Chem. Soc. Dalton Trans., 1973, 858.

16. B. Hall, J.B. Farmer, H.M.M. Shearer, J.D. Sowerby and K. Wade, J. Chem. Soc. Dalton. Trans., 1979, 102.

17. H.M.M. Shearer, R. Snaith, J. D. Sowerby and K. Wade, Chem. Commun., 1971, 1275.

18. J.E. Lloyd, Ph.D. thesis, Univ. of Durham, 1964.

19. W.J. Lehmann, C.O. Wilson Jnr., and I. Shapiro, J. Chem. Phys., 1958, <u>28</u>, 777.

20. W.J. Lehmann, C.O. Wilson Jnr., and I Shapiro, J. Chem. Phys., 1958, <u>28</u>, 781.

21. H.C. Brown and B.C. Subba Row, J. Org. Chem., 1957, 22, 1135.

22. R.C. Lord and E. Neilson, J. Chem. Phys., 1959, 19, 1.

23. H.I. Schlesinger and A.C. Waller, J. Amer. Chem. Soc., 1935, 57, 61.

24. W.J. Lehmann, C.O. Wilson Jnr., and I. Shapiro, J. Chem. Phys., 1961, 34, 783.

25. J.E. Lloyd and K. Wade, J. Chem. Soc., 1964, 1649.

26. E.C. Evers, W.O. Freitag, J.N. Keith, W.A. Kriner, A.G. Mac Diarmid and S. Sujishi, J. Amer. Chem. Soc., 1959, 81, 4493.

27. D.F. Ball, P.L. Goggin and L.A. Larwood, Spectrochim. Acta., 1960, 16, 1358.

28. W. Siebert, R. Fall, T. Renk and A. Ospici, Z. Anorg. Allg. Chem., 1975, 418, 273.

29. J.K. Alford, E.O. Bishop and J.D. Smith, J. Chem. Soc. Dalton Trans., 1976, 920.

30. H.I. Schlesinger and A.B. Burg, Chem. Rev., 1942, 31, 1.

31. H.J. Emeléus and K. Wade, J. Chem. Soc., 1960, 2614.

32. A.B. Burg, "Record of chemical progress" (Kriesge-Hooker Science Library), 1954, 15, 159.

33. J.E. Lloyd and K. Wade, J. Chem. Soc., 1965, 2662.

34. J.R. Jennings, J.E. Lloyd and K. Wade, J. Chem. Soc., 1965, 5083.

35. M.F. Hawthorne, Tetrahedron, 1962, 17, 1171.

36. H.J. Laffer, Inorg. Chem., 1964, 3, 145.

37. V.A. Dorokhov and M.F. Lappert, J. Chem. Soc. (A), 1969, 433.

38. M.R. Collier, M.F. Lappert, R. Snaith and K. Wade, J. Chem. Soc. Dalton Trans., 1970, 370.

39. J.R. Jennings, I. Pattison and K. Wade, J. Chem. Soc. (A), 1969, 565.

40. E.C. Evers, W.O. Freitag, W.A. Kriner, A.G. Mac Diarmid and S. Sujishi, J. Inorg. Nucl. Chem., 1960, 13, 239.

41. E.C. Evers, W.O. Freitag, W.A. Kriner and A.G. MacDiarmid, J. Amer. Chem. Soc., 1959, 81, 5106.

42. B.F. Spielvogel, R.F. Bratton and C.G. Moreland, J. Amer. Chem. Soc., 1972, 92, 8597.

43. B.I. Tikhomirov, A.I. Yukubchik, L.M. Kikhailova and Zh. A. Matveea, J . Gen. Chem. U.S.S.R., 1968, 28, 193.

44. S. Pasynkiewiez and S. Maciaszek, J. Organomet. Chem., 1968, 15, 301.

45. M.F. Lappert in "The chemistry of boron and its compounds". Ed. E.L. Muetterties, Wiley, 1968.

46. C. Summerford and K. Wade, J. Chem. Soc. (A), 1970, 2010.

47. A. Meller and W. Maringgele, Monatsh. Chem., 1968, 99, 2504.

48. H. Nöth and P. Fritz, Z. Anorg. allg. Chem., 1963, 324, 270.

49. H. Hess, Zeit. für Krist., 1963, 118, 361.

50. S. Geller and J.L. Hoard, Acta Cryst., 1951, 4, 399.

51. C.E. Nordman and C.R. Peters, J. Amer. Chem. Soc., 1959, 81, 355.

52. K. Hedberg, M. E. Jones and V. Schomaker, 2nd Intnl. Congr. Cryst., Stockholm, 1953.

53. L.L. Merritt and R.D. Lanterman, Acta. Cryst, 1952, 5, 811.

54. A. Meller and A. Ossko, Monatsh. Chem, 1969, 100, 1187.

55. A Meller and W. Maringgele, Monatsh. Chem., 1970, 101, 753.

56. A. Meller and A. Ossko, Monatsh. Chem., 1971, 102, 181.

57. J. Chatt, R.L. Richards and D.J. Newman, J. Chem. Soc. (A), 1968, 126.

58. C. Summerford, K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1970, 2016.

59. R.J. Abraham and P.J. Loftus, "Proton and Carbon-13 N.M.R. Spectroscopy", Heyden, 1978.

60. F.J. Weigert and J.D. Roberts, Inorg. Chem., 1973, 12, 313.

61. D.J. Hart and W.T. Ford, J. Org. Chem., 1964, 39 363.

62. L.W. Hall, J.D. Odom and P.D. Ellis, J. Amer. Chem. Soc., 1975, 97, 4527.

63. G.C. Levey, R.L. Lichter and G.L. Nelson, "Carbon-13 Nuclear Magnetic Resonance", Wiley-Interscience, 1980.

64. M. Naulet, M.L. Filleux, G.J. Martin and J. Pornet., Org. Magn. Resonance, 1975, 1, 326.

65. L.M. Jackman and D.P. Kelly, J. Chem. Soc. (B), 1970, 102.

66. J.B. Strothers and P.C. Lauterbur, Can. J. Chem., 1967, 45, 225.

67. H. Nöth and B. Wrackmeyer, "Nuclear Magnetic Resonance of Boron Compounds", Eds. P. Diel, E. Fluck and R. Kosfeld, Springer-Verlag, 1978.

68. R.K. Harris and B.E. Mann, "N.M.R. and the Periodic Table", Academic Press, 1978.

69. H. Nöth and H. Vahrenkamp, Chem. Ber., 1967, 100, 3353.

70.

72. H.C. Brown, S.C. Kim and S. Krishnamurthy, J. Org. Chem., 1980, 45, 1.

73. H.C. Brown and S. Krishnamurthy, Tetrahedron, 1979, 35, 567 and refs. therein.

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

75. H.C. Brown, S. Krishnamurthy and J.L. Hubbard, J. Amer. Chem. Soc., 1978, 100, 3343.

76. H.C. Brown and S. Krishnamurthy, J. Amer. Chem. Soc., 1973, 95, 1669.

77. S. Krishnamurthy, R.M. Schubert and H.C. Brown, J. Amer. Chem. Soc., 1973, 95, 8486.

78. H.C. Brown and S.C. Kim, J. Org. Chem., 1978, 42, 1482.

79. H.C. Brown and W.C. Dickason, J. Amer. Chem. Soc., 1970, 92, 709.

80. H.C. Brown and S. Krishnamurthy, J. Amer. Chem. Soc., 1972, 94, 7159.

81. S. Krishnamurthy and H.C. Brown, J. Amer. Chem. Soc., 1976, 98, 3383.

82. H.C. Brown and C.P. Garg, J. Amer. Chem. Soc., 1964, 86, 1085.

83. H. Hoberg and V. Götz, J. Organomet. Chem., 1976, 118, C3.

84. R.M. Silverstein, C.G. Bassler and T.C. Morrill, "Spectrometric identification of organic compounds", 4th Edn., Wiley, 1981.

85. S. Otuska, A. Nakamura and T. Yoshida, J. Organomet. Chem., 1967, 7, 339.

86. R. A. Wilson, Q. Rev. Chem. Soc., 1965, 19, 126.

87. B.N. Storhoff and H. C. Lewis Jnr., Coord. Chem. Rev., 1977, 23, 1.

88. I.R. Beattie, Q. Rev. Chem. Soc., 1963, 17, 382.

89. S.J. Bryan, P.G. Huggett, K. Wade, J. A. Daniels and J. R. Jennings, Coord. Chem. Rev., 1982, 44, 149.

90. B.M. Mikhailov, V.A. Dorokhov and V.I. Serendenko, Dokl. Acad. Nauk. SS SR. Ser. Khim., 1971, 199, 1328.

91. M.M. Midland, J. A. Sinclair and H.C. Brown, J. Org. Chem., 1974, 39, 731.

92. H. Hoberg and V. Götz, J. Organomet. Chem., 1978, 118, C1.

93. H. Hoberg, V. Götz and C. Kruger, J. Organomet. Chem., 1979, 169, 219.

94. H. Hoberg, V. Götz and A. Milchereit, J. Organomet. Chem., 1978, 118, C6.

95. J.B. Farmer, E.A. Petch, R. Snaith, and K. Wade, unpublished observations.

96. J. Keable, D.G. Othen and K. Wade, J. Chem. Soc. Dalton Trans., 1976,/

97. J.B. Farmer, R. Snaith and K. Wade, J. Chem. Soc. Dalton Trans., 1972, 1501.

98. L-H Chan and E.G. Rochow, J. Organomet. Chem., 1969, 9, 231.

99. J. Spencer, Ph.D. Thesis, Univ. of Durham, 1973.

100. R.J. Cook and K. Mislow, J. Amer. Chem. Soc., 1971, 93, 6703.

101. H. Kessler, Angew. Chem. Intnl. Edn., 1970, 9, 219.

102. M. Raban and E. Carlson, J. Amer. Chem. Soc., 1971, 93, 685.

103. H. Kessler and P. Liebfritz, Tetrahedron, 1969, 25, 5127.

104. H. Kessler and P. Liebfritz, Tetrahedron, 1970, 26, 1805.

105. R. Snaith, C. Summerford, K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1970, 2635.

106. C.G. McCarty, "The Chemistry of the Carbon-nitrogen double bond", Interscience, 1970.

107. F. Kerek, G. Ostrogovich and Z. Simon, J. Chem. Soc. (B), 1971, 541.

108. W.A. Anderson and R. Freeman, J. Chem. Phys., 1963, 39, 1518.

109. S.L. Manatt, G.C. Juvinall and D.D. Elleman, J. Amer. Chem. Soc., 1963, 85, 2664.

110. R. Schmidpeter and W. Zeiss, Chem. Ber., 1971, 104, 1199.

111. J.R. Van Wazer and L. Maier, J. Amer. Chem. Soc., 1964, 86, 811.

112. K. Moedritzer, L. Maier and L.C.D. Groenweghe, J. Chem. Eng. Data, 1962, 7, 307.

113. J.R. Van Wazer, C.F. Callis, J.N. Schooley and R.C. Jones, J. Amer. Chem. Soc., 1956, 78, 5715.

114. B. Samuel, R. Snaith, C. Summerford and K. Wade, J. Chem. Soc. (A), 1970, 2019.

115. C. Summerford, Ph.D. Thesis, Univ. of Durham, 1969.

116. I. Pattison, K. Wade, and B.K. Wyatt, J. Chem. Soc., 1968, 837.

117. J.R. Jennings, I. Pattison, C. Summerford, K. Wade, and B.K. Wyatt, Chem. Commun., 1968, 250.

118. C. Summerford and K. Wade, J. Chem. Soc. (A), 1969, 1487.

119. C. Summerford and K. Wade, Unpublished work.

120. R. Snaith, Ph.D. Thesis, Univ. of Durham, 1971.

121. C.J. Sherer, Organomet. Chem. Rev., 1968, 3, 281.

122. H. Nöth, "Progress in Boron Chemistry", Eds. R.J. Brotherton and H. Steinberg, 1970, Vol. 3.

123. G.E. Coates, M.L.H. Green and K. Wade, "Organometallic Compounds", Vol. 1, 3rd Edn., Methuen, 1968, P34.

124. I. Pattison and K. Wade, J. Chem. Soc. (A), 1967, 1098.

125. I. Pattison and K. Wade, J. Chem. Soc. (A), 1968. 842.

126. A. Meller and W. Maringgele, Monatsh. Chem., 1970, 101, 387.

127. Gmelin Handbuch der Anorganishe Chemie, 22, Teil 4, Springer-Verlag, pp. 223-244 and refs. therein.

128. B.M. Mikhailov, G.S. Ter-Sarkisyan, N.A. Nikolaeva and V.G. Kislev, Zh. Obshch. Khim., 1977, 43, 857.

129. A Meller and W. Maringgele, Monatsh. Chem., 1971, 102, 118.

130. A. Meller and A. Ossko, Monatsh Chem., 1970, 101, 1104.

131. A Meller and A. Ossko, Monatsh. Chem., 1971, 102, 121.

132. Gmelin Handbuch der Anorganishe Chemie, Band 22, Teil 4, Springer-Verlag 1975, pp. 181-204 and refs. therein.

133. G.E. Coates, M.L.H. Green and K. Wade, "Organometallic Compounds", 3rd Edn. Vol. 1, Methuen, 1967, pp.35-40.

134. K. Niedereu and J.W. Dawson, "Boron-Nitrogen Compounds", Springer-Verlag, 1966.

135. L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell Univ. Press, 1960.

136. G.J. Bullen and N.H. Clark, J. Chem. Soc., 1970, 992.

137. D.L. Coulson and J.L. Hoard, J. Amer. Chem. Soc., 1952, 74, 1742.

138. H. Hess, Acta Cryst., 1969, B25, 2334.

139. G.J. Bullen, J. Chem. Soc. Dalton Trans., 1981, 511.

140. H. Hess, Angew. Chem. Intnl. Edn., 1971, 10, 518.

141. G.J. Bullen and R.R. Mallinson, J. Chem. Soc. (A), 1970, 2213.

142. G.J. Bullen and N.H. Clark, J. Chem. Soc. (A), 1969, 404.

143. L. Salem, "Molecular Orbital Theory of Conjugated Systems", Benjamin, 1969, P39.

144. K. Wiberg, Tetrahedron, 1968, 24, 1083.

145. D.R. Armstrong, P.G. Perkins and J.J.P. Stewart, J. Chem. Soc., Dalton Trans., 1973, 838.

146. L.J. Bellamy "Infra red spectra of complex molecules" 2nd Edn., Metheun, 1958.

147. J.H. Wotiz and D.E. Mancuso, J. Org. Chem., 1957, 22, 207.

148. D.R. Taylor Chem. Rev., 1967, 67, 317.

149. V.A. Dorokhov and M.F. Lappert, Chem. Commun., 1968, 250.

150. W. Haubold and R. Schaeffer, Chem. Ber., 1971, 104, 1136.

151. H. Nöth and H. Vahrenkamp, Chem., Ber., 1966, 99, 1049.

152. J. Casanova and M. Geisel, Inorg. Chem., 1974, 13, 2783.

153. H . Nöth, Chem. Ber., 1971, 104, 558.

154. W. Becker, W. Beck, H. Nöth and B. Wrackmeyer, Chem. Ber., 1972, 105, 2883.

155. H. Nöth and H. Vahrenkamp, J. Organomet. Chem., 1968, 12, 23.

156. V.V. Negrebetskii, V.S. Bogdanov, A.V. Kessenikh, P.V. Petrovskii, Yu N. Bubnov and B.M. Mikailov, Zh. Obshch. Khim., 1974, 44, 1882.

157. J.W. Emsley, L. Phillips and V. Wray, "Fluorine Coupling Constants", Pergamon, 1977.

158. H. Nöth and B. Wrackmeyer, Chem. Ber., 1981, 114, 1150.

159. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th Edn., Interscience, 1980.

160. R.G. Whitehead, Ph.D. Thesis, Univ. of Durham, 1979.

161. I.M. Trefonas, R.L. Flurry, R. Majeste, E.A. Meyers and R.F. Copeland, J. Amer. Chem. Soc., 1966, 88, 2145.

162. J.L. Hoard and V. Blair, J. Amer. Chem. Soc., 1935, 57, 1985.

163. E.L. Muetterties, " The Chemistry of Boron and its Compounds", Wiley, 1967.

164. L.E. Sutton, "Tables of interatomic distances and configuration of molecules and ions", Special Publication No. 11, The Chemical Society, London, M18, 1958.

165. I.R. Beattie and T. Gilson, J. Chem. Soc. (A), 1964, 229.

166. K.F. Purcell and R.S. Dago, J. Amer. Chem. Soc., 1966, 88, 919.

167. K.F. Purcell, J. Amer. Chem. Soc., 1967, 89, 247.

168. P.L. Pickard and T.L. Tolbert, J. Org. Chem., 1961, 26, 4886.

169. H. Hoberg and J. Barluenga-Mur, J. Organomet. Chem., 1968, 17, 28.

170. H. Hoberg and J. Barluenga-Mur, J. Organomet. Chem., 1968, 17, 30.

171. H. Hoberg and J. Barluenga-Mur, Annal., 1970, 733, 141.

172. T. Hirabayashi, K. Itoh, S. Sakai and Y. Ishii, J. Organomet. Chem., 1970, 21, 273.

173. B. Bogdanovic and S. Konstantinovic, Annal., 1970, 738, 202.

174. K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1969, 1121.

175. R. Ehrlich and J.R. Young, J. Inorg. Nucl. Chem., 1968, 30, 53.

176. W. Kuran and S. Pasynkiewicz, J. Organomet. Chem., 1970, 23, 343.

177. W. Kuran, S. Pasynkiewicz and J. Muszynksi, J. Organomet. Chem., 1970, 25, 23.

178. G.K.J. Gibson and D.W. Hughes, Chem. and Ind. 1964, 544.

179. S. Pasynkiewicz, W. Dahling and B. Tomaszawski, Roczniki Chem., 1962, 36, 1383.

180. S. Pasynkiewicz, W. Kuran and E. Soszynksa, Roczniki Chem., 1964, 38, 1285.

181. E.A. Jeffrey and T. Mole, Aust. J. Chem., 1970, 23, 715.

182. E.C. Ashby and J. Laemmle, J. Org. Chem., 1968, 33, 3398.

183. Y. Baba, Bull. Chem. Soc. Japan, 1968, 41, 2173.

184. H. Hoberg and J. Barluenga-Mur, Synthesis, 1970, 142.

185. H. Hoberg and J. Barluenga-Mur, Synthesis, 1970, 363.

186. R. Snaith, K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1970, 380.

187. K. Wade and B.K. Wyatt, J. Chem. Soc. (A), 1967, 1339.

188. W.S. MacDonald, Acta Cryst., 1969, B25, 1385.

189. J.K. Ruff, J. Amer. Chem. Soc., 1961, 83, 2835.

190. R.A. Kovar and E.C. Ashby Inorg. Chem., 1971, 10, 893.

191. A. Storr and B.S. Thomas, Canad. J. Chem., 1970, 48, 3667.

192. A. Storr, J. Chem. Soc. (A), 1968, 2605.

193. H. Hess, A. Hinderer and S. Steinhauser, Z. anorg. Chem., 1970, 377, 1.

194. J.D. Smith, K. Gosling, G.M. McLaughlin and G.A. Sim, J., Chem. Soc. (D), 1970, 1617.

195. U. Thewalt and I. Kawada, Chem. Ber., 1970, 103, 2754.

196. J.L. Atwood and G.D. Stucky, J. Amer. Chem. Soc., 1970, 92, 285.

197. J.B. Farmer and K. Wade, Internat. Rev. Sci., Inorg. Sec., Vol. 4, 1972.

198. G.M. Sheldrick and W.S. Sheldrick, J. Chem. Soc. (A) 1969, 2279.

199. R. Calas, E. Frainnet and A. Bazouin, Compt. Rend., 1961, 252, 420.

200. C. Kruger, E.G. Rochow and H. Wannagat, Chem. Ber., 1963, 96, 2132.

201. S. Pasynkiewicz and W. Kuran, Roczniki Chem., 1965, 39, 1199.

203. J.B. Farmer, Ph.D. Thesis, Univ. of Durham, 1973.

204. F. Weiss and G. Hencken, J. Organomet. Chem., 1970, 21, 265.

205. R. Amstutz, D. Seebach, P. Seiler, R. Schweizer and J.D. Dunitz, Angew, Chem. Intnl. Edn., 1980, 19, 53.

206. M. F. Lappert, L.M. Engelhardt, C.L. Raston and A.H. White, J. Chem. Soc. Chem. Commun., 1982, 1323.

207. W. Clegg, D.A. Brown, S.J. Bryan and K. Wade, Polyhedron, in press.

208. R.E. Hall and E.P. Schram, Inorg. Chem., 1970, 10, 192.

209. O.T. Beechley, G.E. Coates and G. Kohnstam, J. Chem. Soc., 1965, 3248.

210. M. Witanowski and G.A. Webb, Eds. "Nitrogen NMR", Plenum Press, 1973.

211. M. Witanowski, L. Stefaniak and G.A. Webb, Ann. Rep. NMR Spectros. 1977, 7, 117.

212. C.G. Levey and R.L. Lichter, "^{15}N NMR Spectroscopy" Wiley-Interscience, 1979.

213. J. Mason, Chem. Rev., 1981, 81, 205.

214. M. Karplus and J.A. Pople, J. Chem. Phys., 1963, 38, 2803.

215. J. A. Pople, Discuss. Faraday Soc., 1963, 34, 7.

216. J.A. Pople, Mol. Phys., 1963, 7, 301.

217. M. Witanowski, L. Stefaniak, S. Szymanski and G.A. Webb, Tetrahedron, 1976, 32, 2127.

218. G. Binsch, J.B. Lambert, B. W. Roberts and J.R. Roberts, J. Amer. Chem. Soc., 1964, 86, 5564.

219. J.B. Lambert, W. Oliver and J.D. Roberts, J. Amer. Chem. Soc., 1965, 87, 5085.

220. P. W. Westerman, R.E. Botto and J. D. Roberts, J. Org. Chem., 1978, 43, 2590.

221. N. Nauttet and G.R. Martin, Tetrahedron Lett., 1979, 1493.

222. H. Nöth and B. Wrackeyer, Chem. Ber., 1974, 107, 3070.

223. H. Nöth, W. Tinhof and B. Wrackmeyer, Chem. Ber., 1974, 107, 518.

224. K. Barlos, H. Nöth and B. Wrackmeyer, Z. Naturforsuch, 1978, 33B, 515.

225. D.W.W. Anderson, J.E. Bentham, and R.W.H. Rankin, J. Chem. Soc. Dalton Trans., 1973, 1215.

226. J. Mason, K. Wade, Personal Communication. Now published; D.H. Evans, D.M.P. Mingos, J. Mason and A. Richards, J. Organomet. Chem., 1983, 249, 293.

227. M. Witanowski, L.I. Stefeniak and G.A. Webb, "Nitrogen NMR Spectroscopy", Ann. Rep. NMR Spectrosc., 1981, 11B.

228. G.J. Martin, M.L. Martin and J. -P Gouesnard, "^{15}N NMR Spectroscopy", Vol. 18, NMR, Basic Principles and Progress, Springer-Verlag, 1981.

229. J.A. Pople and D.P. Santry, Mol. Phys., 1964, 8, 1.

230. R. West, J. Organomet. Chem., 1965, 3, 314.

231. M.E. O'Neill and K. Wade in "Comprehensive Organometallic Chemistry". Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982, Vol. 1, P.43.

232. T. Onak in "Comprehensive Organometallic Chemistry". Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982, Vol. 1, P.411.

233. R. Thompson, D.E. Buck, N.N. Greenwood, R.W. Jotham, L.H. Long and J.H. Morris, Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol, 5B1, Boron-Hydrogen Compounds, Longman 1981.

234. R.N. Grimes, "Metal Interactions with Boron Clusters" Plenum, 1982.

235. S. Bresadola in "Metal Interactions with Boron Clusters", Ed. R.N. Grimes, Plenum, 1982.

236. C.R. Kutal, D.A. Owen and L.J. Todd, Inorg. Synth., 1968, 11, 19.

237. M.F. Hawthorne et al., Inorg. Synth., 1967, 10, 91.

238. V.I. Stanko and G.A. Anorova, J. Gen. Chem. USSR., 1967, 37, 2246.

239. T.L. Heying, J.W. Ager, S.L. Clark, R.P. Alexander, S. Papetti, J.A. Reid and S.J. Trotz, Inorg. Chem., 1963, 2, 1097.

240. D. Grafstein, S. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen and M.M. Fein, Inorg. Chem., 1963, 2, 1120.

241. E.L. Muetterties, "Boron-Hydride Chemistry", Academic Press, 1975.

242. V.I. Bregadze and O. Yu. Okhlobystin, Russ. Chem. Rev., 1968, 37, 173.

243. L.I. Zakharkin, V.N. Kalinin and L.S. Podvisotskaya, Izv. Acad. Nauk. SSSR, Ser. Khim., 1968, 2661.

244. R.N. Grimes, "Carboranes" Academic Press, 1970 and refs. therein.

245. L.I. Zakharkin, V.I. Stanko, V.A. Brattsev, Yu. A. Chapovskii, A.I. Kimova, O.Yu. Okhlobystin and A.A. Ponomarenko, Dokl. Acad. Nauk. SSSR, 1964, 155, 1119.

246. L.I. Zakharkin, A.I. L'Vov and L.S. Podvisotskaya, Izv. Acad. Nauk. SSSR , Ser. Khim, 1965, 1905.

247. L.I. Zakharkin, Tetrahed. Lett., 1964, 33, 2255.

248. L.I. Zakharkin and A.V. Karentsev, Zh. Obshch. Khim., 1965, 35, 1123.

249. L.I. Zakharkin and A.G. Karentsev, Zh. Obshch. Khim., 1967, 37, 1211.

250. L.I. Zakharkin, V.I. Stanko and Yu. A. Chapovskii, Izv. Acad. Nauk, SSSR, Ser. Khim., 1964, 582.

251. J.L. Boone, R.J. Brotherton and L.L. Petterson, Inorg. Chem., 1965, 4, 910.

252. V.I. Bregadze, A. Yu. Usyatinskii and N.N. Godovikov, Dokl. Acad. Nauk. SSSR, 1978, 241, 364.

253. L.I. Zakharkin, V.I. Bregadze and O. Yu. Okhlobystin, J. Organomet. Chem., 1965, 4, 211.

254. S. Papetti and T.L. Heying, Inorg. Chem., 1963, 2, 1105.

255. S. Papetti, B.B. Schaeffer, H.J. Troscianiec and T.L. Heying, Inorg. Chem., 1964, 3, 1444.

256. S. Papetti and T.L. Heying, Inorg. Chem., 1964, 3, 1448.

257. N.N. Schwartz, E. O'Brien, S. Karlan and N.M. Fein, Inorg. Chem., 1965, 4, 651.

258. S. Papetti, B.B. Schaeffer, A.P. Grey and T.L. Heying, J. Polymer Sci. (A), 1966, 4, 1623.

259. H. Schroeder, O.G. Schaffling, J.B. Larchar, F.F. Frulla, and T.L. Heying, Rubber Chem. Technol., 1966, 39, 1189.

260. H. Schroeder, S. Papetti, R.P. Alexander, J.F. Siekhaus, and T.L. Heying, Inorg. Chem., 1969, 8, 2444.

261. O.A. Kruglaya, L.I. Zakharkin, B.I. Petrov, G.S. Kalinina and N. S. Vyarankin, Synth. Inorg. Met.-Org. Chem., 1973, 3, 63.

262. L.I. Zakharkin, V.M. Kalinin and E.G Rys, Zh. Obshch. Chim., 1972, 42, 477.

263. L.I. Zakharkin, V.N. Kalinin and E.G. Rys, Zh. Obsh. Khim., 1972, 42, 847.

264. L.I. Zakharkin, V.I. Bregadze and O. Yu. Oklobystin, Izv. Acad. Nauk. SS SR, Ser. Khim., 1964, 1539.

265. A. Yu. Alexandrov, V.I. Bregadze, V.I. Gol'danskii, L.I. Zakharkin, O. Yu. Oklobystin and V.V. Kaprov, Dohl. Acad. Nauk. SSS R, 1965, 165, 593.

266. S. Bresadola, F. Rossetto and G. Tagliavini, Ann. Chim. (Rome) 1968, 58, 598.

267. S. Bresadola, G. Plazzogna, G. Cecchin and G. Togliavini, Gazz. Chim. Ital., 1970, 100, 175.

268. L.I. Zakharkin and N. F. Shemyalkin, Izv. Acad. Nauk. SSS R, Ser. Khim., 1977, 2350.

269. L.I. Zakharkin and N.F. Shemyalkin, Izv. Acad. Nauk.SSSR, Ser. Khim., 1978, 1450.

270. L.I. Zakharkin, Zh. Obshch. Khim., 1964, 34, 4121.

271. L.I. Zakharkin, V.M. Kalinin and L. S. Podivsotskaya, Izv. Acad. Nauk. SSSR, Ser. Khim., 1968, 679.

272. L.I. Zakharkin and G.G. Zhigareva, Zh. Obshch. Khim., 1967, 37, 1707.

273. H.D. Smith, Inorg. Chem., 1967, 8, 676.

274. C.I. Zakharkin, V.I. Bregadze and O. Yu. Okhlobystin, J. Orrganomet. Chem., 1966, 6, 228.

275. L.I. Zakharkin, V.I. Bregadze and O. Yu. Okhlobystin, Zh. Obshch. Khim., 1966, 36, 761.

276. V.I. Pakhomov, A.V. Medvedev, V.I. Bregadze and O. Yu. Okhlobystin, J. Organomet. Chem., 1971, 29, 15.

277. O. Yu. Okhlobystin and L.I. Zakharkin, J. Organomet. Chem., 1965, 3, 257.

278. V.I. Stanko and G.A. Anorova, Zh. Obshch. Khim., 1966, 36, 946.

279. V.I. Stanko, G.A. Anorova, and T.V. Klimova, Zh. Obshch. Khim., 1966, 36, 1174.

280. V.I. Stanko, Zh. Obshch. Khim., 1965, 35, 1139.

281. L.I. Zakharkin, G.G. Zhigareva and A.V. Kazantsev, Zh. Obshch. Khim., 1968, 38, 89.

282. L.I. Zakharkin, V.M. Kalinin and L.S. Podvisotskaya, Izv. Acad. Nauk. SSSR, Ser. Khim., 1968, 688.

283. B.J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon, 1974.

284. J.L. Wardell in "Comprehensive Organometallic Chemistry", Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982.

285. G.D. Stucky, Adv. Chem. Series, 1974, 130, 56.

286. R. Zerger, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 1974, 96, 6048.

287. D. Thoeness and E. Weiss, Chem. Ber. 1978, 111, 3157.

288. J.J. Eisch in " Comprehensive Organometallic Chemistry" Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982.

289. A. Streitwieser Jnr., J. Organomet. Chem., 1978, 156, 1.

290. C. Graham, S. Richtsmeier and D.A. Dixon, J. Amer. Chem. Soc., 1980, 102, 5759.

291. T. Clark, J. Chandrasekhar and P. von R. Schleyer, J. Chem. Soc. Chem. Commun., 1980, 672

292. C.A. Tolman, J. Amer. Chem. Soc., 1970, 92, 2956.

293. E. Weiss, J. Organomet. Chem., 1964, 2, 314.

294. E. Weiss, J. Organomet. Chem., 1965, 4, 101.

295. J. Toney and G.D. Stucky, J. Organomet. Chem., 1970, 22, 241.

296. T. Greiser, J. Koph, D. Thoeness and E. Weiss, J . Organomet. Chem., 1980, 191, 1.

297. D. Thoennes and E. Weiss, Chem. Ber., 1978, 111, 3381.

298. H. Yashuda, M. Yamauchi, A. Nakamura, T. Sei, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jpn., 1980, 53, 1089.

299. W.E. Lindsell in "Comprehensive Organometallic Chemistry", Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982

300. L.I. Zakharkin and L.S. Podvisotskaya, Izv. Acad. Nauk. SSSR, Ser. Khim., 1968, 681.

301. G.E. Coates, M.L.H. Green, P. Powell and K. Wade, "Principles of Organometallic Chemistry", Methuen, 1968.

302. M. Yu. Antipin, N.G. Furmanova, A.I. Yanovskii and Yu. J. Struchov, Izv. Acad. Nauk. SS SR, Ser. Khim., 1978, 1447.

303. J.F. Malone and W.S. Mac Donald, J. Chem. Soc. Chem. Commun., 1970, 280.

304. D.J. Thornhill and A.R. Manning, J. Chem. Soc. Dalton Trans., 1972, 2086.

305. T. Fukamoto, Y. Matsumura and R. Okawara, J. Organomet. Chem., 1974, 69, 437.

306. K. Wade, Adv. Inorg. Chem. Radiochem., 1976, 18, 1.

307. R.E. Williams, Adv. Inorg. Chem. Radiochem., 1976, 18, 67.

308. R.J. Klinger, W. Butler and M.D. Curtis , J. Amer. Chem. Soc. 1975, 97, 3585.

309. M. D. Curtiss and R.J. Klinger, J. Organomet. Chem., 1978, 161, 23.

310. W.I. Bailey, M.H. Chisholm, F.A. Cotton and L. A. Rankel, J. Amer. Chem. Soc., 1978, 100, 5764.

311. D.S. Ginley, C.R. Bock and M. S. Wrighton, Inorg. Chim. Acta, 1977, 23, 85.

312. S.A.R. Knox, R.D. Stansfield, F.G.A. Stone, M.J. Winter, and P. Woodward, J. Chem. Soc. Dalton Trans., 1982, 173.

313. J. A. Beck, S.A.R. Knox, R.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc. Dalton Trans., 1982, 195.

314. M. Green, S.J . Porter and F.G.A. Stone, J. Chem. Soc. Dalton Trans., 1983, 513.

315. L. Busemto, J.C. Jeffrey, R.M. Mills, F.G.A. Stone, M.J. Went and P. Woodward, J. Chem. Soc. Dalton Trans., 1983, 101.

316. M.J. Chetcuti, P.A.M. Chetcuti, J.C. Jeffrey, R.M. Mills, P. Mitrprachuchon, S.J. Pickering, F.G.A. Stone and P. Woodward, J. Chem. Soc. Dalton Trans., 1982, 699.

317. M. Green, J.C. Jeffrey, S.J. Porter, H. Razay and F.G.A. Stone, J. Chem. Soc. Dalton Trans., 1978, 2475.

318. H.W. Sternberg, H. Greenfield, R.A. Friedel, J. Wotiz, R. Markby and I. Wender, J. Amer. Chem. Soc.,1954, 76, 1457.

319. R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 1974, 12, 323.

320. N.N. Greenwood and J.D. Kennedy in "Metal Interactions with Boron Clusters ", Ed. R.N. Grimes, Plenum, 1982.

321. D.F. Gaines and S.J. Hilderbrandt in "Metal Interactions with Boron Clusters", Ed. R.N. Grimes, Plenum, 1982.

322. L.J. Todd in "Metal Interactions with Boron Clusters", Ed. R.N. Grimes, Plenum, 1982.

323. R.N. Grimes in "Organometallic Reactions and Synthesis", Eds. E.I. Becker and M. Tsutsui, Plenum, 1977.

324. G.B. Dunks and M.F. Hawthorne in "Boron Hydride Chemistry", Ed. E.L. Muetterties, Academic Press, 1975.

325. R.N. Grimes, Coord. Chem. Rev., 1979, 28, 47.

326. R.N. Grimes in "Comprehensive Organometallic Chemistry", Eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, 1982.

327. R.N. Leyden, B.P. Sullivan, R.T. Barker and M. F. Hawthorne, J. Amer. Chem. Soc., 1978, 100, 3758.

328. W.R. Hertler,F. Klanberg and E.L. Muetterties, Inorg. Chem. 1967, 6, 1696.

329. R. Hoffman, Angew. Chem. Intnl. Edn., 1982, 21, 711.

330. M.E. O'Neill and K. Wade in "Metal Interactions with Boron Clusters", Ed. R.N. Grimes, Plenum, 1982.

331. L. Mond, H. Hirtz and M. D. Cowap, J. Chem. Soc., 1910, 798.

332. F. Ungvary and L. Marko, Inorg. Chim. Acta, 1970, 4, 324.

333. F. Ungvary and L. Marko, J. Organomet. Chem., 1974, 71, 283.

334. S.C. Watson and J.C. Eastham, J. Organomet. Chem., 1967, 9, 165.