Methyleneamino derivatives of some metals and metalloids

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by

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In memory of my Father

Contents

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Memorandum.

The work described in this thesis was carried out in the University of Durham between October 1971 and July 1974. 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 been submitted to two recent conferences:

"Imino derivatives of boron, silicon and phosphorus"
by E.A. Forman, J. Spencer and K. Wade,
24th International Union of Pure and Applied Chemistry Congress,
Hamburg, September 1973, Abstract 53.

"Di-t-butylmethyleneaminoboranes"
by E.A. Petch and K. Wade,
2nd International Meeting on Boron Chemistry,
Leeds, March 1974, Abstract 71.

Abstract.

This thesis describes the preparation and properties of some methyleneamino derivatives of boron, magnesium and aluminium. The structural implications of their I.R. and ^1H n.m.r. spectra are discussed. As a background to the work, the characteristics of such compounds are discussed and a survey of methyleneamino derivatives of metals and metalloids is presented.

Bis(di-t-butylmethyleneamino)fluoroborane, $(^tBu_2C{:}N)_2BF$, was prepared from boron trifluoride and di-t-butylmethyleneaminolithium and used to synthesise the three compounds $(^tBu_2C{:}N)_3B$, $^tBu_2C{:}NBF_2$ and $(^tBu_2C{:}N)_2BH$. Several compounds in which boron is in a heterocyclic ring system, $^tBu_2C{:}NB\begin{smallmatrix}X\\X\end{smallmatrix}\begin{smallmatrix}Y\\Y\end{smallmatrix}$ and two alkyl(di-t-butylmethyleneamino)boranes, $^tBu_2C{:}NB^tBu_2$ and $(^tBu_2C{:}N)_2BMe$, have been prepared. The I.R and ^1H n.m.r. spectra of these new di-t-butylmethyleneaminoboranes, $(^tBu_2C{:}N)_nBX_{3-n}$, are consistent with their C=N⇌B skeletons being linear, as appropriate for significant N → B dative π-bonding.

The new methyleneaminomagnesium compounds are of the following formula types: $[R_2C{:}NMgX]_n$, $[(R_2C{:}N)_2Mg]_n$, $R_2C{:}NMgBr.2THF$, $LiMg(N{:}CPh_2)_3.OEt_2$ and $LiMg(N{:}CPh_2)_4$. The associated species (n usually = 2) are believed to co-ordinate via bridging methyleneamino groups. The I.R. spectra of compounds containing terminal methyleneamino groups are consistent with the C.N.Mg units being effectively linear.

The preparation of tris(di-t-butylmethyleneamino)alane, $(^tBu_2C{:}N)_3Al$, from aluminium hydride and di-t-butylmethyleneamine has been shown to be more reliable than the reaction between aluminium

trichloride and iminolithium. Similar reactions to prepare mono- and bis-(imino)alanes were less successful, and only once could a bis(imino)alane be isolated as a trimethylamine adduct, $(^{t}Bu_2C{:}N)_2AlH.nNMe_3$. The I.R. and ^{1}H n.m.r. spectra of these two compounds indicate that their C=N⇌Al units are effectively linear, as appropriate for N → Al dative π-bonding. Preliminary studies of reactions between several methylaluminium compounds and di-t-butylmethyleneamine or its lithio derivative have been made.

The preparation and properties of di-t-butylmethyleneaminodimethylamine, $^{t}Bu_2C{:}NNMe_2$, are discussed in Appendix 1. Preliminary investigations of reactions between boron compounds and tetramethylguanidine or its lithio derivative are described in Appendix 2. The experimental techniques used in this research are described in Appendix 3.

Nomenclature.

The Chemical Society have recommended that compounds containing the $>C{=}N-$ group be named as derivatives of the (unknown) parent compound methyleneamine, $CH_2{=}NH$. Thus, depending on the nature of R, $RHC{:}NMX_n$ is an alkyl- or aryl-methyleneamino (or "aldimino") derivative of M, and $R_2C{:}NMX_n$, a dialkyl- or diaryl-methyleneamino (or "ketimino") derivative of M.

The precise nomenclature has been used in chapter headings and in the names of compounds in the experimental sections. However, in the discussion sections the terms "imino", "aldimino" and ketimino" have frequently been used for simplicity wherever such use does not cause confusion.

Chapter 1

Introduction

1. History.

Methyleneamino derivatives of metals, $R^1R^2C{:}NMX_n$, have been known since the beginning of this century when methyleneamino-magnesium and -zinc halides, $R^1R^2C{:}NMX$ (M = Mg,Zn), although not isolated, were described as the product of insertion of a nitrile into an organo-magnesium- or -zinc-halide. (Equation 1.1.) (1).

$$R^1C{:}N + R^2MX \rightarrow R^1R^2C{:}NMX \qquad 1.1$$

Further work showed that this reaction could also be used to prepare other related zinc (3), lithium (2) and aluminium (3) compounds. In all cases, however, interest focussed not on the methyleneamino compounds themselves but on their aldehyde or ketone hydrolysis products (Equation 1.2).

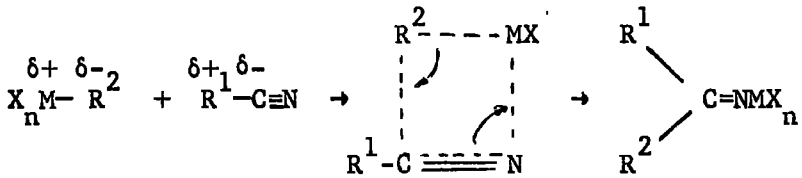
$$R^1R^2C{:}NMX_n + 2H_2O \rightarrow R^1R^2C{:}O + NH_3 + HOMX_n \qquad 1.2$$

The first pure methyleneamino derivative of a metal, butylideneaminodi-i-butylaluminium ($PrCH{:}NAl^iBu_2$) was reported in 1957 (4). Since then, interest in this field has grown considerably, because methyleneamino derivatives have a number of properties that make them useful model compounds with which to explore metal-nitrogen chemistry. Various methods of synthesizing these compounds have been devised, and certain of their reactions have been studied, including co-ordination reactions and reactions of their metal-nitrogen bonds. Particular attention has been paid to their structure - terminally-attached methyleneamino groups have proved useful probes for the study of metal-nitrogen π-bonding. This last aspect features prominently in this thesis.

2. Preparation of methyleneamino derivatives of metals and metalloids, $R^1R^2C{:}NMX_n$

Two main methods have been used to prepare these compounds.

(a) Insertion reactions. These involve the insertion of a nitrile triple bond into a bond between a metal (or metalloid) and a more electronegative element. The reaction may involve a cyclic transition state (Equation 1.3).



1.3

This type of reaction involving many unsaturated substrates has been reviewed (5).

(b) Metathetical reaction of an imine or imino derivative.

(i) Reactions of an imine with a metal hydride or alkyl. These involve the eliminations of hydrogen or an alkane between the reagents and formation of the metal imino compound (Equation 1.4).

$$R^1R^2C{:}NH + R^3MX_n \rightarrow R^1R^2C{:}NMX_n + R^3H \qquad 1.4$$

(ii) Reactions of an imino derivative (of lithium, silicon, sulphur etc.,) with metal halides. These involve the elimination of halogen species and simultaneous formation of the imino metal compound (Equation 1.5)

$$R^1R^2C{:}NY + ZMX_n \rightarrow R^1R^2C{:}NMX_n + YZ \qquad 1.5$$

(Y = Li, $SiMe_3$, SCl, etc., Z = F, Cl, Br)

Reaction 2(b)(ii) has the widest application for the preparation of imino derivatives of metals and metalloids. Iminolithium compounds are suitable starting materials when the product is soluble in a suitable solvent, as the lithium halide formed is readily removed by filtration. Imino derivatives which are only sparingly soluble are more conveniently prepared from starting materials which give volatile halides as side products (e.g. $R^1R^2C{:}NSiMe_3$ gives volatile $XSiMe_3$) as these can be removed by distillation (under reduced pressure if necessary) from the required product.

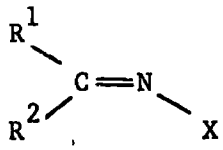
Reactions 2(a) and 2(b)(i) are suitable only for compounds RMX_n where the R - M bond is sufficiently reactive. This activity is achieved for several derivatives of lithium and magnesium, where both methods can be used, and reaction 2(b)(i) has been used to prepare $^tBu_2C{:}NBEt_2$ (See relevant sections later in this chapter)

3. Bonding in methyleneamino derivatives of metals and metalloids.

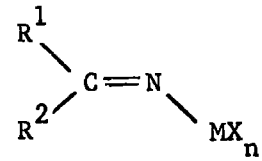
Great interest has been attached to the nature of the bonding between methyleneamino groups and metals and metalloids, especially where there is the possibility of dative π-bonding between nitrogen and the metal or metalloid. Possible structures are shown in Figure 1.1.b-e.

A non-linear structure (Figure 1.1.a) is always observed for oximes $R^1R^2C{:}NOR^3$ (6-12), and hydrazones, $R^1R^2C{:}NNR^3R^4$ (13) and has been demonstrated by ^1H n.m.r. at room temperature for some methyleneamines $R^1R^2C{:}NR^3$ (14-17) and at -30° for $^tBu_2C{:}NH$ (18). However, the bent C=N-M unit (Figure 1.1.b) is believed to occur only in methyleneamino derivatives $R^1R^2C{:}NMX_n$ in which the metal is co-ordinatively saturated. The nitrogen may be regarded as sp^2 hybridised with its lone pair

Figure 1.1



(a)



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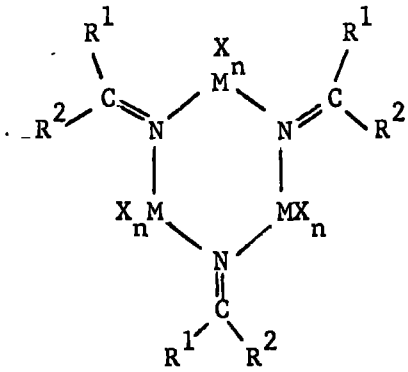
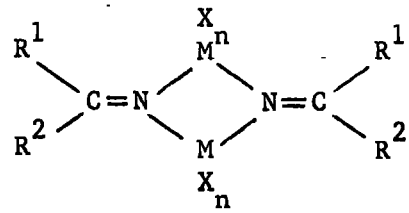
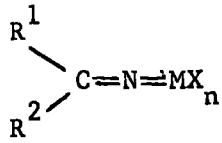


(c)



(d)

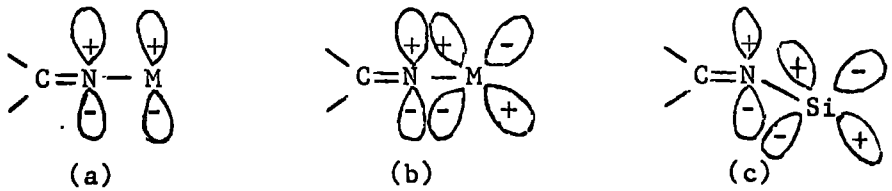


(e)

formally occupying an sp^2 hybrid orbital.

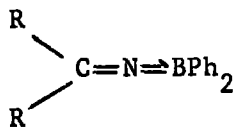
Methyleneamino derivatives $R^1R^2C{:}NMX_n$ of the more electropositive metals and metalloids which can increase their formal co-ordination number tend to associate by means of N → M dative σ-bonds between adjacent monomers. If only the central metal-nitrogen group is considered, association into a cyclic trimer (Figure 1.1.c), requiring little or no change of bond angle is more favourable than dimerisation which involves reduction of the bond angles from ~120° to ~90°. However, steric interference between R^1,R^2 and X is greater in a trimeric structure especially as the sizes of the substituents increase. This steric effect appears to be more important than bond angle strain as association normally afford dimers (Figure 1.1.d). Steric hindrance between R^1,R^2 and X may be sufficient to prevent association entirely, and several monomeric methyleneamino derivatives are now known. In these, co-ordinative saturation of the metal is achieved by N → M dative π-bonding which results in an increase in the bond order between metal and nitrogen, and appropriate shortening of the bond length from that of a single metal-nitrogen bond. (Figure 1.1.e). Maximum overlap between the nitrogen p-orbital containing its lone pair and a vacant metal p - or d - orbital is achieved when the C=N-M unit is linear (Figure 1.2. a and b). However, overlap integrals calculated for a nitrogen-silicon π-bond show that even in a non-linear skeleton, substantial pπ-dπ interaction is still possible (Figure 1.2.c) (19). The steric effects preventing association may be sufficient to dominate the enthalpy difference between the formation of the two N → M σ-bonds in the dimer (Figure 1.1.d) which are stronger than the two N → M π-bonds in two monomers (Figure 1.1.e), although entropy differences

Figure 1.2.

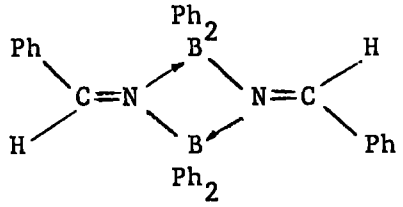


(a) (b) (c)

Figure 1.3



(a)



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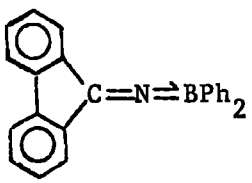

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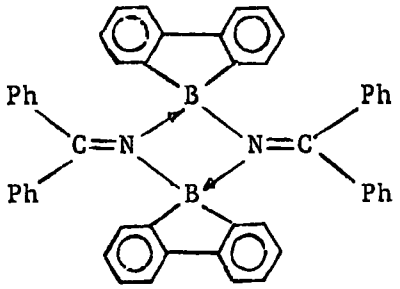


(d)

between monomer and dimer also favour monomer formation as this affords twice as many molecules. Similar arguments have been established for the thermodynamics of phase transitions in a series of dimethylamino-metal derivatives (20).

The influence of steric hindrance on structure is demonstrated by several methyleneaminoboranes. Compounds $R_2C{:}NBPh_2$ (R = Ph, p-tolyl p-ClC_6H_4, p-BrC_6H_4) are all monomeric (Figure 1.3.a), but $[PhCH{:}NBPh_2]_2$ is a dimer (Figure 1.3.b): steric hindrance is reduced sufficiently to allow association by replacing one phenyl group with hydrogen (21). All the di-t-butylmethyleneaminoboranes prepared are monomeric, as the steric requirements of the bulky t-butyl groups always prevent association (18,22,40,52,53). Where the groups on the carbon atom are less bulky, the influence of the other groups, X_n, on the metal on degree of association may be seen. Fluorenylmethyleneaminodiphenylborane is monomeric (Figure 1.3.c), but exchanging the positions of the ligands to give diphenylmethy-leneaminofluorenylborane results in a dimer (Figure 1.3.d) because of the greater steric requirement of the fluorenyl group when nearer the central C=N-B unit (21).

4. Spectroscopic studies of methyleneamino derivatives of metals and metalloids.

(a) Infra-red spectroscopy. The azomethine stretching frequencies (ν(C:N)) of some symmetrical methyleneamines, $R_2C{:}NH$, are given in Table 1.1. Similar information is also available for some non-symmetrical methylene-amines (23). Changes in the stretching frequencies observed when the N-attached hydrogen is replaced by other groups has been used as an indication of the structure of the compound obtained.

Table 1.1.

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), for some methyleneamines $R_2C{:}NH$.

R	ν(C=N)	Ref
Ph	1607	23
p-ClC_6H_4	1590	21
p-tolyl	1611	a
^tBu	1610	21
^nPr	1645	23
C_2F_5	1669	24
CF_3	1701, 1705	25, 26

(a) This work

In general, the adducts $R^1R^2C{:}NR^3.MX_n$ of methyleneamines $R^1R^2C{:}NR^3$ with Lewis acids, MX_n, exhibit higher azomethine stretching frequencies than the free methyleneamines (21,27,28). This may be compared with the increase that invariably occurs in $\nu(C{\equiv}N)$ of nitriles on formation of adducts $RC{\equiv}N.MX_n$ (29). Although this increase in $\nu(C{\equiv}N)$ is believed to arise in part from the mechanical constraint applied to the co-ordinated nitrile (30-32) there is X-ray crystallographic evidence (33,34) that co-ordination is accompanied by a shortening of the C-N bond, i.e. by an increase in its bond order, an effect which apparently reflects slight modification of the hybridisation at nitrogen (35-37). The increase in $\nu(C{=}N)$ on co-ordination of imines is attributed to a similar increase in C=N bond order. Most methyleneamino derivatives of main group metals and metalloids exhibit stretching frequencies higher than the parent imines, and this effect is also rationalised in terms of C-N bond order changes.

The azomethine stretching frequencies of some methyleneamino metal compounds whose structures have been determined crystallographically are given in Table 1.2. Diphenylmethyleneaminodimesitylborane has been shown to contain an almost linear C=N-B unit (CNM angle ~173°) (38)

Table 1.2

Compound	$\nu(C{=}N)$ cm^{-1}	Ref.
$Ph_2C{:}NB(mesityl)_2$	1792	38
$[(^tBu_2C{:}N)_2Be]_2$	1739,1637	39
$Li(^tBu_2C{:}N)_4Al$	1700,1642,1602	40

Both bridging and terminal (almost linear) methyleneamino groups are observed in the structures of bis(di-t-butylmethyleneamino)beryllium (39) and lithium tetrakis (di-t-butylmethyleneamino) aluminate (40). A linear C=N-M unit allows maximum overlap of nitrogen p- and metal p- or d-orbitals and maximum N → M π-dative bonding can occur. (Figure 1.2.a and b) The symmetry of the orbitals is such that conjugation between N-M and C-N π-bonds can occur to give a cumulative π-system similar to those found in compounds listed in Table 1.3. In methyleneamino derivatives of metals with bent C=N-M skeletons, as found in the bridging unit of dimers, (Figure 1.1.d) orbital overlap is not so extensive, and a cumulative π-system over the whole C=N-M unit cannot be so well developed. The nitrogen-metal bond is therefore weaker in compounds having bent C=N-M units than those with linear units, and the higher azomethine stretching frequency is assigned to the latter structure. Thus for $[(^{t}Bu_2C{:}N)_2Be]_2$, the higher frequency, 1739 cm^{-1}, is attributed to the terminal methyleneamino group and the lower, 1637 cm^{-1} to the bridging group.

Azomethine stretching frequencies of compounds $R^1R^2C{:}NMX_n$ higher than ~1700 cm^{-1} are thus attributed to methyleneamino groups linearly bound to the metal and frequencies lower than this are thought to arise from bent C=N-M units.

The azomethine stretching frequencies of some methyleneamino derivatives of transition metals are lower or only slightly higher than that of the parent imines. This has been interpreted in terms of a significant contribution of M → N dπ → pπ* bonding which counteracts any bond-strengthening achieved by N → M σ and pπ → dπ bonding (39).

Within these two general categories of bent or linear C=N-M skeletons, other factors may also influence the changes in absorption frequencies

Table 1.3

Asymmetric stretching frequencies (cm^{-1}) of some cumulatively π-bonded systems

Compound	X=Y=Z	ν(X=Y=Z)	Ref
RN:C:NR	N=C=N	~ 2140	41
$Ph_2C:C:NMe$	C=C=N	1998	42
$R_2C:C:CR_2$	C=C=C	~ 1950	43
$Ph_2C:N:CPh_2^+MXn^-$	C=N=C	~ 1845	44
$^tBu_2C:NBCl_2$	C=N=B	1839	22

in metal-imino compounds $R^1R^2C{:}NMX_n$. They will be outlined here and discussed in detail as appropriate in later chapters.

(i) The nature of the central metal. The more electropositive the metal, the greater is its bond strength to electronegative species. This may be expected to result in a stronger metal-nitrogen bond in compounds $R^1R^2C{:}NMX_n$ and a higher terminal azomethine stretching frequency.

The extent of overlap between the nitrogen lone pair in the p-orbital and a vacant metal p- or d-orbital will be greater when the metal is similar in size to the nitrogen atom, (covalent radius 74 pm (49)) and this will be expected to give a higher $\nu(C{=}N{\rightarrow}M)$ frequency for metals with similar electronegativities.

The mass of the metal will also influence the $\nu(C{=}N{\rightarrow}M)$ frequency; Heavier metals will give lower azomethine frequencies.

The terminal stretching frequencies of several methyleneamino-metal compounds are given in Table 1.4 in decreasing order within their group together with electronegativity (50,51), mass and covalent radii (49) values of the central metals.

It can be seen from the table that no single factor influences the azomethine absorption frequency in all compounds, but some trends are obvious within some groups.

(ii) The nature of the groups X_n. The groups X_n attached to the metal may influence the imino-metal bond by both σ and π effects. Electron-releasing groups are thought to influence the metal-nitrogen bond by weakening the σ bond, and possibly by competing with the lone pair on nitrogen for vacant metal orbitals. Electron-attracting groups will tend to encourage metal-nitrogen bond formation. However, the π-bonding capacity of X may also be an influential factor, as $X \rightarrow M$ back-bonding

Table 1.4.

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some methyleneamino derivatives of some metals.

Compound	ν(C=N)	Properties of metal			Ref
		EN	mass	cov. rad. (pm)	
$(^tBu_2C{:}N)_3B$	1730	2.01	11	82	a
$(^tBu_2C{:}N)_3Al$	1703	1.47	27	118	a
$(^tBu_2C{:}N)_3Ga$	1672	1.82	70	126	45
$[(^tBu_2C{:}N)_2Be]_2$	1746	1.47	9	89	45
$[(^tBu_2C{:}N)_2Zn]_2$	1683	1.66	65	125	45
$[(^tBu_2C{:}N)_2Mg]_2$	1665	1.23	24	136	a
$(Ph_2C{:}N)_4Ge$	1661*	2.02	73	122	46
$(Ph_2C{:}N)_4Si$	1646	1.74	28	111	47
$((CF_3)_2C{:}N)_4Si$	1765†	1.74	28	111	48
$((CF_3)_2C{:}N)_4Ge$	1730†	2.02	73	122	48
$((CF_3)_2C{:}N)_4Sn$	1720†	1.72	119	140	48

* KBr disc

† Liquid film

All other spectra recorded as Nujol mulls

(a) This work

would alter the ability of the metal to accept further electrons from nitrogen. Table 1.5 shows the azomethine stretching frequencies of some substituted methyleneaminoboranes which demonstrate these points.

(iii)The nature of the groups R. The electron-withdrawing or -releasing properties of R also influence azomethine stretching frequencies. Table 1.6 shows the difference in frequencies for related diphenyl- and di-t-butylmethyleneaminoboranes.

(b) Nuclear magnetic resonance spectroscopy. The ^{1}H n.m.r. spectra of methyleneamino derivatives may be used in structural investigations of the nature of the C=N-M skeleton, and can sometimes be used to demonstrate the syn-anti isomerism exhibited by some compounds.

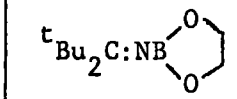
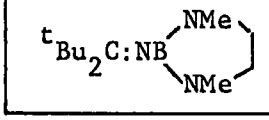
The topic of syn-anti isomerism in methyleneamines has been reviewed (55) and the mechanism involved has also been studied (56). Information is also available about the magnitude of the barriers to inversion in N-alkyl and -aryl methyleneamines (57,58).

In methyleneamino derivatives, $R_2C{:}NMX_n$, with linear C=N-M skeletons (Figure 1.4.a) the groups R are in magnetically equivalent environments (if X_n is also symmetrical with respect to C=N-M) and will have the same chemical shift values. (e.g. when R = t-butyl, all the methyl groups are equivalent, and only one absorption is observed).

The groups R in compounds with non-linear C=N-M units are not equivalent (Figure 1.4.b) and their chemical shifts would be expected to be different.

Table 1.5

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some di-t-butylmethyleneaminoboranes

Compound	ν(C=N)	Ref
$^tBu_2C{:}NBCl_2$	1839	22
$^tBu_2C{:}NBPh_2$	1820†	22
$^tBu_2C{:}NB^nBu_2$	1821	22
$^tBu_2C{:}NBEt_2$	1818	52
$^tBu_2C{:}NBF_2$	1796*	a
	1736	a
	1739†	a

* Pentane solution

† Nujol mull

All others Liquid films

(a) This work

Table 1.6

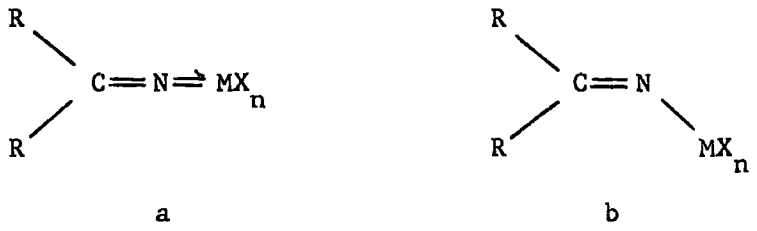
Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of related diphenyl- and di-t-butyl-methyleneaminoboranes.

Compound	ν(C=N)	Ref
$^{t}Bu_2C{:}NBPh_2$	1820	22
$Ph_2C{:}NBPh_2$	1786	54
$^{t}Bu_2C{:}NBEt_2$	1818*	52
$Ph_2C{:}NBEt_2$	1793	54

* Liquid film.

All others Nujol mulls

Figure 1.4.



a b

However, this is not always found, and the n.m.r. spectra of many compounds with bent C=N-M skeletons have only one absorption for both the R groups as a result of rapid inversion between the syn- and anti-isomers (Figure 1.5).

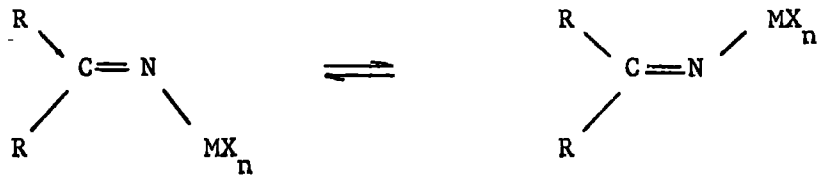


Figure 1.5.

If the rate of inversion of MX_n about nitrogen is high compared with the n.m.r. time scale then the two environments of R cannot be distinguished and only one signal is observed. If the activation energy for the process is low then inversion may be slow enough for the non-equivalence of the R groups to be demonstrated as two peaks of equal intensity on the n.m.r. spectrum. (e.g. The ^1H n.m.r. of $^tBu_2C{:}NH$ at -30^o has two peaks due to t-butyl groups because their different environments can be distinguished (18)).

Syn-anti isomerism is clearly also possible for compounds $R^1R^2C{:}NMX_n$ where $R^1 \neq R^2$ (Figure 1.6),

Figure 1.6.

and has been observed in the low temperature ^{1}H n.m.r. spectrum of the unsymmetrical germanium compound p-$CF_3C_6H_4$(Ph)C:N$GeMe_3$ (59). Below -110^{o}, the Me_3Ge ^{1}H n.m.r. spectrum consists of two overlapping singlets representing the syn- and anti-forms of the compound. Above $\sim -108^{o}$ inversion between the isomers is rapid enough for them to be indistinguishable and only one signal is observed.

The use of ^{11}B n.m.r. spectroscopy in the study of methyleneaminoboranes will be discussed in the next chapter.

(c) Ultra-violet spectroscopy. The only investigation of the U.V. spectra of methyleneamino derivatives of metals and metalloids has been a study of diarylmethyleneamino derivatives of Group IV elements in the range 200 - 400 mμ (60). Two absorptions were observed in each spectrum: a low energy absorption at $\sim$ 350 mμ attributed to the $n \rightarrow \pi^*$ transition of a non-bonding electron on nitrogen, and the other, at $\sim$ 250 mμ, attributed to the $\pi \rightarrow \pi^*$ transition of the conjugate C=N=M system. These two transitions are illustrated in the energy level diagram given in Figure 1.7. (61). Silicon substituents SiX_3 on the nitrogen lower the energy for the $n \rightarrow \pi^*$ transition as a result of $p \rightarrow d$ π-interaction between nitrogen and silicon and the electropositive character of the metal. The π

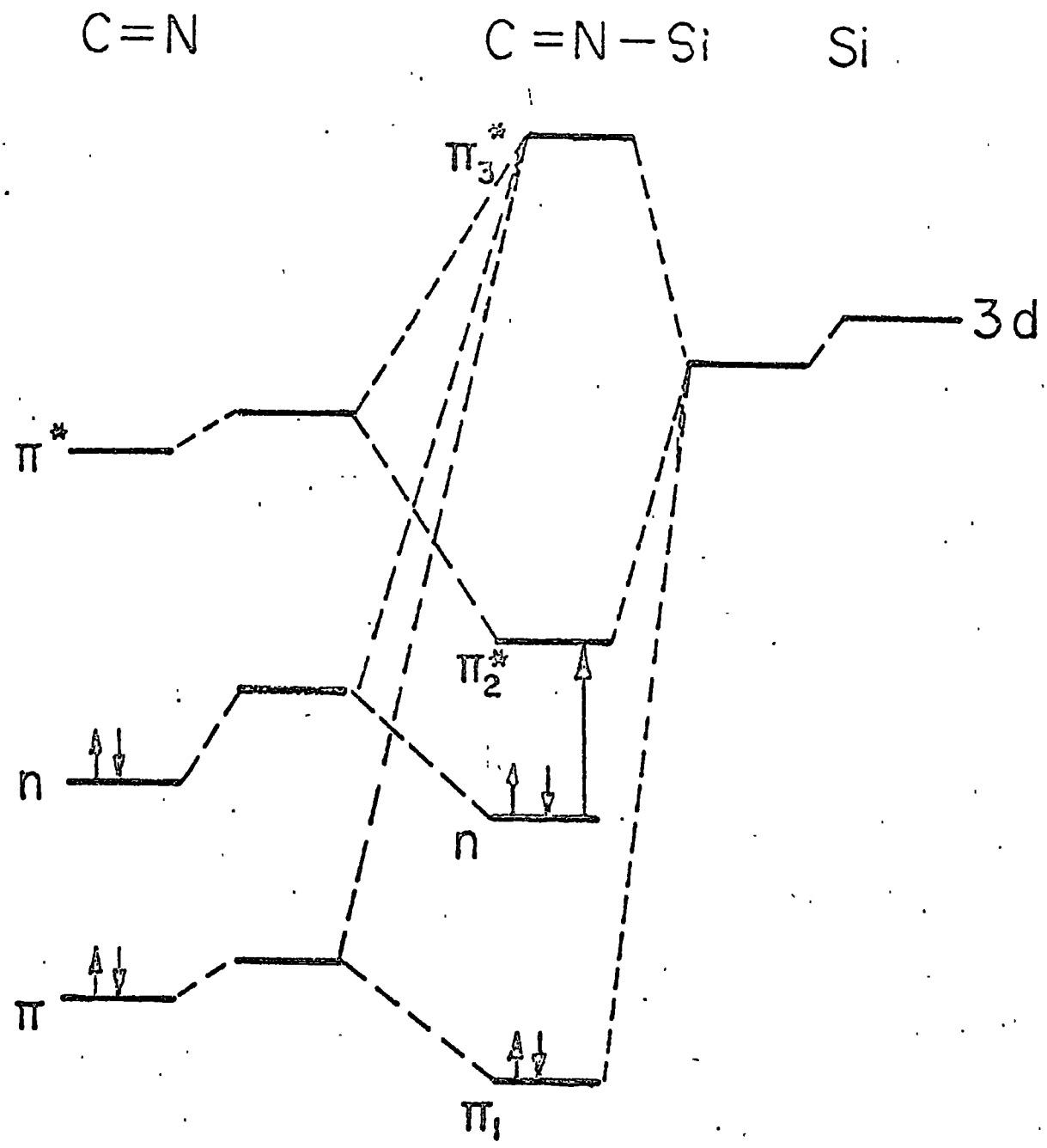


Figure 1.7

Energy levels and transitions for the C=N-Si group.

interaction is greatest in a linear C=N=Si unit, so the influence of SiX_3 on the n → π* transition will be greatest in this circumstance. The n → π* transition frequency did not vary significantly in a series of methyleneaminosilanes $R_2C{:}NSiX_n$ with various groups X on silicon, and this was interpreted in terms of a bent C=N-Si structure. However overlap intergrals calculated for a nitrogen-silicon π-bond show that even in a non-linear C=N-Si skeleton substantial pπ → dπ interaction is possible (19). If the energy of both the π* and the n levels are lowered by almost the same amount as a result of substitution at nitrogen the n → π* transition will be observed at approximately the same frequency for every compound. In this case, the observed results could accommodate both linear and bent C=N-Si structures, consistent with the possibility of pπ → dπ interaction in both cases.

5. Survey of methyleneamino derivatives of metals and metalloids.

Group 1. Methyleneaminolithium compounds have been the most widely-studied of the Group 1 derivatives, both in their own right and as reagents for the preparation of methyleneamino derivatives of other elements.

Preparation. The insertion reaction of a nitrile into lithium carbon bonds (Equation 1.6) has been used to prepare compounds $R^1R^2C{:}NLi$ ($R^1 = R^2 =$ Ph (62), ^{t}Bu (64); $R^1 =$ Ph, $R^2 = NR_2$ (63), Me (62)).

$$R^1C{:}N + R^2Li \rightarrow R^1R^2C{:}NLi \qquad 1.6$$

The first four compounds were obtained in good yield, but the last,

Ph.MeC:NLi was obtained in only ~ 10% yield probably because of the competing oligomerisation or polymerisation of phenyl cyanide which is known to occur in the presence of organolithium compounds (2).

Diphenylmethyleneaminolithium, $Ph_2C{:}NLi$, can be prepared successfully in ether solution, but care must be taken to purify the phenyl lithium and maintain exact stoichiometry to avoid phenyl cyanide polymerisation as described above. Removal of ether from the red solution leaves a yellow, amorphous solid which can only be redissolved readily in strong donor solvents (e.g. T.H.F., pyridine) which can break up the presumably polymeric structure (Figure 1.8.a) to form adducts isolable as dimeric crystalline solids (Figure 1.8.b) (62).

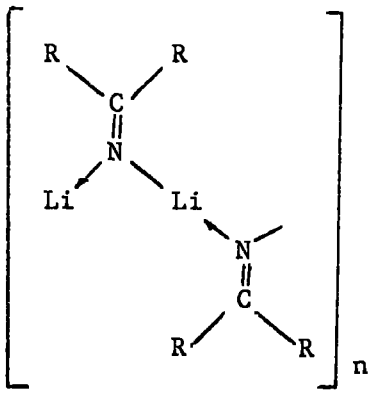
Reaction between alkyl cyanides and alkyllithium compounds do not normally give the required dialkylmethyleneaminolithium (64). Methyl cyanide and excess t-butyl lithium react at -78° by polylithiation to give Li_2C_2HN and two equivalents of isobutane. Methyl or ethyl cyanide and methyl- or ethyl-lithium do not give any of the possible methyleneaminolithium products ($Me_2C{:}NLi$, $Et_2C{:}NLi$, $MeEtC{:}NLi$). Acid reaction of the hydrogen atoms attached to the α-carbon atom of the alkyl cyanide results in the formation of alkane and insoluble involatile materials thought to be polymeric species containing the C=C=N- group (Equation 1.7).

$$R^1CH_2C{:}N + R^2Li \rightarrow (R^1CHC{:}NLi)_n + R^2H \qquad 1.7$$

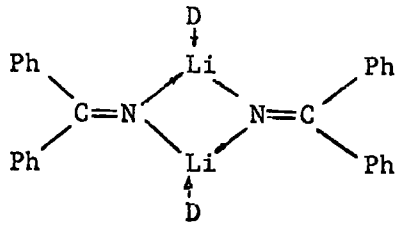
(R^1 = H or Me, R^2 = Me or Et)

However dimethylcyanamide reacted as a protic acid towards methyl lithium, eliminating methane in nearly the proportion required by equation 1.8.

Figure 1.8

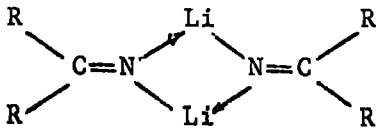


(a)

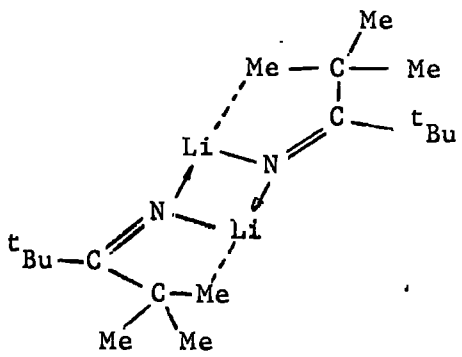


D = donor solvent

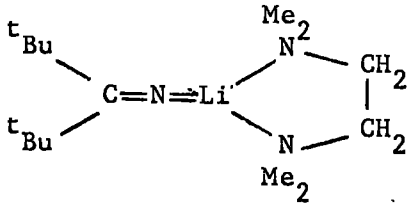
(b)



(c)



(d)



(e)

$$Me_2NC{:}N + MeLi \rightarrow LiCH_2N(Me)C{:}N + MeH \qquad 1.8$$

I

The extreme reactivity of the product I prevented confirmation of its identification by elemental analysis (62).

t-Butyl cyanide, which has no hydrogen atoms on the α-carbon atom does not react with methyl- or ethyl- lithium. However with t-butyl lithium the insertion proceeds smoothly at $\sim -20^{o}$ and di-t-butylmethylene-aminolithium is obtained in quantitative yield (Equation 1.9) (64).

$$^{t}BuC{:}N + {}^{t}BuLi \rightarrow {}^{t}Bu_2C{:}NLi \qquad 1.9$$

Unlike the diarylmethyleneaminolithiums, which once isolated are soluble only in strong donor solvents as 1:1 adducts (62), $^{t}Bu_2C{:}NLi$ can be prepared in a variety of hydrocarbon and ether solvents from which it can be recrystallised as pale yellowish-green needles. The crystals obtained do not readily redissolve in fresh solvent; this property is frequently used to isolate any excess $^{t}Bu_2C{:}NLi$ from reaction mixtures in which it has been used as a starting material.

It is thought that the mechanism of formation of $^{t}Bu_2C{:}NLi$ is similar to that of the reaction between $^{n}BuLi$ and PhCN. Kinetic studies have shown this reaction to be first order in phenyl cyanide and 0.33 order in n-butyl lithium (65). This has been interpreted in terms of a mechanism involving dissociation of the tetrameric n-butyl lithium into reactive monomeric units as the rate-determining step. It is thought that t-butyl lithium is also tetrameric in solution having a cubic structure similar to n-butyl lithium, with substantial C - Li covalent bonding (66-68), so a similar mechanism in the reaction between t-butyl cyanide and t-butyl lithium seems likely.

Di-t-butylmethyleneaminolithium does not form adducts with pyridine or tetrahydrofuran but there is some evidence (an increase in ν(C=N) from 1608 to 1618 cm^{-1}) for its weak interaction with tetramethylethylenediamine, co-ordination probably being from one of the nitrogen atoms of T.M.E.D. to each lithium atom in the iminolithium oligomer (Figure 1.6). A greater increase in ν(C=N) would be expected if both the nitrogen atoms of T.M.E.D. co-ordinated to lithium as this would probably give a monomeric species with a linear C=N≐Li unit (Figure 1.8.e) (52).

Reaction between the appropriate ketimine and an alkyl lithium (usually MeLi or ^{n}BuLi) may be used to prepare compounds $R^1R^2C{:}NLi$ (Equation 1.10).

$$R^1R^2C{:}NH + R^3Li \rightarrow R^1R^2C{:}NLi + R^3H \qquad 1.10$$

($R^1 = R^2$ = Ph (62), p-tolyl (24), t-butyl (52), Me_2N (63,69), CF_3 (24))

This method has been found more convenient for the synthesis of diarylmethyleneamino lithiums required as starting materials, but the first route is more suitable for preparing $^{t}Bu_2C{:}NLi$.

Di-p-tolylmethyleneaminolithium, an orange-yellow solid is a bright orange-red colour when prepared in ether solution. Its solubility properties are similar to those of the diphenyl analogue.

The action of methyl lithium on bis(dimethylamino)methyleneamine (tetramethylguanidine) in ether at ~ -40° affords bis(dimethylamino)-methyleneaminolithium, $(Me_2N)_2C{:}NLi$, which crystallises from toluene solution as off-white plates. Cryoscopic study showed it to be dimeric in benzene solution. Adduct formation with strong donor solvents was not observed (52,69).

Hexafluorodimethylmethyleneamine reacts with methyl lithium in ether at $\sim 0^{\circ}$ to give hexafluorodimethylmethyleneaminolithium (24). Little is know of the properties of this compound. It decomposes explosively at $\sim 25^{\circ}$, and this sensitivity may have restricted further investigations. The electron-withdrawing properties of the perfluoro-alkyl groups confer properties on the compounds which provide an interesting contrast with their hydrocarbon analogues (e.g. Reduced hydrolytic sensitivity, greater volatility, etc.,) (48).

Apparently, the only methyleneamino derivative of any of the other Group 1 metals is diphenylmethyleneaminosodium, $Ph_2C{:}NNa$, prepared in impure form from diphenylmethyleneamine and sodium in liquid ammonia (70). Attempts to prepare the potassium analogue were unsuccessful.

The ease with which the lithio derivatives can be prepared and their suitability as reagents in further syntheses, together with the unsuitability of other alkali metal derivatives as reagents has made further study of their imino derivatives unattractive.

Structure. There has been considerable interest in the strucutre of methyleneaminolithium compounds, since if the are unsolvated, their lithium atoms have a maximum possible co-ordination number of two, unless there is either electron-deficient bridging by nitrogen, or essentially ionic bonding between lithium and nitrogen.

It is thought that diphenyl- and di-p-tolyl-methyleneaminolithium exist as co-ordination polymers in which the units are linked by nitrogen → lithium dative bonds to give a structure like that in Figure 1.8.a. (62). The adducts which are formed with strong donor solvents which can break up this polymer are thought to be dimeric, the smaller unit being

stabilised by co-ordination of solvent molecules to the lithium atoms as shown in figure 1.8.b (62).

Both di-t-butylmethyleneaminolithium and bis(dimethylamino)-methyleneaminolithium are dimeric in benzene, and their structure is thought to be that shown in figure 1.8.c (52). An alternative structure for the first compound (Figure 1.8.d) involving carbon-lithium interaction has been suggested (52). Evidence for this is the similarity between the ^{1}H n.m.r. spectrum of this compound and that of lithium tetrakis-(di-t-butylmethyleneamino)aluminate, known from its X-ray crystal structure to contain such interaction (40).

Reactions. These compounds have been extensively used in the preparation of methyleneamino derivatives of other electropositive elements, by precipitation of an insoluble lithium compound (normally halide) and bond formation between the metal and the methyleneamino group (Equation 1.11).

$$R_2C{:}NLi + XMY_n \rightarrow LiX + R_2CNMY_n \qquad 1.11$$

Individual reactions will be discussed as appropriate in the following sections.

Reactions of methyleneaminolithium compounds with transition metal carbonyl compounds do not always react in so straightforward a manner: these will be described later.

Hexafluourodimethylmethyleneaminolithium reacts with bromine in benzonitrile below 10° to give N—bromohexafluourodimethylmethyleneamine, $(CF_3)_2C{:}NBr$ (24).

With chloro derivatives of Group 1Vb metals, perfluoromethyleneamino compounds are formed, analogous to their hydrocarbon counterparts (48).

Group 11.

Beryllium.

Preparation. Fourteen methyleneaminoberyllium compounds have been isolated. Their methods of preparation, and azomethine stretching frequencies are summarised in Table 1.7.

Six of the compounds were prepared by the straightforward addition of the appropriate iminolithium to beryllium chloride in the required molar ratio. (Equation 1.12 and 1.13).

$$R^1R^2C{:}NLi + BeCl_2 \rightarrow \tfrac{1}{2}[R^1R^2C{:}NBeCl]_2 + LiCl \qquad 1.12$$

($R^1 = R^2$ = p-tolyl (71), ^tBu (45); R^1 = p-tolyl, $R^2 = {}^tBu$ (71))

$$2R^1R^2C{:}NLi + BeCl_2 \rightarrow {}^1/n[(R^1R^2C{:}N)_2Be]_n + 2LiCl \qquad 1.13$$

($R^1 = R^2$ = Ph, p-tolyl; R^1 = p-tolyl, $R^2 = {}^tBu$ (71))

Diphenylmethyleneaminoberyllium chloride was prepared from diphenylmethyleneaminotrimethylsilane and beryllium chloride (Equation 1.14) (71).

$$BeCl_2 + Ph_2C{:}NSiMe_3 \rightarrow \tfrac{1}{2}[Ph_2C{:}NBeCl]_2 + Me_3SiCl \qquad 1.14$$

The second chlorine atom could not be replaced in this way by a further equivalent of the iminosilane.

Reactions between beryllium chloride and two equivalents of di-t-butylmethyleneaminolithium did not give the bis(imino)beryllium $({}^tBu_2C{:}N)_2Be$, but lithium tris(di-t-butylmethyleneamino)beryllate,

Table 1.7

Methyleneamino derivatives of beryllium

Compound	Method of preparation†	ν(C=N) Bridging	ν(C=N) Terminal	Ref
$[Ph_2C{:}NBeCl]_2$	1	1608		71
$[(p\text{-tolyl})_2C{:}NBeCl]_2$	1	1610		71
$[(p\text{-tolyl})BuC{:}NBeCl]_2$	1	1614		71
$[^tBu_2C{:}NBeCl]_2$	1	1626		45
$[Ph_2C{:}NBe^iBu]_2$	2	1610		45
$[Ph_2C{:}NBe^tBu]_2$	2	1648		45
$[^tBu_2C{:}NBe^iBu]_2$	2	1635		45
$[Ph_2C{:}N)_2Be]_n$	1	1627	1732	71
$[((p\text{-tolyl})_2C{:}N)_2Be]_3$	1	1626	1731	71
$[((p\text{-tolyl})^tBuC{:}N)_2Be]_2$	1	1637	1739	71
$[(^tBu_2C{:}N)_2Be]_2$	2	1631	1721	45
$^tBu_2C{:}NBeN(SiMe_3)_2$	3		1734, 1747	45
		ν(C=N)		
$LiBe(N{:}C^tBu_2)_3$	1	1663		45
$Li_2Be(N{:}C^tBu_2)_4$	3	1660, 1709		45

† 1 From beryllium chloride and imino-lithium or -trimethylsilane

2 From beryllium alkyl and methyleneamine

3 Preparation discussed in the text.

$LiBe(N:C^tBu_2)_3$ (42).

Four compounds were prepared by reaction between the appropriate imine and beryllium alkyls (Equations 1.15 and 1.16).

$$R^1_2C:NH + R^2_2Be \rightarrow \tfrac{1}{2}[R^1_2C:NBeR^2]_2 + R^2H \qquad 1.15$$

(R^1 = Ph, R_2 = ^tBu, ^iBu; R^1 = ^tBu, R^2 = ^iBu (45))

$$2R^1_2C:NH + R^2_2Be \rightarrow \tfrac{1}{2}[(R^1_2C:N)_2Be]_2 + 2R^2H \qquad 1.16$$

(R^1 = ^tBu, R^2 = ^iBu (45))

Di-t-butylmethyleneamino-bis(trimethylsilyl)aminoberyllium was prepared from the iminoberyllium chloride and bis(trimethylsilyl)amino-lithium (Equation 1.17).

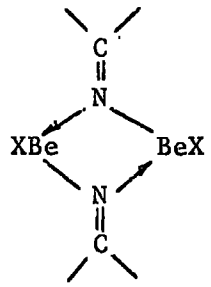
$$\tfrac{1}{2}[^tBu_2C:NBeCl]_2 + (Me_3Si)_2NLi \rightarrow {}^tBu_2C:NBeN(SiMe_3)_2 + LiCl \qquad 1.17$$

The reaction between bis(di-t-butylmethyleneamino)beryllium with two equivalents of di-t-butylmethyleneaminolithium is shown in equation 1.18.

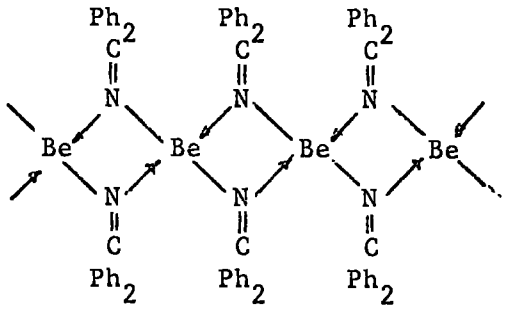
$$[(^tBu_2C:N)_2Be]_2 + 2\,{}^tBu_2C:NLi \rightarrow Li_2Be(N:C^tBu_2)_4. \qquad 1.18$$

Structure. The azomethine stretching frequencies ν(C=N) of the iminoberyllium compounds are a useful guide to their structures. The iminoberyllium chlorides and alkyls are dimeric (by cryoscopy in benzene) and their structure probably involves a four-membered $(BeN)_2$ ring and bridging imino groups (Figure 1.9.a), similar to some related boron, aluminium and gallium compounds $[R_2C:NMCl_2]_2$ (18,72,73) as their azomethine stretching frequencies occur at appropriate values for this. Diphenylmethyleneaminoberyllium is probably polymeric, with a linear

Figure 1.9



(a)



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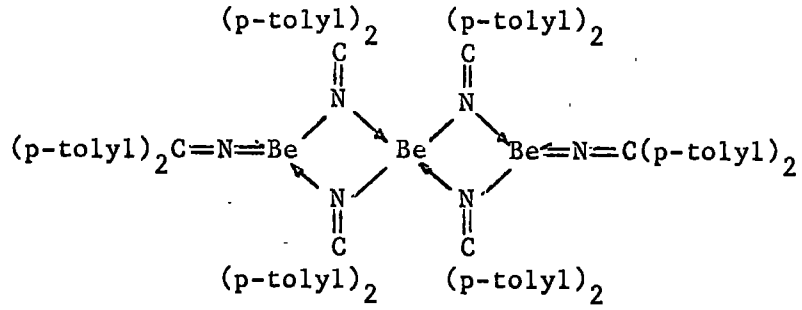

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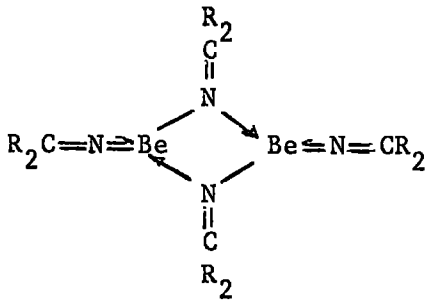

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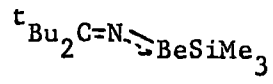

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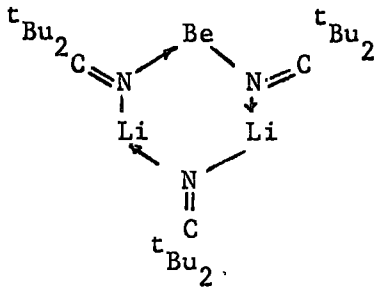


(f)

structure (Figure 1.9.b). The two azomethine stretching frequencies, attributed to bridging and terminal methyleneamino groups, support this (45).

On the basis of its ^1H n.m.r. spectrum (similar to that of $[(Me_2N)_2Be]_3$ (74 - 76)), a linear structure is also proposed for $[(p\text{-tolyl}_2C{:}N)_2Be]_3$ (Figure 1.9.c).

The dimeric bis(imino)beryllium compounds exhibit two azomethine stretching frequencies, the lower attributed to bridging, and the higher to terminal imino groups. The structure consistent with these observations is shown in figure 1.9.d (45), and has been confirmed by X-ray crystallography for $[(^tBu_2C{:}N)_2Be]_2$ (39).

Considerable interest attaches to $^tBuC{:}NBeN(SiMe_3)_2$ as it is apparently the only known monomeric iminoberyllium compound. The complexity of its ^1H n.m.r. spectrum suggests that the C=N-Be unit is not linear (Figure 1.9.e), but the high azomethine stretching frequency would suggest that deviation from linearity is not sufficient to restrict Be → N π-bonding significantly (22). The compound is obtained as a yellow oil which gradually solidifies. It is therefore unsuitable for crystallographic study to determine its structure.

The two lithium beryllates, $LiBe(N{:}C^tBu_2)_3$ and $Li_2Be(N{:}C^tBu_2)_4$, both have absorptions which are not readily assigned to terminal or bridging imino groups. ^1H n.m.r. spectra do not provide evidence for structures similar to any of those of known metallates (e.g. $LiBePh_3$ (77), $LiAl(N{:}C^tBu_2)_4$ (40)). A novel ring system consistent with the spectral data is proposed for $Li_2Be(N{:}C^tBu_2)_4$ (Figure 1.9.f) (22), but it appears that only crystallographic study can show the exact structure of both

the lithium (methyleneamino)beryllates.

Reactions. Apart from the use of mono(imino)beryllium compounds to prepare higher-substituted iminoberyllium species, only the co-ordination properties of methyleneaminoberyllium compounds have been studied; the reactivity of the metal-nitrogen bond has not been investigated.

Reactions between donor molecules and dimeric iminoberyllium compounds have been carried out in an attempt to prepare further monomeric compounds, with linear C=N-Be units.

No reaction was observed between trimethylamine and $[^tBu_2C{:}NBeCl]_2$; steric crowding at beryllium probably restricts co-ordination. There is spectroscopic evidence for some degree of co-ordination between tetramethylethylenediame and $[^tBu_2C{:}NBeCl]_2$, although the complex could not be isolated (45).

Magnesium. Methyleneaminomagnesium compounds have been known since the beginning of this century as intermediates in the preparation of ketones (1) and ketimines (78), but it is only recently that they have been isolated and studied.

Preparation. The insertion of a Grignard reagent into a nitrile has been used to prepare a series of methyleneaminomagnesium compounds (Equation 1.19) (79).

$$R^1C{:}N + R^2MgX \rightarrow R^1R^2C{:}NMgX \qquad 1.19$$

(R^1 = Ph, R^2 = Me, Et, $PhCH_2$; R^1 = cyclopropyl, R^2 = Me, Ph)

Reaction between allylmagnesium bromide and alkyl or aryl halide followed by addition of nitrile also affords methyleneamino magnesium halides (Equation 1.20) (79)

$$CH_2{=}CH{-}CH_2MgX + R^1X \rightarrow R^1MgX + CH_2{=}CHCH_2Br$$
$$\downarrow R^2C{:}N \qquad (1.20)$$
$$^1/_n[R^1R^2C{:}NMgX]_n$$

(X = Br, R^1 = $C_6H_5CH_2$; R^2 = Ph, m-tolyl, cyclopropyl;
R^1 = 1-phenylethyl, R^2 = Ph, m-tolyl;
X = Cl; R^1 = $C_6H_5CH_2$; R^2 = Ph)

Reaction between benzonitrile and diethylmagnesium in ether affords phenylethylmethyleneaminoethylmagnesium (Equation 1.21) (80).

$$PhC{:}N + Et_2Mg \rightarrow {}^1/_n[PhEtC{:}NMgEt]_n \qquad (1.21)$$

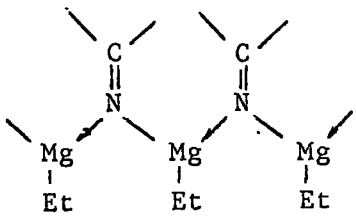
The yellow solid obtained is soluble in benzene, in which it is extensively associated. A similar reaction using t-butyl cyanide afforded a colourless syrup from which the residual ether could not be removed. However, the compound forms a crystalline complex with tetrahydrofuran, $(^tBuEtC{:}NMgEt)_x(THF)_y$.

Reaction between di-i-propylmagnesium and t-butyl cyanide does not yield the methyleneamino compound analogous to those described above, but a crystalline co-ordination complex, $^tBuCN.Mg^iPr_2$, is formed (80).

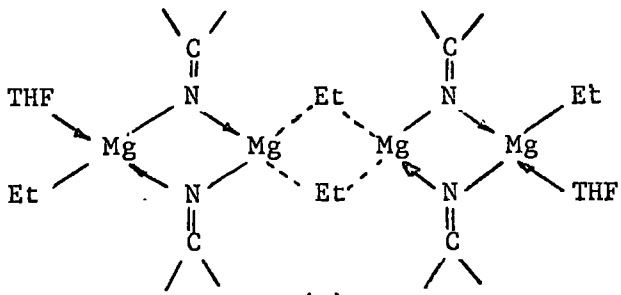
The preparation and properties of several new methyleneaminomagnesium compounds are described in Chapter 3.

Structure. Both the unco-ordinated phenylethylmethyleneaminoethylmagnesium and the ethyl-t-butylmethyleneaminoethylmagnesium - THF complex have low azomethine stretching frequencies (1626 cm^{-1} and 1631 cm^{-1} respectively) suggesting that their polymeric structures contain bridging rather than terminal imino groups (80). A possible structure of $[PhEtC{:}NMgEt]_n$ is shown in figure 1.10.a. It involves dative σ-bonds

Figure 1.10



(a)



(b)

between nitrogen and magnesium in adjacent monomeric units. Figure 1.10.b shows a possible structure for $(^{t}BuEtC{:}NMgEt)_x(THF)_y$ similar to that postulated for aminoethylmagnesium compounds (80) in which the metal is four-co-ordinate, and rapid exchange between terminal and bridging ethylmagnesium groups occur.

So far no crystallographic studies of methyleneamino magnesium compounds have been reported,

The compounds shown in equations 1.19 and 1.20 were prepared in order to investigate the nature of the imine-enamine tautomerism shown in figure 1.11.

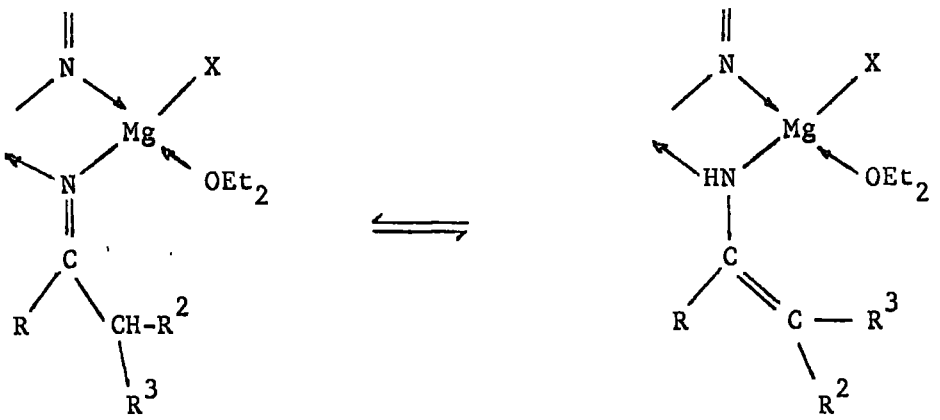


Figure 1. 11

This tautomerism is greatly influenced by the acidity of the protons on the α-carbon. When R^2 and R^3 are hydrogen or alkyl groups or R^2 is hydrogen and R^3 an alkyl group, then only the imino form is obtained (Figure 1.11.a). When R^2 = hydrogen and R^3 is an aryl group,

only the enamine isomer is found (Figure 1.11.b). The ^{1}H n.m.r. spectra of such compounds show a broad vinyl HC= absorption, thought to indicate some degree of bonding between carbon and magnesium as shown in figure 1.12.

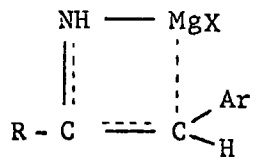


Figure 1.12.

The only compounds obtained in which both isomers were present were those where R^2 = Ph and R^3 = Me.

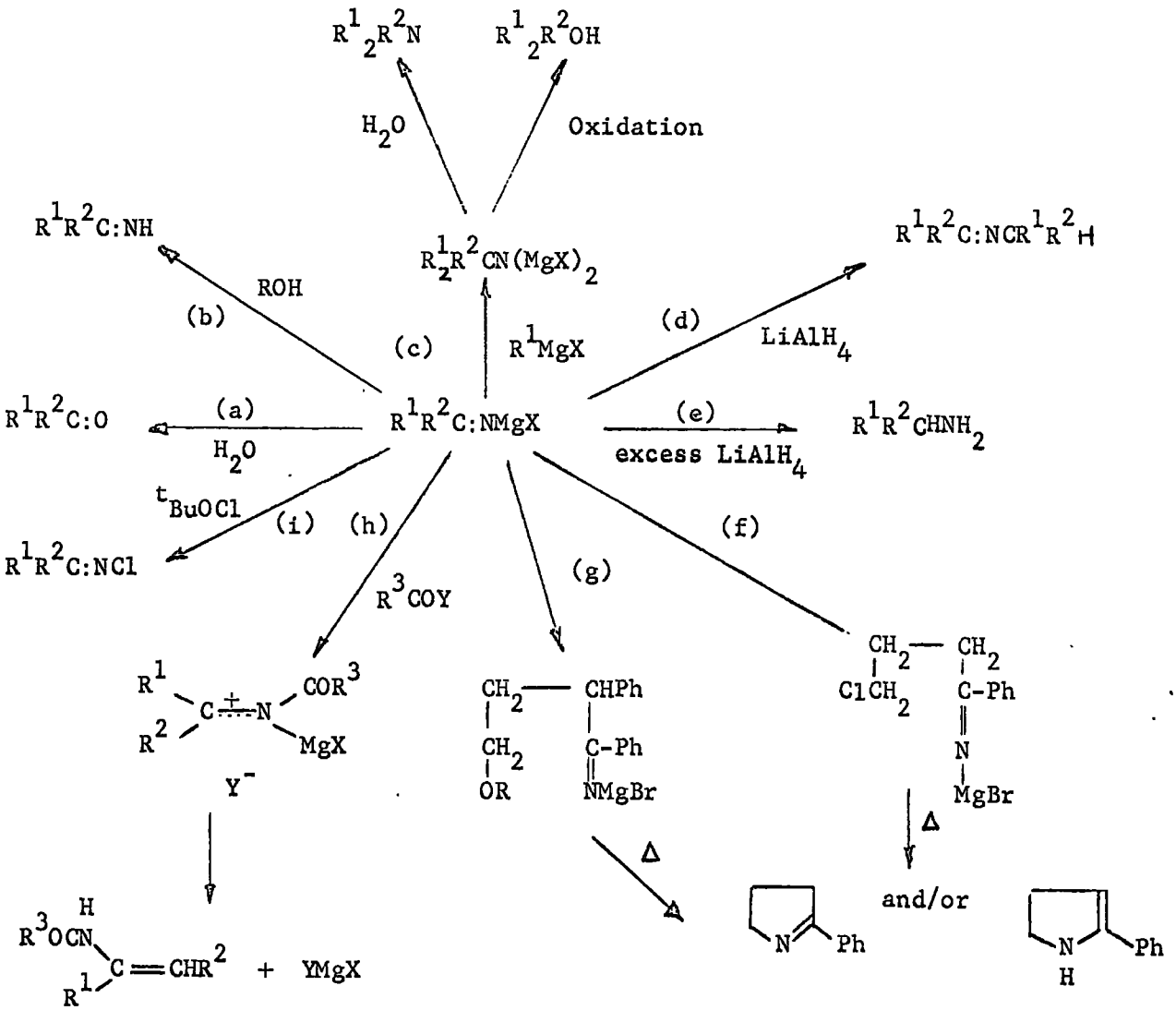
The compounds described in Chapter 3 were prepared in order to study the influence of substituents on the magnesium-nitrogen bond. Only the imino isomer was required, so to avoid any possibility of tautomerisation, groups without hydrogen atoms on the α-carbon were used. The structures of these compounds will be discussed later.

Reactions. The reactions of methyleneamino magnesium compounds are summarised in figure 1.13.

The preparation of ketones (1) or ketimines (78) from Grignard reagents by hydrolysis or alcoholysis are the most widely-known reactions of methyleneaminomagnesium compounds (Figure 1.13.a and b). Grignard reagents can sometimes react with iminomagnesium derivatives to give products which afford tertiary amines or alcohols on hydrolysis or oxidation (Figure 1.13.c) (81). Partial reduction of methyleneamino-Grignard compounds with lithium aluminium hydride gives Schiff's bases (Figure 1.13.d) (82), while complete reduction using excess reagent

Figure 1.13

Reactions of methyleneamino derivatives of magnesium.



yields secondary amines (Figure 1.13.e) (83,84). Pyrolysis of the addition product of phenylmagnesium bromide and 4-chlorobutyronitrile in boiling xylene results in ring closure (Figure 1.13.f) (85). Similar products are obtained from 4-phenoxy- and 4-ethoxy-ethers (Figure 1.13.g) (86). Reactions between ethylphenylmethyleneaminomagnesium bromide and acid chlorides (87) or esters (88) give enamides, probably via an ionic complex (Figure 1.13.h). N-chloro methyleneamines have been prepared by the direct action of t-butyl hypochlorite on methyleneaminogrignards (Figure 1.13.i) (89).

Zinc. Eight methyleneaminozinc compounds are known. Their azomethine stretching frequencies and general methods of preparation are given in Table 1.8.

Five compounds were prepared by reactions between zinc dialkyls and ketimines (Equations 1.22 and 1.23).

$$R^1{}_2Zn + R^2{}_2C{:}NH \rightarrow R^2{}_2C{:}NZnR^1 + R^1H \qquad 1.22$$

(R^2 = Ph, R^1 = Me, Et, Ph(90); R^1 = Me, R^2 = ^{t}Bu (45))

$$R^1{}_2Zn + 2R^2{}_2C{:}NH \rightarrow (R^2{}_2C{:}N)_2Zn + 2R^1H \qquad 1.23$$

(R^1 = Me, R^2 = ^{t}Bu. (45))

Zinc chloride reacted with one or two equivalents of di-t-butylmethyleneaminolithium to give iminozinc chloride or bis(imino)zinc respectively (Equations 1.24 and 1.25).

$$^tBu_2C{:}NLi + ZnCl_2 \rightarrow [^tBu_2C{:}NZnCl]_2 + LiCl \qquad 1.24$$

$$2\,^tBu_2C{:}NLi + ZnCl_2 \rightarrow \tfrac{1}{2}[(^tBu_2C{:}N)_2Zn]_2 + 2LiCl \qquad 1.25$$

Table 1.8

Methyleneamino derivatives of zinc

Compound	Method of preparation†	ν(C=N)	Ref
$[^tBu_2C{:}NZnCl]$	1	1608, 1597	45
$[^tBu_2C{:}NZnMe]_2$	2	1592	45
$[Ph_2C{:}NZnPh]_2$	2, 3	1607	90
$[Ph_2C{:}NZnEt]_2$	2	1611	90
$[Ph_2C{:}NZnMe]_2$	2	1624	90
$[(Ph_2C{:}N)_2Zn]_n$	2	1600	90
$[(^tBu_2C{:}N)_2Zn]_2$	1	1683, 1585	35
$Ph_2C{:}NMe.2py$	4	1613	90

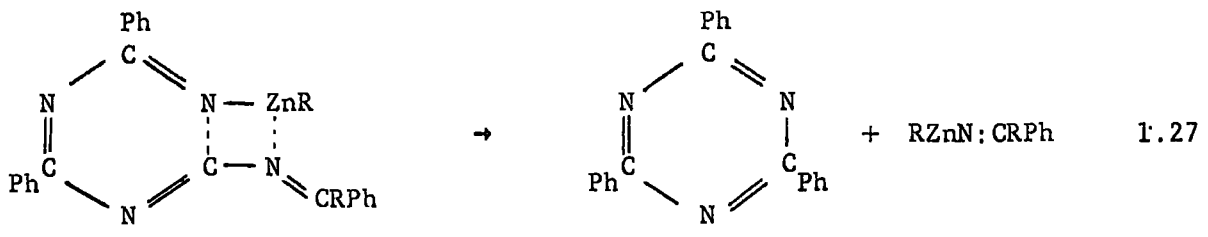
1. From zinc chloride and iminolithium
2. From zinc alkyls and methyleneamine
3. From zinc alkyl and nitrile
4. Preparation described in the text

Benzonitrile and diphenylzinc form an adduct which pyrolyses at 100° to give bis(diphenylmethyleneamino)zinc, presumably via the disproportion of initially-formed diphenylmethyleneaminophenylzinc (Equation 1.26) (90).

$$PhC{:}N + Ph_2Zn \rightarrow PhC{:}N.ZnPh_2 \rightarrow [Ph_2C{:}NZnPh]_2 \rightarrow {}^1/_n[(Ph_2C{:}N)_2Zn]_n + Ph_2Zn \qquad 1.26$$

No evidence of interaction was observed in studies of the systems R_2Zn - $^tBuC{:}N$ (R = Me, Et, Ph) (90). However, heating equimolar mixtures of benzonitrile and dimethylzinc (91) or diethylzinc (90,92) to between 100° and 150° in sealed tubes resulted in the trimerisation of the benzonitrile, The mechanism of the reaction probably involves successive insertions of benzonitrile into initially zinc-carbon and subsequently zinc-nitrogen bonds (Equation 1.27), similar to the polymerisation of benzonitrile in

$$R\text{-}ZnR \xrightarrow{PhC{:}N} R(Ph)C{:}NZnR \xrightarrow{PhC{:}N} R(Ph)C{:}N.CPh{:}NZnR$$



1.27

the presence of organolithium reagents (2).

Attempts to prepare lithium tris(imino)zincates, $LiZn(N{:}CR_2)_3$, analogous to the beryllium compounds described earlier were unsuccessful (45).

Structure. All the monoiminozinc compounds except the pyridine adduct $Ph_2C{:}NZnMe,2py$, dissolve in benzene as dimers, which are thought

to have a planar skeleton based on a four-membered $(ZnN)_2$ ring such as that shown by crystallography for the aminozinc compound $[MeZnNPh_2]_2$ (93) The azomethine stretching frequencies of these compounds occur in the region appropriate for bridging rather than terminal imino groups consistent with the structure shown in figure 1.14.a.

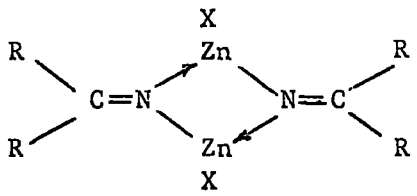
Only one azomethine stretching frequency is observed for bis(diphenylmethyleneamino)zinc, at 1600 cm^{-1}. This is in the region appropriate for bridging imino groups, and suggests that the compound forms a long polymer (Figure 1.14.b) in which the proportion of terminal imino groups which would absorb at higher frequency, is sufficiently small to be undetected spectroscopically (90). The analogous t-butyl compound $[(^tBu_2C{:}N)_2Zn]_2$ being dimeric must have the structure shown in figure 1.14.c; the two types of methyleneamino groups are demonstrated by the two azomethine stretching frequencies observed. (45).

Reactions. Pyridine reacts with diphenylmethyleneaminomethylzinc, breaking up the dimer to form a monomeric bis(pyridine) adduct thought to have the structure shown in figure 1.14.d with tetraco-ordinate zinc, and a terminal imino group (90). The same product was obtained even when the ratio of pyridine to dimer was only 2:1, when a compound similar to the pyridine adduct of phenoxymethylzinc, $(MeZnOPh)_2.2py$. (Figure 1.14.e) (94) was expected.

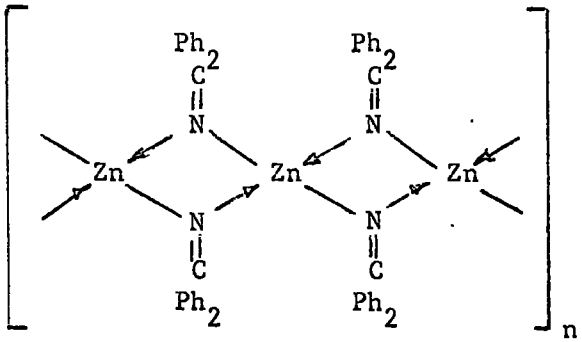
Group III.

Boron. When the chemistry of methyleneaminoboranes was reviewed recently (95), the following iminoboranes were known:
Monomiminoboranes, $[YZC{:}NBR]_n$, with the following substituents (not in all possible combinations):

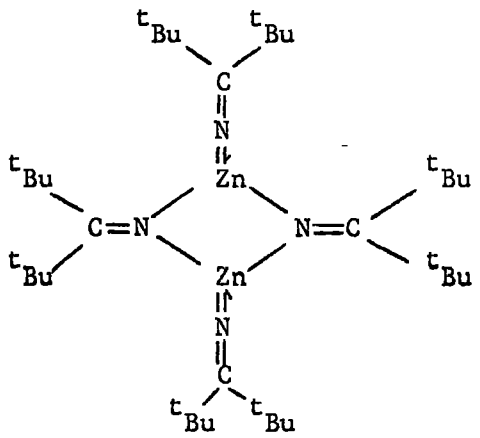
Figure 1.14



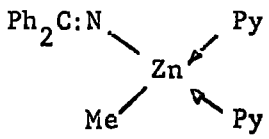
(a)



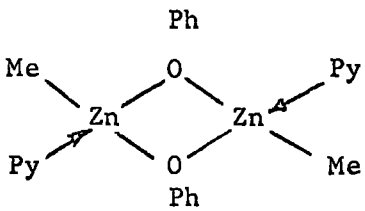
(b)



(c)



(d)



(e)

X = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, C_6H_5, F, Cl, Br, I, N3, mesityl, CH_3S, C_6H_5S.

Y = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9, C_6H_5, F, Cl, Br, CH_2Cl, $CHCl_2$, CCl_3, CHF_2, CF_3, C_2F_5, C_6F_5, CH_2I, 4-CH_3-C_6H_4, 3-CH_3-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-CH_3O-C_6H_4, 4-CN-C_6H_4, C_5H_4NHCl, CH_3OCH_2, CH_3S, i-C_3H_7S.

Z = H, i-C_3H_7, C_6H_5, Cl, Br, I, N_3, NCS, CF_3, $(C_6H_5)_2CBr$, 4-CH_3-C_6H_4, 4-Cl-C_6H_4; CH_3S, C_2H_5S, $ClCH_2S$, C_6H_5S, n-C_4H_9S, sec-C_4H_9S.

R = H, CH_3 C_2H_5, C_3H_7, c-C_4H_9, t-C_4H_9, C_6H_5, F, Cl, Br, I, NCS, mesityl, $(C_6H_5)_2CBr$, $C_6H_4O_2$, 2,2[1]$(C_6H_4)_2$, CH_3S, C_6H_5S.

The bis(methyleneaminoborane, $C_6H_5B(N{:}CPh_2)_2$ and two tris(methyleneamino)-boranes, $B(N{:}CPh_2)_3$ and $B(N{:}C(CF_3)_2)_3$.

The methyleamine-borane adducts, $YZC{:}NH.BX_3$:

X = H, F, CH_3, C_6H_5.

Y = H, t-C_4H_9, C_6H_5, 4-Cl-C_6H_4, 4-C_6H_3-C_6H_4.

Z = t-C_4H_9, C_6H_5, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-C_6H_3-C_6H_4.

and dichloromethyleneamine-borane adducts, $RN{:}CCl_2.BX_3$:

R = C_2H_5, C_6H_5;

X = Cl, Br.

The following methyleneaminoboranes have since been prepared:

$R_2C{:}NBXY$: R = ^{t}Bu, X = Y = Cl, Ph, ^{n}Bu (22).

X = Cl, Y = H, Ph (52).

R = Ph, X = Y = ^{n}Pr, ^{n}Bu (96).

R = CF_3, X = Y = Ph, Cl, Br (97).

$(R_2C{:}N)_2BX$: R = ^{t}Bu, X = Cl, Ph (52).

The preparation and properties of several new methyleneaminoboranes are discussed in Chapter 2.

Preparation. Methyleneaminoboranes can be prepared by all the principal methods described previously. The 1,2 addition of B-X (X = H, C,S, halogen) bonds across the triple bond of nitriles can be used to prepare variously-substituted methyleneaminoboranes (Equation 1.28).

$$RC{:}N + XBY_2 \rightarrow \begin{matrix} R \\ X \end{matrix}\!\!>\!C{:}NBY_2 \qquad 1.28$$

The formation and stability of the product depends on the substituents R and X, and, to a lesser extent, the groups Y (98).

Reaction of the appropriate methyleneamino-lithium or -trimethylsilane with haloboranes has yielded a great number of methyleneaminoboranes (Equation 1.29).

$$nR_2C{:}NY + BX_3 \rightarrow (R_2C{:}N)_nBX_{3-n} + nXY$$
$$(Y = Li, Me_3Si, n= 1\text{-}3.) \qquad 1.29$$

Reaction between two equivalents of diphenylmethyleneaminolithium and boron trichloride yields tris(methyleneamino)borane as a result of disproportionation of initially-formed bis(methyleneamino)chloroborane (Equation 1.30) (21).

$$2Ph_2C{:}N\,Li + BCl_2 \rightarrow (Ph_2C{:}N)_2BCl \rightarrow (Ph_2C{:}N)_3 + [Ph_2C{:}NBCl_2]_2 \qquad 1.30$$

The reaction between an alkylborane and a methyleneamine has been used to prepare two methyleneaminodialkylboranes, $R^1C{:}NBR^2_2$ ($R^1 = {}^tBu$, R^2 = Et (52); R^1 = Ph, R^2 = Me (99)) (Equation 1.31).

$$R^1{}_2C{:}NH + BR^2{}_3 \rightarrow R^1{}_2C{:}NBR^2{}_2 + R^2H \qquad 1.31$$

In a similar reaction between triethylborane and diphenylmethyleneamine, the alkylborane reduced the ketimine to $Ph_2C{:}NCHPh_2$, ethylene being the by-product (99).

Several methyleneaminoboranes have been prepared by special procedures.

Two compounds have been prepared by reacting imine hydrochlorides with sodium tetraphenylborate (Equation 1.32).

$$R_2C{:}NH_2Cl + NaBPh_4 \rightarrow R_2C{:}NBPh_2 + NaCl + 2C_6H_6 \qquad 1.32$$

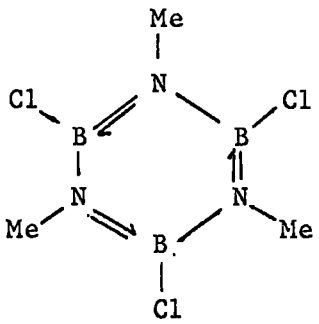
(R = Ph (44), p-tolyl (21)).

Hexafluorodimethylmethyleneaminoboranes can also be obtained by dehydrohalogenation of the (amino)haloboranes with an excess of the parent ketimine (Equation 1.33). (97).

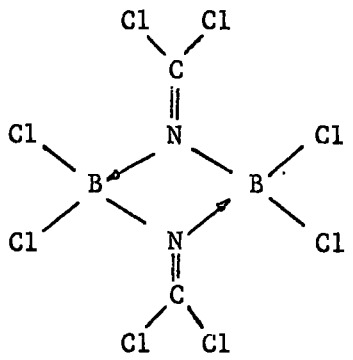
$$(CF_3)_2C{:}NH + BXPh_2 \rightarrow (CF_3)_2CX.NH.BPh_2$$
$$\xrightarrow{(CF_3)_2CNH} (CF_3)_2C{:}NBPh_2 + (CF_3)_2CX.NH_2$$

(X = Br, Cl) 1.33

The compound $[Cl_2C{:}NBCl_2]_2$ is formed by photochemical chlorination of 1,3,5-trimethyl-2,4,6-trichloroborazine, or by interaction of boron trichloride with thiocyanogen trichloride. Reaction between thiocyanogentrichloride and boron tribromide yields $[Cl_2C{:}NBBr_2]_2$ (Equation 1.34) (100).



Cl_2, $h\nu$

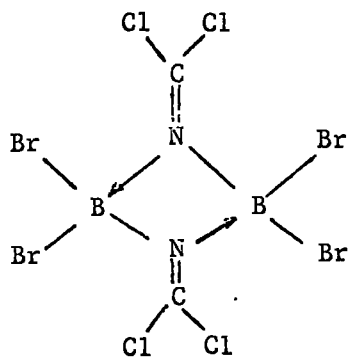


1.34

BCl_3

$Cl\text{-}S\text{-}N{:}CCl_2$

BBr_3



Pyrolysis of the adduct of diphenylketimine with trimethylborane gives the methyleneamino-dimethylborane (Equation 1.35) (101).

$$Ph_2C{:}NH.BMe_3 \xrightarrow{160-200^{\circ}} 1/n[\ Ph_2C{:}NBMe_2]_n + CH_4 \qquad 1.35$$

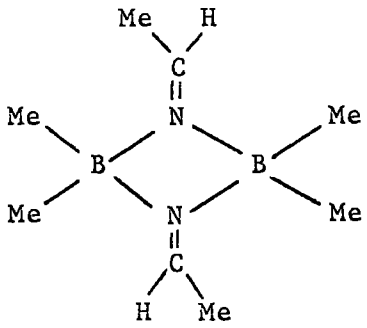
Structure. Methyleneaminoboranes, $[R^1R^2C{:}NBXY]_n$ are normally associated, usually existing as dimeric species in the vapour, solid and solution phases (47,54,72,96,98-100,102-118). Their structures are typified by that of $[MeCH{:}NBMe_2]_2$ (Figure 1.15.a) determined by X-ray crystallography (119). Some higher polymers are also known (21,47,54,72, 101). Monomers (Figure 1.15.b or c) are apparently observed only when the substituents R^1,R^2, X and Y are sufficiently bulky to prevent association (21,44,47,52,54,98,114,115,116,120-122), although they have been noted in the vapour phase of some of the associated species (54,99, 103), on heating solutions of the dimers (112,117) and occasionally as minor constituents of monomer-dimer equilibria in solutions of the dimers (112,114,116).

The structures of the monomeric species are of particular interest since the methyleneamino group, $R^1R^2C{:}N-$, when terminally attached to co-ordinatively unsaturated metals or metalloids (M) in derivatives of the type $R^1R^2C{:}NMX_n$, provide a convenient probe for the study of dative N → M π-bonding.

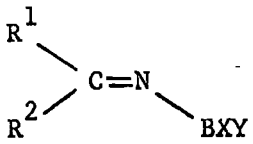
Considerable information has been obtained from a series of di-t-butylmethyleneaminoboranes (22,52,122). The bulk of the t-butyl groups restricts association, and all the compounds are monomeric.

Crystallographic study (38) of diphenylmethyleneaminodimesitylborane, $Ph_2C{:}NB(mesityl)_2$ (47,54,123) has shown that the C=N≐B unit is

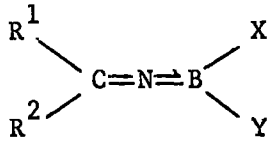
Figure 1.15



(a)

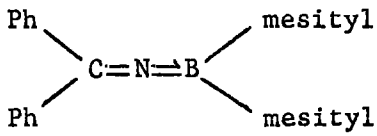


(b)



(c)

Figure 1.16



effectively linear (CNB angle ~173°) (Figure 1.16). The similarity of the azomethine stretching frequency of this compound (1792 cm^{-1}) to those of the di-t-butylmethyleneaminoboranes (1845-1774 cm^{-1}) suggests that they also contain effectively linear C=N=M units, as appropriate for significant N → B pπ → pπ dative bonding.

Table 1.9 shows the variation in azomethine stretching frequency with boron substituents for di-t-butylmethyleneaminoboranes and their diphenylmethyleneamino analogues.

The study of di-t-butylmethyleneaminoboranes is continued in this work.

Reactions. Apart from the use of mono- and bis-(methyleneamino)boranes to prepare other methyleneaminoboranes by changing the boron substituents (21,52) no study of the chemical properties of these compounds has been made.

Aluminium. Methyleneaminoalanes can be prepared by all three general routes described previously.

Insertion of nitriles into aluminium-carbon bonds (Equation 1.36) yield methyleneaminoalanes only when the organic group R^2 is an aryl, or alkyl group other than ethyl, and the nitrile substituent R^1 has no hydrogen atoms on the α-carbon atom.

$$R^1C{:}N + \tfrac{1}{2}[R^2AlX_2]_2 \rightarrow R^1C{:}N.AlR^2X_2 \xrightarrow{\Delta} {}^1/_n[R^1R^2C{:}NAlX_2]_n \qquad 1.36$$

(R^1 = Ph, ^tBu, R^2 = Me, Ph, X = Me, Ph (124,125)

R^1 = Ph, X = Et, R^2 = H (4,124,125))

Pyrolysis of benzonitrile-triethylalane adduct afford both aldimino- and ketimino-alane (Equation 1.37).

Table 1.9

Azomethine stretching frequencies (cm^{-1})

of some related methyleneaminoboranes $[RC:NBXY]_n$

Compound	R = ^tBu			R = Ph		
	ν(C=N)	n	Ref	ν(C=N)	n	Ref
$[R_2C:NBHCl]_n$	1845*	1	52			
$[R_2C:NBCl_2]_n$	1839*	2	22	1590	2	47
$[R_2C:NBPhCl]_n$	1838*	2	52	1612	2	47
$[R_2C:NBPh_2]_n$	1820	1	22	1786	1	47
$[R_2C:NB^nBu_2]_n$	1821*	1	22	1785	1	96
$[R_2C:NBEt_2]_n$	1818*	1	52	1793	1	47
$[(R_2C:N)_2BCl]_n$	1777	1	52			
$[(R_2C:N)_2BPh]_n$	1774	1	52	1672	1	47

* Liquid film. All others recorded as Nujol mulls

$$PhC{:}N + Et_3Al \begin{cases} \xrightarrow{\text{Reduction}} PhHC{:}NAlEt_2 + C_2H_4 \\ \xrightarrow{\text{Addition}} PhEtC{:}NAlEt_2 \end{cases} \qquad 1.37$$

The relative proportions of the products vary with the mole ratios of the reagents (128).

When R^1 = Me or Et, the main products are polymeric materials formed by cleavage of organic groups from aluminium (Equation 1.38) (124,125,129-133).

$$RCH_2C{:}N + R^2AlX_2 \rightarrow RCH_2CN.AlR^2X_2 \qquad 1.38$$

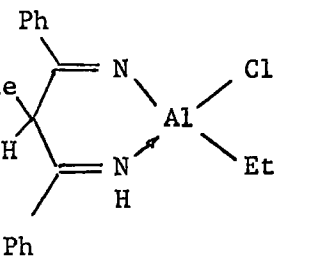
$$\downarrow$$

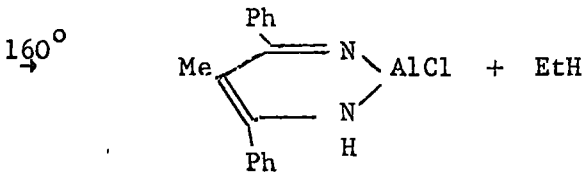
$$^1/_n[RCH{:}CNAlX_2]_n + R^2H \qquad ^1/_n[RCH(AlX_2)CN]_n + R^2H$$

When R^2 = H (124,125,134,135), or Et (124,125,129,130,135), aldimino derivatives $[R^1CH{:}NAlX_2]_n$ are formed, as $EtAlX_2$ can act as a source of $HAlX_2$.

Cyclic compounds can be formed when derivatives $[R^1R^2C{:}NAlXY]_n$ in which R^2 has hydrogen attached to the α-carbon react with unused nitrile (136,137), as shown for example, in equation 1.39.

$$PhC{:}N + PhEtC{:}NAlEtCL \xrightarrow{100^\circ}$$





1.39

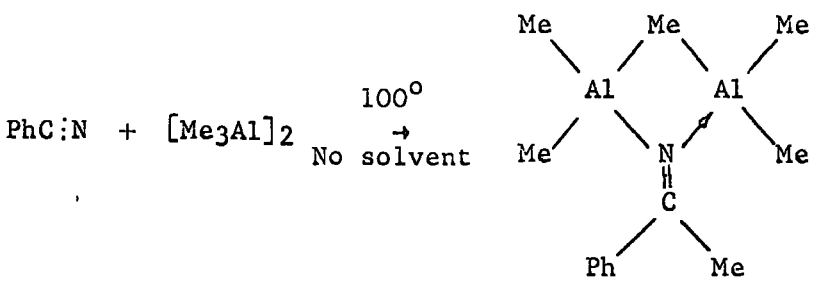
Insertion of nitriles into aluminium-nitrogen bonds also yields methyleneaminoalanes (Equation 1.40).

$$R^1R^2AlNR^3R^4 + R^5C{:}N \rightarrow R^1R^2AlN{:}C(NR^3R^4)R^5 \qquad 1.40$$

(R^5 = Ph; R^1 = R^2 = Et, Cl; R^1 = Et, R^2 = Cl; R^2 = R^4 = Et; R^3R^4 = $(CH_2)_5$; R^3 = Me, R^4 = Ph (127,138,139) R^5 = XC_6H_4 (X = NO_2, Me, OMe, NMe, H), Me, COOEt, CH_2; R^1 = R^2 = Et, R^3 = R^4 = Me (140))

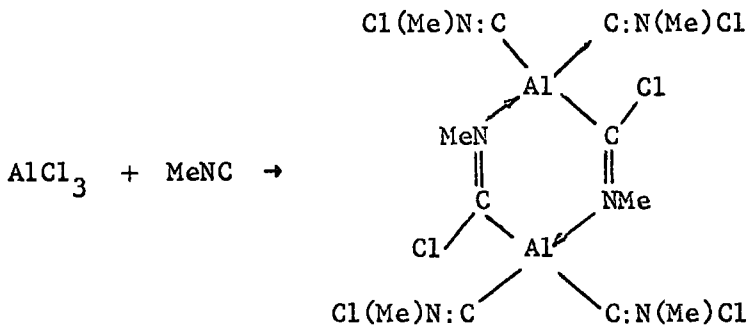
For sterically hindered compounds R_2NAlEt_2 (R = Ph, cyclohexyl), however, reaction with benzonitrile does not give methyleneaminoalanes (126).

Benzonitrile reacts with two equivalents of trimethylalane to give the methyleneaminomethylalane shown in equation 1.41. (152).



1.41

Isocyanides react with aluminium compounds to give cyclic products with $(AlCN)_2$ ring structures, as shown, for example in equation 1:42 (141).



1.42

Methyleneamines and organoaluminium compounds form adducts which produce methyleneaminoalanes on heating (Equation 1.43).

$$R^1{}_2C{:}NH + \tfrac{1}{2}[R^2{}_3Al]_2 \rightarrow R^1{}_2C{:}NH.AlR^2{}_3 \xrightarrow{\Delta} {}^1/_n[R^1{}_2C{:}NAlR^2{}_2]_n + R^2H \qquad 1.43$$

$R^1 = Ph$; $R^2 = Me$, Et, Ph (142)

$R^1 = Me_2N$, $R^2 = Me$, Et (69).

$R^1 = {}^tBu$, $R^2 = Me$, ${}^iBu$ (143)

Reaction between methyleneamino-lithium or -trimethylsilyl compounds and aluminium halides affords methylenaminoalanes (Equation 1.44)

$$nR_2C{:}NY + AlX_3 \rightarrow (R_2C{:}N)_nAlX_{3-n} + nXY \qquad 1.44$$

$n = 1$; $R = Ph$; $X = Cl$, Br; $Y = Li$, Me_3Si (18).

$X = Cl$, $Y = Li$, $R = {}^tBu$ (18), Me_2N (69).

$n = 3$; $R = Ph$, ${}^tBu$, $Y = Li$; $X = Cl$ (18,144).

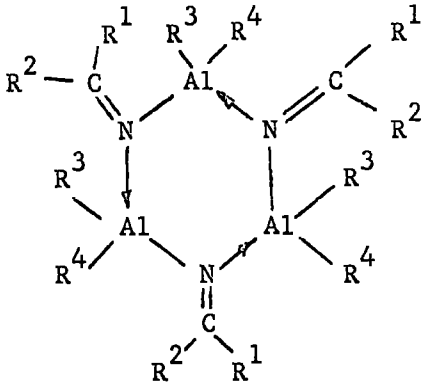
Mono- and tris-(methyleneamino)alanes were also obtained when two moles of iminolithium reacted with aluminium trichloride, apparently as a result of disproportionation of initially-formed bis(methyleneamino)-aluminium chloride (Equation 1.45).

$$2R_2C{:}NLi + AlCl_3 \rightarrow (R_2C{:}N)_2AlCl + 2LiCl$$
$$2(R_2C{:}N)_2AlCl \rightarrow \tfrac{1}{2}[R_2C{:}NAlCl_2]_2 + (R_2C{:}N)_3Al \qquad 1.45$$

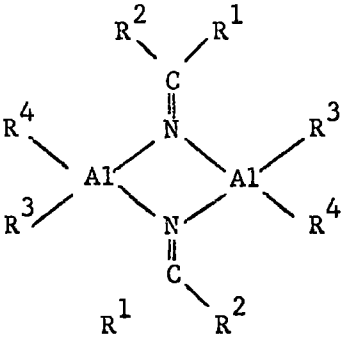
$R = {}^tBu, Ph$ (18,144).

Structure. All the mono(methyleneamino)alanes are dimeric, $[R^1R^2C{:}NAlR^3R^4]_2$. Even those with bulky substituents (e.g. ${}^tBu$) are associated, unlike their boron counterparts. A trimeric structure $[R^1R^2C{:}NAlR^3R^4]_3$ (Figure 1.17.a), as found in some related azides $[R_2AlN_3]_3$ (146), aminoalanes, $[R_2NAlH_2]_3$ (147), and in $[Me_2AlNHMe]_3$ (148), would have

Figure 1.17



(a)



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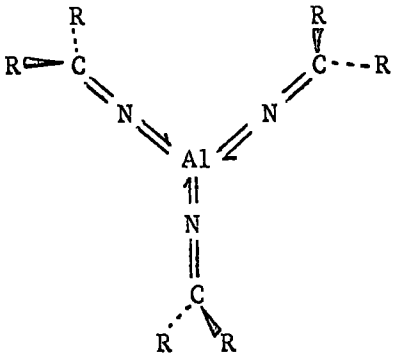

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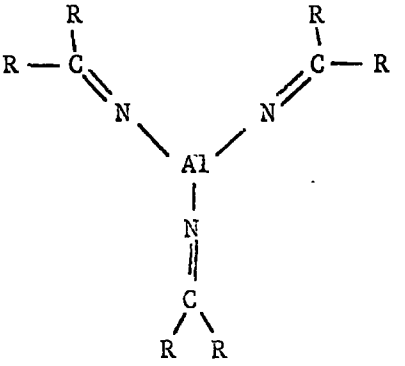

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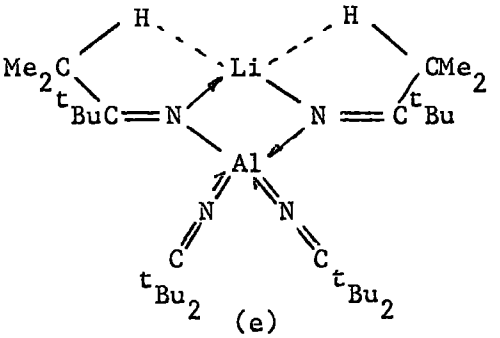


(e)

allowed a greater Al-N-Al angle, releasing the strain at the nitrogen atom. However, kinetic studies of nitrile / trialkylalane systems have indicated that dialkylmethyleneaminoalanes are thermodynamically most stable as dimers (145). Crystallographic studies of $[^{t}BuMeC{:}NAlMe_2]_2$ (153) and $[p\text{-}Br\text{-}C_6H_4.PhC{:}NAlPh_2]_2$ (149) have shown that they are dimers with bridging rather than terminal methyleneamino groups. Their azomethine stretching frequencies (1634 cm^{-1} (124) and 1660 cm^{-1} (131) respectively) are in the same region as those found for other methyleneaminoalanes (Selected examples are given in table 1.10) which are therefore also thought to have bridging methyleneamino groups (Figure 1.17.b)

The tris(methyleneamino)alanes, $(R_2C{:}N)_3Al$, are monomeric, and on the basis of their azomethine stretching frequencies, shown in table 1.11, the C-N-Al skeleton is thought to be linear with a considerable degree of N → Al dative π-bonding. Linearity of the C=N≓Al units would cause the C-attached substituents to adopt a "paddle-wheel" orientation normal to the AlN_3 plane (Figure 1.17.c). This is the configuration with minimum steric hindrance between the substituents. A completely planar structure (Figure 1.17.d) would not only involve steric hindrance between substituents, but the nitrogen 2p orbital would then be in an orientation with zero overlap with the aluminium 3d orbital.

A crystallographic study of lithium tetrakis(di-t-butylmethyleneamino)-aluminate, $Li(^{t}Bu_2C{:}N)_4Al$, shows that the aluminium atom is surrounded by a distorted tetrahedron of methylenamino groups, two terminally attached, with the near-linear C-N-Al skeletons and short Al-N distances appropriate for appreciable N → Al (p → d) dative π-bonding, the other two bridging the aluminium to the lithium, which is also apparently involved in a novel type of Li---H-C interaction. (Figure 1.17.e) (40).

Table 1.10

Azomethine stretching frequencies (cm^{-1}) of some methyleneaminoalanes $[R^1R^2C{:}NAlR^3R^4]_2$

R^1	R^2	R^3 R^4	ν(C=N)	Ref
^tBu	H	Me	1661	125
Ph	H	Me	1630	125
^tBu	H	Et	1656	125
Ph	H	Et	1633	125
Me	Me	Me	1658	125
Ph	Ph	Ph	1604	18
Ph	Ph	Me	1616	18
Me_2N	Ph	Et	1573	140
Me_2N	Me	Et	1578	140
Ph	Ph	Cl	1593	18
^tBu	^tBu	Cl	1664	18

Table 1.11

Azomethine stretching frequencies (cm^{-1}) of tris(methyleneamino)alanes

Compound	ν(C=N)	Ref
$(Ph_2C{:}N)_3Al$	1686	18
$(^tBu_2C{:}N)_3Al$	1703	a

(a) This work

Reactions. The $(AlN)_2$ rings of dimeric methyleneaminoalanes appear to resist cleavage by donor molecules. Diphenylmethyleneaminodichloroalane, $[Ph_2C{:}NAlCl_2]_2$, is unaffected by pyridine below 100°, but in boiling toluene disproportionation apparently occurs, as the adduct $AlCl_3$.py can be isolated from the mixture (18).

Some aldiminoalanes have been found to react with a tenfold excess of nitriles to exchange the groups on nitrile and methyleneamine (Equation 1.46) (150).

$$Cl_nEt_{2-n}AlN{:}CHR^1 + R^2C{:}N \rightarrow Cl_nEt_{2-n}AlN{:}C(N{:}CHR^2)R^1 \rightarrow Cl_nEt_{2-n}AlN{:}CHR^2 + R^1C{:}N \qquad 1.46$$

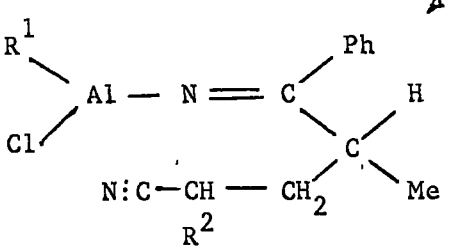
Amidines may be prepared from methyleneaminoalanes and nitriles as shown for example in equation 1.47 (138).

$$Et_2AlNEt_2 + PhC{:}N \rightarrow Et_2AlN{:}CPhNEt_2 \xrightarrow{\text{hydrolysis}} PhC(:NH)NEt_2 \qquad 1.47$$

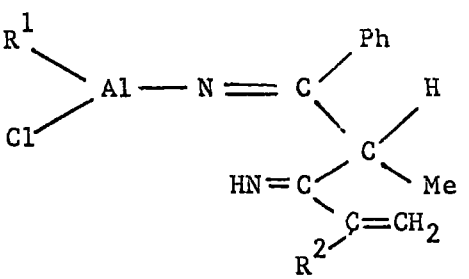
Reaction of phenylethylmethyleneaminoalanes with vinyl cyanides occurs as shown in equation 1.48

$$ClR^1AlN{:}CPhEt \; (R^1 = Et, Cl) \; + \; CH_2{:}CR^2C{:}N \; (R^2 = H, Me) \qquad 1.48$$

A



B



Reaction A involves addition of the C_α-H of the alane to the C=C bond in vinyl cyanide; reaction B involves addition to the C=N bond (151).

Gallium. Methyleneaminogallium species were first prepared by pyrolysis of triethylgallium-nitrile adducts (Equation 1.49, Table 1.12) (154).

$$R^1C{:}N + Et_3Ga \rightarrow R^1C{:}N.GaEt_3 \xrightarrow{\Delta} \tfrac{1}{2}[R^1HC{:}NGaEt_2]_2 + C_2H_4 \qquad 1.49$$

(R^1 = Ph, ^tBu)

Pyrolysis of adducts of trimethylgallium did not, however, afford methyleneaminogallanes (Table 1.12) (154). This preparation of aldiminogallanes is similar to that of their aluminium counterparts (124,126,128, 130).

Reaction between diphenylmethyleneamine and organogallium compounds also affords methyleneaminogallanes (Equation 1.50) (155).

$$Ph_2C{:}NH + R_3Ga \rightarrow Ph_2C{:}NH, GaR_3 \xrightarrow{100-120^\circ} RH + \tfrac{1}{2}[Ph_2C{:}NGaR_2]_2 \qquad 1.50$$

(R = Me, Et, Ph)

This route is analogous to that used to prepare corresponding boron (99) and aluminium (142,143,156) derivatives, although the ease of elimination of RH decreases in the sequence Al > Ga > B which is the sequence in which the M(δ+)-C(δ-) bond polarity decreases. This is in accord with the reverse order of electronegativity of these elements (B,2.01;Ga,1.82; Al,1.47 (50)).

Metathetical reactions between gallium trichloride and methyleneaminolithium reagents have also been used to prepare methyleneaminogallanes (Equation 1.51).

Table 1.12

Trialkylgallane-nitrile adducts

Adduct	Pyrolysis temp., °C	Products
$MeC{:}N.GaMe_3$	145	$CH_4 + [Me_2GaNC_2H_2]_n$
$^tBuC{:}N.GaMe_3$	150	$^tBuC{:}N + Me_3Ga$
$PhC{:}N.GaMe_3$	118	$Me_3Ga + Ph_3C_3N_3$
$^tBuC{:}N.GaEt_3$	158	$C_2H_4 + \frac{1}{2}[^tBuHC{:}NGaEt_2]_2$
$PhC{:}N.GaEt_3$	158	$C_2H_4 + \frac{1}{2}[PhHC{:}NGaEt_2]_2$

$$mR_2C{:}NLi + GaCl_3 \rightarrow {}^1/n[(R_2C{:}N)_mGaCl_{3-m}]_n \qquad 1.51$$

(m = 3, R = Ph, ^tBu (45)

m = 1, R = Ph (73) ^tBu (52))

When two equivalents of di-t-butylmethyleneaminolithium were used, tris(di-t-butylmethyleneamino)gallane was obtained (45). The reaction, probably involves a disproportionation similar to that observed for related aluminium (R = Ph (18), ^tBu (52)) and boron (R = Ph (21)) compounds.

Gallium trichloride treated with four and five molar equivalents of di-t-butylmethyleneaminolithium afforded $LiGa(N{:}C^tBu_2)_4$ and $Li_2Ga(N{:}C^tBu_2)_5$ respectively. Conductimetric titration confirmed their existence in solution (45).

Structure. Molecular weight determinations have shown that the monomethyleneaminogallanes are dimeric. Comparison of their azomethine stretching frequencies (Table 1.13) with those of related dimeric aluminium and boron compounds suggest that the structure of the methyleneaminogallanes is similar, with planar four-membered $(GaN)_2$ rings (Figure 1.18.a).

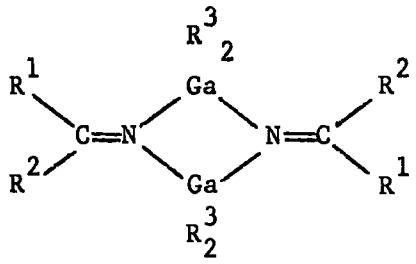
The high azomethine stretching frequencies observed for the monomeric tris-(di-t-butyl-) and -(diphenyl-methyleneamino)gallanes suggest that the structure is planar, with significant N → Ga dative π-bonding (Figure 1.18.b), but the presence of other absorptions in the region appropriate for bridging methyleneamino groups presents an inconsistency. Only a single absorption is observed for all the t-butyl groups is observed in the ^1H n.m.r. spectrum of $(^tBu_2C{:}N)_3Ga$, and this evidence supports a planar structure with terminally-attached imino groups which are

Table 1.13

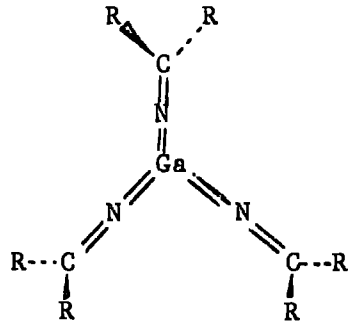
Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of methyleneaminogallanes

Compound	ν(C=N)	Ref
$[PhHC{:}NGaEt_2]_2$	1688, 1633	154
$[^tBuHC{:}NGaEt_2]_2$	1658	154
$[Ph_2C{:}NGaMe_2]_2$	1626	155
$[Ph_2C{:}NGaEt_2]_2$	1613	155
$[Ph_2C{:}NGaPh_2]_2$	1612	155
$[Ph_2C{:}NGaCl_2]_2$	1591	73
$[^tBu_2C{:}NGaCl_2]_2$	1647	52
$(Ph_2C{:}N)_3Ga$	1645, 1620	45
$(^tBu_2C{:}N)_3Ga$	1672, 1653sh, 1613	45
$LiGa(N{:}C^tBu_2)_4$	1673, 1649, 1629, 1616	45
$Li_2Ga(N{:}C^tBu_2)_5$	1670, 1656sh, 1626sh, 1612	45

Figure 1.18



(a)



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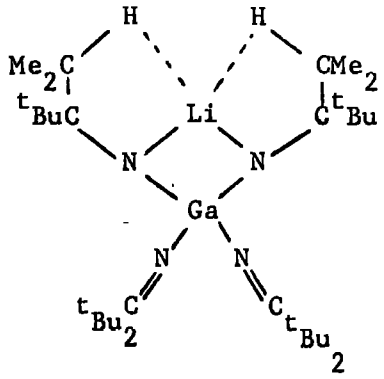

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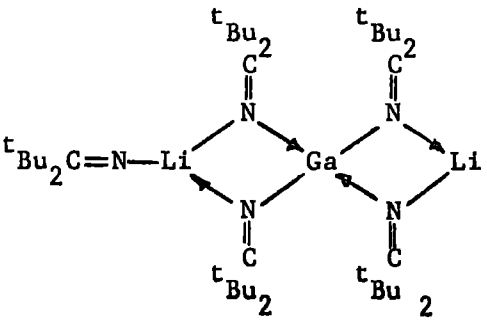

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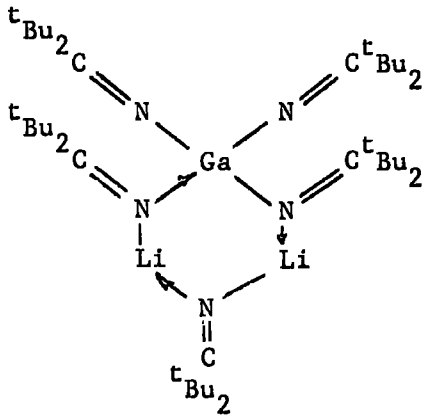


(e)

magnetically equivalent.

Lithium tetrakis(di-t-butylmethyleneamino)gallate, $LiGa(N{:}C^tBu_2)_4$, is probably isostructural with its aluminium counterpart (40) (Figure 1.18.c). The structures for $Li_2Ga(N{:}C^tBu)_5$ shown in figure 1.18.d and e are consistent with its I.R. spectrum which suggests the presence of both bridging and terminal imino groups, but not with its ^1H n.m.r. spectrum, where two absorptions of equal intensity were observed.

Group IV.

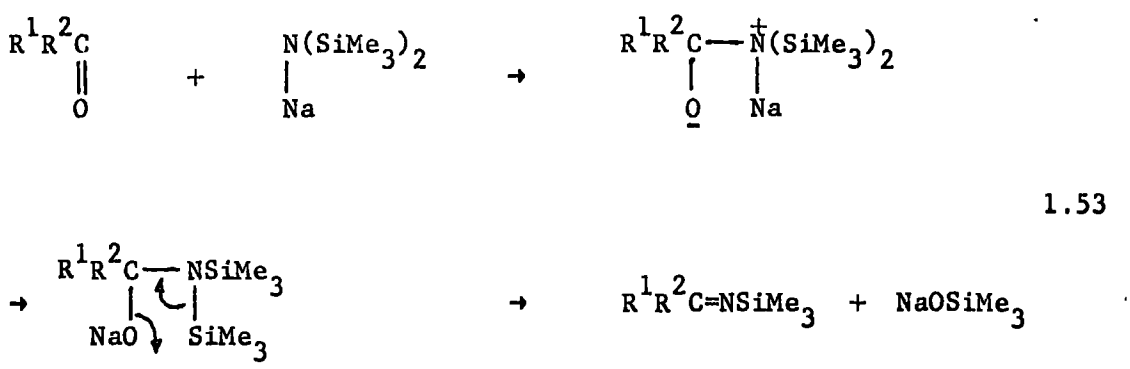
Silicon. Several methods have been used to prepare methyleneaminosilanes.

Insertion reactions of nitriles into silicon-nitrogen and silicon-hydrogen bonds have been used in the preparation of methyleneaminosilanes (Equation 1.52)

$$R^1C{:}N + R^2SiX_3 \rightarrow R^1R^2C{:}NSiX_3 \qquad 1.52$$

(R^1 = Ph, R^2 = H (157), R^1 = OR, R^2 = NR_2, NHR, $NHSiMe_3$, $NMeSiMe_3$ (158))

The reaction between sodium bis(trimethylsilyl)amide, $NaN(SiMe_3)_2$ and non-enolisable carbonyl species also afford methyleneaminosilanes (Equation 1.53).



1.53

($R^1R^2C{=}O$ = aldehyde or ketone (159), R^1 = Ph, R^2 = $OSiMe_3$, OCOPh, $NHSiMe_3$ (160), R^1 = Cl, R^2 = Ph, C_5H_4N, ^tBu, OMe, OEt (161))

Metathetical reactions of halosilanes and methyleneaminolithium compounds have been used to prepare methyleneaminosilanes (Equation 1.54)

$$nR^1R^2C{:}NLi + R^3_{4-m}SiCl_m \rightarrow (R^1R^2C{:}N)_nSiR^3_{4-m}Cl_{m-n} + nLiCl \quad 1.54$$

(n = 1-3, R^1 = R^2 = alkyl, aryl; R^3 = alkyl, aryl (45-47,52,60,162,163)

n = 1-4. R^1 = R^2 = CF_3, R^3 = Me (48,164)

n = 1, R^1, R^2 = alkyl, aryl, R^3 = NR_2, OR (60), alkyenyl (52,60)

n = 1, R^1 = Ph, R^2 = NR^4R^5 (165))

When R^1 or R^2 have C_α-hydrogen atoms imine - enamine tautomerisation (23) results in a mixture of products (60). Ligand isomerisation can also occur in amino(methyleneamino) compounds (Figure 1.19) (165).

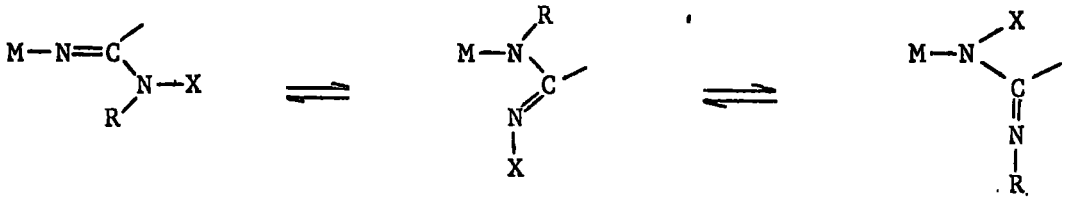


Figure 1.19

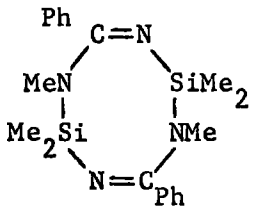
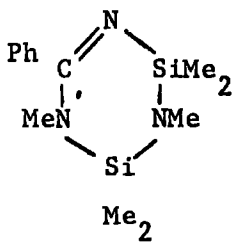
Di-p-tolylmethyleneaminotrimethylsilane has been prepared by reaction between di-p-tolylmethyleneamine and dimethylaminotrimethylsilane (Equation 1.55) (60).

$$(p\text{-tolyl})_2C{:}NH + Me_2NSiMe_3 \rightarrow (p\text{-tolyl})_2C{:}NSiMe_3 \rightarrow Me_2NH \quad 1.55$$

The stability of methyleneaminochlorosilanes, $(R^1_2C{:}N)_nSiR^2_{4-m}Cl_{m-n}$, to disproportionation varies with m and R^1. Diphenylmethyleneaminodichloro-

methylsilane, ($Ph_2C{:}NSiMeCl_2$) and diphenylmethyleneaminotrichlorosilane, ($Ph_2C{:}NSiCl_3$) could not be isolated from appropriate reaction mixtures: $(Ph_2C{:}N)_2SiMeCl$ and $(Ph_2C{:}N)_2SiCl_2$ respectively were obtained (162). However, all the di-t-butylmethyleneaminosilanes, $^tBu_2C{:}NSiMe_nCl_{3-n}$ (n = 0-3) have been isolated (162). Diphenylmethyleneaminochlorodimethylsilane $(Ph_2C{:}N)SiMe_2Cl$ has been isolated and characterised but it slowly disproportionates at room temperature, forming $(Ph_2C{:}N)_2SiMe_2$ (60).

Bis- (60,162), tris- (60) and tetrakis- (47) diphenyl- and bis- and tris-di-p-tolyl- (46) methyleneaminosilanes have been prepared, but the di-t-butylmethyleneaminosilanes, $^tBu_2C{:}NSiMe_nCl_{3-n}$ (n = 0-2) will not undergo further substitution of chlorine (162).

Other specific reactions have been used to prepare several other methyleneaminosilanes: $Me_3SiN{:}C(OSiMe_3)R$; R = Ph (166), $CH_2{:}CH$ (167) and cyclic compounds  and  (168).

Structure. With the exception of the cyclic compounds shown above, methyleneaminosilanes are monomeric. Azomethine stretching frequencies for some selected compounds are given in table 1.14.

Diarylmethyleneamino silanes are thought to have a bent Si-N-C skeleton (Figure 1.20.a) on the basis of their U.V. spectra, and low azomethine stretching frequency (60). However, some degree of $p\pi \rightarrow d\pi$ dative bonding is still possible in bent Si-N-C systems (19), and this

Table 1.14

Azomethine stretching frequencies,

ν(C=N) (cm^{-1}), of some methyleneaminosilanes.

Compound	R = Ph	R = ^{t}Bu	R = CF_3
$R_2C{:}NSiMe_3$	1642	1735	1765
$R_2C{:}NSiMe_2Cl$	1660, 1653	1736	
$R_2C{:}NSiMeCl_2$		1736	
$R_2C{:}NSiCl_3$		1729	
$(R_2C{:}N)_2SiMeCl$	1645, 1630		
$(R_2C{:}N)_2SiCl_2$	1656		
$(R_2C{:}N)_2SiMe_2$			1770
$(R_2C{:}N)_3SiMe$			1774
$(R_2C{:}N)_4Si$			1786

is indicated by an azomethine stretching frequency higher rather than lower than that of the parent imine.

Di-t-butylmethyleneaminosilanes however have higher azomethine stretching frequencies, and their ^1H n.m.r. spectra have only one absorption due to the t-butyl groups, indicating that they may contain effectively linear Si-N-C units (Figure 1.20.b) (45,52,162).

Germanium, tin and lead. Methyleneamino derivatives of germanium, tin and lead have been prepared by metathetical reactions between iminolithium and appropriate metal halides (Equations 1.56 and 1.57)

$$nR^1R^2C{:}NLi + R^3_{4-n}MCl_n \rightarrow (R^1R^2C{:}N)_nMR^3_{4-n} + nLiCl \qquad 1.56$$

($R^1 = R^2 = {}^tBu$, p-tolyl, CF_3; R^3 = Me; M = Sn; n = 1 (169);

$R^1 = R^2 = CF_3$; R^3 = Me; M = Ge, Sn; n = 1 - 4 (48);

$R^1 = R^2$ = Ph; n = 1; R^3 = Ph; M = Ge, Sn, Pb, R^3 = Me;

M = Ge, Sn (60);

R^1 = Ph; $R^2 = NMe_2$; n = 1, R^3 = Me, M = Ge, Sn; Sn; R^2 = $NMeSiMe_3$; M = Ge, Sn, Pb (165))

$$nR^1{}_2C{:}NLi + GeX_4 \rightarrow (R^1{}_2C{:}N)_nGeX_{4-n} + nLiX \qquad 1.57$$

(X = Br; n = 4; R^1 = Ph, p-tolyl; X = Cl; n = 3; R = ^tBu;

$R^1 = {}^tBu$; n = 2; X = Br, Cl; n = 1; X = Br (46))

Higher substitution of the bulky imino groups is observed at germanium than at silicon (e.g. Three $^tBu_2C{:}N$- ligands can be accommodated round germanium (46), but only one such ligand can be attached to silicon (162)). This is attributed to the greater covalent radius of germanium (122 pm) than silicon (111 pm) (49).

Several compounds have been prepared by insertion of nitriles into metal-nitrogen and -oxygen bonds (Equation 1.58).

$$R^1C{:}N + R^2MR^3_3 \rightarrow R^1R^2C{:}NMeR^3_3 \qquad 1.58$$

(R^1 = Ph; M = Sn, R^2 = NMe_2, R^3 = Me; (170,171);

M = Pb, R^2 = NEt_2 R^3 = Bu (172);

R^1 = CCl_3 M = Sn, R^2 = OMe (173);

M = Pb, R^2 = OMe, $OPbPh_3$ (174))

Structure. All these compounds are monomeric. The azomethine stretching frequency of some methyleneamino derivatives of these Group 1V elements are given in table 1.15.

The diphenyl- and bis(trifluouromethyl)-methyleneamino derivatives are thought to have a bent C-N-M skeleton as their I.R. and U.V. spectra are similar to those of their silicon counterparts. The di-t-butylmethyleneamino derivatives may have a linear structure, as they exhibit azomethine stretching frequency rather higher than those of the corresponding diaryl compounds, and only one signal is observed in their ^1H n.m.r. spectra, but evidence for this structure is not conclusive, since the spectrum of p-$CF_3C_6H_4$(Ph)C:$NGeMe_3$ shows a singlet at room temperature, which splits into a doublet below -110°, indicating that the compound has a non-linear C-N-Ge unit with non-equivalent t-butyl groups (59).

Reactions. Methyleneamino(trimethyl)stannanes react with protic acids as shown in equation 1.59 (169)

$$Me_3SnN{:}CR_2 + HA \rightarrow Me_3SnA + HN{:}R_2 \qquad 1.59$$

(A = OH, N^nBu_2, PhC:C, C_6F_5)

Transition metal hydrides may also react in this way, but other products are sometimes formed and this suggests that the mechanisms of the reactions differ.

Table 1.15

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some methyleneamino derivatives of germanium and tin $(R_2C{:}N)_nM_{4-n}$

Compound	R			
	Ph	CF_3	^tBu	p-tolyl
$R_2C{:}NGeMe_3$	1630	1730		
$R_2C{:}NSnMe_3$	1613	1720		1611sh, 1596
$R_2C{:}NGePh_3$	1633			
$R_2C{:}NSnPh_3$	1613			
$R_2C{:}NGeBr_3$			1624	
$(R_2C{:}N)_2GeMe_2$		1730		
$(R_2C{:}N)_2SnMe_2$		1719		
$(R_2C{:}N)_2GeCl_2$			1645	
$(R_2C{:}N)_2GeBr_2$			1646	
$(R_2C{:}N)_3GeMe$		1733		
$(R_2C{:}N)_3ShMe$		1717		
$(R_2C{:}N)_3GeCl$			1652	
$(R_2C{:}N)_4Ge$	1661	1730		1651
$(R_2C{:}N)_4Sn$		1717		

Methyleneaminostannanes can be used to prepare imino derivatives of transition metals (Equation 1.60) (169).

$$Me_3SnN{:}CR_2 + ClML \rightarrow LMN{:}CR_2 + Me_3SnCl \qquad 1.60$$

These compounds will be discussed later.

Methyleneaminostannes also react with unsaturated species: the reaction is catalysed by the free imine probably formed by hydrolysis of the starting material by traces of moisture. (Equation 1.61) (169).

$$\begin{array}{ccccc} Me_3SnN{:}CR_2 & + & X{:}Y & \rightarrow & Me_3Sn\text{-}X\text{-}Y\text{-}N{:}CR_2 \\ H_2O \downarrow & & & & \uparrow\ Me_3SnN{:}CR_2\ (-HN{:}CR_2) \\ HN{:}CR_2 & & & \rightarrow & HX\text{-}Y\text{-}N{:}CR_2 \end{array} \qquad 1.61$$

(X, Y = PhNCO, CH_2CHCN; R = Ph, CF_3)

Bis(trifluoromethyl)methyleneamino(trimethyl)stannane reacts with bromine to give the bromo-stannane and -imine (Equation 1.62) (169).

$$(CF_3)_2C{:}NSnMe_3 + Br_2 \rightarrow (CF_3)_2C{:}NBr + Me_3SiBr \qquad 1.62$$

Reactions of methyleneamino-germanium and -lead compounds have apparently not been investigated.

Group V.

Phosphorus. Diphenylmethyleneaminophosphines were first prepared from chlorophosphines and the parent ketimine (Equation 1.63) (176).

$$PX^1X^2Cl + R^1R^2C{:}NH \xrightarrow{Et_3N} X^1X^2P{:}NCR^1R^2 + Et_3N.HCl \qquad 1.63$$

(X^1 = Cl, Me, Ph; X^2 = Cl, Me, Ph, OMe;
R^1 = Ph, OEt; R^2 = Ph, OMe, OEt)

Metathetical reactions between methyleneaminolithiums and chlorophosphines also result in methyleneaminophosphines (Equations 1.64 and 1.65).

$$nR^1{}_2C{:}NLi + R^2{}_{3-n}PCl_n \rightarrow (R^1{}_2C{:}N)_nPR^2{}_{3-n} + nLiCl \qquad 1.64$$

($n = 1$, $R^2 = Ph$, $R^1 = {}^tBu$ (46,52) $R^1 = Ph$, p-tolyl (46)

$R^2 = Cl$, $R^1 = Ph$, p-tolyl (46).

$n = 3$, $R^2 = Cl$, $R^1 = Ph$, p-tolyl (46), $R^1 = CF_3$ (164))

$$nR_2C{:}NLi + POCl_3 \rightarrow OPCl_{3-n}(N{:}CR^1{}_2)_n + nLiCl \qquad 1.65$$

($R = Ph$, p-tolyl, t-Bu; $n = 1 - 3$ (46))

Reaction between $((CF_3)_2C{:}N)_3P$ and chlorine or oxygen afforded tris-(imino)phosphorus^{V} compounds (Equation 1.66) (164).

$$((CF_3)_2C{:}N)_3P^{III} + X_2 \rightarrow ((CF_3)_2C{:}N)_3P^{V}X_2 \qquad 1.66$$

Structure. The low azomethine stretching frequencies quoted for methyleneaminophosphines (Table 1.16) (46,52) indicate that their P-N=C skeletons are bent. The frequencies are similar to those for related silanes which are thought to have non-linear Si-N-C units (60). ^{31}P n.m.r. spectra have been recorded and interpreted for some methyleneaminophosphines (46).

Reactions. Methyleneaminophosphines are both electrophilic (at carbon) and nucleophilic (at phosphorus).

Some methyleneaminophosphorus^{III} compounds react with sulphur to give phosphorus^{V} compounds (Equation 1. 67) (177)

$$Ph_2P{:}NCR^1R^2 + S \rightarrow Ph_2P(S)N{:}CR^1R^2 \qquad 1.67$$

($R^1 = Ph$, $R^2 = Ph$, OMe, OEt, $R^1 = R^2 = OEt$.)

Reactions with methyl iodine yields ionic products (Equation 1.68)

$$PN{:}CR^1R^2 + MeI \rightarrow X^1X^2\overset{+}{P}MeN{:}CR^1R^2\bar{I} \qquad 1.68$$

($X = Ph$, Me, Cl; $R^1 = R^2 = Ph$, OEt; $R^1 = Ph$, $R^2 = OMe$, OEt)

Table 1.16

Azomethine stretching frequencies $\nu(C{=}N)$ (cm^{-1}) of some methyleneamino derivatives of phosphorus $(R_2C{:}N)_nPX_{3-n}$ and $(R_2C{:}N)_nPOX_{3-n}$

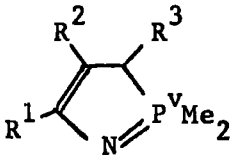
Compound	R			
	Ph	CF_3	^tBu	p-tolyl
$R_2C{:}NPCl_2$	1650		1678	1630
$R_2C{:}NPPh_2$	1608		1647	1612
$(R_2C{:}N)_3P$	1607	1717		1612
$(R_2C{:}N)_3PO$	1619	1750	1670	1620
$(R_2C{:}N)_2POCl$	1660		1667	1618
$R_2C{:}NPOCl_2$	1650		1655	1607
$(R_2C{:}N)_3PCl_2$		1742		

Some of these ionic compounds lose alkyl iodide on heating (Equation 1.69) (176).

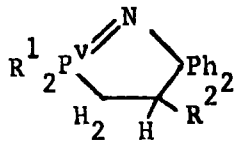
$$Ph_2MeP\overset{+}{N}:CR^1R^2\bar{I} \xrightarrow{\Delta} Ph_2PN:C(R^2)(Me) + R^1I \qquad 1.69$$

(R^1 = Ph, OEt, R^2 = alkoxy)

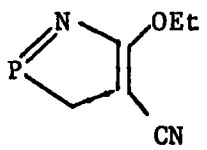
Reactions of methyleneaminophosphines with unsaturated species yield heterocyclic products in which the oxidation state of phosphorus may be 111 or V (Equations 1.70 - 1.74).

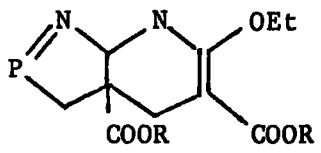
$$Me_2PN:CR^1OMe + R^2CH:CHR^3 \rightarrow$$  1.70 (178)

(R^1 = Ph, OEt; R^2 = CN, COMe, COPh, COCH:CHPh, COOMe, COOEt; R^3 = H, Me, Ph)

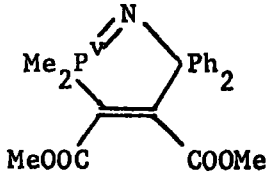
$$R^1{}_2PN:CPh_2 + CH_2C:CHR^2 \rightarrow$$  1.71 (179)

(R^1 = Ph, Me, OMe; R^2 = CN, COOMe)

$$Ph_2PN:C(OEt)_2 + CH_2:CHCN \rightarrow$$  1.72 (177)

$$Ph_2PN:C(OEt)_2 + CH_2:CHCOOR \rightarrow$$  1.73 (177)

Ring compounds are also formed by reaction with acetylenedicarboxylates (Equation 1.74) (179).

$$Me_2PN:CPh_2 + MeOOC\text{-}C{:}C\text{-}COOMe \rightarrow$$  1.74

Arsenic. Tris(hexafluoromethylmethyleneamino)arsenic has been prepared from $AsCl_3$ and $(CF_3)_2C{:}NLi$ (Equation 1.75) (164).

$$AsCl_3 + 3(CF_3)_2C{:}NLi \rightarrow ((CF_3)_2C{:}N)_3As + 3LiCl \qquad 1.75$$

Its azomethine stretching frequency is observed at 1710 cm^{-1}

Transition Metals. The work described in this thesis is concerned with methyleneamino derivatives of main group metals and metalloids, but for completeness a brief summary of transition metal derivatives is given in this survey.

Preparation. Metathetical reactions between methyleneamino-lithium, -silicon or -tin compounds and transition metal halides afford imino derivatives of transition metals (Equation 1.76).

$$L_nMX + R^1R^2C{:}NY \rightarrow L_nMN{:}CR^1R^2 + XY \qquad 1.76$$

The following compounds have been prepared in this way:

π-$C_5H_5M(CO)_2N{:}CR^1R^2$ M = Mo, W; $R^1 = R^2 = {}^tBu$ (180), p-tolyl (181), Ph (182), p-$CF_3C_6H_4$, p-$MeOC_6H_4$ (183); R^1 = Ph, $R^2 = {}^tBu$ (184) p-tolyl (183) M = Mo, $R^1 = R^2 = {}^tBu$ (185).

$(\pi$-$C_5H_5)_2M(Cl)N{:}CR^1R^2$ M = Ti, Zr; $R^1 = R^2$ = Ph, ^tBu (186); M = Ti, $R^1 = R^2 = CF_3$ (187, 188), p-tolyl (186), R^1 = Ph, R^2 = Me (186).

$[(\pi$-$C_5H_5)_2M(CO)N{:}CPh_2]_2$ M = Mo, W (182).

π-$C_5H_5MoCO(Ph_3P)N{:}C^tBuPh$ (184).

π-$C_5H_5MCOI_2(N{:}C^tBuPh)$ M = Mo, W (184).

π-$C_5H_5Fe(CO)N{:}C^tBu_2$ (190).

$Fe(CO)_3N{:}C^tBuPh$ (190)

cis-$(X_2PhP)_2$ $Pt(Cl)N{:}CR_2$ R = CF_3, X = Ph (187, 188), Me (187), X = Ph, R = Ph (188).

trans-$(X_2PhP)_2Pt(Y)N{:}C(CF_3)_2$ Y = H, X = Ph, Me (187); Y = $SnMe_3$; X = Ph (188)

$(Me_2PhP)_2PtN{:}C(CF_3)_2$ (187).

$(Ph_3P)_3RhN{:}C(CF_3)_2$ (187).

$(^tBu_2C{:}N)_2NiL^1L^2L^1L^2$ = various fluorocarbons (189).

$Fe_2(CO)_6INC{:}R^1R^2R^1$ = R^2 = Ph, p-tolyl; R^1 = Ph, R^2 = ^tBu (190).

$[Fe_2(CO)_6N{:}CR_2]_2$ R = Ph, p-tolyl (191).

$Mn(CO)_4N{:}CPh_2$ (187).

Other methods have been used to prepare various other transition metal methyleneamino derivatives. Two examples are given in equations 1.77 and 1.78. (192).

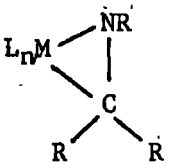
$$trans\text{-}[ReCl_3(NMe)(PPh_2R)_2] + 2py \rightarrow ReCl_2(N{:}CH_2)py(PPh_2R)_2 + py.HCl \quad (R = Ph, Me, Et) \qquad 1.77$$

$$trans\text{-}[ReCl_3(NMe)(PMe_2Ph)_2] + PMe_2Ph + NEt_3 \rightarrow ReCl_2(N{:}CH_2)(PMe_2Ph)_3 + NEt_3.HCl \qquad 1.78$$

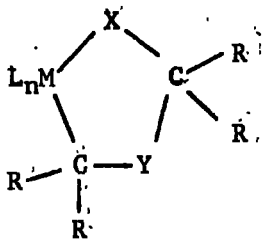
In general, the interest in these compounds has been the influence of the methyleneamino groups on other ligands bonded to the metal.

Crystallographic studies have shown that in $\pi\text{-}C_5H_5Mo(CO)_2N{:}C^tBu_2$ the C-N-Mo skeleton is effectively linear (CNMo angle $\sim 172^o$) (39) while in $Fe_2(CO)_6INCPh_2$ (190) and $[Fe_2(CO)_6N{:}C(p\text{-tolyl})_2]_2$ (191) the methyleneamino groups bridge between the metal atoms.

Methyleneamines and their derivatives also react with transition metal compounds to form three- or five-membered ring structures (188, 199, 200) (Figures 1.21.a and 1.21.b respectively), or may form aza-allyl, -allene, or -olefine derivatives of the transition metal (Figures 1.21.c - e respectively) (181, 182, 187, 193 - 200).



(a)



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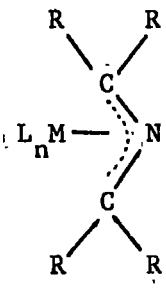

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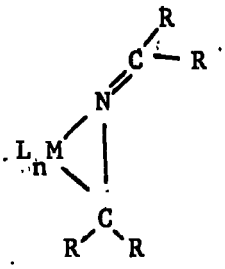

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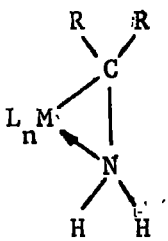


(e)

Figure 1.21

Chapter 2

Methyleneamino derivatives of boron

This chapter describes the preparation and properties of a series of new di-t-butylmethyleneaminoboranes, $^{t}Bu_2C{:}NBXY$ Aspects of their I.R., ^{11}B n.m.r., ^{1}H n.m.r. and mass spectra are discussed and compared with those of other similar compounds.

1. Experimental.

(a) Preparation of bis(di-t-butylmethyleneamino)fluoroborane, $(^{t}Bu_2CN)_2BF$.

A solution of 20 mmole di-t-butylmethyleneaminolithium in 20 ml. hexane was prepared and added to a solution of boron trifluoride diethyl etherate (2.84 g, 20 mmole) in 20 ml hexane at -196°. The solution was allowed to warm to room temperature with stirring. Lithium fluoride began to precipitate out of the mixture at ~ -20°. The mixture was stirred for 2 hours, then solvent was removed. The off-white solid residue was extracted with pentane, and the lithium fluoride filtered off. White, needle-shaped crystals (m.p. 70-72°, subl. 90-110°, 0.05 mm Hg) were obtained by refridgerating the filtrate at -15° for several hours. The crystals were identified as monomeric bis(di-t-butylmethyleneamino-fluoroborane, $(^{t}Bu_2C{:}N)_2BF$.

(Found: C, 69.93; H, 11.72; B, 3.22; F, 6.24; N, 9.17%; M, 306. $C_{18}H_{36}N_2BF$ requires C, 69.672; H, 11.964; B, 3.484; F, 6.122; N, 9.028%; M, 310.310).

ν_{max} (contact film) 2960s, 2932s, 2878s, 1750s, 1487s, 1465m, 1394s, 1373s, 1320s, 1291s, 1262s, 1210m, 1136w, 1048m, 10302, 971s, 937w, 870w, 837m, 643m, 604m, 540w cm^{-1}.

A similar reaction between di-t-butylmethyleneaminolithium and

boron trifluoride (uncoordinated) also gave the bis(imino)fluoroborane, $(^tBu_2C{:}N)_2BF$.

(b) Attempts to prepare di-t-butylmethyleneaminodifluoroborane, $^tBu_2C{:}NBF_2$.

(i) Reaction between equimolar proportions of boron trifluoride diethyl etherate and di-t-butylmethyleneaminolithium.

A solution of 20 mmole di-t-butylmethyleneaminolithium was prepared and added to a solution of boron trifluoride diethyl etherate (2.84 g, 20 mmole) in 20 ml hexane at -196°. The mixture was allowed to warm up, with stirring. At ~ -20° a white precipitate was formed. The mixture was stirred at room temperature for several hours. Solvent was removed and the residue was extracted with hexane, giving an off-white solid and a very pale yellow solution. The crystals obtained from the solution were identified (by I.R. spectrum and elemental analysis) as bis(di-t-butylmethyleneamino)-fluoroborane, $(^tBu_2C{:}N)_2BF$. The off-white residue was shown (by flame test) to contain boron and lithium, and its I.R. spectrum suggested the presence of lithium tetrafluoroborate.

(ii) Reaction between boron trifluoride diethyl etherate and di-t-butylmethyleneaminolithium.

(Mole ratio 2:1; see Discussion (Section 2) for reasons for this and subsequent mole ratios).

A solution of 20 mmole di-t-butylmethyleneaminolithium in 30 ml hexane was added to a solution of boron trifluoride diethyl etherate (5.68 g, 40 mmole) in 30 ml hexane at -196°. The mixture

was treated as in the experiment above. Again, the product obtained was bis(di-t-butylmethyleneamino)fluoroborane, $(^tBu_2C{:}N)_2BF$.

(iii) Reaction between boron trifluoride and di-t-butylmethyleneaminolithium (mole ratio 1:1).

Boron trifluoride (3.39 g, 50 mmole) was condensed onto a solution of 49.5 mmole di-t-butylmethyleneaminolithium in 200 ml hexane at -196° in vacuo. The mixture was warmed to room temperature and stirred overnight. The evacuated flask was let down to an atmosphere of nitrogen, and the mixture was treated as in the previous experiments. Bis(di-t-butylmethyleneamino)-fluoroborane was obtained as a crystalline solid, and the amorphous residue was again shown to contain lithium tetrafluoroborate.

(iv) Reaction between boron trifluoride and di-t-butylmethyleneaminolithium (mole ratio 2:1)

Boron trifluoride (2.71 g, 40 mmole) was condensed onto a solution of 20 mmole di-t-butylmethyleneaminolithium in 100 ml hexane at -196° in vacuo. The mixture was warmed to room temperature and stirred overnight. The evacuated flask was refilled with nitrogen. An I.R. spectrum of the colourless solution showed an absorption at 1750 cm^{-1}, indicating the presence of bis(di-t-butylmethyleneamino) fluoroborane, which was not isolated.

(v) Reaction between di-t-butylmethyleneaminolithium and excess boron trifluoride.

A solution of di-t-butylmethyleneaminolithium (22 mmole) was

prepared in 80 ml pentane, and frozen to -196°. Boron trifluoride (67.8 g, 90 mmole) was condensed onto this. The mixture was allowed to melt, then stirred and slowly warmed to room temperature. An I.R. spectrum of the solution showed bands in the region appropriate for C=N⇒B stretch at 1796m and 1750s cm^{-1} attributed to mono- and bis-(imino)fluoroborane, $^{t}Bu_2C{:}NBF_2$ and $(^{t}Bu_2C{:}N)_2BF$, respectively. The solution was again frozen to -196° and more BF_3 (2.71 g, 40 mmole) was added. The mixture was warmed as before, and an I.R. spectrum of the solution run. Peaks were observed at the same frequencies, but their relative intensities were reversed (i.e. 1796s, 1750m). Boron trifluoride was bubbled through the stirred solution at room temperature for ~4 hours. An I.R. spectrum of the yellow solution showed only one absorption in the C=N⇒B stretching region, at 1796 cm^{-1}, attributed to <u>di-t-butylmethyleneaminodifluoroborane,</u> $^{t}Bu_2C{:}NBF_2$.

ν_{max} (Pentane solution) 1870w, 1796s, 1448s, 1406s, 1262m, 1138m, 1110w, 1066w, 1046m, 1027m, 971s, 917m, 908s, 867s, 800w, br, 764m, 725s, 652w, 631m, 616sh, 602sh, 534w, 509w, cm^{-1}.

Solvent was removed from the solution to give a clear yellow viscous liquid which was distilled at 100-110°, 0.2 mm Hg to give a clear pale yellow liquid which decomposed almost immediately to a white solid, identified by its I.R. spectrum as <u>bis(di-t-butylmethyleneamino)fluoroborane,</u> $(^{t}Bu_2C{:}N)_2BF$.

(vi) <u>Reaction between bis(di-t-butylmethyleneamino)fluoroborane and excess boron trifluoride.</u>

Boron trifluoride was bubbled through a solution of bis(di-t-butylmethyleneamino)fluoroborane (2.48 g, 8 mmole) in 60 ml toluene for

~ 2 hours. This orange-yellow solution was used to obtain the n.m.r. spectral data for di-t-butylmethyleneaminodifluoroborane, $^{t}Bu_2C{:}NBF_2$. Attempted purification by distillation of the liquid obtained after solvent was removed was unsuccessful.

(c) Attempts to prepare tris(di-t-butylmethyleneamino)-borane, $(^{t}Bu_2C{:}N)_3B$.

(i) Reaction between boron trifluoride diethyl etherate and di-t-butylmethyleneaminolithium (mole ratio 1:3).

A solution of boron trifluoride diethyl etherate (2.84 g, 20 mmole) in 80 ml toluene was added to a solution of 60 mmole di-t-butylmethyleneaminolithium in 20 ml toluene at -196°. The mixture was warmed to room temperature and stirred for several hours. An I.R. spectrum of the yellow solution obtained showed an absorption at 1735 cm^{-1} attributed to the required product. Absorptions at 1608 and 1750 cm^{-1} indicated the presence of di-t-butylmethylene-aminolithium and bis(di-t-butylmethyleneamino)fluoroborane respectively. The solution was refluxed for 4 days, after which the I.R. spectrum showed absorptions at 1735 and 1608 cm^{-1} suggesting the presence of tris(di-t-butylmethyleneamino)borane, and di-t-butylmethyleneamino-lithium. Attempts to isolate the tris(imino) borane afforded moist yellow crystals, which showed an I.R. absorption at 1735 cm^{-1} attributed to $\nu(C{=}N{\rightarrow}B)$, but elemental analyses of these crystals were unsatisfactory. Sublimation of these crystals yielded a very small quantity of moist yellow sublimate (Principal ν_{max} at 1800 and 1745 cm^{-1}) which was not identified, and a white residue (Principal ν_{max} at 1735 cm^{-1}) probably impure $(^{t}Bu_2C{:}N)_3B$.

(ii) Reaction between boron trifluoride diethyl etherate and di-t-butylmethyleneaminolithium (mole ratio 4:3).

Boron trifluoride diethyl etherate (5.68 g, 40 mmole) was added to a solution of 30 mmole di-t-butylmethyleneaminolithium in 40 ml petroleum ether (100-120°) at -196°. The mixture was warmed to room temperature and stirred overnight. An I.R. spectrum of the cloudy, pale yellow liquid showed absorptions at 1750 and 1608 cm^{-1} due to bis(imino)fluoroborane and iminolithium respectively. The mixture was refluxed for 36 hours. I.R. spectra run at regular intervals indicated the gradual formation of the required product. After a further 12 hours' refluxing the spectrum showed a decrease in tris(imino)borane concentration and an increase in that of the bis(imino)fluoroborane. Only bis(di-t-butylmethyleneamino)fluoroborane could be isolated from this mixture.

(iii) Reaction between bis(di-t-butylmethyleneamino)fluoroborane and di-t-butylmethyleneaminolithium.

A solution of di-t-butylmethyleneaminolithium (3.55 mmole) in 25 ml 100-120° pet. ether was added to a frozen solution of bis(di-t-butylmethyleneamino)fluoroborane (1.101 g, 3.55 mmole) in 25 ml 100-120° pet. ether at -196°. The solution was allowed to warm to room temperature and stirred. An I.R. spectrum of the solution showed that the starting materials were unchanged. The solution was refluxed for 36 hours, then solvent was removed and replaced with hot pentane. The solution was filtered, concentrated, then refridgerated at -15°. Colourless, chunky crystals were formed. These were identified as tris(di-t-butylmethyleneamino)-borane, $(^tBu_2C{:}N)_3B$, m.p. 84-86°, subl. 90-100°, 0.01 mm Hg.

(Found: C, 75.85; H, 11.14; B, 2.46; N, 9.42%; M, 446

$C_{27}H_{54}N_3B$ requires C, 75.14; H, 12.61, B, 2.51, N, 9.74%;

M, 431.53).

ν_{max} (KBr disc) 3004sh, 2988s, 2954s, 2912s, 2872m, 1788sh, 1763sh, 1730s, 1482s, 1456w, 1388m, 1366s, 1362s, 1253s, 1204w, 1169s, 1047m, 1026w, 965s, 934w, 833s, 636m, 583w, 522w, 413w cm^{-1}.

(d) Preparation of bis(di-t-butylmethyleneamino)borane, $(^tBu_2C{:}N)_2BH$.

A solution of bis(di-t-butylmethyleneamino)fluoroborane (6.21 g, 20 mmole) in 15 ml ether was added to a solution of lithium aluminium hydride (0.76 g, 20 mmole) in 60 ml ether frozen to -196°. The mixture was warmed to room temperature and stirred for 18 hours. The cloudy white suspension was filtered, then the filtrate was reduced to half its original volume. White needle-shaped crystals were obtained from this solution after refridgeration at -15°. These were isolated and identified as bis(di-t-butylmethyleneamino)-borane $(^tBu_2CN)_2BH$, m.p.80-82°.

(Found: C, 74.24; H, 12.93; B, 3.6; N, 9.54%; F, absent.

$C_{18}H_{37}N_2B$ requires C, 73.96; H, 12.76; B, 3.70; N, 9.58%)

ν_{max} (Nujol mull) 2502w, 2452m, 1760s, br, 1482s, 1376sh, 1366s, 1320m, 1290s, 1262m, 1240w, 1208m, 1095m, 1045s, 1020m, 968s, 933w, 832s, 800w, br, 640w, 608w, 547w, 518w cm^{-1}.

(e) Reaction between bis(di-t-butylmethyleneamino)fluoroborane and sodium borohydride.

A solution of bis(di-t-butylmethyleneamino)fluoroborane (7.91 g,

25.5 mmole) in 50 ml hexane was added to a solution of ~95% pure sodium borohydride (1.017 g, ~25.5 mmole) in 50 ml hexane at -196°. The mixture was warmed to room temperature and stirred for 18 hours. An I.R. spectrum of the reaction mixture showed that the starting materials were unchanged. The mixture was refluxed for 8 hours then filtered and recrystallised. Bis(di-t-butylmethyleneamino)-fluoroborane, identified by its I.R. spectrum, was obtained.

(f) Reaction between di-t-butylmethyleneaminodichloroborane and t-butyl lithium (mole ratio 1:2)

Di-t-butylmethyleneaminodichloroborane (5.64 g, 25.4 mmole), prepared as described in the literature (22), was added by syringe to a solution of t-butyl lithium in pentane (50.8 ml of a 1.0 M solution, 50.8 ml) frozen to -196°. The mixture was allowed to reach room temperature then refluxed for 18 hours. Lithium chloride was filtered off, and the solvent was removed to leave a clear yellow oil which was distilled at 100-120°, 0.05 mm Hg, and identified as di-t-butylmethyleneaminodi-t-butylborane, $^{t}Bu_2C{:}NB^{t}Bu_2$.

(Found C, 77.12; H, 13.82; B, 4.1; N, 5.16%

$C_{17}H_{36}BN$ requires C, 76.97; H, 13.68; B, 4.08; N, 5.28%)

ν_{max} (Liquid film) 2964s, 2942s, 2918sh, 2900sh, 2865s, 1812v.s, 1769w, 1755sh, 1488s, 1454sh, 1391s, 1385m, 1366s, 1362sh, 1302w, 1279m, 1210m.br, 1162w, 1086v.w, 1045m, 1029w, 1023m, 971s, 954s, 934w, 886w, 840m, 661w, 652w, 552w, 522w, 433w cm^{-1}.

(g) Preparation of bis(di-t-butylmethyleneamino)methylborane, $(^{t}Bu_2C{:}N)_2BMe$.

Methyl lithium (3.4 ml of a 2.2 m solution, 7.48 mmole) was

added to a frozen (-196°) solution of 7.43 mmole of bis(di-t-butylmethyleneamino)fluoroborane in 50 ml 100-120° pet. ether. The mixture was allowed to warm up. A white precipitate was formed at ~ -10°. The mixture was stirred at room temperature for ~ 2 hours. Solvent was removed and the white residue extracted with hot pentane. Lithium fluoride was removed by filtration. Removal of solvent from the filtrate left a pale yellow clear liquid identified as bis(di-t-butylmethyleneamino)methylborane, $(^tBu_2C{:}N)_2BMe$.

(Found: B, 3.5; N, 8.9%.

$C_{19}H_{39}BN_2$ requires B, 3.53; N, 9.15%)

ν_{max} (Liquid film) 2984sh, 2955s, 2920s, 2872m, 1745s, 1483s, 1460m, 1390s, 1368s, 1315sh, 1289s, 1261s, 1204m, 1101m, 1044s, 1030sh, 968s, 934m, 878sh, 869w, 836m, 823sh, 806m,br, 708w, br, 643m, 617sh, 605m, 538w cm^{-1}.

(h) Reaction between bis(di-t-butylmethyleneamino)fluoroborane and n-butyl- and t-butyl-lithium.

Solutions of n-butyl lithium (3.9 ml of a 2.54 m solution, 10 mmole) and t-butyl lithium (10 ml of a 1.0 m solution, 10 mmole) were added to solutions of bis(di-t-butylmethyleneaminofluoroborane (3.10 g, 10 mmole) in 100-120° pet. ether at -196°. The mixtures were allowed to reach room temperature and stirred overnight. No precipitate was observed in either solution. The solutions were refluxed for several days, after which they were allowed to cool and crystallise. Bis-(di-t-butylmethyleneamino)fluoroborane, identified by its I.R. spectrum, was recovered from both solutions.

(i) Reaction between triethylborane and di-t-butylmethyleneaminolithium (mole ratio 1:3)

A solution of triethylborane (102 ml of a 1.0 m solution, 102 mmole) was added to a solution of di-t-butylmethyleneamine (4.81 g, 34 mmole) in 40 ml ether. The mixture was warmed to room temperature and stirred overnight. The I.R. spectrum of the solution showed that the starting materials were unchanged. Toluene (~ 50 ml) was added, the ether was pumped off and the solution was refluxed for five days. The I.R. spectrum showed a large peak at 1814 cm^{-1} attributed to di-t-butylmethyleneaminodiethylborane (52), and a weak absorption at 1730 cm^{-1} attributed to tris(di-t-butylmethyleneamino)borane, and a large peak at 1604 cm^{-1} attributed to unchanged di-t-butylmethyleneamine. Solvent was removed, leaving a clear yellow viscous liquid. This was distilled at ~ 75°, ~ 0.005 mm Hg to give a clear colourless liquid identified by its I.R. spectrum as di-t-butylmethyleneaminodiethylborane $^{t}Bu_2C{:}NBEt_2$ The small amount of yellow residue was identified by its I.R. spectrum as impure tris(di-t-butylmethyleneamino)borane, $(^{t}Bu_2C{:}N)_3B$.

(j) Preparation of 2-di-t-butylmethyleneamino-1,3,2-benzodioxaborole, $^{t}Bu_2C{:}NB$ 

To a solution of 2-chloro-1,3,2-benzodioxaborole, (1.97 g, 12.8 mmole), prepared as described in the literature (54, 205) in hexane at -196° was added a solution of di-t-butylmethyleneaminolithium (13 mmole) in 25 ml hexane. The mixture was allowed to reach room temperature and stirred for ~ 1 hour. A white precipitate was formed in a colourless solution. Solvent was removed and the residue was

extracted with fresh hexane, from which white needles were obtained after refridgeration. These were identified as 2-di-t-butylmethylene-amino-1,3,2-benzodioxaborole, $^{t}Bu_2C{:}NB\langle^{O}_{O}\rangle C_6H_4$ m.p. 270-330° d. (Found: C, 69.77; H, 8.71; B, 4.4; N, 5.25%; M, 271. $C_{15}H_{22}BNO_2$ requires C, 69.52; H, 8.56; B, 4.17; N, 5.41; O, 12.31%; M 259.16).

ν_{max} (Nujol mull) 1780s, 1762sh, 1481s, 1417m, 1404w, 1352sh, 1344s, 1336sh, 1239s, 1125w, 1102w, 1082w, 1064w, 1050w, 1036w, 1008w, 976w, 939w, 913w, 884m, 870w, 809m, 741s, 646w cm^{-1}.

(k) Preparation of 2-di-t-butylmethyleneamino-1,3,2-dioxaborolane, $^{t}Bu_2C{:}NB\langle^{O}_{O}\rangle CH_2CH_2$

A solution of di-t-butylmethyleneaminolithium (40 mmole) in 40 ml hexane was added to 2-chloro-1,3,2-dioxaborolane (4.16 g, 39 mmole), prepared as described in the literature (226), suspended in 20 ml THF at -196°. The mixture was warmed to room temperature, and on vigorous shaking a dense white precipitate was formed during an exothermic reaction solvent was removed to leave a white semi-solid which was extracted with pentane/THF. A few fine white needles of a compound (not identified) which did not contain boron were obtained from this solution. Removal of solvent from their mother liquor left a yellow oil which was distilled at ~80°, ~0.05 mm Hg to give a very pale yellow liquid identified as 2-di-t-butylmethyleneamino-1,3,2-dioxaborolane, $^{t}Bu_2C{:}NB\langle^{O}_{O}\rangle CH_2CH_2$

(Found: B, 5.27; N, 6.46%.

$C_{11}H_{22}BNO_2$ requires B, 5.12; N, 6.64%)

ν_{max} (Liquid film) 2956s, 2910s, 2872s, 1798sh, 1736s, 1527w, 1500sh, 1482s, 1432w, 1412m, 1389s, 1366s, 1338w, 1299s, 1220s, 1247m, 1216m, 1198m, 1135w, 1085sh, 1064sh, 1044s, 1030sh, 967s, 934m, 884w, 846sh, 836m, 800w, 689w, 660m, 614m, 540w, 455w cm^{-1}.

(1) Preparation of 2-di-t-butylmethyleneamino-4,5-diphenyl-1,3,2-dioxaborole, $^{t}Bu_2C{:}NB\langle^{O}_{O}\rangle C_2Ph_2$

2-Chloro-4,5-diphenyl-1,3,2-dioxaborole was prepared from boron trichloride and benzoin in a manner similar to that described for the preparation of the related 2-phenyl-4,5-diphenyl-1,3,2-dioxaborole (233). A solution of this compound (2.88 g, 11.22 mmole) in 40 ml hexane at -196° was added a solution of 11.28 mmole di-t-butylmethyleneaminolithium in 20 ml hexane. The mixture was allowed to warm up, and at ~ -20° a white precipitate was formed in a brown solution. The mixture was stirred overnight at room temperature then solvent was removed and replaced with fresh hexane. Lithium chloride was filtered off and solvent was removed from the pinkish-brown filtrate leaving a pink solid identified as 2-di-t-butylmethyleneamino-4,5-diphenyl-1,3,2-dioxaborole, $^{t}Bu_2C{:}NB\langle^{O}_{O}\rangle C_2Ph_2$

(Found: B, 2.94; N, 3.68%

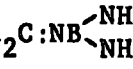
$C_{23}H_{38}BNO_2$ requires B, 2.99; N, 3.88%.)

ν_{max} (Hexane solution) 1770sh, 1756s, 1604w, 1413m, 1341w, 1307w, 1288m, 1256s, 1246sh, 1212m, 1179w, 1167w, 1136m, 1062s, 1046w, 1026m, 1000v.w, 971m, 935m, 907m, 890m, 884m, 868w, 834w, 822w, 803w, 794w, 760s, 724s, 692s, 674m, 678w, 657w cm^{-1}.

(m) Preparation of 2-di-t-butylmethyleneamino-1,3,2-benzodiazaborole, $^{t}Bu_2C{:}NB$ 

2-Chloro-1,3,2-benzodiazaborole was prepared as described in the literature (227).

To a suspension of this compound (1.31 g, 10.5 mmole) in 60 ml benzene frozen to -196° was added a solution of 10.5 mmole di-t-butylmethyleneaminolithium in 40 ml benzene. The mixture was stirred at room temperature overnight, then solvent was removed and the off-white solid extracted with hexane. Removal of solvent from the clear brown solution obtained after filtering off the lithium chloride left an amorphous brown solid. Vacuum sublimation of this solid at 80-85°, 0.05 mm Hg afforded a small quantity of long (~ 2 cm) colourless needle crystals tentatively identified by their I.R. spectrum as 2-di-t-butylmethyleneamino-1,3,2-diazaborole, $^{t}Bu_2C{:}NB$  , and a small quantity of a clear colourless liquid identified by its I.R. spectrum as di-t-butylmethyleneamine, $^{t}Bu_2C{:}NH$. An orange residue, thought to be a borazine derivative, remained in the sublimation vessel.

$^{t}Bu_2C{:}NB$  ν_{max} (Nujol mull) 1745s, 1510s, 1485sh, 1393m, 1324w, 1319w, 1269m, 1219w, 1046m, 1028m, 969m, 956sh, 934m, 880m, 837w, 759sh, 740s, 724sh, 610w, br, 549w,br, 450w, br cm^{-1}.

(n) Preparation of 2-di-t-butylmethyleneamino-1,3-dimethyl-1,3,2-diazaborolane, $^{t}Bu_2C{:}NB$ 

2-Chloro-1,3-dimethyl-1,3,2-diazaboralane (0.78 g, 5.9 mmole), prepared as described in the literature (236), was dissolved in 20 ml

hexane and the solution was frozen to -196°. Di-t-butylmethyleneaminolithium (6.1 mmole) in 20 ml hexane was added. On warming to room temperature a white precipitate was formed in a pale yellow solution. The very pale yellow glassy solid obtained from this solution was identified as 2-di-t-butylmethyleneamino-1,3-dimethyl-1,3,2-diazaborolane, $^{t}Bu_2C{:}NB\begin{smallmatrix}NMe\\NMe\end{smallmatrix}$, m.p. 57-59°.

(Found B, 4.33; N, 17.85%,

$C_{11}H_{24}BN_3$ requires B, 4.56; N, 17.72%)

ν_{max}(Nujol mull) 1764sh, 1739s, 1396s, 1375w, 1364m, 1320m, 1298m, 1259m, 1218m, 1190w, 1030s, v.br, 966w, 945w, 933w, 876w, 839w, 802m, 721w, 625m, 583w, 540w, 487w cm^{-1}.

(o) Preparation of B-tris(di-t-butylmethyleneamino)borazine, $[^{t}Bu_2C{:}NB.N.H]_3$

B-trichloroborazine (1.65 g, 8.99 mmole) was dissolved in 60 ml hexane and the solution frozen to -196°. Di-t-butylmethyleneaminolithium (27 mmole) in 25 ml hexane was added. On warming to room temperature a white precipitate formed during ~ 30 minutes. Removal of solvent left a pale yellowish-green fluffy solid which was extracted with pentane to give a pale green solution. Solvent was removed, leaving a flocculent white solid identified as B-tris(di-t-butylmethyleneamino)borazine, $[^{t}Bu_2C{:}NB.N.H]_3$ m.p. 240-245°d.

(Found: B, 6.32; N, 17.14%.

$C_{27}H_{57}B_3N_6$ requires B, 6.51; N, 16.87%.)

ν_{max}(Nujol mull) 3452m, 1764sh, 1736s, 1608v.w, 1480sh, 1300w.br, 1105m, 1044m, 1030sh, 967m, 931w, 875w, 828w, 800w, 721m, 617w, 540w cm^{-1}.

2. Discussion.

(a) Preparation of methyleneaminoboranes. The new methyleneaminoboranes are listed in Table 2.1 together with their azomethine stretching frequencies. The methods of preparation of these and the other known di-t-butylmethyleneaminoboranes are summarised in figure 2.1. Hydrocarbon or ether solutions of the reagents were mixed at -196°, allowed to reach room temperature, and stirred for a few hours. In some cases (see experimental section), several hours' reflux at ~ 120° was required.

(i) The $BF_3/{}^tBu_2C{:}NLi$ system. When iminolithium was added to solutions of boron trifluoride (either the unco-ordinated compound or its diethyl etherate) in mole ratios between 2:1 and 2:3, the principal product obtained was the bis(imino)fluoroborane, $({}^tBu_2C{:}N)_2BF$. When three equivalents of iminolithium were used there was evidence for the formation of some tris(imino)borane, $({}^tBu_2C{:}N)_3B$, but the compound could not be isolated. These observations are an interesting contrast to the BCl_3 / ${}^tBu_2C{:}NLi$ system, where stoichiometric reactions between the reagents afforded ${}^tBu_2C{:}NBCl_2$ and $({}^tBu_2C{:}N)_2BCl$ (Equation 2.1), but the tris(imino)-borane could not be prepared in a similar manner (52).

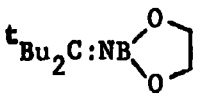
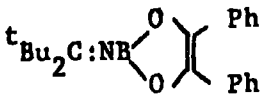
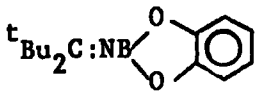
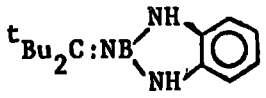
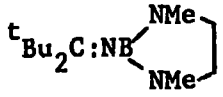
$$n\,{}^tBu_2C{:}NLi + BCl_3 \rightarrow ({}^tBu_2C{:}N)_nBCl_{3-n} + nLiCl \qquad 2.1$$

$(n = 1,2)$

The influence of the mole ratios of boron trifluoride and iminolithium ($^tBu_2C{:}NLi$) on the products obtained has been studied, and the information gained used to develop methods of preparation of the mono- and tris-(imino)-boranes, ${}^tBu_2C{:}NBF_2$ and $({}^tBu_2C{:}N)_3B$, from the readily-obtainable bis(imino)-borane, $({}^tBu_2C{:}N)_2BF$.

Table 2.1

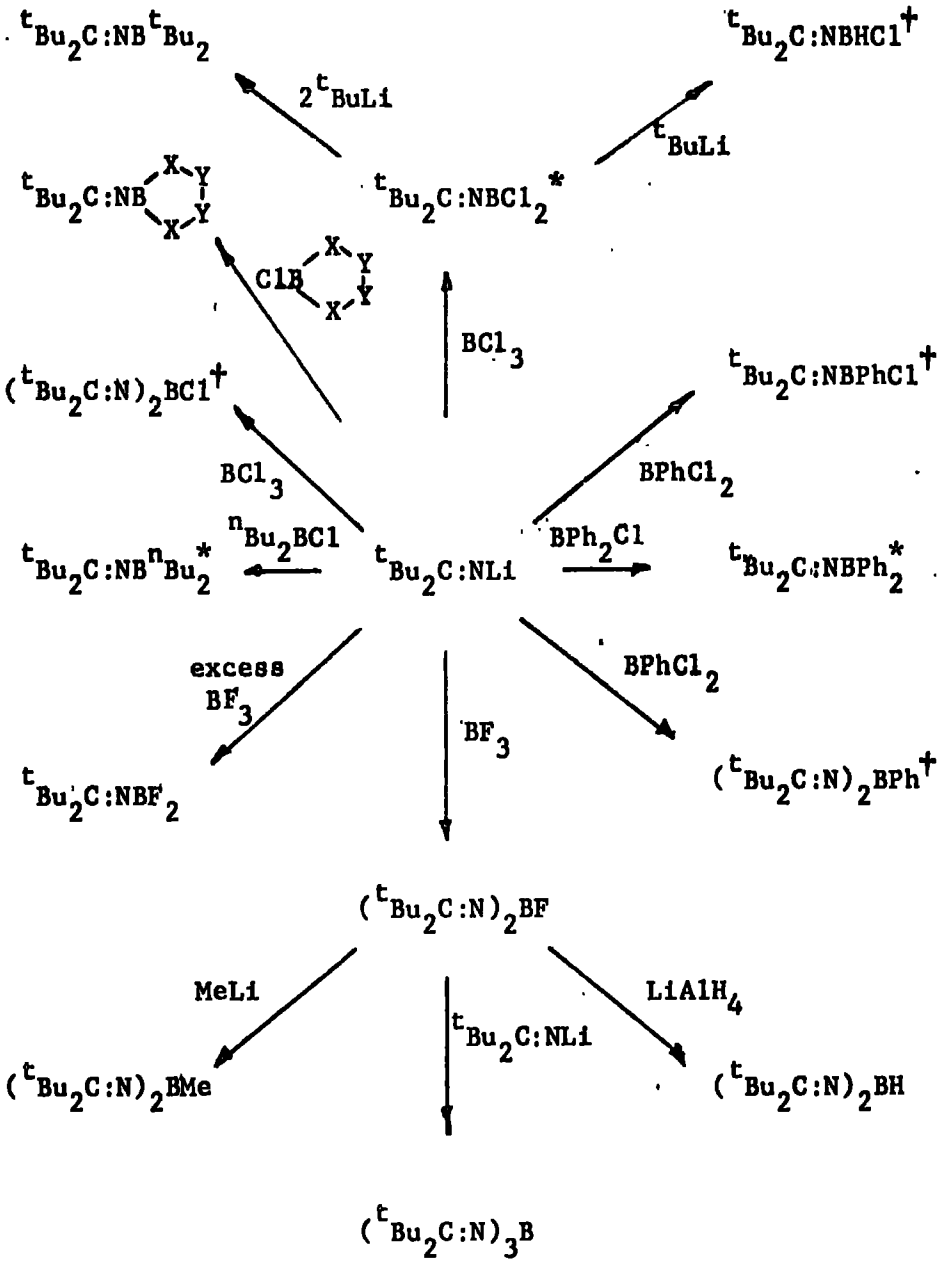
Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of the new di-t-butylmethyleneaminoboranes

Compound	ν(C=N)	Δν*	Phase
$^tBu_2C{:}NBF_2$	1796	186	Pentane solution
$(^tBu_2C{:}N)_2BF$	1750	140	Contact film
$(^tBu_2C{:}N)_3B$	1730	120	KBr disc
$(^tBu_2C{:}N)_2BH$	1760	150	Nujol mull
$(^tBu_2C{:}N)_2BMe$	1745	135	Liquid film
$^tBu_2C{:}N)B^tBu_2$	1812	102	Liquid film
	1736	126	Liquid film
	1756	146	Nujol mull
	1780	170	Nujol mull
	1745	135	Nujol mull
	1739	129	Nujol mull
$(^tBu_2C{:}NB.N.H)_3$	1736	126	Nujol mull

* $\Delta\nu = \nu(C{=}N)^tBu_2C{:}NBXY - \nu(C{=}N)^tBu_2C{:}NH$

Figure 2.1

Preparation of di-t-butylmethyleneaminoboranes



$^tBu_2C{:}NH + Et_3B \rightarrow {}^tBu_2C{:}NBEt_2^\dagger$

* Reference 22 † Reference 52

All others, this work

Reactions between BF_3 and $^tBu_2C{:}NLi$ in mole ratios between 2:1 and 2:3 afforded $(^tBu_2C{:}N)_2BF$ and depending on the stoichiometry, lithium fluoride, lithium tetrafluoroborate, or a mixture of the two (Equations 2.2 - 2.4).

$$2\,^tBu_2C{:}NLi + BF_3 \rightarrow (^tBu_2C{:}N)_2BF + 2LiF \qquad 2.2$$

$$2\,^tBu_2C{:}NLi + 3BF_3 \rightarrow (^tBu_2C{:}N)_2BF + 2LiBF_4 \qquad 2.3$$

$$2\,^tBu_2C{:}NLi + 2BF_3 \rightarrow (^tBu_2C{:}N)_2BF + LiBF_4 + LiF \qquad 2.4$$

The ease of preparation of bis(di-t-butylmethyleneamino)fluoroborane contrasts with the difficulty of preparation of its chloro or phenyl counterparts. Attachment of the secondimino group to $RBCl_2$(R = Cl, Ph) required several hours at 95° in toluene solution (Equation 2.5) (52).

$$2\,^tBu_2C{:}NLi + RBCl_2 \rightarrow (^tBu_2C{:}N)_2BR + 2LiCl \ (R = Ph, Cl) \qquad 2.5$$

However, bis(imino)fluoroborane is formed readily at or below room temperature in reactions between BF_3 and $^tBu_2C{:}NLi$ in various mole ratios as described above. The small size of the fluorine atom presumably allows the bulky di-t-butylmethyleneamino groups to be more easily accommodated round boron in $(^tBu_2C{:}N)_2BF$ than in the chloro or phenyl analogues which require a higher temperature and longer reaction time for their preparation.

As reaction between equimolar proportions of BF_3 and $^tBu_2C{:}NLi$ did not afford mono(imino)fluoroborane as was expected by analogy with the preparation of the related chloroborane, the reaction between iminolithium (1 mol) and borontrifluoride (3 mols) designed to give complete formation of iminodifluoroborane and lithium tetrafluoroborate was attempted. Again, however, the product isolated was $(^tBu_2C{:}N)_2BF$. It would seem therefore that the stability of the bis(imino)fluoroborane, rather than

the formation of lithium tetrafluoroborate as an alternative by-product, is the controlling factor; any mono-substituted compound which may be formed apparently disproportionates rapidly to $(^tBu_2C{:}N)_2BF$ and BF_3 (Equation 2.6)

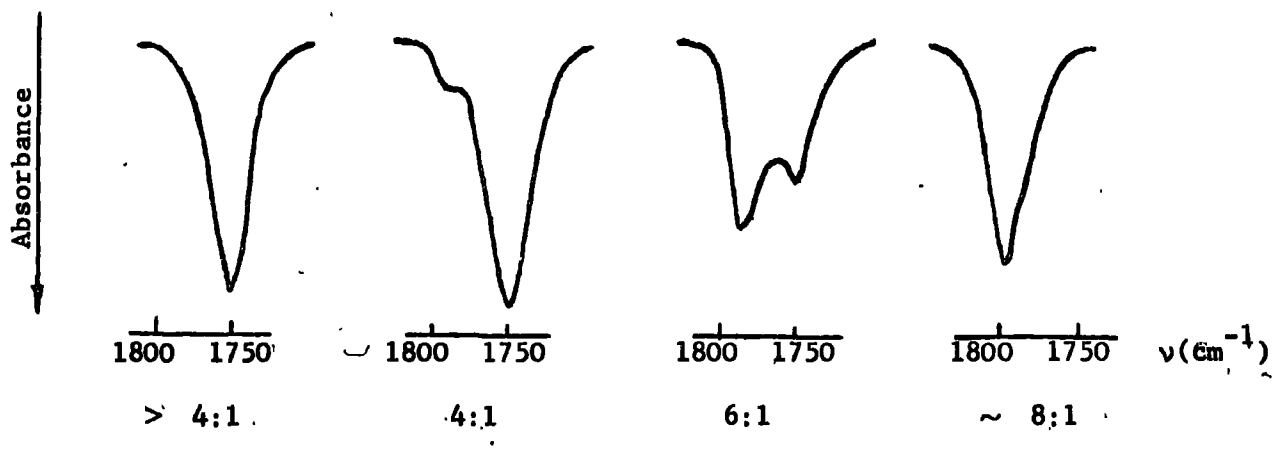
$$^tBu_2C{:}NLi + 2BF_3 \rightarrow {}^tBu_2C{:}NBF_2 + LiBF_4$$
$$\downarrow$$
$$\tfrac{1}{2}(^tBu_2C{:}N)_2BF + \tfrac{1}{2}BF_3 \qquad 2.6$$

I.R. spectra recorded during a study of a controlled addition of boron trifluoride to iminolithium indicated that at a mole ratio of 4:1 some mono(imino)difluoroborane, $^tBu_2C{:}NBF_2$, was present together with bis(imino)fluoroborane, $(^tBu_2C{:}N)_2BF$. The concentration of $^tBu_2C{:}NBF_2$ is greatly increased at mole ratio 6:1, and above the ratio of ~8:1, complete formation of iminodifluoroborane is achieved (Figure 2.2). Little, if any, bis(imino)fluoroborane is present and the disproportionation described by equation 2.7 is completely suppressed.

$$2\,^tBu_2C{:}NBF_2 \rightarrow (^tBu_2C{:}N)_2BF + BF_3 \qquad 2.7$$

Figure 2.2

I.R. spectra recorded during the preparation of $^tBu_2C{:}NBF_2$



Di-t-butylmethyleneaminodifluoroborane, a clear, pale yellow liquid, could be distilled, but it decomposed so rapidly into $(^tBu_2C{:}N)_2BF$ and BF_3 that investigations of its properties as a neat liquid could not be made. This instability is similar to that of dimethylaminodifluoroborane, Me_2NBF_2, which when heated with trimethylamine disproportionates to the bis(amino)fluoroborane and the trimethylamine adduct of BF_3 (Equation 2.8) (201).

$$Me_2NBF_2 \xrightarrow{Me_3N} (Me_2N)_2BF + BF_3.NMe_3 \qquad 2.8$$

Preparation of iminodifluoroborane from bis(imino)fluoroborane and excess boron trifluoride provides a cleaner, more direct route avoiding contamination by lithium salts. Again however, purification of the required compound resulted in its rapid disproportionation no longer prevented by the presence of excess BF_3.

Several routes to tris(di-t-butylmethyleneamino)borane were investigated. An I.R. spectrum of the product obtained from reaction between boron trifluoride (1 mol) and iminolithium (3 mol.) (Equation 2.9) indicated the presence of the required tris(imino)borane, but attempts at purification were unsuccessful.

$$3\,^tBu_2C{:}NLi + BF_3 \rightarrow (^tBu_2C{:}N)_3B + BLiF \qquad 2.9$$

Reaction between boron trifluoride (4 mol) and iminolithium (3 mol) (Equation 2.10) afforded some tris(imino)borane after 36 hours' refluxing at $\sim 120^{\circ}$, but further refluxing appeared to cause its decomposition and subsequently only bis(imino)fluoroborane could be isolated from the reaction mixture.

$$3\,^tBu_2C{:}NLi + 4BF_3 \rightarrow (^tBu_2C{:}N)_3B + 3LiBF_4 \qquad 2.10$$

Reaction between bis(imino)fluoroborane and lithium fluoride did not give tris(imino)borane and lithium tetrafluoroborate (Equation 2.11): the reagents were recovered unchanged.

$$3(^{t}Bu_2C{:}N)_2BF + LiF \not\rightarrow 2(^{t}Bu_2C{:}N)_3B + LiBF_4 \qquad 2.11$$

As described previously in connection with the preparation of iminodifluoroborane, it seems in this case also that is is the stability of the bis(imino)fluoroborane rather than the formation of lithium tetrafluoroborate which dominates these reactions.

The tris(imino)borane, $(^{t}Bu_2C{:}N)_3B$, was prepared from bis(imino)-fluoroborane (1 mol) and iminolithium (1 mol) (Equation 2.12)

$$(^{t}Bu_2C{:}N)_2BF + {}^{t}Bu_2C{:}NLi \rightarrow (^{t}Bu_2C{:}N)_3B + LiF \qquad 2.12$$

Complete reaction is achieved after ~ 36 hours at ~ 120^{o} in 100 - 120^{o} pet. ether. These vigorous conditions contrast with the ease of preparation of the related compound, $(Ph_2C{:}N)_3B$: reaction between boron-tribromide or -trichloride and three equivalents of imino-lithium or -trimethylsilane is complete after a short time at room temperature (Equation 2.13) (21,47, 54,62)

$$3Ph_2C{:}NY + BX_3 \rightarrow (Ph_2C{:}N)_3B + 3XY \qquad 2.13$$

$$(Y = Li, SiMe_3, X = Br, Cl)$$

The relative stabilities of the two iminofluoroboranes, $^{t}Bu_2C{:}NBF_2$ and $(^{t}Bu_2C{:}N)_2BF$, and $(^{t}Bu_2C{:}N)_3B$ are opposite to those of the related diphenyliminoboranes, $(Ph_2C{:}N)_nBCl_{3-n}$ $(n = 1 - 3)$. The bis(imino)chloroborane, $(Ph_2C{:}N)_2BCl$ is believed to be unstable with respect to disproportionation into iminodichloroborane and tris(imino)borane (Equation 2.14), and it has not been isolated (21,47).

$$2(Ph_2C{:}N)_2BCl \rightarrow \tfrac{1}{2}[Ph_2C{:}NBCl_2]_2 + (Ph_2C{:}N)_3B \qquad 2.14$$

Diphenylmethyleneaminodichloroborane, $Ph_2C{:}NBCl_2$, is a crystalline solid, and its lattice energy is thought to be a driving force in the disproportionation reaction. Tris(diphenylmethyleneamino)borane, $(Ph_2C{:}N)_3B$ is a waxy yellow solid, and although its formation may not actively encourage the disproportionation reaction, experiments with scale models suggest that there is little steric hindrance between the methyleneamino groups.

In contrast, iminodifluoroborane, $^tBu_2C{:}NBF_2$ is a liquid and the bis(imino)fluoroborane, $(^tBu_2C{:}N)_2BF$, is a crystalline solid, whose lattice energy probably provides the driving force for the disproportionation of the mono(imino)derivative (Equation 2.15).

$$2\,^tBu_2C{:}NBF_2 \rightarrow (^tBu_2C{:}N)_2BF + BF_3 \qquad 2.15$$

Previous attempts to prepare tris(di-t-butylmethyleneamino)borane, $(^tBu_2C{:}N)_3B$, from BCl_3, $^tBu_2C{:}NBCl_2$ and $(^tBu_2C{:}N)_2BCl$ with three, two and one equivalents of iminolithium respectively were all unsuccessful (52). This was attributed to steric crowding between the t-butyl groups in the product, and the stability of $(^tBu_2C{:}N)_2BCl$, which does not disproportionate to $(^tBu_2C{:}N)_3B$ and $^tBu_2C{:}NBCl_2$ in the same manner that $(Ph_2C{:}N)_2BCl$ readily disproportionates to $[Ph_2C{:}NBCl_2]_2$, a crystalline solid, and $(Ph_2C{:}N)_3B$ (Equation 2.14). The fact that $(^tBu_2C{:}N)_3B$ can be prepared as a stable crystalline solid indicates that steric hindrance between the alkyl groups in the product is not a significant feature in its preparation. It is thought therefore that the smaller fluorine atom allows more ready access of the third methyleneamino group to the central metal atom than does the larger chlorine, and formation of a transition

state probably involving four-co-ordinate boron (Figure 2.3). The large chlorine atom presumably prevents formation of the postulated transition state, but the smaller fluorine does not.

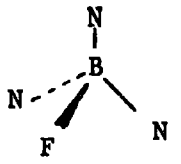


Figure 2.3.

(ii) Other acyclic methyleneaminoboranes. Bis(di-t-butylmethyleneamino)borane, $(^tBu_2C{:}N)_2BH$, was prepared by reducing bis(imino)fluoroborane with lithium aluminium hydride (Equation 2.16).

$$(^tBu_2C{:}N)_2BF \xrightarrow{LiAlH_4} (^tBu_2C{:}N)_2BH \qquad 2.16$$

A similar reaction between lithium aluminium hydride and di-t-butyliminodichloroborane, an attempt to prepare the iminoborane, $^tBu_2C{:}NBH_2$, apparently resulted in ligand exchange between boron and aluminium, and the required compound was not obtained. Using sodium borohydride as the reducing agent so that any ligand exchange may still result in the required product was also unsuccessful. Reaction between equimolar proportions of bis(imino)fluoroborane and sodium borohydride (Equation 2.17) did not afford $^tBu_2C{:}NBH_2$ either, and so far this compound has not been prepared.

$$(^tBu_2C{:}N)_2BF + NaBH_4 \not\rightarrow 2\,^tBu_2C{:}NBH_2 + NaF \qquad 2.17$$

Ligand exchange reactions such as those used to prepare aminoboranes (Equation 2.18) (202) have not yet been attempted in the preparation of methyleneaminoboranes.

$$H_3B.NR^1_3 + 2HNR^2 \rightarrow HB(NR^2_2)_2 + 2H_2 + NR^1_3 \qquad 2.18$$

Reaction between bis(di-t-butylmethyleneamino)fluoroborane and methyl lithium afforded the bis(imino)methylborane, $(^tBu_2C{:}N)_2BMe$, a very pale yellow liquid (Equation 2.19).

$$(^tBu_2C{:}N)_2BF + MeLi \rightarrow (^tBu_2C{:}N)_2BMe + LiF \qquad 2.19$$

Precipitation of lithium fluoride began at $\sim -20^o$, and the reaction was complete after $\sim$ 2 hours at room temperature. In contrast to the ease with which $(^tBu_2C{:}N)_2BMe$ can be prepared, methyl lithium does not react with diphenylmethyleneaminophenylchloroborane, $Ph_2C{:}NBPhCl$ (96); presumably the chlorine and phenyl groups on the central boron atom are sufficiently bulky to prevent close approach of the methyl group.

No reaction occurred between bis(di-t-butylmethyleneamino)fluoroborane and n-butyl- or t-butyl-lithium, even during several hours' reflux at $\sim 120^o$, and $(^tBu_2C{:}N)_2BF$ was recovered from the reaction mixtures. This contrasts with the reaction between di-t-butylmethyleneaminodichloroborane and n-butyl- and t-butyl-lithium (52). With two equivalents of n-butyl lithium, the iminodi-n-butylborane, $^tBu_2C{:}NB^nBu_2$, is obtained (Equation 2.20)

$$^tBu_2C{:}NBCl_2 + 2^nBuLi \rightarrow {}^tBu_2C{:}NB^nBu_2 + 2LiCl \qquad 2.20$$

However, reaction between the iminochloroborane and one equivalent of t-butyl lithium affords iminochloroborane, $^tBu_2C{:}NBHCl$ and butene (Equation 2.21) (52).

$$^tBu_2C{:}NBCl_2 + {}^tBuLi \rightarrow {}^tBu_2C{:}NBHCl + C_4H_8 + LiCl \qquad 2.21$$

The mechanism of this reaction may involve initial production of radicals (Equation 2.22) (52), such as those detected in reactions between alkyl halides and alkyl lithiums (203).

$$^{t}BuLi + {}^{t}Bu_2C{:}NBCl_2 \rightarrow {}^{t}Bu\cdot + {}^{t}Bu_2C{:}NBCl + LiCl$$

$$^{t}Bu\cdot \rightarrow H\cdot + C_4H_8$$

$$H\cdot + {}^{t}Bu_2C{:}NBCl\cdot \rightarrow {}^{t}Bu_2C{:}NBHCl \qquad 2.22$$

It is surprising that no reaction occurs between bis(imino)fluoroborane and the two butyl lithiums, especially in view of the successful preparation of the tris(imino)borane, $(^{t}Bu_2C{:}N)_3B$, unobtainable from the chloroboranes. A possible explanation is that methyl and di-t-butylmethyleneamino groups can approach the central metal close enough for reaction to occur but the butyl groups are too bulky to do so, the terminal methyl group of the n-butyl group interfering with the t-butyl groups of the methyleneamino ligand and the t-butyl group as a whole being too bulky for sufficiently close approach if a transition state involving four-co-ordinate boron is required. Experiments with scale models support these arguments.

As a radical mechanism is invoked for the reaction between $^{t}BuLi$ and $^{t}Bu_2C{:}NBCl_2$, the lack of reaction between $^{t}BuLi$ and $(^{t}Bu_2C{:}N)_2BF$ may also be explained in terms of the greater boron-fluorine than boron-chlorine bond strength which limits formation of $(^{t}Bu_2C{:}N)_2B\cdot$ radicals, and subsequently $(^{t}Bu_2C{:}N)_2BH$ in a manner similar to that described by equation 2.22 for the preparation of $^{t}Bu_2C{:}NBHCl$.

Reaction between two equivalents of t-butyl lithium and iminochloroborane, $^{t}Bu_2C{:}NBCl_2$, afforded iminodi-t-butylborane, $^{t}Bu_2C{:}NB^{t}Bu_2$ (Equation 2.24). This was a rather unexpected product, as one equivalent of $^{t}BuLi$ reacted with $^{t}Bu_2C{:}NBCl_2$ to give $^{t}Bu_2C{:}NBHCl$ (Equation 2.23) (52), and the similar reaction using two equivalents of t-butyl lithium was therefore expected to be a suitable preparation of $^{t}Bu_2C{:}NBH_2$.

$$^{t}Bu_2C{:}NBCl_2 + {}^{t}BuLi \rightarrow {}^{t}Bu_2C{:}NBHCl + C_4H_8 + LiCl \qquad 2.23$$

$$^{t}Bu_2C{:}NBCl_2 + 2\,{}^{t}BuLi \rightarrow {}^{t}Bu_2C{:}NB{}^{t}Bu_2 + 2LiCl \qquad 2.24$$

The preparation of $^{t}Bu_2C{:}NB{}^{t}Bu_2$ probably does not proceed via a free-radical mechanism, which, by analogy with equation 2.22 would be expected to give $^{t}Bu_2C{:}NBH_2$. In a similar reaction reported previously between $^{t}Bu_2C{:}NBCl_2$ and two equivalents of $^{t}BuLi$, some iminoborane, $^{t}Bu_2C{:}NBH_2$, was thought to be formed, but it could not be isolated and characterised (52). Further work is necessary to determine the precise reaction conditions which govern the formation of the two compounds $^{t}Bu_2C{:}NB{}^{t}Bu_2$ and $^{t}Bu_2C{:}NBH_2$.

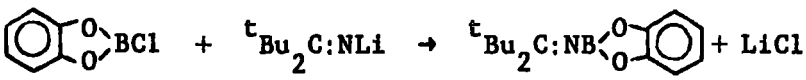
There is an interesting comparison between the iminodibutylborane, $^{t}Bu_2C{:}N{}^{t}Bu_2$, and the tributylboranes. Tri-t-butylborane, although reported as the product of reaction between $^{t}BuMgCl$ and BF_3, (234), does not exist: steric hindrance between the t-butyl groups prevents its formation, and such reactions have been shown to yield di-i-butyl-t-butyl-borane, $^{i}Bu_2B{}^{t}Bu$, or tri-i-butylborane, $^{i}Bu_3B$ (235). When three butyl groups are attached to boron it seems that only one bulky t-butyl group can be accommodated, and if necessary, isomerisation of other butyl groups occurs to reduce their steric hindrance. In constrast, two bulky t-butyl groups can be accommodated at boron when the third ligand is a methyleneamino group, as the t-butyl groups on carbon are sufficiently remote from the centre of the molecule to cause excessive congestion.

When triethylborane (1 mol) and di-t-butylketimine (3 mols) were heated in toluene at $\sim 95^{o}$ for seven days, the principle product, isolated from the reaction mixture by distillation after removal of solvent, was iminodiethylborane, $^{t}Bu_2C{:}NBEt_2$. This distillate was identified by its

I.R. and ^1H n.m.r. spectra (52). It is interesting to note that in the previous report of the preparation of $^tBu_2C{:}NBEt_2$, attempted distillation caused decomposition (52).

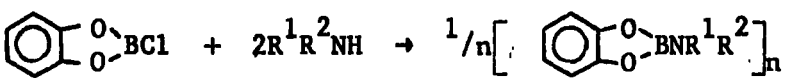
(iii) Heterocyclic methyleneaminoboranes. Preparation of the heterocyclic compounds involved metathetical reactions between di-t-butylmethyleneaminolithium and the chloro derivative of the appropriate boron heterocycle. Reactions of iminolithium with chloroboranes appear to be much cleaner than those with fluoroboranes. Lithium fluoride seems to precipitate out of reaction mixtures as a more finely-divided powder than lithium chloride, which is therefore more easily removed by filtration.

2 di-t-butylmethyleneamino-1,3,2-benzodioxaborole was prepared from 2-chloro-1,3,2,-benzodioxaborole and iminolithium (Equation 2.25)

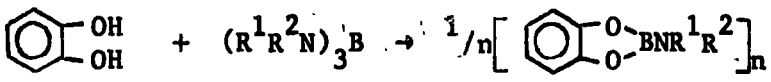


2.25

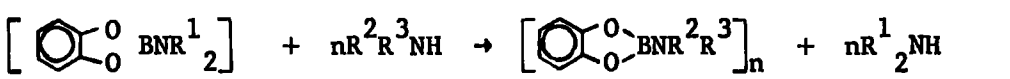
Similar aminodioxaborole derivatives have been prepared from 2-chloro-1,3,-2-benzodioxaborole and the appropriate primary on secondary amine, which is used in excess to remove the HCl formed as the amine hydrochloride (Equation 2.26) (204 - 206). Reactions between catechol and tris(amino)-boranes (Equation 2.27), and ligand exchange between aminodioxaborole and a secondary amine (Equation 2.28) have also been used to prepare related amino compounds (204).



2.26

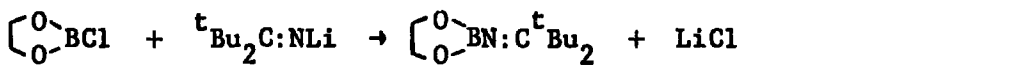


2.27



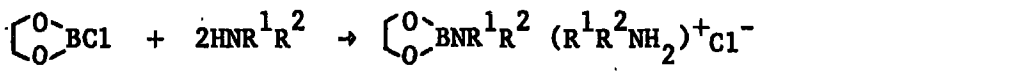
2.28

2-di-butylmethyleneamino-1,3,2-dioxaborolane was prepared by reaction between iminolithium and 2-chloro-1,3,2-dioxaborolane (Equation 2.29)



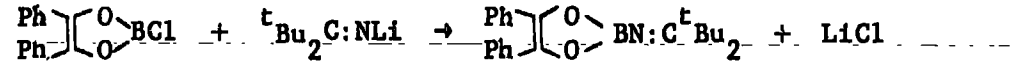
2.29

This preparation is similar to that of the related amino compounds (Equation 2.30). (207).

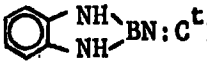


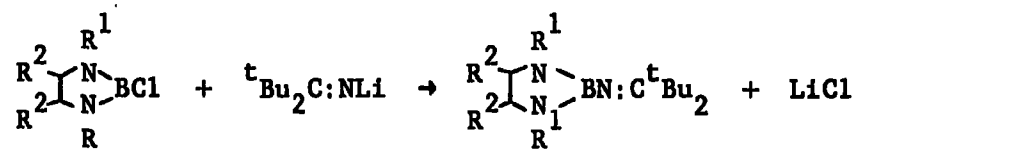
2.30

Reaction between iminolithium and the appropriate chloroborane afforded $^{t}Bu_2C{:}NB\langle O_O\rangle C(Ph)_2$ (Equation 2.31)



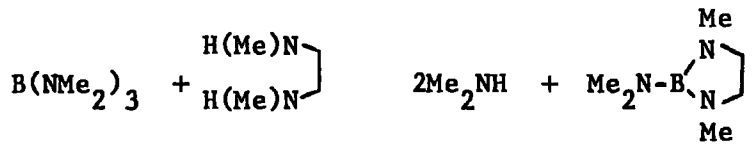
2.31

Preparation of the two compounds  and was achieved by reaction between the appropriate 2-chlorodiazaborole and iminolithium (Equation 2.32)



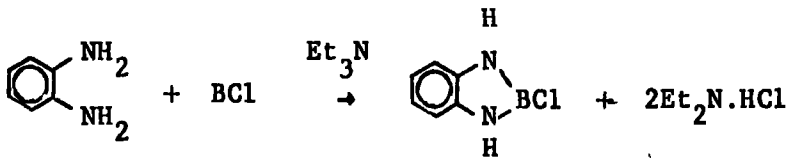
2.32

The preparation of 1,3-dimethyl-2-imino-1,3,2-diazaboracyclopentane was straightforward; the reaction was complete after a few hours at room temperature. Preparation of a similar 2-amino-1,3,2-diazaboracyclopentanes by transamination reaction between tris(amino)boranes and ethylenediamine (Equation 2.33) require the more forcing conditions of several hours' refluxing in pentane (208).



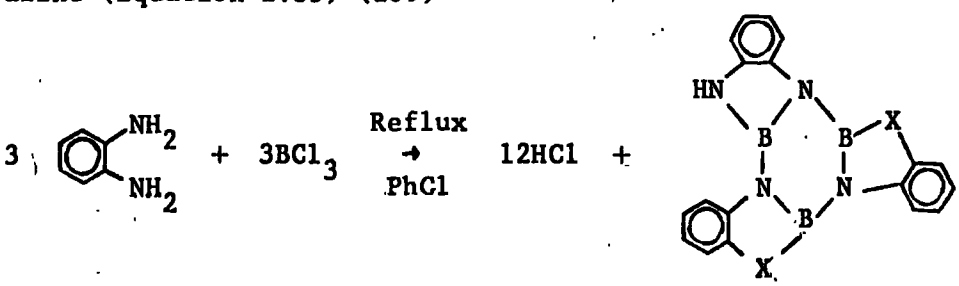
2.33

2-chloro-1,3,2-benzodiazaborole was prepared from o-phenylenediamine and boron trichloride in hexane and triethylamine at room temperature (Equation 2.34)



2.34

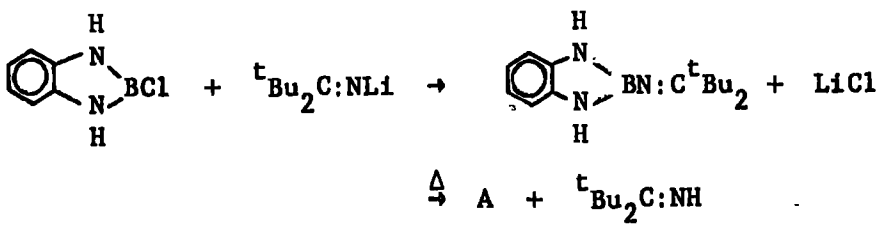
At higher temperatures, these reagents afford the tris(2-borabenzazolo)-borazine (Equation 2.35) (209)



2.35

A.

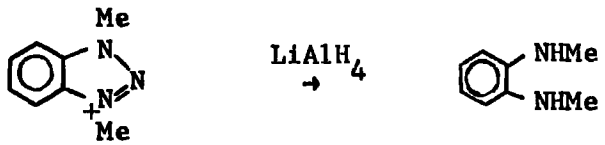
Reactions between di-t-butylmethyleneaminolithium and 2-chloro-1,3,2-benzodiazaborole gave a brown solid identified as the impure iminobenzo-diazaborole but attempted purification by sublimation caused decomposition to the free ketimine and a solid thought to be the trimer A shown in equation 2.35 (Equation 2.36).



2.36

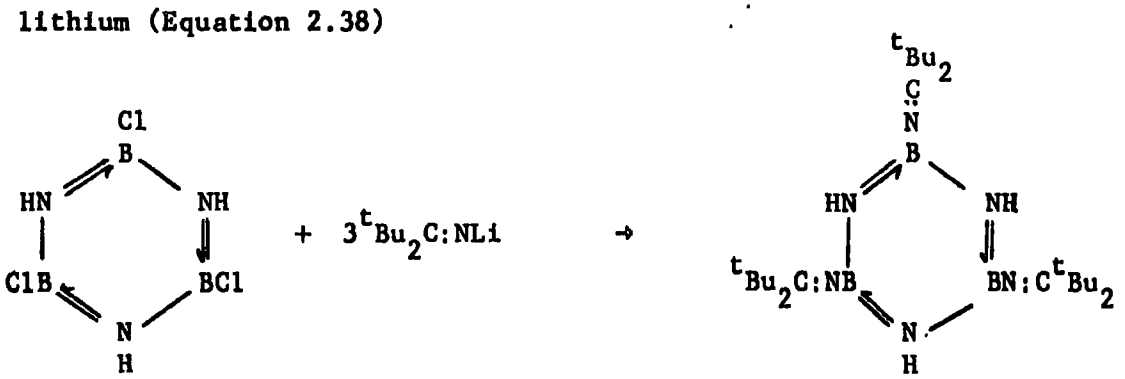
Substitution of one hydrogen on the nitrogen atoms would prevent this

trimerisation. The preparation of N,N'-dimethyl-o-phenylenediamine by reduction of 1,3-dimethylbenzotriazolium ion with lithium aluminium hydride (Equation 2.37) has been reported (210) and this could be used to prepare the 2-chloro-, and hence the 2-imino-1,3,2-benzodiazaborole.



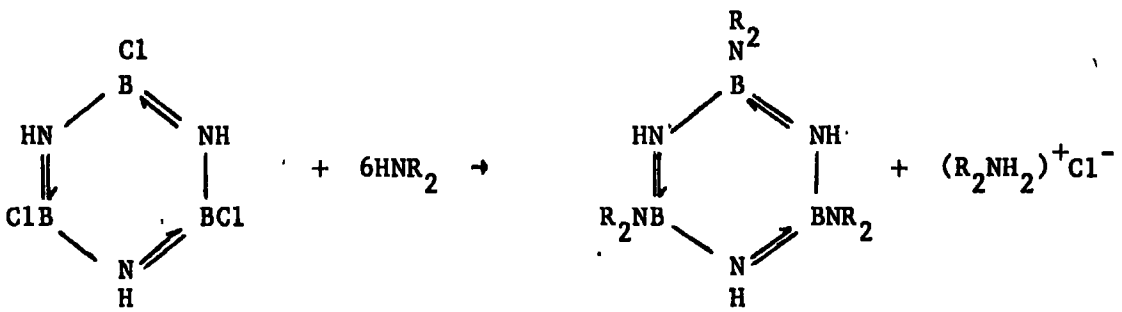
2.37

B-tris(di-t-butylmethyleneamino)borazine was prepared by the reaction of B-trichloro-borazine and three equivalents of di-t-butyl methyleneamino-lithium (Equation 2.38)



2.38

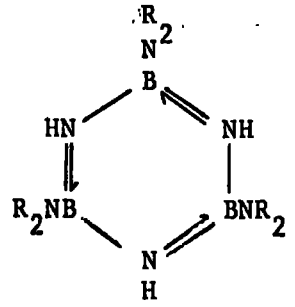
B-aminoborazines can be similarly prepared from B-chloroborazines and appropriate amines (Equation 2,39) (211),



2.39

but are more easily prepared from boron trichloride and the appropriate amine (Equation 2.40) (211,212).

$$BCl_3 + NR_3 \rightarrow BCl_3.NR_3 \quad \S \quad \text{(2.40)}$$

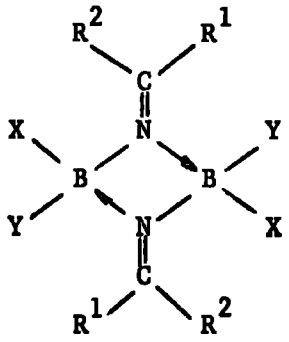


(b) Structure and spectroscopic properties of methyleneaminoboranes.

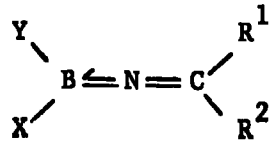
(i) Steric effects. There is considerable evidence that the degree of association of methyleneaminoboranes, $[R^1R^2C{:}NBXY]_n$, depends on the bulk of the substituents R^1, R^2, X and Y.

The influence of R^1 and R^2 is demonstrated by a series of highly-halogenated methyleneaminoboranes. The compounds $[R^1R^2C{:}NBXY]_2$ (R; R^2 = halogen; X, Y = halogen, Ph, Bu) (110 - 113), $[F_3C(R)C{:}NBXY]_2$ (R, X, Y = halogen) (102), and $[R^1ClC(R^2)C{:}NBXY]_2$ (R^1, R^2 = halogen, X, Y = halogen, Me) (114), are dimeric (Figure 2.4.a) while compounds $Cl_3C(R)C{:}NBXY$ (R, X = halogen, Y = halogen, Ph, Me) (112, 120) are monomeric at or above room temperature (Figure 2.4.b), apparently because the bulky CCl_3 group restricts association. A series of carbon-sulphur-substituted methyleneaminoboranes, $[R^1(R^2S)C{:}NB(SR^3)_2]_n$, prepared either by thioboration of nitriles or thiocyanates (115, 116), or by reaction of C-halogenated methyleneaminoboranes with alkylthiols (116, 121), also shows the influence of the bulk of R^1. When R^1 = FCH_2 (115, 116), the compounds are dimeric (n = 2), but when R^1 = Cl_3C , MeS or ^iPrS (115, 121), they are monomeric (n = 1). Iminoboron derivatives of catechol also demonstrate the influence of R^1 and R^2 on the degree of association. 2-Diphenylmethyleneamino-1,3,2-benzodioxaborole is dimeric (Figure 2.4.c) (21), but the related di-t-butylimino compound is a monomer (Figure 2.4.d), presumably

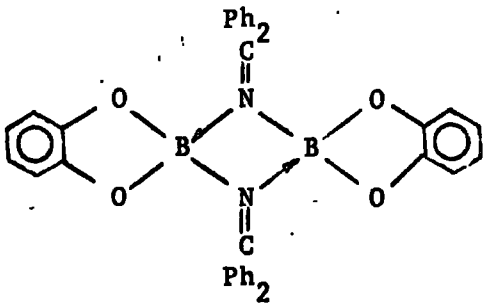
Figure 2.4



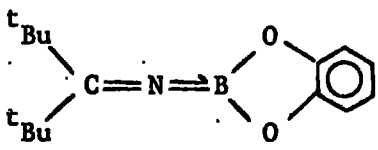
(a)



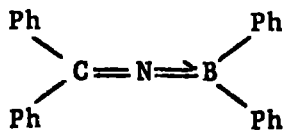
(b)



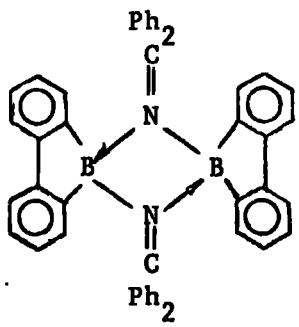
(c)



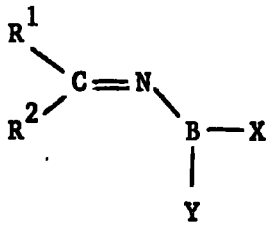
(d)



(e)



(f)



(g)

because the bulky t-butyl groups prevent association.

The groups X and Y have a greater influence on degree of association than R^1 and R^2, as they are nearer the centre of the molecule. For example, diphenylmethyleneaminodiphenylborane, $Ph_2C{:}NBPh_2$, is monomeric (Figure 2.4.e) (21,47,54), but when the phenyl groups on boron are linked together, as in $[Ph_2C{:}NBC_{12}H_8]_2$ steric hindrance is reduced sufficiently to allow association (Figure 2.4.f) (21). All the known di-t-butylmethyleneaminoboranes are monomeric (22,52,122); the t-butyl groups presumably always provide sufficient steric hindrance to prevent association, however small X and Y

Monomeric species are much more widely observed in aminoboranes, R^1R^2NBXY (213 - 215), as the groups R^1 and R^2 are much closer to the central boron atom than they are in methyleneaminoboranes, so their steric influence is greater.

(ii) <u>N → B dative π-bonding in monomeric methyleneaminoboranes</u>. When one methyleneamino group is attached to boron, and the other two groups have little or no π-bonding capacity, then maximum N → B pπ → pπ dative bonding, giving an N → B bond formally of order two, is possible.

With two methyleneamino groups, the maximum N-B bond order for each group is formally 1.50 (σ-bond order 1.00, π-bond order 0.50). However, these N-B bond orders may be influenced by the other groups attached to boron.

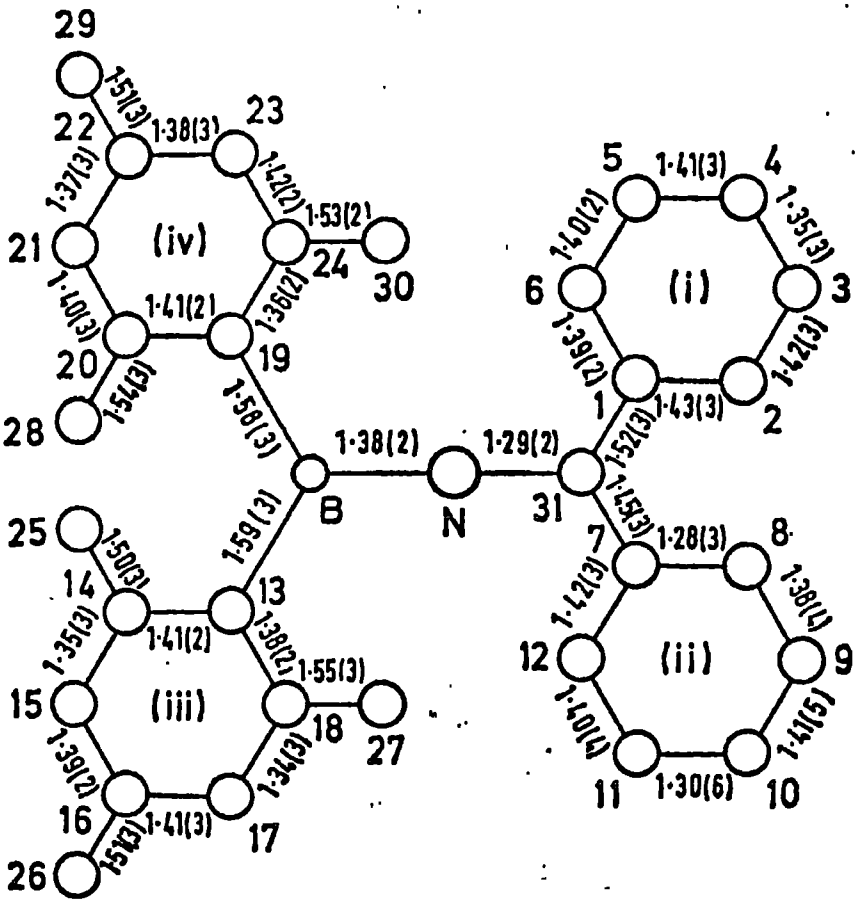
If the groups X in compounds $R_2C{:}NBX_2$ can π-bond to boron, the B-X bond orders themselves can be expected to be greater than one, and the B-N bond order therefore cannot be as high as two. Groups X more electronegative than nitrogen may, by an inductive effect, encourage strengthening of the B-N bond, but this will be modified if back-bonding from X to B increases the B-X bond order as described above. The influence of X in

bis(imino)boranes, $(R_2C{:}N)_2BX$, is similar to, but less marked than that in mono(imino)boranes, $R_2C{:}NBX_2$, because the range of B-N bond order is smaller in the former (1.50 - 1.33) than the latter (2.00 - 1.33) as the maximum B-N π-bond order in bis(imino)boranes is half that in mono(imino)-boranes.

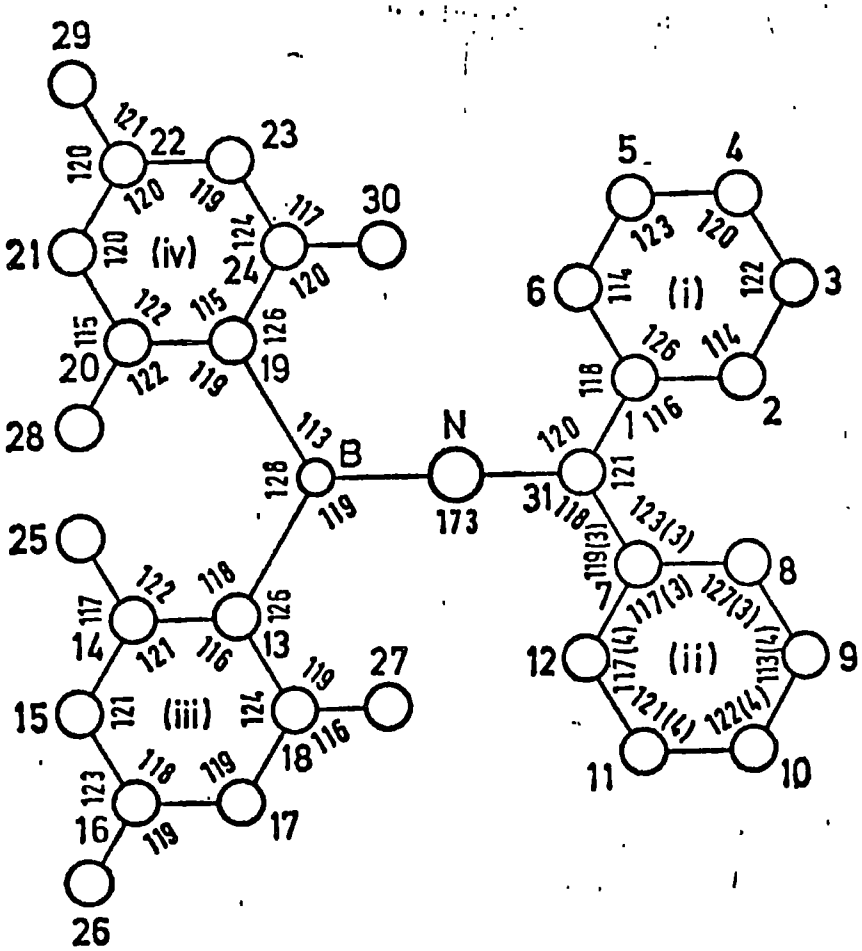
When three methyleneamino groups are attached to boron, co-ordinative saturation of the metal is achieved with a bond order of 1.33 (σ-bond order 1.00, π-bond order 0.33) between boron and each nitrogen.

(iii) Azomethine stretching frequencies of methyleneaminoboranes. The azomethine stretching frequencies of the monomeric methyleneamino-boranes may sometimes be a useful guide to the extent of N → B pπ → pπ dative bonding in these compounds (Chapter 1, section 4a). The X-ray crystal structure of diphenylmethyleneaminodimesitylborane, $Ph_2C{:}NB(mesityl)_2$ (Figure 2.5), shows that the C-N-B unit is effectively linear (CNB angle 173 ± 2^{o}), and the short B-N distance (138 pm, bond order 1.59, calculated using the LCAO method) indicates the degree of dative π-bonding (38). The high azomethine stretching frequency of this compound (ν(C=N≐B) at 1792 cm^{-1} (21)) reflects the allene-like structure of the C=N≐B unit. Monomeric methyleneaminoboranes with similar azomethine stretching frequencies, such as those prepared in this work (Table 2.1) and reported elsewhere (22,52) are thought therefore to have similar structures with linear C=N≐B skeletons. Small variations in ν(C=N≐B) between these compounds may well reflect variations in the extent of N → B dative π-bonding. However, other factors, particularly the mass of substituents on boron, may also be expected to influence the azomethine stretching frequencies, and so mask the effect of N → B dative bonding variations.

Figure 2.5. Crystal structure of $Ph_2C{:}NB(mesityl)_2$ (38)



Bond lengths (Å)



Bond angles

The azomethine stretching frequencies of di-t-butylmethyleneamino-chloro- and -fluoro-boranes (Table 2.2) clearly show the influence of dative X → B π-bonding. Although fluorine is more electronegative than chlorine (4.10 and 2.83 respectively (50)), back-bonding from a filled p-orbital on fluorine to the vacant p-orbital on boron, facilitated by the similar sizes of these atoms (Covalent radii 64 and 81 pm respectively (49)), means that the B-N bond order in iminofluoroboranes is likely to be less than in the related iminochloroboranes which would explain their lower azomethine stretching frequencies. This explanation is supported

Table 2.2

Azomethine stretching frequencies ν(C=N) (cm^{-1}) of di-t-butylmethyleneamino-chloro- and -fluoro-boranes.

Compound	X = Cl	X = F
$^tBu_2C{:}NBX_2$	1839	1796
$(^tBu_2C{:}N)_2BX$	1776	1750

by the calculated greater reorganisation energy of BF_3 than BCl_3, attributed to the contribution to boron-fluorine bond strength by F → B dative π-bonding (216). For the same reason, BCl_3 is a better lewis acid than BF_3 (175).

The azomethine stretching frequencies of some other related mono- and bis-(methyleneamino)boranes are given in Table 2.3.

Variations in the stretching frequencies of methyleneaminoboron compounds $^tBu_2C{:}NBX_2$ in which boron is bonded to elements in the top row

Table 2.3

Azomethine stretching frequencies (cm^{-1}) of some methyleneaminoboranes

Compound	ν(C=N)	Ref
$^{t}Bu_2C{:}NBHCl$	1845	52
$^{t}Bu_2C{:}NBPhCl$	1838	52
$^{t}Bu_2C{:}NBPh_2$	1820*	22
$^{t}Bu_2C{:}NB^{n}Bu_2$	1821	22
$^{t}Bu_2C{:}NBEt_2$	1818	52
$^{t}Bu_2C{:}NB^{t}Bu_2$	1812	a
$(^{t}Bu_2C{:}N)_2BH$	1760*	a
$(^{t}Bu_2C{:}N)_2BMe$	1745	a
$(^{t}Bu_2C{:}N)_2BPh$	1774*	52

* Nujol mulls: all others recorded as liquid films

(a) This work

of the periodic table are small. While some changes in $\nu(C{=}N{\rightarrow}B)$ appear to follow changes in the electronegativity of X, others do not, presumably because the influence of other factors such as the mass and rigidity of X on $\nu(C{=}N{\rightarrow}B)$ is significant (Table 2.1).

The azomethine stretching frequencies of compounds in which boron is in an aromatic or potentially aromatic ring system are of interest since they may reflect the extent of participation of the boron atoms in the aromatic system. If the boron receives electrons from the ring system and is less able to accept dative π-bonding from the methyleneamino group, this might result in a bent C=N-B unit (Figure 2.4.g) indicated by a low azomethine stretching frequency. This was not observed, indicating that in the compounds prepared, the $C{=}N{\rightarrow}B$ unit is effectively linear and N → B dative π-bonding is still possible.

Tris(di-t-butylmethyleneaminoborane), $(^{t}Bu_2C{:}N)_3B$, has the lowest azomethine stretching frequency (1730 cm^{-1}) observed so far for di-t-butylmethyleneaminoboranes, and this is in accord with the relatively low N-B bond order (~ 1.33) expected for this compound (see section 2(b)(ii)) Maximum overlap of the boron and nitrogen p-orbitals will be achieved if the compound adopts a "paddle-wheel" structure in which the t-butyl groups are perpendicular to the plane of the BN_3 unit (Figure 2.6).

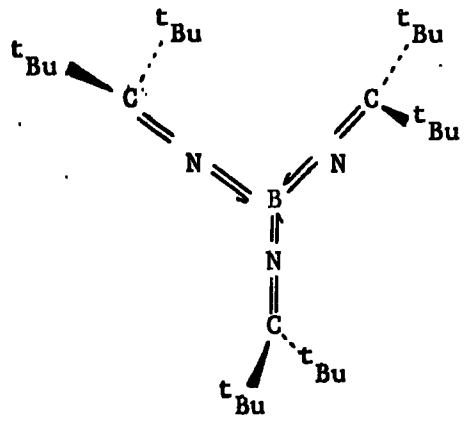


Figure 2.6.

An X-ray crystallographic study of this compound is in progress.

In a recent study of a related compound, $((CF_3)_2C{:}N)_3B$, its ^{19}F n.m.r. spectrum recorded at -30° showed a single absorption, but at $+30^{\circ}$ a multiplet was observed (164). The implication of these data, that all the fluorine atoms are in magnetically-equivalent environments at low but not at high temperatures, is puzzling.

Other compounds in which boron is bonded to three nitrogen atoms have similar azomethine stretching frequencies to that of the tris(imino)borane, $(^tBu_2C{:}N)_3B$, indicating that the other nitrogen-bound ligands contribute to the BN_3 π-system to a similar extent as the methyleneamino group.

Incidentally, it is interesting to note that the differences between the azomethine stretching frequencies of di-t-butylmethyleneaminoboranes, $^tBu_2C{:}NBXY$, and the parent ketimine, $^tBu_2C{:}NH$, are significantly greater (20 - 30 cm^{-1}) than those between corresponding diphenylmethyleneaminoboranes, $Ph_2C{:}NBXY$ and $Ph_2C{:}NH$. (Table 2.4)

Table 2.4

Azomethine stretching frequencies, $\nu(C{=}N{\rightarrow}B)$ cm^{-1}, of some related methyleneaminoboranes

Compound	R = Ph			R = ^{t}Bu		
	$\nu(C{=}N{\rightarrow}B)$	$\Delta\nu$	Ref	$\nu(C{=}N{\rightarrow}B)$	$\Delta\nu$	Ref
$R_2C{:}NH.BF_3$	1628	21	27	1672	62	64
$R_2C{:}NBPh_2$	1786	179	54	1820	210	22
$R_2C{:}NB^nBu_2$	1785	178	96	1821	211	22
$R_2C{:}NBEt_2$	1793	186	54	1818	208	52

$$\Delta\nu = \nu(C{=}N{=}B) - \nu(C{=}N)R_2C.NH$$

$\nu(C{=}N)$ $R_2C{:}NH$ R = Ph, 1607 cm^{-1} (23)

R = ^tBu, 1610 cm^{-1} (64)

(iv) B-N stretching frequencies of methyleneaminoboranes. The azomethine stretching frequencies of methyleneaminoboranes, $\nu(C{=}N)$ or $\nu(C{=}N{\rightarrow}B)$, as discussed in the previous section are always observed at higher frequencies than isolated C=N bonds as a result of coupling between the C=N and N=B bonds in the linear C=N→B unit. This coupling between adjacent double bonds may also be expected to influence the N→B stretching frequency.

The spectra of linear systems X=Y=Z in which three atoms are linked by double bonds may be expected to show two absorptions, assignable to symmetric, $\vec{X} = Y = \vec{Z}$ vibrations of X and Z about the central atom Y. These vibrations are found respectively at lower and higher frequencies than those of isolated X=Y and Y=Z units. The antisymmetric and symmetric stretching frequencies of some linear X=Y=Z systems are given in table 2.5

Table 2.5

Symmetric and antisymmetric stretching frequencies (cm^{-1}) of some cumulatively π-bonded systems (41).

System	antisymm.	sym.
C=C=C	~ 1950	~ 1070*
N=C=N	~ 2160	~ 1130*
$N{=}\overset{+}{N}{=}\overset{-}{N}$	~ 2100	~ 1290 - 1250
N=C=O	~ 2270	~ 1350

* Raman spectrum only.

The C=N≐B unit, being isoelectronic with an allene skeleton, may also be expected to exhibit two stretching frequencies. The higher-frequency absorption, the azomethine stretching frequency already referred to, is readily identified and assigned. It occurs in the region ~ 1700 - 1850 cm^{-1}, and has been used as a guide to the nature of the bonding between the methyleneamino group and the central metal. No attention seems to have been paid to the lower-frequency vibration, ν(B≐N), which should in principle be a more direct guide to the nature of the bonding between boron and the methyleneamino and other ligands.

The B≐N stretching frequency, ν(B≐N), has been neglected apparently because it is difficult to assign with certainty. Characteristically the symmetric stretching frequency of X=Y=Z systems is lower than ν(X=Y) or ν(Y=Z). The stretching frequencies ν(B≐N) of aminoboranes, R_2NBXY, occur in the region ~ 1360 - 1530 cm^{-1} (214), and the data in table 2.5 would suggest that the symmetric vibration of a linear C=N≐B unit, ν(B≐N), may have a frequency in the region ~ 900 - 1300 cm^{-1}.

The spectrum of di-t-butylmethyleneamine, $^tBu_2C{:}NH$, was compared with that of one of its simplest boron derivatives, $^tBu_2C{:}NBCl_2$, and tentative assignments of the bands were made (Table 2.6). Particular attention was paid to the region below 1600 cm^{-1}. Four bands, assignable to various vibrations of the alkyl groups, were common to both compounds with only minor variations in frequency. A strong band at 1287 cm^{-1}, with a shoulder at 1307 cm^{-1} was present in the spectrum of $^tBu_2C{:}NBCl_2$ but not in that of $^tBu_2C{:}NH$. At lower frequency, four bands assignable to various alkyl deformation modes are again common to both spectra. The strong bands at 649 (694sh) and 461 (475sh) cm^{-1} in the spectrum of $^tBu_2C{:}NBCl_2$ are assigned to $B\text{-}Cl_2$ antisymmetric and symmetric stretches respectively.

The peak at 1287 (1307sh) cm^{-1} is tentatively assigned to the symmetric

Table 2.6

I.R. spectra of di-t-butylmethyleneamine and di-t-butylmethyleneaminochloroborane

$^tBu_2C{:}NH$	$^tBu_2C{:}NBCl_2$	Assignment
3378w		N-H stretch
2994sh	2976s	C-H stretch
2959v.s	2941m	
2920sh	2924sh	
2874s	2878m	
	1951w	
1689w		C=N stretch
1610v.s	1773sh	
	1653w	
	1515sh	CH_3 deformation
	1481s	asymm.
	1480s	
	1395s	
1370s	1370s	symm. C-H deformation
1326m		
	1307sh	B=N-stretch
	1287s	

Table 2.6 continued

$^{t}Bu_2C{:}NH$	$^{t}Bu_2C{:}NBCl_2$	Assignment
1218s		hydrocarbon bending vibration
1195s	1199m	
1054m	1048s	
1031m	1029m	
1026sh		
977w	976m	
952m	935m	
930m	909m,br	
877s	871s,br	
842w	833m	
783m		
719m	730w	
	694sh	antisymm $B-Cl_2$ stretch
	649s	
544m	552m,br	
	475sh	symm. $B-Cl_2$ stretch
	461m,br	

stretching mode $\nu(B{=}N)$. Comparison of this frequency with those of the symmetric stretching frequencies of the other X=Y=Z systems in table 2.5 would suggest that this is not unreasonable. It is rather higher than that of allene, as expected on the grounds of the difference in coupling in the two cumulative double-bond systems.

Confirmation of the assignment of the absorptions at 1287 cm^{-1} to the symmetric stretching frequency, $\nu(B{=}N)$, in $^{t}Bu_2C{:}NBCl_2$ could be made by study of the same compound containing ^{10}B-enriched boron. Shift of the position of the peak to the higher frequency at which the shoulder is observed, 1307 cm^{-1}, would confirm its assignment, as in the original spectrum vibration of the bond between nitrogen and the less-abundant ^{10}B isotope.

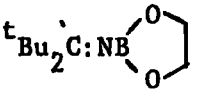
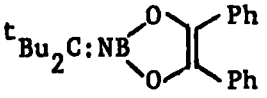
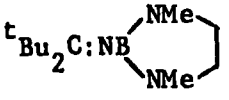
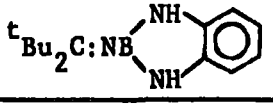
The spectra of some other methyleneaminoboranes were also compared with that of $^{t}Bu_2C{:}NH$ in the appropriate region, and tentative assignments of $\nu(B{=}N)$ for each are given in table 2.7, together with their azomethine stretching frequencies.

It appears that the values of $\nu(B{=}N)$ do not cover so wide a range as those of $\nu(C{=}N)$, nor do their variations from compound to compound follow precisely the same pattern, but as the differences in $\nu(B{=}N)$ are small, and even the interpretation of some $\nu(C{=}N)$ values is sometimes speculative, this feature is not considered particularly significant.

However, values of $\nu(B{=}N)$ for bis(imino)boranes, $(^{t}Bu_2C{:}N)_2BX$, are lower than those of their mono(imino)borane counterparts, $^{t}Bu_2C{:}NBX_2$, and $\nu(B{=}N)$ for $(^{t}Bu_2C{:}N)_3B$ is the lowest of all. This general trend is the same as that observed for $\nu(C{=}N)$ values. The interpretation of these differences in $\nu(C{=}N)$ with number of methyleneamino groups in terms of boron-nitrogen bond order as described earlier would therefore seem to be equally applicable to similar variations in $\nu(B{=}N)$.

Table 2.7

Skeletal stretching frequencies, ν(B=N) and ν(C=N) (cm^{-1}), of some di-t-butylmethyleneaminoboranes

Compound	ν(B=N)	ν(C=N)
$^tBu_2C{:}NBCl_2$	1287	1839
$^tBu_2C{:}NBPhCl$	1314	1838
$^tBu_2C{:}NBPh_2$	1304	1820
$^tBu_2C{:}NBEt_2$	1292	1818
$^tBu_2C{:}NB^nBu_2$	1294	1821
$^tBu_2C{:}NB^tBu_2$	1302	1812
$^tBu_2C{:}NBHCl$	1294	1845
$(^tBu_2C{:}N)_2BF$	1291	1750
$(^tBu_2C{:}N)_2BCl$	1271	1777
$(^tBu_2C{:}N)_2BH$	1290	1760
$(^tBu_2C{:}N)_2BPh$	1295	1774
$(^tBu_2C{:}N)_2BMe$	1289	1745
$(^tBu_2C{:}N)_3B$	1253	1730
	1299	1736
	1288	1756
	1269	1739
	1298	1745

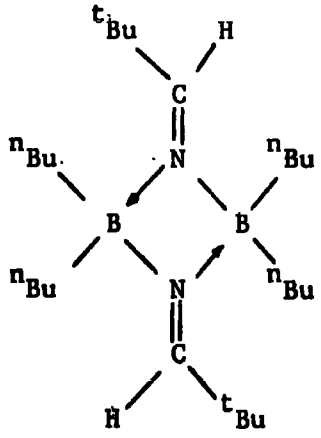
It is interesting to note however that $\nu(B\equiv N)$ for $(^tBu_2C{:}N)_2BF$ is higher than that for $(^tBu_2C{:}N)_2BCl$. This order of frequencies is the reverse of that of their azomethine stretching frequencies but is the same as that of the $\nu(B\equiv N)$ values of related fluoro- and chloro-aminoboranes Table 2.8) (237).

Table 2.8

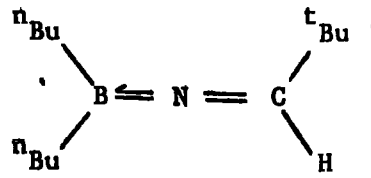
Skeletal stretching frequencies (cm^{-1}) for some related amino- and methyleneamino-haloboranes

Compound	ν(C=N)		ν(B≡N)	
	F	Cl	F	Cl
$^tBu_2C{:}NBX_2$	1796	1839 (22)		1287 (22)
$(^tBu_2C{:}N)_2BX$	1750	1777 (52)	1291	1271 (52)
Me_2NBX_2			1595 (237)	1548 (237)

(v) ^{11}B n.m.r. spectra of methyleneaminoboranes. The use of ^{11}B n.m.r. spectroscopy for determining the co-ordination number of boron is well-established (218), and has been employed to distinguish the monomeric form of $^tBuCH{:}NB^nBu_2$ (chemical shift -38.8 ± 0.5 ppm relative to $BF_3.OEt_2$) from its dimer (-7.4 ± 0.4 ppm). In the dimer (Figure 2.7.a), the boron atoms are four-co-ordinate and are more magnetically shielded, so their signal appears at higher field than the less-well shielded three-co-ordinate boron atom in the monomer (Figure 2.7.b). (219)



(a)



(b)

Figure 2.7

In addition to the co-ordination number of boron, ^{11}B chemical shifts are also sensitive to the degree to which the vacant p-orbital of the trigonal sp^2-hybridised boron atom is occupied (175). If there is little or no dative π-bonding into the vacant boron p-orbital electron density at the central metal is clearly significantly less than if the p-orbital is fully occupied: in this situation electron density at boron is similar to that in compounds where there is a tetrahedral arrangement of four ligands around sp^3-hybridised boron.

There is already considerable evidence that the shielding of the boron nucleus increases with the increase in double-bond character of the B-X bond (221, 222).

^{11}B n.m.r. is particularly useful in the study of methyleneaminoboranes because of this sensitivity of the chemical shift to electron density at boron as a result of B-X multiple bonding as this provides information about the effect of the ligands on the environment of the central atom. Table 2.9 gives ^{11}B n.m.r. data for some di-t-butylmethyleneaminoboranes, and some related compounds.

Table 2.9

^{11}B n.m.r. data for di-t-butylmethyleneaminoboranes and some related compounds

Compound	δ p.p.m.	Ref
$^tBu_2C{:}NBCl_2$	-11.3 ±0.2	22
$(^tBu_2C{:}N)_2BCl$	- 5.9 ±0.2	a
$^tBu_2C{:}NBF_2$	+18.5 ±0.2	a
$(^tBu_2C{:}N)_2BF$	- 6.0 ±0.2	a
$(^tBu_2C{:}N)_3B$	- 6.3 ±0.7	a
* $^tBu_2C{:}NB^nBu_2$	-17.6 ±1.0	22
* $^tBu_2C{:}NBPh_2$	-13.6 ±2.0	22
$^tBu_2C{:}NB^tBu_2$	-15.1 ±0.4	a
$(^tBu_2C{:}N)_2BH$	+ 3.5 (J_{B-H} = 135Hz)	a
$(^tBu_2C{:}N)_2BMe$	- 8.6 ±0.2	a
$(^tBu_2C{:}NB.N.H)_3$	- 2.0 ±0.5	a
BF_3	+24.0	221
† BCl_3	-11.8	221
† $EtBF_2$	-10.7	220
$EtBCl_2$	-45.6	220
$PhBCl_2$	-36.3	220
$CH_2{:}CHBCl_2$	-35.8	220
$(Et_2N)_3B$	-12.9	223
* $(Et_2NB.N.H)_3$	- 9.4	228
$(MeO)_2BH$	- 8.7 (J_{B-H} = 141 Hz)	222
$Me_3N.BH_3$	+24.9 (J_{B-H} = 97 Hz)	225

(a) This work.

Shifts measured relative to external $B(OMe)_3$ except those marked * which were measured relative to $BF_3.OEt_2$ and transferred to the $B(OMe)_3$ reference scale using the conversion.

$$\delta_{B(OMe)_3} = \delta_{BF_3.OEt_2} + 17.4 \text{ p.p.m}$$

and those marked † which were measured relative to BCl_3 and transferred using the conversion.

$$\delta'_{B(OMe)_3} = \delta_{BCl_3} - 29.6 \text{ p.p.m}$$

The differences in chemical shift between di-t-butylmethyleneamino-dichloro- and -difluoro-boranes are the most striking examples of the usefulness of this technique. The high shift values observed for both the iminofluoroboranes confirm that back-bonding from fluorine to boron p-orbitals increases electron density at boron, reducing the N → B dative π-bonding from the methyleneamino ligand, as indicated by the lower azomethine stretching frequencies for the fluoro- than the chloro-iminoboranes. This effect of the difference of π-bonding capacities of fluorine and chlorine is clearly demonstrated by the chemical shift values of the two boron trihalides (BF_3, +24.0 ppm, BCl_3 -11.8 ppm). Back-donation from the filled p_z-orbital of fluorine to the empty p-orbital of boron significantly alters the electron density at boron (221). This effect is also shown by the ethyldihaloboranes, $EtBCl_2$ and $EtBF_2$ whose chemical shifts are -45.6 ppm and -10.7 ppm respectively, showing that F → B dative π-bonding significantly increases the electron density (and hence the magnetic shielding) at boron (220).

The large difference between the chemical shifts of the two iminofluoroboranes, $^tBu_2C{:}NBF_2$ and $(^tBu_2C{:}N)_2BF$ apparently reflects the different capacities of the methyleneamino group and fluorine to π-bond to boron. In $^tBu_2C{:}NBF_2$, where one imino group is bonded to boron, F → B back-bonding significantly increases electron density at boron. The low N-B bond order in the compound is reflected by its azomethine stretching frequency, which is considerably lower than that of the related chloroborane. However, when a second fluorine atom is replaced by the methyleneamino group ($(^tBu_2C{:}N)_2BF$), ^{11}B n.m.r. shows that electron density at boron is very much lower than in $^tBu_2C{:}NBF_2$, and is similar to that in $(^tBu_2C{:}N)_2BCl$.

The effect of π-bonding on chemical shift is also demonstrated by alkyl-, aryl-, and vinyl- dichloroboranes (220). Ethyldichloroborane has a lower chemical shift (-45.6 ppm) than phenyl- and vinyl-dichloroborane (-36.3 ppm

and -35.8 ppm respectively) indicating that in the latter two compounds the boron atoms are more shielded than in $EtBCl_2$, suggesting that C → B π-bonding may be an important shielding factor. The differences between the shifts observed for $^tBu_2C{:}NB^nBCl_2$ (-17.6 ppm) (22), $^tBu_2C{:}NB^tBu_2$ (-15.5 ppm), and $^tBu_2C{:}NBPh_2$ (-13.6 ppm) (22), although rather smaller than those described above, still suggest that the phenyl group participates in some degree of C → B π-bonding. However, their I.R. spectra show that $^tBu_2C{:}NBPh_2$ has a slightly higher stretching frequency (1820 cm^{-1}) than $^tBu_2C{:}NB^tBu_2$ (1812 cm^{-1}) but slightly lower than $^tBu_2C{:}NB^nBu_2$ (1821 cm^{-1}). As the ^{11}B n.m.r. shift differences are small, and the azomethine stretching frequency is less sensitive to changes in X in compounds $^tBu_2C{:}NBX_2$, this reversal in order of magnitude of I.R. frequencies is not considered to be of particular significance, especially as the spectra were recorded in different phases (see Table 2.1).

Single peaks were observed in the spectra of $(^tBu_2C{:}N)_3B$ and $(^tBu_2C{:}NB.N.H)_3$ at -6.3 ppm and -2.0 ppm respectively. These chemical shift values, which indicate that electron density at boron is fairly high, support the interpretation of the low azomethine stretching frequencies of these compounds in terms of extensive N → B dative π-bonding.

The postulated "paddle-wheel" structure of $(^tBu_2C{:}N)_3B$ allows maximum overlap of the nitrogen and boron p-orbitals, but a similar structure for tris(amino)boranes with the alkyl groups perpendicular to the plane of the BN_3 unit means that the nitrogen p-orbital is perpendicular to the vacant p-orbital on boron, and N → B dative π-bonding will not be so extensive as in tris(imino)boranes. This difference in N → B dative π-bonding is reflected in the chemical shifts of $(^tBu_2C{:}N)_3B$ (^{11}B = -6.3 ppm) and $(Et_2N)_3B$ (^{11}B = -12.9 ppm (223)) which indicate that such bonding is rather less

extensive in the tris(amino)- than in the tris(imino)-borane, where such bonding results in greater shielding of boron.

Similarly, the spectrum of $(^{t}Bu_2C{:}NB.N.H)_3$ (^{11}B = -2.0 ppm) shows an absorption at higher field than $(Et_2NB.N.H)_3$ (^{11}B = -9.4 ppm (228)) as a result of the difference in capacity of the two ligands to π-bond to boron. A study of the influence of the amino group on aromaticity in various B- and N-aminoborazine was inconclusive (228), although it has been shown that aromaticity is not influenced by substitution of chlorine or alkyl groups for hydrogen (229). A more extensive study is required to determine whether the N → B dative π-bonding from methyleneamino groups in iminoborazines can influence the aromaticity of the borazine ring.

^{11}B chemical shift values of 2-amino-1,3,2-diazaboracycloalkanes have been interpreted in terms of a set of additive substituent contributions (230) which depend on their mesomeric effects rather than electronegativity (231). Unfortunately, ^{11}B n.m.r. spectra could not be obtained for the iminodiaza- and dioxa-boracyclopentane compounds as a similar method of interpretation may be useful. The similarity of their azomethine stretching frequencies makes interpretation of their I.R. spectra somewhat speculative.

The ^{11}B n.m.r. spectrum of bis(di-t-butyl)methyleneaminoborane, $(^{t}Bu_2C{:}N)_2BH$, shows a doublet centred at +3.5 ppm, with peaks at 0.0 ppm and 7.0 ppm as a result of spin coupling between the ^{11}B and ^{1}H nuclei. The coupling constant (J_{B-H} = ~135 Hz) is similar to that for $(MeO)_2BH$ (^{11}B = -8.7 ppm, J_{B-H} = 141Hz (222)). The magnitude of the coupling between hydrogen and another magnetic nucleus depends on the s character in the bond between the two species; smaller coupling constants are obtained for sp^3- than sp^2-hybridised boron (224). For example, in $Me_3N.BH_3$, where the boron is sp^3-hybridised, J_{B-H} = 97Hz, while in borazole, where the boron is sp^2-

hybridised, J_{B-H} = 138Hz (225). The value of J_{B-H} for $(^tBu_2C{:}N)_2BH$ is thus consistent with the boron being sp^2-hybridised.

^{11}B n.m.r. is thus extremely useful in the study of methyleneaminoboranes as the indication of electron density at boron given by the spectra shows the influenece of other groups on boron much more effectively than I.R. spectra.

(vi) ^1H n.m.r. spectra of methyleneaminoboranes. The ^1H n.m.r. spectra of the new methyleneaminoboranes were recorded as benzene or toluene solutions or neat liquids at $+33^\circ$ and at temperatures down to -80°. Details of the spectra are given in Table 2.10, together with those for some other di-t-butylmethyleneaminoboranes (22,52). In all cases the t-butyl absorption was a sharp singlet which did not change significantly in shape or chemical shift when the solutions were cooled. The single absorption observed for both the t-butyl groups in the methyleneamino ligand indicates that their environments are magnetically equivalent. The high azomethine stretching frequency observed for these compounds indicates at linear C=N≐B skeleton which gives the t-butyl groups identical environments (Figure 2.4.a). The alternative limiting structure for the monomeric species has a bent C=N-B unit and non-equivalent t-butyl groups (Figure 2.4.g) would give a single absorption in the ^1H n.m.r. spectrum only if inversion at nitrogen were more rapid than the n.m.r. timescale (see Chapter 1, section 4b). Such a structure is unlikely for these methyleneaminoboranes as the azomethine stretching frequencies of the compounds would be lower than are observed.

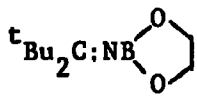
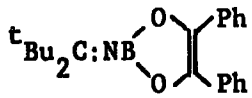
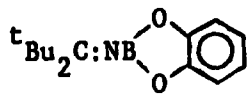
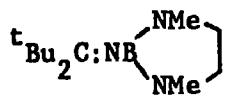
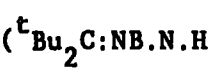
The narrow range of observed shift values indicates that the t-butyl groups are little affected by changes in electron density at boron and in the N-B bond. This is not unexpected as the groups are three bonds away from the central boron atom, and the electronic changes effected at boron by varying the ligands attached to it will not be very influential over

Table 2.10

^{1}H n.m.r. spectroscopic data for di-t-butylmethyleneaminoboranes.

Compound	τ values p.p.m.	
$^tBu_2C{:}NBF_2$	9.42s	
$^tBu_2C{:}NBCl_2$*	8.92s	
$^tBu_2C{:}NBHCl$*	8.95s	BH proton not observed
$^tBu_2C{:}NBPhCl$*	8.89s	2.74c (3), 2.24c (2)
$^tBu_2C{:}NBPh_2$*	8.86s	2.75c (6), 2.31c (4)
$^tBu_2C{:}NBEt_2$*	8.89s	
$^tBu_2C{:}NB^nBu_2$*	8.85	8.4 - 9.2c
$^tBu_2C{:}NB^tBu_2$	9.17s (18)	8.92s (18)
$(^tBu_2C{:}N)_2BF$	9.38s	
$(^tBu_2C{:}N)_2BCl$*	8.80s	
$(^tBu_2C{:}N)_2BH$	9.54s	BH proton not observed
$(^tBu_2C{:}N)_2BMe$	8.91s	methyl group not observed
$(^tBu_2C{:}N)_2BPh$*	8.73s (7)	2.69c (1)
$(^tBu_2C{:}N)_3B$	9.18s	

Table 2.10 continued

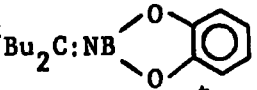
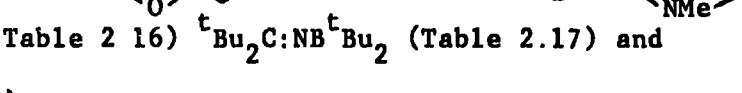
Compound	τ values p.p.m.	
	9.05s (18)	~ 6.5c (~ 2)
	9.68s	4.73c (v. weak)
	9.38s (18)	3.77 (4)
	9.25s (18)	8.00s (5) 7.39c (~ 3)
	9.51s	NH protons not observed

$\tau(Me_4Si)$ = 10.00 p.p.m.

s = singlet, c = complex. Relative intensities in brackets

* Spectra recorded using TMS as internal reference standard (52). All others refer to external TMS.

such a distance.

(vii) Mass spectra of methyleneaminoboranes. The mass spectra of several of the new methyleneaminoboranes were recorded. The same fragments found in the mass spectrum of $^{t}Bu_2C{:}NH$ (Table 2 11 (52)) were present in all the spectra. Some other features were common to most spectra and to those described previously (22, 52). A feeble monomeric parent peak was observed as the species with the higher m/e value. Initial fragmentation normally involved loss of a butyl group as the source of the most abundant fragments. As observed previously (52), alkyl groups on boron tended to lose alkene to form B-H species, but the t-butyl groups of the methyleneamino ligand did not eliminate butene to leave C-H species so readily. These features are illustrated by details of the mass spectra of $(^{t}Bu_2C{:}N)_2BF$ (Table 2.12) $(^{t}Bu_2C{:}N)_2BH$ (Table 2.13)  (Table 2.14),  (Table 2.15), $(^{t}Bu_2C{:}N)_3B$ (Table 2 16) $^{t}Bu_2C{:}NB^{t}Bu_2$ (Table 2.17) and  (Table 2.18).

(c) Reactions of some di-t-butylmethyleneaminoboranes. With the exception of $(^{t}Bu_2C{:}N)_3B$, all the di-t-butylmethyleneaminoboranes prepared in this work are hydrolysed by atmospheric moisture to di-t-butylketone and the appropriate boric acid derivative (Equation 2.41).

$$(^{t}Bu_2C{:}N)_nBX_{3-n} + nH_2O \rightarrow {}^{t}Bu_2C{:}NH + (HO)_nBX_{3-n} \quad (\downarrow H_2O \rightarrow {}^{t}Bu_2C{:}O) \qquad 2.41$$

In this respect $(^{t}Bu_2C{:}N)_2BF$ differs from $(^{t}Bu_2C{:}N)_2BCl$, which gives $(^{t}Bu_2C{:}N)_2BOH$ on hydrolysis (Equation 2.42) (52).

$$(^{t}Bu_2C{:}N)\,Cl + H_2O \rightarrow (^{t}Bu_2C{:}N)_2BOH + HCl \qquad 2.42$$

This provides a further example of the differences between the properties of

Table 2.11

Mass spectroscopic results for $^{t}Bu_2C{:}NH$ (52)

m/e	Relative Intensity	Assignment
142	0.1	$^{t}Bu_2C{:}NH_2$
141	1	$^{t}Bu_2C{:}NH$
126	2.5	$^{t}Bu(Me_2C)C{:}NH$
84	46	$^{t}BuCNH$
68	26	$Me_2C{:}C{:}N$
59	28	$^{t}BuH_2$
58	4	^{t}BuH
57	84	^{t}Bu
56	15	C_4H_8
43	10	MeCHNH
42	53	MeCNH
41	100	MeC:N
39	37	HCCN
29	18	$H_2C{:}NH$
27	21	HC:N
16	2	MeH
15	12	Me

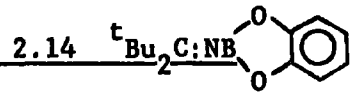
^{11}B-containing fragments in the mass spectra of several di-t-butylmethyleneamines

Table 2.12 $(^tBu_2C{:}N)_2BF$

m/e	Rel. Int.	Assignment
310	~ 1	$(^tBu_2C{:}N)_2BF$
279	4	$(^tBu_2C{:}N)(C_8H_{15})BF$
253	33	$(^tBu_2C{:}N)(^tBuC{:}N)BF$
196	36	$(^tBuC{:}N)_2BF$
170	8	$^tBuC{:}NBF$

Table 2.13 $(^tBu_2C{:}N)_2BH$

m/e	Rel. Int.	Assignment
292	4	$(^tBu_2C{:}N)_2BH$
277	2	$(^tBu_2C{:}N)_2BH$ minus CH_3
235	88	$(^tBu_2C{:}N)(^tBuC{:}N)BH$
180	24	$(^tBuHC{:}N)_2BH$
178	20	$(^tBuC{:}N)_2BH$
177	24	$(^tBuC{:}N)_2B$
151	1	$^tBu_2C{:}NB$

Table 2.14 $^{t}Bu_2C{:}NB$ 

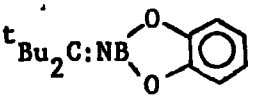
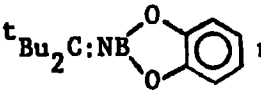
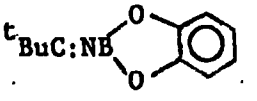
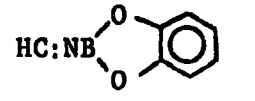
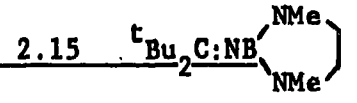
m/e	Rel. Int.	Assignment
259	4	$^{t}Bu_2C{:}NB$ 
244	< 1	$^{t}Bu_2C{:}NB$  minus CH_3
202	12	$^{t}BuC{:}NB$ 
146	6	$HC{:}NB$ 

Table 2.15 $^{t}Bu_2C{:}NB$ 

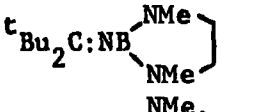
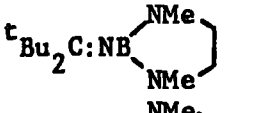
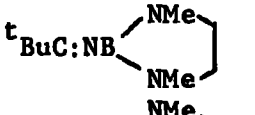
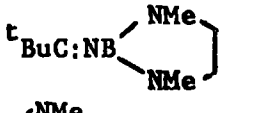
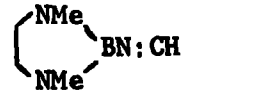
m/e	Rel. Int	Assignment
237	7	$^{t}Bu_2C{:}NB$ 
222	2	$^{t}Bu_2C{:}NB$  minus CH_3
180	67	$^{t}BuC{:}NB$ 
164	3	$^{t}BuC{:}NB$  minus CH_4
124	100	

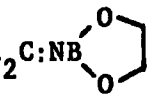
Table 2.16 $(^tBu_2C{:}N)_3B$

m/e	Rel. Int.	Assignment
431	< 1	$(^tBu_2C{:}N)_3B$
415	< 1	$(^tBu_2C{:}N)_3B$ minus CH_4
374	7	$(^tBu_2C{:}N)_2BN{:}C^tBu$
291	100	$(^tBu_2C{:}N)_2B$
260	6	$(^tBuC{:}N)_3B$
235	15	$^tBuHC{:}NBN{:}C^tBu_2$
204	4	$(^tBuC{:}N)_2BN{:}CH$
179	8	$(^tBuHC{:}N)_2B$

Table 2.17 $^{t}Bu_2C{:}NB^{t}Bu_2$

m/e	Rel. Int.	Assignment
209	12	$^{t}Bu_2C{:}NBH^{t}Bu$
166	2	$^{t}Bu_2C{:}NBHCH_2$
152	8	$^{t}Bu_2C{:}NBH$
124	11	$^{t}Bu_2C{:}NBHCH_2$ minus C_3H_6
110	13	$^{t}BuMeC{:}NBH$

Table 2.18 $^{t}Bu_2C{:}NB$

m/e	Rel. Int.	Assignment
211	< 1	$^{t}Bu_2C{:}NB$ 
152	< 1	$^{t}Bu_2C{:}NBH$

imino-chloro- and imino-fluoro-boranes which result from the differences between boron-chlorine and -fluorine bonds. This behaviour is similar to that of the boron trihalides: BCl_3 is completely hydrolysed by atmospheric moisture to boric acid and HCl, but BF_3 is less readily hydrolysed, forming boric acid only in a considerable excess of water.

The use of bis(di-t-butylmethyleneamino)fluoroborane to prepare other methyleneamino)boranes is discussed in section 2(a).

Tris(di-t-butylmethyleneamino)borane is remarkably stable towards hydrolysis: no significant decomposition was observed after ~ 4 weeks exposure to the atmosphere, and complete hydrolysis to boric acid was achieved only with a considerable excess of water (Equation 2.43).

$$(^tBu_2C{:}N)_3B + 3H_2O \rightarrow 3\,^tBu_2C{:}NH + B(OH)_3$$
$$\downarrow H_2O$$
$$^tBu_2C{:}O \qquad 2.43$$

The stability of $(^tBu_2C{:}N)_3B$ is further demonstrated by its apparent lack of lewis acid or base properties. ^1H n.m.r. and I.R. studied of $(^tBu_2C{:}N)_3B$ in good donor solvents (acetonitrile, benzonitrile, collidene) gave no evidence of co-ordination. Similarly, when refluxed at ~ 120° in pet. ether with one equivalent of $^tBu_2C{:}NLi$ there was no evidence for the formation of any $LiB(N{:}C^tBu_2)_4$ (Equation 2.44).

$$(^tBu_2C{:}N)_3B + {}^tBu_2C{:}NLi \not\rightarrow LiB(N{:}C^tBu_2)_4 \qquad 2.44$$

This contrasts with the behaviour of di-t-butylmethyleneaminoaluminium compounds: $(^tBu_2C{:}N)_3Al$ is very readily hydrolysed; lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C{:}{}^tBu_2)_4$ is readily formed from aluminium chloride and four equivalents of iminolithium (40); and in the preparation of the tris(imino)alane, $(^tBu_2C{:}N)_3Al$, lithium must be rigorously

excluded as $LiAl(N:C^tBu_2)_4$ is the more stable compound and is formed preferentially whenever possible (see Chapter 4). Attempts to prepare a four-co-ordinate iminoboron compound by reaction between $^tBu_2C:NBCl_2$ and $(C_5H_{11})_2NCl$ were also unsuccessful.

Tris(dimethylamino)borane reacts with $(MeCN)_3BW(CO)_3$ to give a π-donor complex, $(Me_2N)_3BW(CO)_3$ (Figure 2.8.) (217).

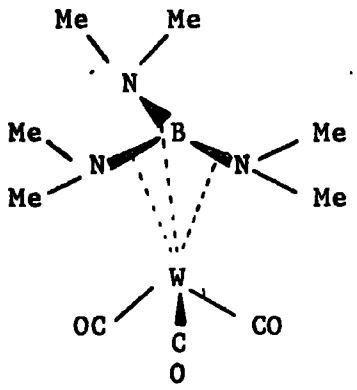


Figure 2.8.

Attempts to carry out similar reactions between molybdenum and tungsten carbonyl compounds and $(^tBu_2C:N)_3B$ at high temperature, and using U.V. radiation were unsuccessful: no evidence of complex formation was observed in the I.R. ^1H n.m.r., or ^{11}B n.m.r. spectra of the reaction mixtures.

It seems likely that the bulk of the t-butyl groups prevents sufficiently close approach of the metal carbonyl species for complex formation: In addition, the nitrogen-metal bond strength in a π-complex similar to that in figure 2.8. would not be as strong as in the parent iminoborane as the nitrogen p-orbital is in a suitable orientation to overlap with boron, but not the transition metal. This is the opposite situation to that in the aminoborane-metal carbonyl complex, as the nitrogen p-orbital is perpendicular to the vacant boron p-orbital so overlap of these orbitals is small but is suitably orientated for overlap with a d-orbital in the transition metal,

and N → W dative π-bonding is favoured.

3. Summary of the new methyleneaminoboranes.

The new di-t-butylmethyleneaminoboranes are listed in table 2.1. They are monomeric, and their I.R. ^{1}H n.m.r. and ^{11}B n.m.r. spectra are consistent with the methyleneamino group being linearly-bound to boron. Some interpretation of the spectra of some compounds has been made in terms of the influence of other groups on boron on the extent of N → B dative π-bonding.

Tris(di-t-butylmethyleneamino)borane is the first example of a crystalline tris(imino)borane. It is thought to have a "paddle-wheel" structure with the t-butyl groups projecting from the plane of the planar $(>C{:}N)_3B$ unit: such a structure allows maximum overlap of the filled p-orbital on nitrogen and the vacant p-orbital on boron.

Chapter 3

Methyleneamino derivatives of magnesium

This chapter describes the preparation and properties of some new methyleneamino derivatives of magnesium. Aspects of their I.R. and ^1H n.m.r. spectra are discussed and compared with those of related compounds.

1. Experimental.

(a) Reactions of i-propylmagnesium bromide.

A solution of i-propylmagnesium bromide in diethyl ether was prepared in the usual manner from magnesium turnings and i-propyl bromide. Unreacted magnesium was allowed to settle then the solution was standardised using excess dilute sulphuric acid and titrating the unused acid with sodium hydroxide solution.

(i) Reaction between i-propylmagnesium bromide and diphenylmethyleneamine.

A solution of i-propylmagnesium bromide (17.2 ml of a 0.88 M solution, 15.1 mmole) in diethyl ether was added to a solution of diphenylmethyleneamine (2.74 g, 15.1 mmole) in 80 ml diethyl ether at -196°. The mixture was allowed to warm up. At ~ -20° a pale yellow solid began to form in the yellow solution. This solid continued to form as the mixture gradually warmed to room temperature. The mixture was stirred overnight then solvent was removed from the pale yellow suspension. The creamy-coloured solid was recrystallised from THF as large pale yellow crystals identified as diphenylmethyleneaminomagnesium bromide-di-THF, $Ph_2C{:}NMgBr.2THF$, m.p. 165 - 180°d. (Found: C, 56.72; H, 5.00; Br, 20.2; Mg, 5.71; N, 3.56%; M, 379. $C_{21}H_{36}BrMgNO_2$ requires C, 58.85; H, 6.11, Br, 18.64; N, 3.27%; M, 438.76).

ν_{max}(Nujol mull) 1630s, 1596m; 1576m, 1550sh, 1489w, 1443s, 1400w, 1367w, 1349sh, 1334w, 1309w, 1295w, 1285v.w, 1250m, 1240sh, 1180w, 1157w, 1147w, 1076m, 1027s, 1002w, 958w, 934m, 922m, 915sh, 899m, 873s, 840sh, 790s, 779s, 728w, 703sh, 699s, 673sh, 650s, 620w, 609w, 500s, 467s, 402m cm^{-1}.

(ii) Reaction between i-propylmagnesium bromide and di-p-tolylmethyleneamine.

A solution of i-propylmagnesium bromide (18.1 ml of a 0.91 N solution, 16.5 mmole) in diethyl ether was added to a solution of di-p-tolylmethyleneamine (3.46 g, 16.5 mmole) in 60 ml diethyl ether at -196^{o}. The mixture was allowed to warm up. As the mixture was melting a deep yellow-coloured suspension was formed. At $\sim -20^{o}$ then solid dissolved to give a yellow solution, then at $\sim 0^{o}$ an off-white suspension was formed. The mixture was stirred at room temperature overnight, then solvent was removed and the pale yellow powdery solid was recrystallised from THF. The pale yellow needle-shaped crystals obtained were identified as di-p-tolylmethyleneaminomagnesium bromide-di-THF, $(p\text{-tolyl})_2C{:}NMgBr.2THF$. m.p. decomposes above $\sim 190^{o}$.
(Found: C, 58.23; H, 5.87; Mg, 5.11; N, 3.25%.
$C_{23}H_{30}BrMgNO_2$ requires C, 60.49; H, 3.07; Mg, 5.32; N, 3.07%).
ν_{max}(Nujol mull). 1910v.w, 1805v.w, 1624s, 1602s, 1568m, 1560sh, 1504m, 1402v.w, 1346v.w, 1320sh, 1308m, 1288m, 1272w, 1255s, 1230s, 1217sh, 1209m, 1183sh, 1179m, 1141w, 1118sh, 1109m, 1070w, 1031s, 1020s, 955sh, 948w, 919s, 877s, 842sh, 830sh, 825s, 783s, 749s, 745sh, 683s, 675sh, 631m, 601s, 526w, 472s, 455sh, 340sh, 365w, cm^{-1}.

(iii) Reaction between i-propylmagnesium bromide and di-t-butylmethyleneamine.

A solution of i-propylmagnesium bromide (15.6 ml of a 0.88 M solution, 13.7 mmole) in diethyl ether was added to a solution of di-t-butylmethyleneamine (1.94 g, 13.8 mmole) in 80 ml diethyl ether at -196°. The mixture was allowed to warm to room temperature. During ~ 1 hour a greenish-yellow colour developed. The solution was stirred overnight at room temperature, then reduced to ~ half its volume. Hexane was added, and a greenish suspension was formed. This redissolved on slight heating. The light green crystals obtained from this solution were identified as di-t-butylmethyleneaminomagnesium bromide $[^{t}Bu_2C{:}NMgBr]_2$, m.p. 142 - 157°d.

(Found: Mg, 9.26; N, 5.27%; M, 423.

$C_9H_{18}BrMgN$ requires Mg, 9.95; N, 5.73% M, 488.94).

ν_{max}(Nujol mull). 1667sh, 1618s, 1595s, 1408sh, 1386s, 1314s, 1335v.w, 1292w, 1262w, 1237w, 1209m, 1196m, 1152s, 1123m, 1091s, 1040s, 1000m, 954s, 930sh, 896s, 875sh, 838m, 799sh, 782s, 738w, 725m, 675sh, 664m, 620w, 600sh, 577m, 516w, 483s, 409m cm^{-1}.

(b) Reactions of diethylmagnesium.

During the preparation of ethylmagnesium bromide solution from ethyl bromide and magnesium turnings in diethyl ether the reaction vessel was shielded from light as recommended in literature (276). Unreacted magnesium was filtered off, and the solution of ethylmagnesium bromide was standardised in the usual way.

Diethylmagnesium can be prepared from this solution by adding dioxan, which forms an insoluble complex with magnesium bromide (277, 278).

Dioxan (12.06g, 137 mmole) was added to a solution of ethylmagnesium bromide (80 ml of a 0.86 M solution, 69 mmole) in diethyl ether at $\sim 0^{o}$. A copious white precipitate formed immediately. The mixture was stirred at room temperature for 24 hours then allowed to stand for a further 24 hours to let the precipitate settle. The clear colourless solution was decanted from the precipitate and standardised by titrating a known volume of the solution with a 1.0 M solution of sec-butanol in xylene, using 1,10-phenanthroline as indicator (279).

(i) Reaction between diethylmagnesium and diphenylmethyleneamine (mole ratio 1:2).

A solution of diphenylmethyleneamine (8.8 g, 48.6 mmole) in 80 ml diethyl ether was added to a solution of diethylmagnesium (70.5 ml of a 0.34 M solution, 24 mmole) in diethyl ether at -196^{o}. A deep maroon colour developed immediately. The mixture was stirred at room temperature for $\sim$ 18 hours during which time a brick-red suspension formed. Solvent was removed and the brick-red powdery solid was recrystallised from THF. The deep red crystals obtained were identified as bis(diphenylmethyleneamino)magnesium trimer-bis-THF, $[(Ph_2C{:}N)_2Mg]_3.2THF$ m.p. $\sim 90^{o}$d.

(Found: Mg, 5.77; N, 6.17%.

$C_{86}H_{46}Mg_3N_6O_2$ requires Mg, 5.61; N, 6.47%)

ν_{max}(Nujol mull) 1484v.w, 1650m, 1612s, 1573m, 1408v.w, 1310w, 1302sh, 1281w, 1240m, 1224m, 1170w,br, 1072m, 1068sh, 1028m, 1000w, 966w, 949m, 906m, 890m, 850w, 787w, 764m, 725w, 706sh, 699s, 682sh, 668v.w, 650m, 640sh, 625sh, 605v.w, 510w, 495sh, 466m, 455sh cm^{-1}.

(ii) Reaction between diethylmagnesium and di-p-tolylmethyleneamine (mole ratio 1:2).

A solution of di-p-tolylmethyleneamine (6.47 g, 31 mmole) in 80 ml diethyl ether was added to a solution of diethylmagnesium (44 ml of a 0.34 M solution, 15 mmole) in diethyl ether at -196°. A deep orange-brown colour developed immediately. At ~0°, a clear orange solution was formed but during 18 hours at room temperature an orange suspension was formed. Solvent was removed, and the orange powdery solid recrystallised from THF as deep orange crystals identified as bis(di-p-tolylmethyleneamino)magnesium, $[((p\text{-tolyl})_2C{:}N)_2Mg]_n$ (n probably = 2) m.p. 153-4° d.

(Found: Mg, 5.27; N, 6.40%.

$C_{30}H_{28}MgN_2$ requires Mg, 5.51; N, 6.35%).

ν_{max}(Nujol mull) 1657m, 1616m, 1600s, 1565m, 1501w, 1308w, 1287w, 1254m, 1240m, 1225sh, 1209w, 1178m, 1173sh, 1150v.w, 1125m, 1113m, 1107sh, 1070m, 1034m, 1020m, 950v.w, 921m, 904w, 890v.w, 877w, 825s, 805sh, 784m, 745sh, 740s, 725w, 685sh, 672m, 633w, 618sh, 601m, 573w, 500sh, 483s, 476s, 327sh cm^{-1}.

(iii) Reaction between diethylmagnesium and di-t-butylmethyleneamine (mole ratio 1:2).

A solution of di-t-butylmethyleneamine (5.02 g, 35.5 mmole) in 20 ml diethyl ether was added to a solution of diethylmagnesium (50 ml of a 0.34 M solution, 17 mmole) at -196°. As the solution warmed to room temperature, a lime-green colour developed. The solution was stirred overnight at room temperature, then solvent was removed and the pale green fluffy solid was recrystallised from hexane/diethyl ether

to give pale green crystals identified as bis(di-t-butylmethyleneamino)-magnesium, $[(^tBu_2C{:}N)_2Mg]_n$ (n probably = 2) m.p. decomposes above ~ 120°.
(Found: Mg, 8.40; N, 9.6%.
$C_{18}H_{36}MgN_2$ requires Mg, 8.48; N, 9.77%).
ν_{max}(Nujol mull) 1720sh, 1665s, 1604s, 1398m, 1322s, 1355m, 1320m, 1260s, 1230sh, 1204s, 1125sh, 1098s,br, 1020w, 1037s, 1020sh, 953s, 930s, 905sh, 877m, 801s, 731w, 720sh, 706w, 680w, 663m, 616sh, 585s,br, 560sh, 543w, 493m, 435sh, 405m cm^{-1}.

(iv) Reaction between diethylmagnesium and di-t-butylmethyleneamine (mole ratio 1:1).

A solution of diethylmagnesium (39 ml of a 0.33 M solution, 12 mmole), in diethyl ether was added to a solution of di-t-butylmethyleneamine (1.71 g, 12 mmole) in 80 ml diethyl ether at -196°. The mixture was allowed to reach room temperature and stirred for ~ 3 hours. Solvent was removed from the pale green solution to leave a pale greenish-yellow solid which recrystallised from hexane/diethyl ether as pale green crystals identified as di-t-butylmethyleneaminoethylmagnesium $[^tBu_2C{:}NMgEt]_n$ (n probably = 2) m.p. decomposes above ~ 105°.
(Found: Mg, 12.35; N, 6.67%.
$C_{11}H_{23}MgN$ requires Mg, 12.56; N, 7.23%).
ν_{max}(Nujol mull) 1605s, 1586sh, 1386s, 1364s, 1300w,br, 1263m, 1245v.w, 1223sh, 1209m, 1153w, 1125m, 1100s, 1060sh, 1047s, 1023w, 955s, 925m, 900sh, 894m, 801s, 737w, 724w, 665s, 615sh, 581s, 510m, 585sh, 408m cm^{-1}.

(c) Reactions of ethylmagnesium bromide.

A solution of ethylmagnesium bromide in diethyl ether was prepared

and standardised as outlined in section b.

(i) Reaction between ethylmagnesium bromide and diphenylmethyleneaminolithium.

A solution of ethylmagnesium bromide (15.5 ml of a 0.81 M solution, 12.0 mmole) in diethyl ether was added to a solution of diphenylmethyleneaminolithium (12.8 mmole) in 25 ml diethyl ether at -196°. As the mixture warmed up its colour changed from the characteristic deep red of diphenylmethyleneaminolithium to olive green, and an off-white precipitate gradually formed.

Solvent was removed and the green residue was extracted with hexane/diethyl ether. Lithium bromide was filtered off. Green crystals were obtained from the filtrate and identified as diphenylmethyleneaminoethylmagnesium, $[Ph_2C{:}NMgEt]_n$ (n probably = 2) m.p. ~85° d.

(Found: Mg, 9.35; N, 5.72%.

$C_{15}H_{15}MgN$ requires Mg, 10.41; N, 6.00%).

ν_{max}(Nujol mull) 1619s, 1594w, 1576m, 1308w, 1280v.w, 1260m,br, 1240sh, 1225sh, 1193w, 1182w, 1153w, 1141v.w, 1123sh, 1091w, 1073w, 1049m, 1025sh, 1000w, 968w, 932m, 918w, 901m, 834w, 800sh, 789w, 777m, 736w, 721w, 700s, 649m, 600w, 510m,br, 469m cm^{-1}.

(ii) Reaction between ethylmagnesium bromide and di-p-tolylmethyleneaminolithium.

A solution of ethylmagnesium bromide (14.0 ml of a 0.81 M solution, 11.3 mmole) in diethyl ether was added to a solution of di-p-tolylmethyleneaminolithium (11.4 mmole) in 25 ml diethyl ether at -196°. As the mixture was warmed to room temperature a white precipitate formed in a

green solution. The mixture was stirred overnight then solvent was removed, and the green residue extracted with hexane/diethyl ether. Removal of solvent from the solution obtained afforded an extremely moisture-sensitive yellowish-green microcrystalline solid. A red colour developed on the surface of the solid even when it was stored in an atmosphere of nitrogen. The green solid was identified as

<u>di-p-tolylmethyleneaminoethylmagnesium,</u> $[(p\text{-tolyl})_2C{:}NMgEt]_n$

(n probably = 2) m.p. ~ 110 d.

(Found: Mg, 9.18; N, 5.02%.

$C_{17}H_{19}MgN$ requires Mg, 9.29; N, 5.35%).

ν_{max}(Nujol mull) 1618s, 1600s, 1565w, 1560sh, 1510sh, 1504w, 1401v.w, 1308w, 1287w, 1260m, 1240sh, 1210w, 1179m, 1151w, 1112w, 1090v.w, 1050m, 1030w, 952w,br, 921s, 825s, 800sh, 783m, 742s, 720sh, 678m, 633w, 615sh, 601s, 577v.w, 477s cm^{-1}.

<u>(iii) Reaction between ethylmagnesium bromide and di-t-butylmethyleneaminolithium.</u>

A solution of ethylmagnesium bromide (25.4 ml of a 0.81 m solution, 20.6 mmole) in diethyl ether was added to a solution of di-t-butylmethyleneaminolithium (20.6 mmole) in 40 ml diethyl ether at -196°. The mixture was allowed to warm to room temperature, and a white precipitate formed in a lime-green solution during ~ 18 hours. Solvent was removed and the green solid was extracted with fresh ether, and lithium bromide was filtered off. Attempted crystallisation of the solution was unsuccessful (cf. section (b)(iv)). Removal of solvent afforded a pale yellow solid identified by its I.R. spectrum as

<u>di-t-butylmethyleneaminoethylmagnesium</u> $[{}^{t}Bu_2C{:}NMgEt]_n$ (section (b)(iv)).

(d) Reactions of phenylmagnesium bromide.

A solution of phenylmagnesium bromide in diethyl ether was prepared and standardised in the usual way.

(i) Reaction between benzonitrile and phenylmagnesium bromide.

A solution of benzonitrile (2.66 g, 25.8 mmole) in 20 ml diethyl ether was added to a solution of phenylmagnesium bromide (30 ml of a 0.87 M solution 26.0 mmole) in diethyl ether at -196°. The mixture was warmed to room temperature and stirred overnight. Solvent was removed from the pale yellow suspension to leave a pale yellow solid which was recrystallised from THF and identified by its I.R. spectrum as diphenylmethyleneaminomagnesium bromide-di-THF $Ph_2C{:}NMgBr.2THF$ (see section (a)(i)).

(ii) Reaction between diphenylmethyleneaminolithium and phenylmagnesium bromide.

A solution of phenylmagnesium bromide (17.5 ml of a 0.87 M solution, 15.2 mmole) in diethyl ether was added to a solution of diphenylmethylene aminolithium (15 mmole) in 80 ml diethyl ether at -196°. As the mixture warmed to room temperature its colour changed from red through brown and yellow to green, and an off-white precipitate was formed. The mixture was stirred overnight at room temperature then solvent was removed and the yellowish residue was extracted with toluene. A small quantity of yellow rather powdery crystals were obtained. Their elemental analyses were very poor, so this material is only tentatively identified as diphenylmethyleneaminophenylmagnesium, $[Ph_2C{:}NMgPh]_n$ (n probably = 2).

ν_{max}(Nujol mull) 1618s, 1598w, 1591sh, 1576m, 1554v.w, 1490w, 1411w,

1400m,br, 1310w, 1286w, 1235w, 1232w, 1191v.w, 1160sh, 1151w, 1090w, 1077w, 1057m, 1030w, 1003v.w, 941m, 925v.w, 909m, 895sh, 855w, 835v.w, 792m, 789m, 630v.w, 601s, 680m,br, 654m, 640w, 625v.w, 605w, 510w, 471m, 466sh, 455sh, 438w cm^{-1}.

(iii) Reaction between di-t-butylmethyleneaminolithium and phenylmagnesium bromide.

A solution of phenylmagnesium bromide (25 ml of a 0.87 M solution, 21.8 mmole) in diethyl ether was added to a solution of di-t-butylmethyleneaminolithium (21.8 mmole) in 60 ml hexane at -196°. As the mixture warmed to room temperature, an off-white suspension slowly formed in the yellow solution. The mixture was stirred overnight then solvent was removed and the pale yellow solid was extracted with fresh hexane. Attempted crystallisations of the hexane solution were all unsuccessful, so solvent was removed to leave an off-white powdery solid. As in the previous experiment, elemental analyses were very poor, so this compound is only tentatively identified as di-t-butylmethyleneaminophenylmagnesium, $[{}^{t}Bu_2C{:}NMgPh]_n$ (n probably = 2) m.p. decomposes above ~185°.
ν_{max}(Nujol mull) 1609sh, 1614sh, 1605s, 1578sh, 1488s, 1415m, 1385s, 1312s, 1300sh, 1270m, 1228w, 1204w, 1165v.w, 1124m, 1069w, 1045sh, 1037m, 1021w, 1014sh, 1002v.w, 990v.w, 951w, 800w, 764m, 737m, 708s, 702sh, 675sh, 665s, 629w, 584w, 490w,br, 435v.w, 401w cm^{-1}.

(e) Reaction between bis(diphenylmethyleneamino)magnesium and diphenylmethyleneaminolithium.

A solution of diphenylmethyleneaminolithium (15 mmole) in 50 ml diethyl ether was added to a solution of bis(diphenylmethyleneamino)magnesium

(15 mmole) in 60 ml diethyl ether prepared as described previously (section (b)(i)). During ~ 3 hours the colour of the solution gradually changed from red to orange to yellow, and a yellow precipitate formed during ~ 18 hours. Solvent was removed leaving a yellow powdery solid, which could not be recrystallised from either diethyl ether or THF. The solid was identified as the lithium tris(diphenylmethyleneamino)-magnesate diethyl etherate $LiMg(N:CPh_2)_3.Et_2O$ m.p. decomposes ~ 120°

(Found: Li, 1.41; Mg, 3.78; N, 6.53%.

$C_{43}H_{40}AlLiN_3O$ requires Li 1.01; Mg 3.76; N, 6.50%).

ν_{max}(Nujol mull) 1623s, 1595sh, 1575m, 1486sh, 1467sh, 1460s, 1445sh, 1377s, 1377sh, 1307w, 1260sh, 1235m, 1071w, 1047w, 1028w, 933w, 900m, 789w, 773m, 723w, 700s, 676w, 640m, 620w, 608w, 496sh, 475w cm^{-1}.

The intensities of the peaks quoted here are relative. As strong a mull as possible was prepared, but the spectrum obtained was still very weak.

(f) Preparation of dilithium tetrakis(diphenylmethyleneamino)magnesate, $Li_2Mg(N:CPh_2)_4$.

A solution of diphenylmethyleneaminolithium (0.6 mmole) in 10 ml diethyl ether was added to a suspension of lithium tris(diphenylmethylene-amino)magnesate -diethyl ether (0.40 g, 0.6 mmole) in 30 ml diethyl ether, and the mixture was stirred overnight. The cloudy yellow solution was filtered, and solvent removed to leave an opaque orange syrup. Distillation of this material at 130°, ~ 0.8 mm Hg afforded a small quantity of a yellow liquid whose I.R and ^1H n.m.r. spectra were consistent with its identity being dilithium tetrakis(diphenylmethylene-amino)magnesate. There was not sufficient material for elemental analyses.

ν_{max}(liquid film) 3100sh, 3080v.w, 3062w, 3030w, 1658s, 1652sh, 1618sh, 1598s, 1577sh, 1567s, 1362s, 1318m, 1298sh, 1277s, 1195s, 1177m, 1150m, 1062m, 1029m, 1000w, 971v.w, 940w, 930m, 920sh, 890s, 847w, 810w, 788s, 762s, 739w, 721w, 696s, 670w, 639m, 623s, 523w, 440w cm^{-1}.

(g) Reactions between diphenylmethyleneaminomagnesium bromide and phenyl isocyanate.

(i) Mole ratio 1:1.

Phenyl isocyanate (0.56 g, 4.7 mmole was added slowly to a solution of diphenylmethyleneaminomagnesium bromide (Ph_2C:NMgBr.2THF) (1.99 g, 4.7 mmole) in 40 ml THF. The solution immediately became darker yellow in colour. It was stirred at room temperature for ~1 hour then solvent was removed. Attempted recrystallisation of the yellow solid from THF/hexane was unsuccessful. The creamy-white powder obtained was identified as the THF adduct of the product of insertion, Ph_2C:NC(:O)N(Ph)MgBr.THF m.p. 156-158° d.

(Found: Br, 18.02; Mg, 5.75; N, 5.81%)

$C_{24}H_{23}BrMgN_2O_2$ requires Br, 18.18; Mg, 5.53; N, 6.37%).

ν_{max}(Nujoll mull) 1720m, 1635s, 1597m, 1579w, 1532s, 1490w, 1450s, 1400sh, 1321m, 1297w, 1261w, 1182w, 1167m, 1076m, 1032s, 1004w, 990w, 954w, 918w, 885m, 802sh, 792w, 770sh, 761s, 715sh, 700s, 679w, 640w, 626w, 612v.w, 604v.w, 550sh, 542w, 500sh cm^{-1}.

(ii) Mole ratio 1:2.

This experiment was carried out in the same manner as that described in section (g)(i) using two equivalents of phenyl isocyanate. The off-white solid obtained was thought to be the product of a second insertion

reaction, $Ph_2C{:}NC(:O)N(Ph)C(:O)N(Ph)MgBr.THF$, m.p. 172-178 d.

(Found: Br; 14.62; Mg, 3.63; N, 6.23%.

$C_{31}H_{28}BrN_3MgO_3$ requires Br, 14.20; Mg, 4.32; N, 7.47%)

ν_{max}(Nujol mull) 1725m, 1688s, 1594s, 1585m, 1580m, 1495m, 1467sh, 1460s, 1450sh, 1379m, 1368w, 1322m, 1215w,br, 1180w,br, 1160sh, 1073w, 1035m, 918w, 889m, 819w, 813w, 790v.w, 773m, 766sh, 759m, 742w, 721w, 708sh, 702m, 692m, 676v.w, 641v.w, 617v.w, 601w, 545sh, 540w, 511v.w cm^{-1}.

(h) Reaction between t-butylmagnesium chloride and t-butyl cyanide.

A solution of t-butylmagnesium chloride (~ 100 mmole) in diethyl ether was prepared from t-butyl chloride and magnesium. The reaction was started by adding ~ 2ml t-butyl chloride to the magnesium in ~ 20 ml diethyl ether, adding a crystal of iodine and refluxing the mixture for ~ 2 hours. The preparation was completed, and the solution standardised in the usual way.

A solution of t-butyl cyanide (3.22 g, 27 mmole) in 20 ml diethyl ether was added to a solution of t-butylmagnesium chloride (40 ml of a 0.68 M solution, 27 mmole) in diethyl ether. The mixture was allowed to reach room temperature. A white precipitate slowly formed in a colourless solution. An I.R. spectrum of this solution showed peaks at 2272 and 2238 cm^{-1} attributed to coordinated and free t-butyl cyanide and peaks in the region appropriate for C=N stretching vibrations at 1665 and 1640 cm^{-1}.

The white solid was filtered off and solvent removed from the filtrate. A white gelatinous material remained.

ν_{max}(Contact film) 2980-2840s,br, 2390-2320s,br, 2672s, 2615m, 2272s, 2220w,sh, 1940w, 1665s, 1641m, 1578w, 1476s, 1460s,br, 1435sh, 1389s, 1370s, 1360w, 1350w, 1325w, 1288w, 1260m, 1240s, 1207s, 1191m, 1168sh, 1145m, 1110sh, 1089m, 1040m,sh, 998s, 958m, 938m, 899m, 884w, 833w, 800s, 782s, 766sh, 698m, 636m, 688m, 510m, 462w, 410w cm^{-1}.

This reaction has been repeated several times with similar results.

On one occasion, the mixture was gently heated to $\sim 40^{\circ}$. After a few minutes a bright yellow colour suddenly developed but the I.R. spectrum of this solution was no different from that recorded before heating.

Work is still in progress to isolate and identify the products of the reaction between t-butyl cyanide and t-butylmagnesium chloride and to study its mechanism.

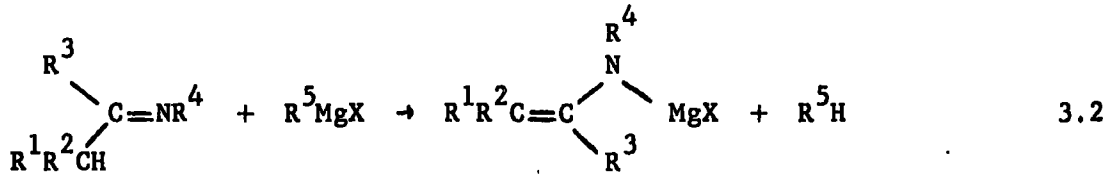
2. Discussion.

(a) Preparation of methyleneaminomagnesium compounds. The new methyleneaminomagnesium compounds are listed in table 3.1 together with their azomethine stretching frequencies. In the procedure found most convenient, hydrocarbon or ether solutions of the reagents were mixed at -196°, allowed to reach room temperature and stirred for a few hours. The reactions studied were those between Grignard reagents and nitriles, methyleneaminolithium compounds, or methyleneamines, and between diethylmagnesium and methyleneamines.

(i) Insertion reactions. The chemistry of organomagnesium compounds has been widely studied, but methyleneaminomagnesium species have received little attention although they have long been known as the product of insertion of nitriles into Grignard reagents (Equation 3.1)

$$R^1C{:}N + R^2MgX \rightarrow R^1R^2C{:}NMgX \qquad 3.1$$

Until this present work, the reaction between Grignard reagents and nitriles was the only established route to the imine form of methyleneaminomagnesium compounds, although N-substituted enamino Grignards have been prepared from Grignard reagents and Schiff's bases containing C_α-hydrogen (Equation 3.2) (238)



imine enamine

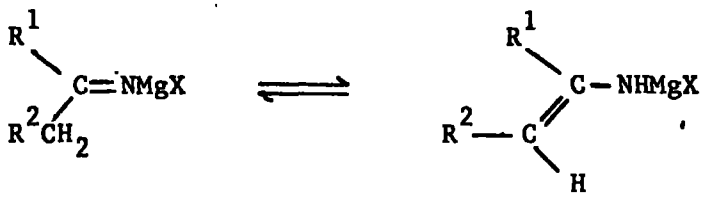
In a recent study of the imine - enamine tautomerisation of methyleneaminomagnesium compounds (Equation 3.3), several new imino-Grignard reagents were prepared (79).

Table 3.1

Azomethine stretching frequencies ν(C=N) (cm^{-1}), of the new methyleneaminomagnesium compounds

Compound	ν(C=N)	
	Terminal	Bridging
$Ph_2C{:}NMgBr.2THF$	1630	
$(p\text{-tolyl})_2C{:}NMgBr.2THF$	1624	
$[Ph_2C{:}NMgBr]_m$		1620
$[{}^tBu_2C{:}NMgBr]_2$		1618
$[Ph_2C{:}NMgEt]_n$		1619
$[(p\text{-tolyl})_2C{:}NMgEt]_n$		1618
$[{}^tBu_2C{:}NMgEt]_n$		1605
$[Ph_2C{:}NMgPh]_n$		1618
$[{}^tBu_2C{:}NMgPh]_n$		1605
$[(Ph_2C{:}N)_2Mg]_3.2THF$	1650	1612
$[((p\text{-tolyl})_2C{:}N)_2Mg]_n$	1657	1616
$[({}^tBu_2C{:}N)_2Mg]_n$	1665	1604
$LiMg(N{:}CPh_2)_3.OEt_2$	1623	
$Li_2Mg(N{:}CPh_2)_4$	1658	1598

n probably = 2 (see text).



3.3

All the preparations involved reaction between a Grignard reagent and a nitrile, but an interesting modification to the general technique, using a "cyclic reactor" has been described for some compounds (79).

In this modification, amalgamated magnesium is prepared from magnesium and mercuric chloride solution, packed into a vertical glass column, then covered with ether. Allyl bromide is added to form allylmagnesium bromide. Allyl or aryl halide is added, then the new Grignard reagent is reacted with a solution of the required nitrile either by allowing the Grignard reagent to run into a refluxing solution of the nitrile in ether, or by slowly adding the nitrile to the Grignard reagent (Equations 3.4 and 3.5).

$$R^1X + CH_2{=}CH{-}CH_2MgBr \rightarrow R^1MgX + CH_2{=}CH{-}CH_2Br \qquad 3.4$$

$$R^1MgX + R^2C{:}N \rightarrow {}^1/_n[R^1R^2C{:}NMgX]_n \qquad 3.5$$

(X = Br; $R^1 = C_6H_5CH_2$; R^2 = Ph, m-tolyl, cyclopropyl, R^1 = 1-phenylethyl, R^2 = Ph, m-tolyl.

X = Cl, $R^1 = C_6H_5CH_2$; R^2 = Ph).

Several other compounds $R^1R^2C{:}NMgX$ (X = Cl, R^1 = Ph; R^2 = Me, p-xylyl, $C_6H_5CH_2$; R^1 = Me; R^2 = cyclopropyl; X = Br; R^1 = Ph; R^2 = Et, cyclopropyl), were prepared by the usual procedure of addition of a nitrile to an ether solution of a Grignard reagent followed by several hours' reflux. No evidence was presented that these forcing conditions were necessary. In the present work it was found that for the reaction between benzonitrile and phenylmagnesium bromide, and the other general

preparative routes to methyleneamino derivatives of magnesium, reaction was complete after a few hours at room temperature. Several colour changes were frequently observed when the reaction mixtures, prepared at low temperature, were warmed to room temperature, but for these reactions no colour change was observed during the period of stirring at room temperature and I.R. spectra of the solutions showed that no starting materials remained.

Two nitrile insertion reactions were attempted in this work. The insertion of benzonitrile into phenylmagnesium bromide afforded diphenylmethyleneaminomagnesium bromide, which could be crystallised from T.H.F. as $Ph_2C{:}NMgBr.2THF$.

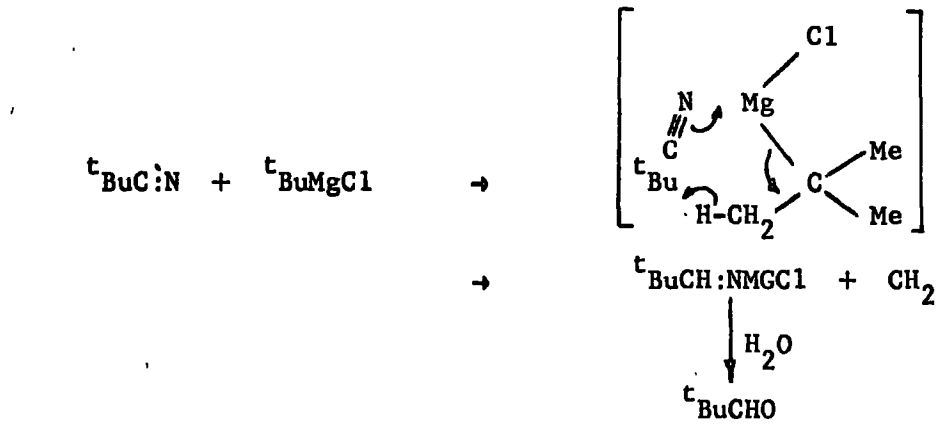
The reaction between t-butyl cyanide and t-butylmagnesium chloride did not proceed so readily.

In previous investigations of this system, interest focussed on the products obtained after hydrolysis of the reaction mixture, rather than the initially-formed magnesium nitrogen compounds.

When t-butyl cyanide and t-butylmagnesium chloride were stirred at room temperature for four months, and the mixture hydrolysed, 60% of the t-butyl cyanide was recovered and 7% of the aldehyde ^tBuCHO was obtained (Equation 3.6) (272).

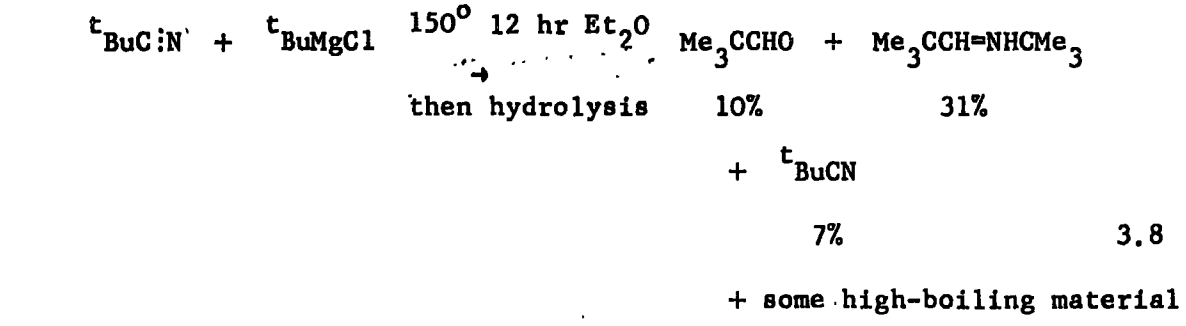
$$^tBuC{:}N + {}^tBuMgCl \xrightarrow[\text{room temp.}]{\text{4 months}} \text{60\% recovery of } {}^tBuCN + \text{then hydrolysis } 7\% \ {}^tBuCHO \qquad 3.6$$

The mechanism proposed for this reaction is shown in equation 3.7. (272).



3.7

Hydrolysis of the products obtained when t-butyl cyanide and t-buytlmagnesium chloride were heated to 150° in ether solution in an autoclave afforded the products shown in equation 3.8. (261). No di-t-butylketone $^{t}Bu_2C{:}O$, the expected product if di-t-butylmethylene-aminomagnesium chloride were the intermediate, was obtained.



3.8

As this work was carried out some time ago, experimental and spectroscopic techniques were probably not adequate for any study of the iminomagnesium intermediates further work on this system may be fruitful.

In the reaction between t-butyl cyanide and t-butylmagnesium chloride carried out in the present work, ether solutions of the reagents were mixed at -196° and allowed to warm to room temperature. A white solid gradually formed in a clear, colourless solution. An I.R. spectrum of this solution showed a large peak in the region appropriate for C=N stretching vibrations at 1665 cm^{-1}, and a smaller peak at 1640 cm^{-1}

Absorptions attributed to C=N stretching vibrations of t-butyl cyanide were observed at 2272 amd 2238 cm^{-1}, the former being considerably more intense than the latter. These data suggest that the room-temperature reaction between t-butyl cyanide and t-butylmagnesium chloride may not be as slow as previous workers have suggested (272).

The absorption at 2272 cm^{-1} is attributed to t-butyl cyanide co-ordinated to the Grignard reagent, and that at 2238 cm^{-1} is attributed to a small amount of unco-ordinated t-butyl cyanide. The shift to higher frequency on co-ordination characteristic of nitriles (29), is similar to that observed on co-ordination of methyleneamines to Lewis acids (64).

The I.R. spectrum of the gum obtained on removal of solvent from this solution did not have an absorption at 2238 cm^{-1}, indicating that the unco-ordinated t-butyl cyanide could be readily removed, but that which was co-ordinated to the Grignard reagent apparently could not.

The absorption at 1665 cm^{-1} is in the region appropriate for C=N stretching vibrations, and could arise either from $^{t}Bu_2C{:}NMgCl$ or $^{t}BuCH{:}NMgCl$ species.

The ^{1}H n.m.r. spectrum of a benzene solution of this gum showed two main peaks, one at higher and one at lower field than a solution of t-butyl cyanide itself in benzene (9.33 τ). The peak at lower field, 9.03 τ is in the region appropriate for t-butyl groups in methyleneamino derivatives of metals and metalloids, and is consistent with the formation of $^{t}Bu_2C{:}NMgCl$ or $^{t}BuCH{:}NMgCl$ species.

When a sample of the gum was exposed to the atmosphere for a few seconds, vigorous effervescence was seen, but no change in the positions or relative intensities of the peaks between 2300 and 1600 cm^{-1} was seen.

This suggests that there was still some unreacted Grignard reagent present in the gum, and that it is this rather than any iminomagnesium chloride formed, which is destroyed by hydrolylic cleavage of the ^{t}Bu-Mg bonds.

An I.R. spectrum of the products of methanolysis of material obtained from a similar reaction showed a peak in the C=N stretching region at 1665 cm^{-1}, at considerably higher frequency than that of $^{t}Bu_2C{:}NH$ (1610 cm^{-1}). This suggests that one iminomagnesium compound formed initially may be the aldimino derivative, ^{t}BuCH:NMgCl, as inferred in the mechanism proposed by earlier workers (Equation 3.7) (272) rather than ketimine derivative which may have been expected by analogy with the related PhC:N / PhMgBr system.

Survey of Reactions between Grignard reagents and nitriles. The mechanisms of reactions between Grignard reagents and unsaturated species (ketones in particular) have been the subject of great controversy and a brief account of the main points of discussion provides a useful background to the work described in this thesis.

The greatest difficulty has been in identifying the reactive species of the Grignard reagent. Two recent reviews of papers dealing with the composition of Grignard reagents in solution and its relevance to reaction mechanisms and stereochemistry indicate the variety of opinions, some more reliable than others, on this topic (239, 240).

The Schlenk equilibrium (Equation 3.9) (241) was the first attempt to describe solutions of Grignard reagents in terms of their properties, and reflects the fact that at that time it had just been shown that the degree of association of Grignard reagents was concentration-dependent

(242), and that magnesium bromide could be precipitated out of an ether solution of a Grignard reagent by forming its dioxan complex (241).

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg.X_2Mg \qquad 3.9$$

The structure of the dimeric species was first suggested as the unsymmetrical $R_2MgX_2Mg.L_2$ where L is a donor solvent molecule (243). Despite the fact that the evidence on which this assumption was based also supported a symmetrical $[RMgX]_2.L_2$ structure, the unsymmetrical structure was more widely used. Exchange studies between $^{28}MgBr_2$ and Et_2Mg, later shown to be unsatisfactory, suggested that RMgX does not exist in solution, and that Grignard reagents are best represented by the unsymmetrical structure $R_2MgX_2Mg.L_2$ (244).

This description of Grignard reagents was widely accepted for many years, but when it was shown that Grignard reagents are monomeric in T.H.F. over a wide concentration range, and when the presence of EtMgCl, Et_2Mg and $MgCl_2$ species in solutions of EtMgCl in T.H.F. was established, the structure $R_2MgX_2Mg.L_2$ was seriously questioned, as the new information suggested that equilibrium 3.10 (245) represented the species present in solutions of ethylmagnesium chloride, and probably other Grignard reagents.

$$2RMgX.L_2 \rightleftharpoons R_2Mg.L_2 + MgX_2.L_2 \qquad 3.10$$

It had also been shown that in ether ethylmagnesium chloride is associated, so the equilibrium described by equation 3.10 must be extended to include dimers and possibly higher oligomers (e.g. Equation 3.11) (246).

$$L.EtMgCl_2MgEt.L \underset{-2L}{\overset{2L}{\rightleftharpoons}} 2EtMgCl.L_2 \rightleftharpoons Et_2Mg.L_2 + Mg.L_2 \qquad 3.11$$

X-ray crystallographic studies of $PhMgBr.2Et_2O$ (247) and $EtMgBr.2Et_2O$ (248) showed that they were both monomeric in the crystalline phase, with

the four ligands adopting tetrahedral arrangements around magnesium. This is further evidence for the existence of monomeric Grignard reagent species, but does not mean these are necessarily the only species possible in solution as the same compound in different phases may adopt different structures.

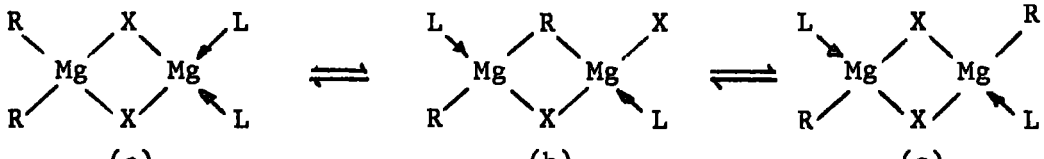
Conclusive evidence for the existence of monomeric $RMgX.L_2$ species in solution was obtained when ebullioscopic measurements established the presence of EtMgBr in ether solution, from which it could be precipitated as its bis(triethylamine) adduct, $EtMgBr.2NEt_3$,(249).

From the vast amount of data in the literature, only a few definite conclusions can be drawn about the composition of Grignard reagents in ether solutions.

In T.H.F. there is relatively little association, and the monomeric species present are $RMgX.2THF$, $R_2Mg.2THF$ and $MgX_2.2THF$.

In diethyl ether, association does occur, and is extensive at concentrations above 0.3 M. The principal monomeric species is $RMgX.2Et_2O$, and only small amounts of $MgX_2.2Et_2O$ and $R_2Mg.2Et_2O$ are present.

Possible structures for the dimer are shown in figure 3.1.



(a) (b) (c)

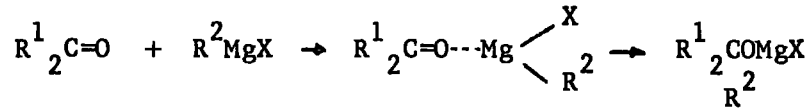
Figure 3.1

It is likely that all three structures may be present in solution. Structure (c) is expecting to predominate, possibly rearranging to a limited extent via (b) to (a)

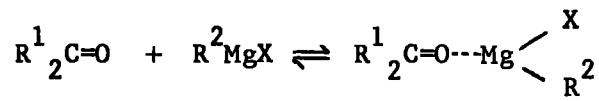
The controversy over the mechanism of reactions between Grignard reagents and unsaturated species has reflected the uncertainty about the

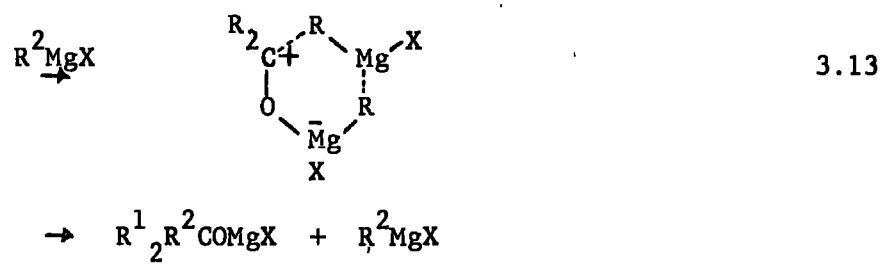
structure of Grignard.

Early studies of the ketone - Grignard reagent system described straightforward mechanisms involving RMgX species in both unimolecular (Equation 3.12) (250) and third-order (Equation 3.13) (251) processes.



3.12



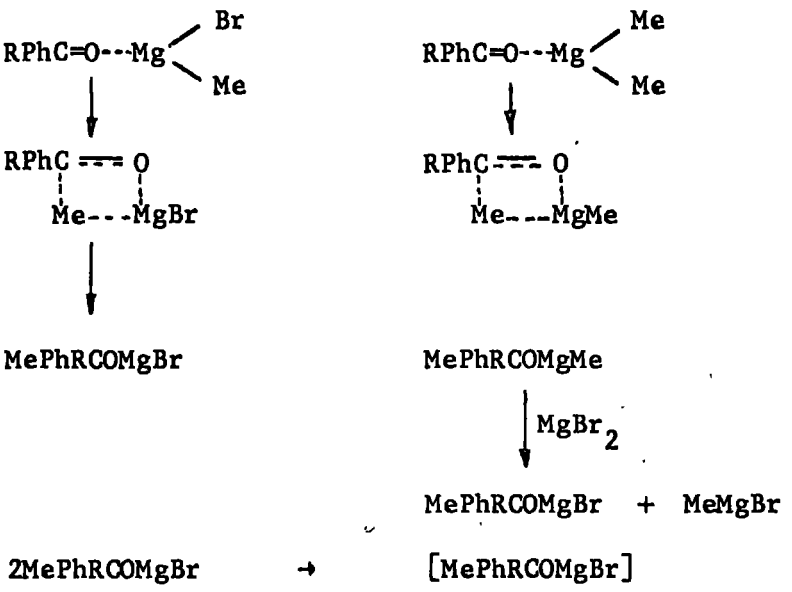


3.13

This and similar work was criticised when the Grignard reagent was thought to be $R_2MgX_2Mg.L_2$, and complex mechanisms using this species were invoked (80, 252, 253). It is clear however, that none of the kinetic data reported is entirely consistent with the mechanisms deduced from them.

Since the report describing the presence of monomeric species in diethyl ether solution, these species have again featured in the proposed mechanisms of reactions of Grignard reagents. The general improvement in experimental techniques also means that kinetic data may be more reliable than when the early work was done.

Kinetic data obtained during a recent rigorous study of the reaction between 2-methylbenzophenone and methylmagnesium bromide were interpreted in terms of the mechanism shown in equation 3.14, involving both MeMgBr and MeMg as reactive species, but only one product, MePhRCOMg (R = 2-methylphenyl) was obtained (254).

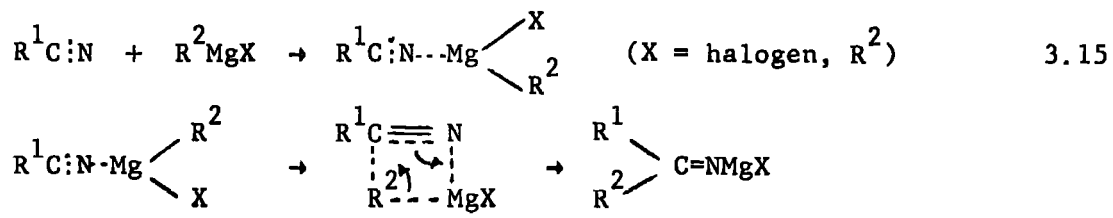


3.14

Controversy still remains over the mechanisms of some reactions of Grignard reagents, but it is clear that in recent years considerable progress has been made.

Although detailed inferences about the mechanism of reaction between Grignard reagents and nitriles cannot be made from those of ketone - Grignard reagent systems, some similarities may be expected.

It seems likely that the first stage of the reaction involves co-ordination of the nitrogen atom of the nitrile to the magnesium of the Grignard reagent. By analogy with equation 3.14, formation of a four-membered transition state is the likely next step, and rearrangement of this as shown to give the iminomagnesium compound seems reasonable (Equation 3.15).



(X = halogen, R^2) 3.15

Clearly if X = R^2, then the product will be an imino-alkyl- or -aryl-magnesium rather than an iminomagnesium halide. A mechanism similar to that described above for the ketone - Grignard reagent system in which MePhRCOMgMe reacts further with $MgBr_2$ to form $[MePhRCOMgBr]_2$ may also be possible for reactions between Grignard reagents and nitriles. Confirmation of this would require a kinetic study of nitrile - Grignard reagent systems more detailed and quantitative then those previously reported (80, 253).

The reaction between benzonitrile and phenylmagnesium bromide gave the required methyleneaminomagnesium halide apparently uncontaminated by species $[R^1{}_2C{:}NMgR^2]_2$, but whether this was because the reaction proceeded simply in the manner shown by equation 3.15 (X = halogen), or whether species $R^1{}_2C{:}NMgR^2$ were involved in a mechanism similar to that described by equation 3.14 remains an open question. There was no I.R. spectroscopic evidence from this reaction to support the formation of a nitrile - Grignard reagent adduct, as I.R. spectra were recorded after the reagent has been mixed at -196° and warmed to room temperature did not show any peaks attributable to free or complexed nitrile. The I.R. spectra of the solution and its solute obtained from reaction between t-butyl cyanide and t-butylmagnesium chloride however, clearly showed the presence of complexed nitrile, and this seems to be the first evidence that such co-ordination, long postulated, is indeed the first step in reactions

between nitriles and Grignard reagents.

Reactions between di-i-propylmagnesium and t-butyl cyanide however, has been reported to give a crystalline co-ordination complex, $^{i}Pr_2Mg.N{:}C^{t}Bu_2$ which was stable at its melting point (120°) (Equation 3.16) (80). Its I.R. spectrum had an absorption at 2259 cm^{-1}, assigned to ν(C≡N). Although this complex did not rearrange to form the methyleneamino compound in a manner similar to that observed for related alkylalluminium-nitrile complexes (Equation 3.17) (135), it is at least evidence that co-ordination between nitriles and magnesium alkyls can occur.

$$^{t}BuC{:}N + {}^{i}Pr_2Mg \rightarrow {}^{t}BuC{:}N.Mg^{i}Pr_2 \xrightarrow{-X} {}^{t}Bu^{i}PrC{:}NMg^{i}Pr_3 \qquad 3.16$$

$$R^1C{:}N + R^2AlX_2 \rightarrow R^1C{:}N.AlR^2X_2 \xrightarrow{\Delta} R^1R^2C{:}NAlX_2 \qquad 3.17$$

Two other general routes to methyleneamino derivatives of metals and metalloids, reaction between inimolithium and a metal halide ($R_2C{:}NLi + MX_n$) or between an imine and a metal alkyl ($R^2C{:}NH + RMX_m$), have not been described previously for the preparation of methyleneamino derivatives of magnesium, although their use in the preparation of derivatives of two other Group 11 metals, beryllium and zinc, is well-established (see Chapter 1).

Grignard reagents were used as the magnesium halide species in reactions with methyleneaminolithium compounds (Equation 3.

$$R^1{}_2C{:}NLi + R^2MgBr \rightarrow R^1{}_2C{:}NMgR^2 + LiBr \qquad 3.18$$

R^1 = Ph, ^{t}Bu, R^2 = Ph; R^1 = Ph, p-tolyl, ^{t}Bu, R^2 = Et)

The reactions proceeded smoothly and were complete after a few hours at room temperature. Separation of the required product from lithium

bromide by-product was rather difficult, as the only solvents which would dissolve the iminomagnesium compounds (ether, THF) also dissolved some lithium halide which later precipitated out of solution during attempted crystallisation. The sensitivity to hydrolysis of the methyleneaminomagnesium compounds meant that successive recrystallisations over a period of several days, although removing the lithium halide, resulted in some decomposition of the iminomagnesium compound, and the uncontaminated material had to be carefully selected by hand, in an atmosphere of nitrogen, from decomposition products, for analysis and spectroscopic study.

Reactions between alkylmagnesium compounds and imines avoid this problem of contamination by unwanted by-products and were indeed found to be the most successful routes to methyleneaminomagnesium compounds. For example, i-propylmagnesium bromide was used to prepare methyleneaminomagnesium bromides (Equation 3.19), while diethylmagnesium was used in the preparation of methyleneamino ethylmagnesium and bis(methyleneamino)-magnesium compounds (Equation 3.20)

$$^{i}PrMgBr + R_2C{:}NH \rightarrow R_2C{:}NMgBr + {}^{i}PrH \quad (R = Ph, p\text{-toly}, {}^{t}Bu) \qquad 3.19$$

$$Et_2Mg + nR_2C{:}NH \rightarrow (R_2C{:}N)_nMgEt_{2-n} + nEtH \qquad 3.20$$

$(n = 1, R = {}^{t}Bu;\ n = 2, R = Ph, p\text{-tolyl}, {}^{t}Bu)$

Evolution of alkane was apparently complete at or below room temperature, but the reaction mixtures were stirred at room temperature for a few hours to ensure complete reaction.

Reactions involving diphenylmethyleneamine, $Ph_2C{:}NH$, were the most successful: in all cases they gave good yields of products which were readily isolated as crystalline solids. Reactions involving di-p-tolyl-

methyleneamine also gave good yields, but the products were less-readily purified, and those with di-t-butylmethyleneamine gave rather lower yields of products which, in some cases, were very difficult to purify.

This difference in reactivity of these three methyleneamines has also been observed in the series of methyleneamino phosphorus compounds, $XnP(N:CR_2)_{3-n}$ (N = 0, 2; X = Ph, Cl) and $Cl_nOP(N:CR_2)_{3-n}$ (n = 0, 2). Preparation of $Ph_2PC:N^tBu_2$ requires the reagents to be refluxed in hexane for several days, and $P(N:C^tBu_2)_3$ could not be prepared. Preparations of all the other related diphenyl- and di-p-tolyl-methyleneaminophosphorus compounds were complete at room temperature (46).

In general, for the magnesium compounds, as with the phosphorus compounds, details of the preparative techniques were developed using the diphenylmethyleneamino ligand, then the more spectroscopically-useful compounds with di-p-tolyl- and di-t-butyl-methyleneamino ligands were prepared by similar methods.

Lithium tris(diphenylmethyleneamino)magnesate- ether adduct, $LiMg(N:CPH_2)_3.Et_2O$ was prepared by adding one equivalent of diphenylmethyleneaminolithium to a solution of bis(diphenylmethyleneamino)magnesium in ether prepared in situ (Equation 3.21).

$$^1/n[(Ph_2C:N)_2Mg]_n + Ph_2C:NLi \xrightarrow{Et_2O} LiMg(N:CPh_2)_3.Et_2O \qquad 3.21$$

Addition of a second equivalent of iminolithium afforded the dilithium tetrakis(imino)magnesate $Li_2Mg(N:CPh_2)_4$ (Equation 3.22).

$$LiMg(N:CPh_2)_3.Et_2O + Ph_2C:NLi \rightarrow Li_2Mg(N:CPh_2)_4 \qquad 3.22$$

The related lithium beryllates were prepared from beryllium chloride and di-t-butylmethyleneaminolithium in mole ratios of 1:3 and 1:4

(Equations 3.23 and 3.24) lithium tris(di-t-butylmethyleneamino)beryllate was also obtained unexpectedly from the reaction between beryllium chloride and two equivalents of iminolithium (Equation 3.25) (45).

$$BeCl_2 + 3\,{}^tBu_2C{:}NLi \rightarrow LiBe(N{:}C{}^tBu_2)_3 + 2LiCl \qquad 3.23$$

$$BeCl_2 + 4\,{}^tBu_2C{:}NLi \rightarrow Li_2Be(N{:}C{}^tBu_2)_4 + 2LiCl \qquad 3.24$$

$$BeCl_2 + 2\,{}^tBu_2C{:}NLi \rightarrow \tfrac{1}{2}LiBe(N{:}C{}^tBu_2)_3 + \tfrac{1}{2}[{}^tBu_2C{:}NBeCl]_2 + {}^3/2LiCl \qquad 3.25$$

(b) Structure and spectroscopic properties of methyleneaminomagnesium compounds. The structures and spectra of methyleneaminomagnesium compounds had received little attention before this work, although some related zinc and beryllium compounds have been studied. Interesting comparisons may be drawn between the methyleneamino derivatives of these three Group 11 elements, and some other related organometallic compounds.

(i) Structure. The influence of the bulk of substituents on the degree of association of methyleneamino derivatives of Group 11 elements is clearly demonstrated by the series of bis(imino) metal compounds $[(R_2C{:}N)_2M]_n$, which may be dimers (n = 2), trimer (n = 3), or higher polymers.

Bis(di-t-butylmethyleneamino)beryllium is a dimer, $[({}^tBu_2C{:}N)_2Be]_2$, presumably because the bulky t-butyl groups restrict further association. Its structure, determined by X-ray crystallography (Figure 3.2) (39) contains the four-membered $(MN)_2$ ring (M = Be), analogous to those in related Group 111 methyleneamino derivatives (M = B, Al, Ga) (see relevant sections of Chapters 1 and 2). A similar structure is postulated for the bis(di-t-butylmethyleneamino)zinc dimer, $[({}^tBu_2C{:}N)_2Zn]_2$ (45).

Bis(diphenylmethyleneamino)-beryllium and -zinc are apparently

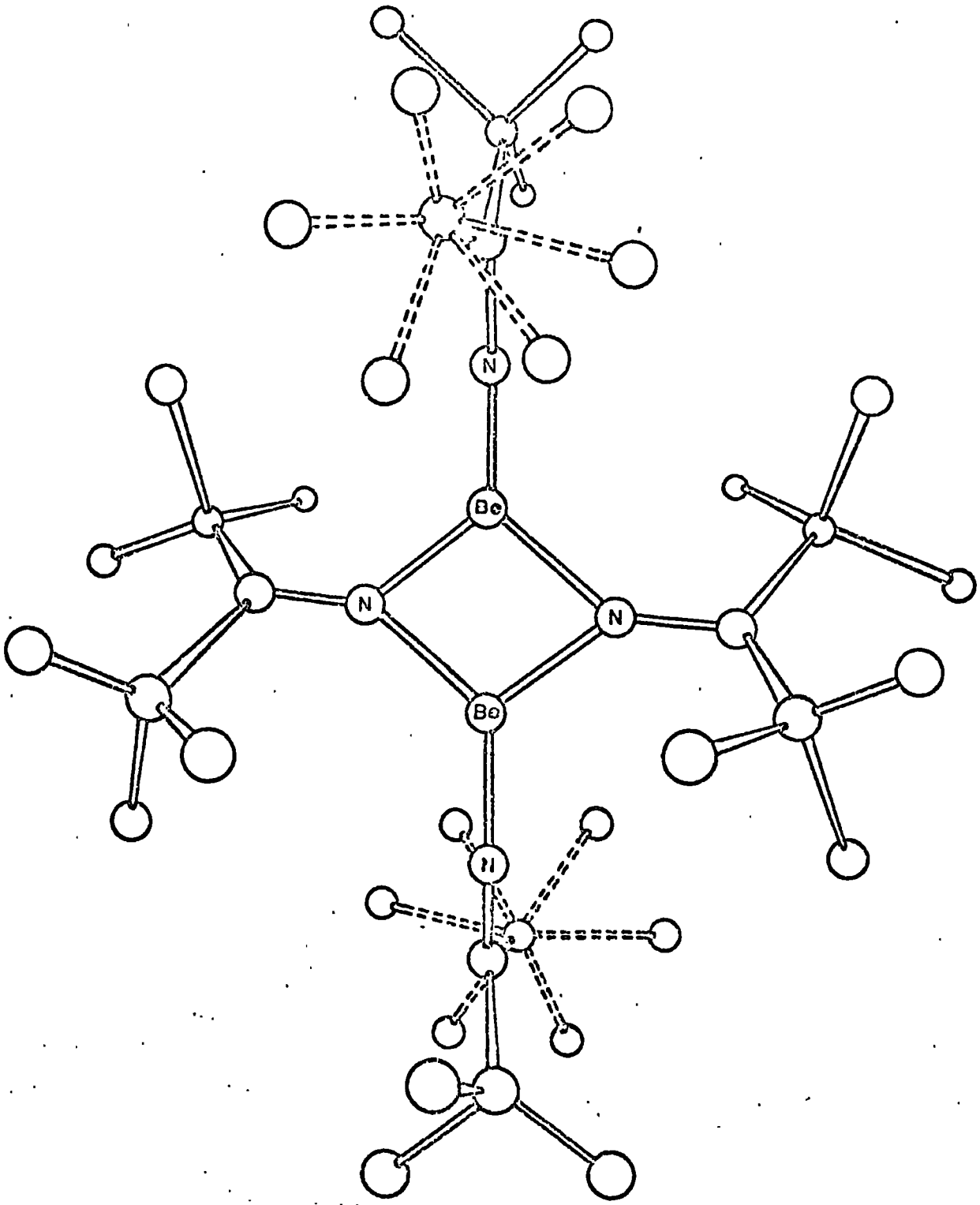


Figure 3.2

$[(^{t}Bu_2C{:}N)_2Be]_2$ (39)

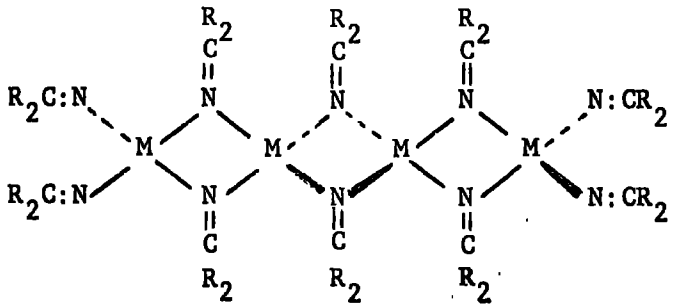
polymeric, $[(Ph_2C{:}N)_2M]_m$ (M = Be, Zn). Their structures probably involve four-membered $(MN)_2$ rings similar to those already established, and described above, for $[(^tBu_2C{:}N)_2Be_2$ and dimeric methyleneamino derivatives of Group 111 metals $[R_2C{:}NMX_2]_2$ (M = B, Al, Ga) (See Chapter 2). In the polymers, a mutually-perpendicular arrangement of adjacent $(MN)_2$ rings is more likely on both steric and bonding considerations than a planar structure, and the structure proposed is shown in figure 3.3.a.

Bis(di-p-tolylmethyleneamino)beryllium is apparently trimeric in benzene, $[(p\text{-tolyl})_2C{:}N)_2Be]_3$. Presumably the slightly greater bulk of the p-tolyl than the phenyl group is sufficient to make this compound less extensively associated than $[(Ph_2C{:}N)_2Be]_m$, Its structure is thought to involve two mutually-perpendicular $(BeN)_2$ rings (Figure 3.3.b) as found in other trimeric beryllium-nitrogen compounds (e.g. $[(Me_2N)_2Be]_3$ (Figure 3.3.c.) (74-76)). The similarity of the ^1H n.m.r. spectra of $[((p\text{-tolyl})_2C{:}N)_2Be]_3$ and these related compounds is evidence for the similarity of their structures.

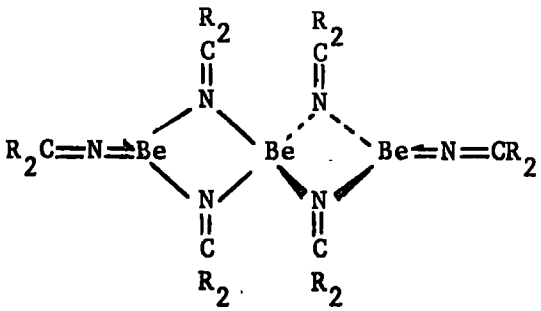
The structures of the bis(methyleneamino)magnesium compounds differ in some ways from those of beryllium and zinc described above. Magnesium is larger than either of these two metals, (Covalent radii Mg, 136 pm; Zn, 125 pm; Be, 89 pm (49)), and is the least electronegative (Mg, 1.23; Zn, 1.66; Be, 1.47 (50)). These properties mean that magnesium may have a higher co-ordination number than the other two elements, and may more readily accept electrons from donor molecules.

Bis(diphenylmethyleneamino)magnesium is thought to be a trimer which crystallises with two molecules of THF, $[(Ph_2C{:}N)_2Mg]_3.2THF$. By analogy with the compounds described above, its structure is thought to be that

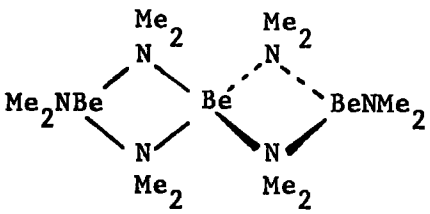
Figure 3.3.



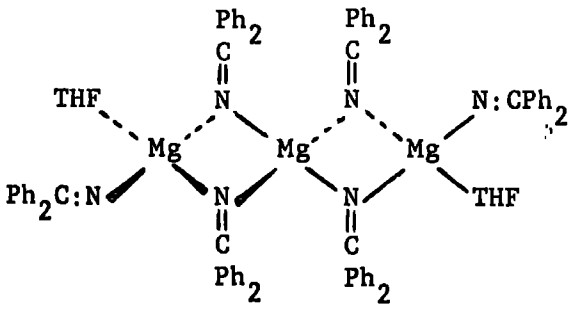
(a)



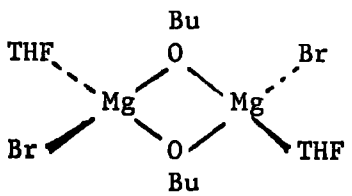
(b)



(c)



(d)

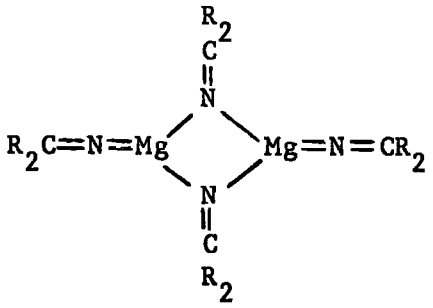


(e)

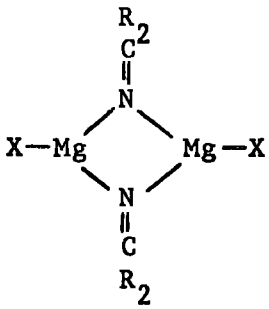
shown in figure 3.3.d, with two mutually-perpendicular $(MgN)_2$ rings. The structure of another THF-solvated magnesium compound, $[^tBuOMgBr]_2.2THF$, determined by X-ray crystallography (255), involves a four-membered planar $(MgO)_2$ ring and the two other species bonded to magnesium adopt trans positions in a plane perpendicular to that of the ring (Figure 3.3.e). Similar structures are proposed for many other compounds $[R^1MgX]_2.2R^2{}_2O$, e.g. $[^tBuMgS^iPr]_2.2Et_2O$ (256), $[BrMgO^iPr]_2.2Et_2O$ (257) and $[EtMgOCEt_3]_2.2THF$ (260). The structure proposed for $[(Ph_2C{:}N)_2Mg]_3.2THF$ with the two different terminal ligands adopting trans positions is rather similar.

Bis(di-p-tolylmethyleneamino)magnesium and bis(di-t-butylmethyleneaminomagnesium however, crystallise without co-ordinated solvent molecules, $[((p\text{-tolyl})_2C{:}N)_2Mg]_n$ and $[(^tBu_2C{:}N)_2Mg]_n$, presumably because the p-tolyl and t-butyl groups, bulkier than phenyl, prevent close approach of solvent molecules. On the basis of their I.R. spectra, in which the intensities of the absorptions due to C=N stretching vibrations in terminal and bridging methyleneamino groups are similar, they are thought to be dimeric (n = 2). Their structures (Figure 3.4.a) are presumably similar to that of $[(^tBu_2C{:}N)_2Be]_2$. Similar structures, with bridging methyleneamino groups (Figure 3.4.b) are proposed for the other dimeric methyleneamino derivatives $[R^1R^2C{:}NMX]_2$ of Group 11 elements which are unsolvated in the solid state (M = Be, X = Cl, $R^1 = R^2$ = Ph, p-tolyl, ^tBu, R^1 = p-tolyl, $R^2 = {}^tBu$; X = $R^1R^2C{:}N$, R^1 = p-tolyl, $R^2 = {}^tBu$. M = Zn, $R^1 = R^2$ = Ph, X = Me. Et, Ph; $R^1 = R^2 = {}^tBu$, X = Me, Cl; M = Mg; X = Br, $R^1 = R^2 = {}^tBu$). Cryoscopic molecular weight determinations could not be made for the magnesium compounds $[R_2C{:}NMgX]_n$ R = Ph, p-tolyl, ^tBu, X = Et; R = Ph,

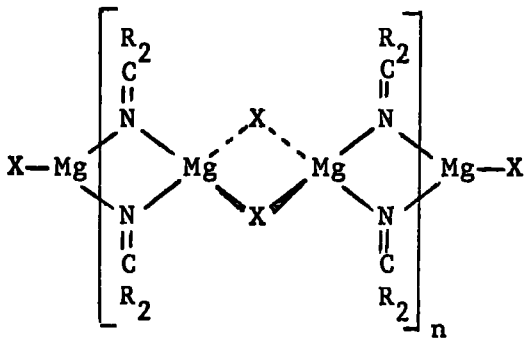
Figure 3.4



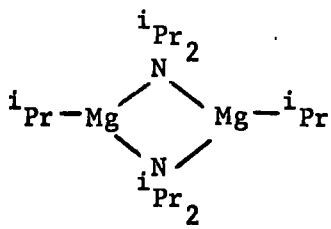
(a)



(b)



(c)



(d)

^{t}Bu, X = Ph as they were apparently not sufficiently soluble in benzene. A possible difficulty however is that some hydrolysis may have occurred, and the small amount of hydrolysis product was insoluble in benzene. However, by analogy with the related compound $[^{t}Bu_2C{:}NMgBr]_2$ and the other dimeric methyleneamino derivatives they are thought to be dimeric, although clearly they could be higher oligomers.

In structures $[R^1R^2C{:}NMX]_2$ and $[(R^1R^2C{:}N)_2M]_2$, the metal is three-co-ordinate. This is not unusual for beryllium and zinc, but is for magnesium whose compounds normally tend to adopt a structure which allows co-ordination of four ligands to magnesium as in the other magnesium compounds described above.

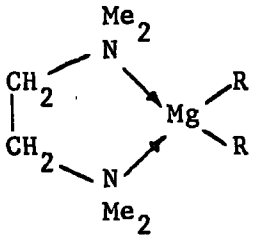
The dimeric di-t-butylmethyleneaminomagnesium compounds described here however are further examples of species containing three-co-ordinate magnesium. If the iminomagnesium compounds $[R_2C{:}NMgX]_n$ whose molecular weights could not be determined cryoscopically are oligomers ($n > 2$), (Figure 3.4.c) the terminal magnesium atoms will still be three-co-ordinate, although clearly the others would be four-co-ordinate. Co-ordination state three was first found for magnesium in the structure of di-t-propylamino-i-propylmagnesium dimer, $[^{i}Pr_2NMg^{i}Pr]_2$ (80). The most likely structure of this compound (Figure 3.4.d) involves bridging amino rather than alkyl groups as nitrogen, with a lone pair of electrons, is a better bridging atom than a carbon atom which is fully co-ordinated. Similarly the structures of the new iminomagnesium compounds are also likely to have bridging methyleneamino groups.

When prepared in diethyl ether, diphenyl- and di-p-tolyl-methylene-aminomagnesium bromide can only be isolated as amorphous yellow solids which are not sufficiently soluble in benzene for cryoscopic molecular

weight determinations. They are thought therefore to be either dimeric, with structures similar to those above, or, more likely, as they, unlike the other compounds $[R_2C{:}NMgX]_n$ are also insoluble in ether, higher oligomers with both imino and bromine bridges (Figure 3.5.a). However, although these compounds are insoluble in diethyl ether, they can be crystallised from THF as bis(ether) complexes, $R_2C{:}NMgBr.2THF$.

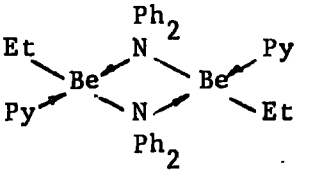
Similar depolymerisations have been described for reactions of magnesium alkyls with NNN'N'-tetramethylethylenediamine (Equation 3.26) (258, 259), diphenylaminoethylberyllium with one and two equivalents of pyridine (Equations 3.27 and 3.28) (260), and diphenylmethyleneamino-methylzinc with pyridine (Equation 3.29) (90).

$$[R_2Mg]_n + nMe_2N.C_2H_4.NMe_2 \rightarrow$$

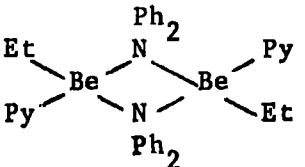


3.26

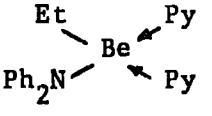
$$[Ph_2NBeEt]_n + nPy \rightarrow$$



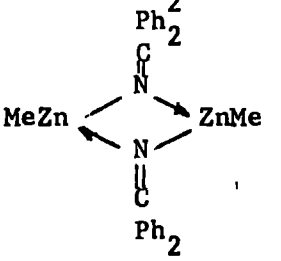
3.27



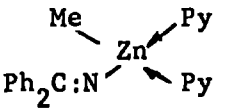
$+ 2Py \rightarrow 2$



3.28

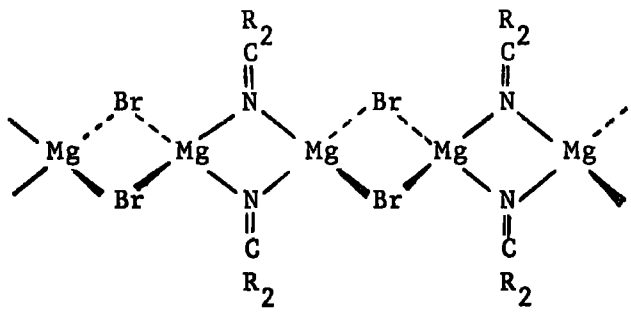


$+ 2Py \rightarrow$

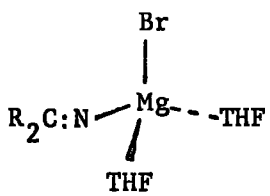


3.29

Figure 3.5



(a)



(b)

In the monomeric species, the four ligands presumably adopt an approximately tetrahedral arrangement around the central metal (Figure 3.5.b).

A preliminary X-ray crystallographic study of $Ph_2C{:}NMgBr.2THF$ has shown that the crystals are monoclinic, with the following properties: a = 1799 pm, b = 1063 pm, c = 2198 pm, $\beta = 114^{o}\ 15^{1}$, $\rho = 1.48$ g cm^{-3} Z = 8, space group C^{6}_{2h} (262). Work on determining the full crystal structure of the compound is in progress.

The related lithium compound, di-t-butylmethyleneaminomagnesium bromide, however, crystallises from ether as an unsolvated species, $[{}^{t}Bu_2C{:}NMgBr]_2$. The bulk of the t-butyl groups would be expected to prevent association into higher polymers and also to limit the approach of solvent molecules.

The two lithium diphenylmethyleneaminomagnesium compounds, $LiMg(N{:}CPh_2)_3.Et_2O$ and $LiMg(N{:}CPh_2)_4$, are monomeric. In both compounds the magnesium is presumably four-co-ordinate. This contrasts with the related beryllium compounds $LiBe(N{:}C^{t}Bu_2)_2$ and $Li_2Be(N{:}C^{t}Bu)_4$, in which the central atom is respectively three- and four-co-ordinate. The combination of the larger, more electropositive central metal, and the less bulky methyleneamino group in $LiMg(N{:}CPh_2)_3.Et_2O$ allows ready access to the magnesium for the neutral co-ordinating ether molecule.

The structures of these four compounds have not been determined. The three compounds in which the central metal is presumable four-co-ordinate, $LiMg(N{:}CPh_2)_3.Et_2O$, $Li_2Mg(N{:}CPh_2)_4$ and $Li_2Be(N{:}C^{t}Bu_2)_4$, are thought to involve a tetrahedral arrangement of the ligands around the metal, similar to that found for lithium tetramethylberyllate, $Li_2Be(Me)_4$

(263) although lithium tris- and tetra-alkylmagnesates, $LiMgR_3$ and Li_2MgR_4 are described extensively in the patent literature as catalysts in acrylonitrile polymerisation, no crystal structures of these, or any compounds which may be similar to the methyleneaminomagnesates have been reported.

(ii) Azomethine stretching frequencies of methyleneaminomagnesium compounds. The main feature of the azomethine stretching frequencies of the methyleneamino derivatives of magnesium and the two other Group II metals that have been investigated, beryllium and zinc, is that their values do not cover as wide a range as those observed for the Group III elements' derivatives. Most of the known imino derivatives of Group III elements are associated, usually as dimers, but some higher oligomers are known, and the stretching frequencies of the imino groups in these compounds generally appear to be less influenced by changes in the other ligands attached to the central metal than are the terminal groups in related monomeric compounds of Group III derivatives.

The terminal and bridging azomethine stretching frequencies for the known bis(methyleneamino) derivatives of Group III elements, $[(R_2C{:}N)_2M]_n$, are given in table 3.2. The variations in the stretching frequencies do not appear to show a simple relationship to the nature of either the methyleneamino group or the central metal.

Diphenylmethyleneamino derivatives of magnesium generally have ν(C=N) (terminal) values greater than ν(C=N) for the parent diphenylmethyleneamine, though the difference in frequencies, $\Delta\nu$, is less than $\Delta\nu$ for related di-t-butylmethyleneamino compounds. This feature is in line with that observed for methyleneamino derivatives of Group III

Table 3.2

Terminal and bridging azomethine stretching frequencies (cm^{-1}) of bis(methyleneamino) derivatives, $[(R_2C{:}N)_2M]_n.mTHF$ of Group 11 elements.

M	ν(C=N) Terminal			ν(C=N) Bridging		
	Ph	p-tolyl	^tBu	Ph	p-tolyl	^tBu
Be	1732	1731	1721	1627	1626	1631
Mg	1650	1657	1664	1612	1616	1605
Zn			1683	1600		1585

ν(C=N) $Ph_2C{:}NH$ 1607 cm^{-1} (23) $^tBu_2C{:}NH$ 1610 cm^{-1} (64)

elements (see Chapter 2).

The terminal azomethine stretching frequencies of the two beryllium compounds $[(Ph_2C{:}N)_2Be]_n$ and $[(^tBu_2C{:}N)_2Be]_2$ differ from those of their parent ketimines by 125 and 111 cm^{-1} respectively, the greater difference being observed for the diphenyl- rather than the di-t-butyl-iminoberyllium compound

The crystal structure of bis(di-t-butylmethyleneamino)beryllium, $[(^tBu_2C{:}N)_2Be]_2$, shows that the C-N-Be angle for the terminal methyleneamino group is 160.5°, less than the 180° which is appropriate for maximum overlap by beryllium and nitrogen p-orbitals (39). Such a distortion from linearity is necessary to accommodate all the t-butyl groups around the metal atoms, and it seems that it is only this steric effect, rather than other, electronic considerations which prevents the bond being linear. The observed value of ν(C=N⇌Be) is therefore likely to be lower than it would have been if the bond were linear. This is probably why ν(C=N⇌Be) for this compound is lower than that for $[(Ph_2C{:}N)_2Be]_n$ in which there is less steric hindrance between the imino groups and the terminal C=N-Be bond is probably linear.

Experiments with scale models suggest that in bis(di-t-butylmethyleneamino)magnesium the t-butyl groups can be accommodated without distortion as the central metal atom is larger, so the C=N-Mg skeleton for the terminally-attached methyleneamino group is thought to be effectively linear. A similar situation probably obtains for the p-tolyl derivative, $[((p\text{-tolyl})_2C{:}N)_2Mg]_2$. The other bis(imino)magnesium compound, $[(Ph_2C{:}N)_2Mg]_3.2THF$, in which the methyleneamino groups are less bulky than in $[(^tBu_2C{:}N)_2Mg]_2$ and $[((p\text{-tolyl})_2C{:}N)_2Mg]_2$ is also thought to have

linearly-bound terminal methyleneamino groups as the co-ordinated solvent molecules probably do not cause significant steric hindrance.

Comparison of the terminal stretching frequencies of similar zinc compounds cannot be made as the terminal azomethine stretching frequency of $[(Ph_2C{:}N)_2Zn]_n$ is apparently too weak to be observed.

The terminal stretching frequencies of compounds $[(R_2C{:}N)_2Mg]_n.mTHF$ are lower than those of the related beryllium compounds, presumably because the changes resulting from the greater mass of magnesium than beryllium offset the bond strength differences. However, the terminal stretching frequency of $[(^tBu_2C{:}N)_2Zn]_2$ is intermediate between those of the related di-t-butylmethyleneamino derivatives of beryllium and magnesium. As zinc is the heaviest and least electropositive of the three elements, this observation seems somewhat anomalous, as the terminal azomethine stretching frequency of $[(^tBu_2C{:}N)_2Mg]_2$ would have been expected to be the lowest of the three compounds if these were the only criteria.

The azomethine stretching frequencies of the bridging groups in the eight compounds $[(R_2C{:}N)_2M]_n$ (M = Be, Mg, R = Ph, p-tolyl, ^tBu; M = Zn; R = Ph, ^tBu) however, seem to vary with the mass of the central metal in the expected manner: the heavier the metal, the lower the stretching frequency. However, as observed for the terminal stretching frequencies, the differences between the bridging azomethine stretching frequencies and the parent ketimines are not those expected by analogy with derivatives of Group 111 elements. Five of the compounds have frequencies higher than the parent ketimines, but the azomethine stretching frequencies of three of the compounds. $[(^tBu_2C{:}N)_2Mg]_2$, $[(^tBu_2C{:}N)_2Zn]_2$ and $[(Ph_2C{:}N)_2Zn]_2$

are lower than those of the parent ketimine.

The stretching frequency of the monomeric THF adduct of diphenylmethyleneaminomagnesium bromide, $Ph_2C{:}NMgBr.2THF$, is significantly higher than that observed for the amorphous solid obtained before recrystallisation (Table 3.3). If the unsolvated species does have the polymeric structure described above (Figure 3.3.a), then its azomethine stretching frequency is clearly that of bridging methyleneamino groups. The solvated, monomeric species necessarily has terminally-attached imino groups, and the observed difference in the stretching frequencies of the two types of compound, monomeric and polymeric, are consistent with this.

The I.R. spectra of the three compounds $Ph_2C{:}NMgBr.2THF$, $(p\text{-tolyl})_2C{:}NMgBr.2THF$ and $[(Ph_2C{:}N)_2Mg]_3.2THF$ all have absorptions in the region appropriate for linear methyleneamino groups. In these compounds the magnesium is four-co-ordinate, and its 2p orbitals are filled. Dative N → Mg π-bonding in linear C=N-Mg units is formally possible if magnesium 3d orbitals are involved.

The C=N stretching frequencies of the terminal methyleneamino groups in the two monomers $R_2C{:}NMgBr.2THF$ (R = Ph, p-tolyl), are considerably lower than those of similar groups in the related trimer and dimer, $[(Ph_2C{:}N)_2Mg]_3.2THF$ and $[((p\text{-tolyl})_2C{:}N)_2Mg]_2$. This may be due to steric effects. In the monomers the two ligands which differ from those on the terminal magnesium atoms in the bis(imino) derivatives, bromide and THF, may result in more crowding at the metal atom than the two other imino groups bonded to magnesium in the oligomers. Some bending of the C=N-M skeleton similar to that observed for $[(^tBu_2C{:}N)_2Be]_2$ may be required to

Table 3.3.

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some related diarylmethyleneaminomagnesium compounds.

Compound	ν(C=N)
$Ph_2C{:}NMgBr.2THF$	1630
$[Ph_2C{:}NMgBr]_n$	1620
$(p\text{-tolyl})_2C{:}NMgBr.2THF$	1624
$[(Ph_2C{:}N)_2Mg]_3.2THF$	1650, 1612
$[(p\text{-tolyl})_2C{:}N)_2Mg]_2$	1657, 1618

accommodate the other ligands around magnesium in the monomer and this will result in a lower stretching frequency than would be observed if the skeleton were linear, as is thought to be the case in the bis(methyleneamino)magnesium compounds.

The azomethine stretching frequencies of the other dimeric methyleneaminomagnesium compounds are given in table 3.4 together with those of some related beryllium and zinc compounds.

In the series of compounds $[R_2C:NMX]_2$, where X is an alkyl or aryl group, the azomethine stretching frequencies of the di-t-butylmethyleneamino derivatives of magnesium and zinc, $[^tBu_2C:NMgEt]_2$, $[^tBu_2C:NMgPh]_2$ and $[^tBu_2C:NZnMe]_2$ are all lower than those of the corresponding diphenylmethyleneamino derivatives. This order is similar to that observed for the stretching frequencies of the bridging methyleneamino groups of the bis(imino)- magnesium and -zinc compounds (Table 3.2). However, the series of beryllium compounds $[R_2C:NBX]_2$ where X is chlorine or i-butyl shows the expected variations in azomethine stretching frequencies in the imino-beryllium compounds and the parent ketimine are greater for di-t-butyl- than for diphenyl-methyleneamino derivatives.

As observed for the di-t-butylmethyleneamino-alkyl- and -aryl-boranes, $^tBu_2C:NBX_2$ (X = Et (52), Ph, ^nBu (22)), there is no significant difference between the stretching frequencies of the methyleneamino-alkyl- and -aryl-derivatives of Group 11 elements.

It is interesting to note that for the two pairs of compounds $[Ph_2C:NMEt]_2$ and $[Ph_2C:NMPh]_2$ (M = Mg, Zn), the stretching frequencies of the two zinc compounds are both lower than those of the corresponding magnesium derivatives. This order is also observed for the bridging

Table 3.4

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of dimeric methyleneamino derivatives of Group 11 elements, $[R_2C:NMX]_2$.

Compound	M	Ph	p-tolyl	^tBu
$[R_2C:NMCl]_2$	Be	1608	1610	1626
	Zn			1597, 1608
$[R_2C:NMBr]_2$	Mg			1618
$[R_2C:NMMe]_2$	Zn	1624		1592
$[R_2C:NMEt]_2$	Mg	1619	1618	1605
	Zn	1611		
$[R_2C:NM^iBu]_2$	Be	1610		1635
$[R_2C:NM^tBu]_2$	Be	1648		
$[R_2C:NMPh]_2$	Mg	1618		1605
	Zn	1607		

azomethine stretching frequencies of the bis(imino) compounds $[(R_2C{:}N)_2M]_n$ (R = Ph, ^tBu; M = Mg, Zn). It seems that for these bridging azomethine vibrations, the mass of the central metal may be the most important influence, while this clearly cannot be so for the terminal stretching frequencies of the bis(imino) compounds.

It seems therefore that while the azomethine stretching frequencies of diphenyl- and di-t-butyl-methyleneaminoberyllium compounds vary in a similar manner to those of related Group III compounds, those of the methyleneamino derivatives of zinc and magnesium do not. As in many cases the differences in azomethine stretching frequencies between related compounds are small, detailed interpretation is not justified.

The azomethine stretching frequencies of the two lithium magnesates $LiMg(N{:}CPh_2)_3.Et_2O$ and $Li_2Mg(N{:}CPh_2)_4$, and the related lithium beryllates $LiBe(N{:}C^tBu_2)_3$ and $Li_2Be(N{:}C^tBu_2)_4$ are particularly interesting because of the structural and bonding features they imply (Table 3.5).

The stretching frequency of $LiBe(N{:}C^tBu_2)_3$ is rather lower than those of other imino groups terminally-attached to beryllium, and this has been interpreted (45) in terms of the steric requirements of the three bulky ligands around the central metal forcing the methyleneamino units into positions in which the C-N-Be skeletons are slightly bent, so N → Be dative π-bonding is less than in a linear structure. A similar explanation for the azomethine stretching frequency of $LiMg(N{:}CPh_2)_3.Et_2O$, which is also rather lower than those of other terminal diphenylimino ligands, seems reasonable.

The two dilithium metallates, $Li_2Be(N{:}C^tBu_2)_4$ and $Li_2Mg(N{:}CPh_2)_4$, both have azomethine stretching frequencies in the region appropriate for

Table 3.5

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some related methyleneamino derivatives of magnesium and beryllium

Compound	Terminal	Bridging
$Ph_2C{:}NMgBr.2THF$	1630	
$[(Ph_2C{:}N)_2Mg]_3.2THF$	1650	1612
$LiMg(N{:}CPh_2)_3.Et_2O$	1623	
$LiMg(N{:}CPh_2)_4$	1658, 1598	
$^tBu_2C{:}NBeN(SiMe_3)_2$	1734, 1747	
$[(^tBu_2C{:}N)_2Be]_2$	1721	1631
$LiBe(N{:}C^tBu_2)_3$	1633	
$Li_2Be(N{:}C^tBu)_4$	1709, 1660	

linearly-attached terminal imino groups (1709 and 1658 cm^{-1} respectively). The azomethine stretching absorptions oberved at lower frequency are clearly consistent with bent C=N-M units also being present in the molecule.

(iii) ^1H n.m.r. spectra of methyleneaminomagnesium compounds. Details of the ^1H n.m.r. spectra recorded at $+33^o$ of the new methyleneaminomagnesium compounds are given in table 3.6. As observed for the spectra of the boron compounds described in Chapter 2, the spectra of related methyleneaminomagnesium compounds are too similar for any conclusions about the influence of other ligands on the nature of the nitrogen - magnesium bond to be drawn, but several features of the spectra are of interest.

In the spectrum of (p-tolyl)$_2$C:NMgBr.2THF, the two complex absorptions of equal intensity observed at 3.00 and 3.38 τ are attributed to protons on the aromatic ring of the p-tolyl groups. A peak due to the methyl protons of the p-tolyl groups is observed at 8.43 τ. The peaks at 6.90 and 9.21 τ attributed to co-ordinated THF are in the appropriate relative intensities to the other peaks for the formula of the molecule to be as shown above.

The peaks due to co-ordinated THF in the spectrum of Ph_2C:NMgBr.2THF are of rather lower relative intensity than would be required by the formula. This may suggest that some THF is only weakly-co-ordinated, and may be lost during prolonged storage. Two peaks were observed in the region appropriate for protons on an aromatic ring. The higher-field absorption at 3.34 τ was more intense than that at lower field at 3.00 τ in the ratio 3.2. Comparison of this spectrum with that of

Table 3.6

^{1}H n.m.r. spectroscopic data for the new methyleneamino derivatives of magnesium.

Compound	τ values p.p.m
$Ph_2C{:}NMgBr.2THF$	2.88c, 3.34c (15), 6.90c, 9.20c (16)
$(p\text{-tolyl})_2C{:}NMgBr.2THF$	3.38c, 3.00c (12), 8.43s (6), 6.90c, 9.21c (16)
$[^tBu_2C{:}NMgBr]_2$	9.28s
$[Ph_2C{:}NMgEt]_n$*	3.54c 9.63c
$[(p\text{-tolyl})_2C{:}NMgEt]_n$*	8.37s, 9.35c, 9.67c (Phenyl protons not observed)
$[^tBu_2C{:}NMgEt]_n$*	9.28s (Ethyl protons not observed)
$[^tBu_2C{:}NMgPh]_n$	3.36c (5), 9.23s (24)
$[(Ph_2C{:}N)_2Mg]_3.2THF$	3.13c, 3.45c (5), 7.25c, 9.28c (1)
$[((p\text{-tolyl})_2C{:}N)_2Mg]_n$	3.34c, 3.54c, 3.68c (7), 8.46s (7)
$[(^tBu_2C{:}N)_2Mg]_n$	9.15s (1), 9.27s (1)
$LiMg(N{:}CPh_2)_3.OEt_2$*	3.45c
$Li_2Mg(N{:}CPh_2)_4$	3.04, 2.59c

n probably = 2

$\tau(Me_4Si)$ = 10.00 p.p.m (external reference standard)

s = singlet,

c = complex

Relative intensities in brackets. * Very weak, poorly-resolved spectrum

$(p\text{-tolyl})_2C{:}NMgBr.2THF$ suggests that the protons in the para positions in $Ph_2C{:}NMgBr.2THF$ absorb at 3.34 τ.

The spectra of the dimeric di-t-butylmethyleneaminomagnesium compounds $[{}^tBu_2C{:}NMgX]_2$ (X = Br, Ph, Et) all show single absorptions due to the t-butyl groups, consistent with their proposed structure, with bridging methyleneamino groups in which the t-butyl groups are in magnetically-equivalent environments. A broad peak due to the protons of the phenyl groups was observed in the spectrum of $[{}^tBu_2C{:}NMgPh]_2$, but no peaks attributable to ethyl groups were observed in the spectrum of $[{}^tBu_2C.NMgEt]_2$. However, the signal due to the t-butyl groups in this compound was very weak, even when as concentrated solution of the compound as possible was used, so it is not surprising that the triplet and quartet signals, relative intensities 3 and 2 respectively, expected for the ethyl groups are not observed when the single absorption due to the t-butyl groups, relative intensity 18, is only just visible.

The spectra of the dimeric diphenylmethyleneaminomagnesium compounds, $[Ph_2C{:}NMgX]_2$ (X = Br, Et), show fairly broad, poorly-resolved multiplets due to the phenyl groups. Diphenylmethyleneaminophenylmagnesium, $[Ph_2C{:}NMgPh]_2$, was not sufficiently soluble for its ^1H n.m.r. spectrum to be recorded.

In the spectra of $[Ph_2C{:}NMgEt]_2$ and $[(p\text{-tolyl})_2C{:}NMgEt]_2$, only very weak signals were observed, even though solutions as concentrated as possible were used. The spectrum of $[Ph_2C{:}NMgEt]_2$ showed a weak broad

peak at ~ 3.54 τ attributed to protons in the aromatic ring, and another at ~ 9.63 τ attributed to the ethyl group. A similar spectrum was obtained for $[(p\text{-tolyl})_2C{:}NMgEt]_2$: weak peaks were observed at ~ 3.65 (aromatic protons), 8.37 (methyl protons of p-tolyl group) and 9.67 (ethyl group) τ.

The spectra of the bis(di-t-butylmethyleneamino) derivatives of the three Group II elements (Table 3.7) show an interesting variation. The spectra of the beryllium and zinc compounds both have three peaks of relative intensities 1:1:2 (45). This is consistent with the structure determined for $[(^tBu_2C{:}N)_2Be]_2$ (39), and postulated for $[(^tBu_2C{:}N)_2Zn]_2$ (45), in which the bond angle between the terminal methyleneamino group and the metal is sufficiently less than 180° that the two t-butyl groups on each imino ligand are not in magnetically equivalent environments and so do not have the same chemical shift. The two peaks of relative intensity 1 are therefore attributed to t-butyl groups in the different environments of the terminal imino ligands, and the single peak, relative intensity 2, at higher field, is attributed to the magnetically-equivalent t-butyl groups of the bridging imino ligands.

However, in the ^1H n.m.r. spectrum of bis(di-t-butylmethyleneamino)-magnesium, $[(^tBu_2C{:}N)_2Mg]_2$, two peaks of equal intensity, one attributed to bridging and the other to terminal methyleneamino groups, are observed. As only one signal is observed for all the t-butyl groups of the terminal methylenamino groups in $[(^tBu_2C{:}N)_2Mg]_2$, the C=N-Mg skeleton must be effectively linear, so that all the t-butyl groups are equivalent. As discussed in the previous section, the covalent radius of magnesium is rather larger than those of beryllium and zinc, so steric crowding which

Table 3.7

^{1}H n.m.r. spectroscopic data for bis(di-t-butylmethyleneamino) derivatives of beryllium, zinc and magnesium

Compound	τ values p.p.m.
$[(^tBu_2C{:}N)_2Be]_2$	8.69 (1), 8.71 (1), 8.77 (2)
$[(^tBu_2C{:}N)_2Zn]_2$	8.64 (1), 8.68 (1), 9.03 (2)
$[(^tBu_2C{:}N)_2Mg]_2$*	9.15 (1), 9.27 (1)

$\tau(Me_4Si)$ = 10.00 p.p.m.

* Measured using TMS as external reference standard: others measured using TMS as internal reference standard (45). Relative intensities in brackets.

results in some distortion from linearity of the terminal imino groups in the beryllium and (probably) zinc compounds $[(^tBu_2C{:}N)_2Be]_2$ and $[(^tBu_2C{:}N)_2Zn]_2$ is presumably sufficiently reduced in the magnesium compound $[(^tBu_2C{:}N)_2Mg]_2$ for the C=N-Mg unit to be linear, the shape which allows maximum N → Mg dative π-bonding.

In the spectrum of $[(p\text{-tolyl})_2C{:}N)_2Mg]_2$ however, only one signal due to the methyl groups is observed, presumably because they are too remote from the centre of the molecule for their environments to be sufficiently different to be detected in this way.

The spectrum of $[(Ph_2C{:}N_2Mg]_3.2THF$ shows peaks due to co-ordinated THF in relative intensities appropriate for the above formula. Two complex peaks are observed in the region appropriate for protons in an aromatic ring, at 3.13 and 3.45 , and as observed for $Ph_2C{:}NMgBr.2THF$ the peak at higher field is more intense than that at lower field in the ratio 3.2.

The two absorptions due to co-ordinated THF in the three compounds $Ph_2C{:}NMgBr.2THF$, $(p\text{-tolyl})_2C{:}NMgBr.2THF$ and $[Ph_2C{:}N)_2Mg]_3.2THF$ occur at higher field than the corresponding peaks in the free compound (Table 3.8), and in all cases the separation of the peaks is greater than in unco-ordinated THF.

This shift is in the opposite direction to that observed in the spectra of THF solutions of BH_3 and BF_3 recorded at low temperature, where peaks due to co-ordinated solvent were observed at lower field than those due to free solvent (Table 3.9) (273).

In the trimer $[(Ph_2C{:}N)_2Mg]_3.2THF$, the shift of the peak due to hydrogens on the α-carbons of THF is slightly greater than that of the

Table 3.8

^{1}H n.m r. spectroscopic data for THF complexes of methyleneaminomagnesium compounds

Compound	τ values p.p.m.				
	Δ_α	α	Separation	β	Δ_β
THF		6.82	2.00	8.82	
$Ph_2C{:}NMgBr.2THF$	0.08	6.90	2.30	9.20	0.38
$(p\text{-tolyl})_2C{:}NMgBr.2THF$	0.08	6.90	2.31	9.21	0.39
$[(Ph_2C{:}N)_2Mg]_3.2THF$	0.53	7.25	2.03	9.28	0.46

α hydrogens on α-carbon atoms

β hydrogens on β-carbon atoms

$\Delta_\alpha = \tau_\alpha$ (compound) $- \tau_\alpha$ (THF)

$\Delta_\beta = \tau_\beta$ (compound) $- \tau_\beta$ (THF)

Table 3.9

Chemical shift differences on co-ordination of boron compounds to THF

Compound	Temp.	Δ_α	Δ_β
BH_3.2.5THF	-45^o	0.34	0.23
BF_3.5THF	-80^o	0.68	0.36

$\Delta_\alpha = \tau_\alpha$ (complex) $- \tau_\alpha$ (THF)

$\Delta_\beta = \tau_\beta$ (complex) $- \tau_\beta$ (THF)

Spectra recorded in THF.

Shifts measured with reference to internal TMS.

peak due to hydrogens on the β-carbons. A greater shift for the α- than the β-hydrogens is also observed for in the spectra of the BX_3/THF systems: it would be expected that the hydrogens nearest the site of co-ordination would be influenced to a greater extent than those more remote. This apprently is not the case in the monomeric compounds Ph_2C:NMgBr.2THF and $(p\text{-tolyl})_2C$:NMgBr.2THF, for which a slightly greater shift to higher field is observed for hydrogens on the β-carbon atoms.

It has been shown that the apparent electronegativity of oxygen in diethyl ether decreases rather than increases, on co-ordination to triethyl-gallium and -aluminium (274). Since the number of lone pairs on oxygen is reduced from two to one on co-ordination, a significant change in the magnetic anisotropy and hence the apparent electronegativity and shielding of the methylene protons may occur, and this may offset the change in shielding power due to a change in electron withdrawing power (274). This change in shielding as a result of magnetic anisotropy changes may account for the observed changes in chemical shift observed on co-ordination of THF in iminomagnesium compounds, but it is still not clear why the shifts of peaks due to co-ordinated THF should be in opposite directions in boron (273) and magnesium systems.

The spectra of the related lithium beryllates $LiBe(N{:}C^tBu_2)_3$ and $Li_2Be(N{:}C^tBu_2)_4$ are both well-resolved (45). However, the structures proposed on the basis of their ^1H n.m.r. spectra are inconsistent with their I.R. spectra and vice versa (45), and it seems that X-ray crystallographic studies are required to determine their structures.

No structural information can be gained from the spectrum of the lithium magnesate $LiMg(N{:}CPh_2)_3.Et_2O$ as only a broad weak absorption due

to the phenyl groups was observed. No peaks due to the co-ordinated ether were observed, even though as concentrated a solution as possible was used, but as the peaks due to the phenyl groups were very weak, this is not too surprising.

The spectrum of the dilithium magnesate $Li_2MgCN:CPh_2)_4$ was recorded in ether rather than deuterobenzene in an attempt to obtain a better spectrum. Two peaks, one an unresolved weak complex at $\sim 2.6\ \tau$ and a sharper peak at $3.05\ \tau$, were observed. As the spectrum of the two lithium magnesates were recorded in different solvents, comparison of the observed chemical shift values cannot be made.

(iv) Mass spectra of methyleneaminomagnesium compounds. The mass spectra of the methyleneaminomagnesium compounds did not show any peaks due to magnesium-containing fragments, even when recorded using a low source temperature and low accelerating potential. The only identifiable peaks were due to methyleneamino groups and their fragmentation.

However, the mass spectra of several methyleneamino derivatives of the other two Group 11 elements did contain peaks other than methyleneamino-group fragmentations.

In the spectrum of bis(di-t-butylmethyleneamino)zinc, $[(^tBu_2C:N)_2Zn]_2$ the peak with the highest $^m/e$ value was identified as the monomer fragment $(^tBu_2C:N)_2Zn$. Only two other peaks corresponding to zinc-containing fragments could be identified (45). Parent peaks were observed in the spectra of two beryllium compounds, $[Ph_2C:NBe^iBu]_2$ and $[^tBu_2C:NBe^iBu]_2$. Several beryllium-containing fragments have been identified in these spectra and those of several other methyleneamino derivatives of beryllium (45).

(c) Reactions of methyleneaminomagnesium compounds. All the new methyleneaminomagnesium compounds are readily hydrolysed by atmospheric moisture, but these reactions were not studied in detail. Controlled hydrolysis of methyleneamino derivatives of Grignard reagents is of course a well-established preparation of ketimines and aldimines. Vigorous hydrolysis affords ketones or aldehydes (264).

Reactions between one and two equivalents of phenyl isocyanate and diphenylmethyleneaminomagnesium bromide, $Ph_2C{:}NMgBr.2THF$, were carried out to determine whether the metal-nitrogen bond will undergo further insertion.

Diphenylmethyleneaminomagnesium bromide reacted with one mole of phenyl isocyanate to give the insertion product $BrMgN(Ph)C(:O)N{:}CPh_2.THF$ (Equation 3.26)

$$Ph_2C{:}NMgBr.2THF + PhNCO \rightarrow BrMgN(Ph)C(:O)N{:}CPh_2.THF \qquad 3.26$$

Similar insertion reactions have been described for two unsaturated species (PhNCO and $CH_2{:}CHCN$) with methyleneamino derivatives of tin (Equation 3.27 (169).

$$Me_3SnN{:}CR_2 + Y{:}Z \rightarrow Me_3SnYZN{:}CR_2 \qquad 3.27$$

(R = Ph, CF_3; Y:Z = PhN:CO, CH_2:CHCN)

These reactions are thought to be catalysed by trace amounts of free methyleneamine formed by hydrolysis of the metal derivative (see Chapter 1) and probably proceed via a polar transition state (Figure 3.7). The reaction of the iminomagnesium compound may proceed in a similar manner.

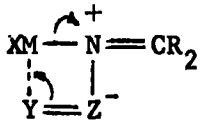


Figure 3.7

The observed order of reactivity of the two tin compounds studied,

$Me_3SnN:CPh_2$ > $Me_3SnN:C(CF_3)_2$ is consistent with such a transition state, as in $Me_3SnN:CPh_2$ the metal-nitrogen bond is more polar than in $Me_3SnN:C(CF_3)_2$.

When two equivalents of phenyl isocyanate were added to $Ph_2C:NMgBr.2THF$, a further insertion into the magnesium-nitrogen bond apparently occurs to give a compound whose elemental analyses are consistent with the formula $BrMgN(Ph)C(:O)N(Ph)C(:O)N:CPh_2.THF$ but the detailed structure of the compound is not known.

3. Summary of the new methyleneaminomagnesium compounds. Several new methyleneamino derivatives of magnesium have been prepared. The unsolvated mono(imino)magnesium compounds, $[R_2C:NMgX]_n$ (R = Ph, p-tolyl, ^tBu; X = Et; R = Ph, ^tBu; X = Ph; R = ^tBu, X = Br), are thought to be dimeric (n = 2), and their C=N stretching frequencies indicate that the imino groups occupy bridging rather than terminal positions. The C=N stretching frequencies of the terminal methyleneamino groups in the monomeric mono(imino)magnesium compounds $R_2C:NMgBr.2THF$ (R = Ph, p-tolyl), the bis(imino)magnesium compounds $[(R_2C:N)_2Mg]_n$ (R = Ph, p-tolyl, n probably = 2) and $[(Ph_2C:N)_2Mg]_3.2THF$ and the lithium magnesates $LiMg(N:CPh_2)_3.OEt_2$ and $Li_2Mg(N:CPh_2)_4$ are consistent with the C.N.Mg units being effectively linear.

Chapter 4

Methyleneamino derivatives of aluminium

This chapter describes the preparation and properties of some methyleneamino derivatives of aluminium. Aspects of their I.R., ^1H n.m.r. and mass spectra are discussed and compared with those of related compounds.

The preparation of tris(di-t-butylmethyleneamino)aluminium is discussed in detail, with reference to previous reports of this compound.

Attempted preparation of the methyleneaminoalanes $[^tBu_2C{:}NAlH_2]_n$ and $[(^tBu_2C{:}N)_2AlH]_n$ presented several difficulties, not all of which could be overcome.

Preliminary investigations of several methyleneamino derivatives of aluminium have been carried out in this laboratory by Mr. B. Hall. An account of this work, which has not been reported elsewhere is included in this thesis to allow a full account of the present state of methyleneamino-aluminium chemistry to be given.

1. Experimental.

(a) Attempts to prepare tris(di-t-butylmethyleneamino)alane, $(^tBu_2C{:}N)_3Al$.

(i) Reaction between aluminium trichloride and di-t-butylmethyleneaminolithium (mole ratio 1:3).

A solution of di-t-butylmethyleneaminolithium (45.5 mmole) in 60 ml diethyl ether was added to a solution of aluminium trichloride (2.02 g, 15.1 mmole) in 50 ml diethyl ether at -196°. The mixture was allowed to warm up. At ~0° a white precipitate was formed in the yellow solution. The mixture was stirred at room temperature for ~2½ hours. No further changes were noticed. The ether was pumped off and the yellow residue was extracted with pentane. Lithium chloride was filtered off. The first crop of yellow crystals obtained from the

pentane solution contained lithium and chlorine (0.2 and ~2.5% respectively). The Al:N ratio in this material was ~1:3.3 (5.13 and 8.8% respectively). It was thought that this material was a mixture of $LiAl(N:C^tBu_2)_4$ and $[^tBu_2C:NAlCl_2]_2$ (52,18).

The second crop of yellow crystals obtained from the pentane solution were identified as lithium tetrakis(di-t-butylmethyleneamino)aluminate by its I.R. spectrum (52) and elemental analyses

(Found: Al, 4.2; Li, 1.1; N, 9.6%.

$C_{36}H_{72}AlLiN_4$ requires Al, 4.5; Li, 1.2; N, 9.4%).

This reaction was repeated several times with similar results.

(ii) Reaction between aluminium trichloride and di-t-butylmethyleneaminolithium (mole ratio 1:2.5).

A solution of 56.5 mmole di-t-butylmethyleneaminolithium in 50 ml diethyl ether was added to a solution of aluminium trichloride (3.0 g, 22.6 mmole) in 40 ml diethyl ether frozen to -196°. The mixture was allowed to warm up. Lithium chloride began to precipitate out of the yellow solution at ~0°. The mixture was stirred at room temperature overnight, then the ether was pumped off. The yellow residue was extracted with pentane and lithium chloride was removed by filtration. Removal of solvent from the filtrate left a deep yellow gelatinous solid whose I.R. and ^1H n.m.r. spectra indicated that it contained both lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N:C^tBu_2)_4$ (52) and di-t-butylmethyleneaminolithium dichloride, $[^tBu_2C:NAlCl_2]_2$ (18). Qualitative tests for lithium and chlorine were positive.

(iii) Reaction between tri-i-butylaluminium and diphenylmethyleneamine (mole ratio 1:3).

Diphenylmethyleneamine (6.5 g, 35.9 mmole) was added to a solution of tri-i-butylaluminium (2.37 g, 12 mmole) in 100 ml toluene at room temperature, and the mixture was stirred overnight. An I.R. spectrum showed that no reaction had occurred, so the solution was refluxed for 7 days. I.R. spectra recorded each day showed that no reaction had occurred, and diphenylmethyleneamine was recovered from the reaction mixture.

(iv) Reaction between tri-i-butylaluminium and di-t-butylmethyleneamine (mole ratio 1:3).

Di-t-butylmethyleneamine (9.6 g, 68 mmole) was added to a solution of tri-i-butylaluminium (4.49 g, 22.7 mmole) in 100 ml toluene. The experiment was carried out as in the reaction described above. Again, I.R. spectra showed that no reaction had occurred.

(v) Reaction between trimethylaluminium and diphenylmethyleneamine (mole ratio 1:3).

Diphenylmethyleneamine (8.8 g, 4.9 mmole) was added to a solution of trimethylaluminium (1.17 g, 1.7 mmole) in 100 ml toluene at -196°. The mixture was allowed to warm to room temperature then refluxed for ~ 28 hours. Solvent was removed and the yellowish residue was extracted with hexane to leave a white solid identified by its I.R. spectrum, melting point and elemental analyses as diphenylmethyleneaminodimethylaluminium, $[Ph_2C{:}NAlMe_2]_2$ (142).

(Found: Al, 11.16; N, 6.21%

$C_{15}H_{16}AlN$ requires Al, 11.37; N, 5.90%).

(vi) Reaction between aluminium hydride and di-t-butylmethyleneamine (mole ratio 1:3).

A solution of aluminium hydride in diethyl ether was prepared from aluminium trichloride and lithium aluminium hydride solutions as described in the literature (271) and standardised by adding a known volume to an excess of iodine in benzene solution and determining the unused iodine with sodium thiosulphate solution (275).

Aluminium hydride solution (30 ml of a 0.72 M solution, 21.6 mmole) was added to a solution of di-t-butylmethyleneamine (9.15 g, 65 mmole) in 40 ml diethyl ether at -196°. Vigorous effervescence was observed during this addition. As the mixture warmed to room temperature it became slightly cloudy, and a lemon-yellow colour developed. The mixture was stirred overnight to ensure complete reaction, then it was filtered. The white chunky crystals which formed in the filtrate were isolated and identified as tris(di-t-butylmethyleneamino)alane, $(^{t}Bu_2C{:}N)_3Al$ m.p. softened ~170° then became glassy solid ~190°.
(Found: Al, 5.94; N, 9.5%; Li, absent.
$C_{27}H_{54}AlN_3$ requires Al, 6.03; N, 9.39%).
ν_{max}(Nujol mull) 1738sh, 1703s, 1606w, 1580m, 1478s, 1466sh, 1462sh, 1456sh, 1405sh, 1396w, 1385s, 1380sh, 1375sh, 1363s, 1350sh, 1322w, 1276m, 1262w, 1220m, 1207sh, 1191w, 1178v.w, 1150m, 1093s, 1045m, 1021m, 960w, 945m,br, 930sh, 913m, 876w, 860w, 802m, 780w, 765sh, 754w, 738w, 600m, 575w, 545sh, 538m, 500sh, 487w, 455w, 423w cm^{-1}.

(b) Reaction between tris(di-t-butylmethyleneamino)alane and di-t-butylmethyleneaminolithium.

A solution of di-t-butylmethyleneaminolithium (5 mmole) was

prepared in 40 ml diethyl ether and added to a solution of tris(di-t-butylmethyleneamino)alane (2.17 g, 4.8 mmole) in 60 ml diethyl ether frozen to -196°. The mixture was allowed to warm to room temperature and stirred for ~ 1 hour. Solvent was removed and the yellow solid was recrystallised from toluene to give yellow crystals of lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C^tBu_2)_4$, identified by their I.R. spectrum (52).

(c) Attempts to prepare the di-t-butylmethyleneaminoalanes $^tBu_2C{:}NAlH_2$ and $(^tBu_2C{:}N)_2AlH$.

(i) Reaction between di-t-butylmethyleneamine and aluminium hydride (mole ratio 1:1).

Di-t-butylmethyleneamine (0.55 g, 3.9 mmole) was added to a solution of aluminium hydride (40 ml of a 0.097 M solution) in diethyl ether at -196°. The mixture was allowed to warm to room temperature and stirred for ~ 2 hours. Attempts to obtain an I.R. spectrum of this solution were unsuccessful as extensive decomposition occurred in the solution cell. Some ether was removed from the solution, in which some white crystalline solid and a dark gelatinous material slowly formed. The white solid was isolated and studied.

(Found: Al, 12.44; N, 21.3%.

$^tBu_2C{:}NAlH_2$ ($C_9H_{20}AlN$) requires Al, 15.94; N, 8.28%)

ν_{max} 3248m, 3236m, 1918s,br, 1855m,br, 1817m,br, 1570v.w, 1403s, 1300m, 1261m, 1211m, 1159w, 1083m, 1041s, 1019m, 959s, 945s, 919w, 866s, 840w,br, 830m, 788m, 755w, 722m, 680s,br, 625w,sh, 596m, 448w cm^{-1}.

The ^1H n.m.r. spectrum of this material recorded as a toluene solution showed a singlet absorption at 9.47 τ with a shoulder at 9.33 τ.

This material could not be identified, but was clearly not the required iminoalane.

(ii) Reaction between di-t-butylmethyleneamine and aluminium hydride (mole ratio 2:1).

Di-t-butylmethyleneamine (1.1 g, 7.8 mmole) was added to a solution of aluminium hydride (40 mls of a 0.097 M solution) in diethyl ether at -196°. The mixture was allowed to reach room temperature stirred for ~2 hours during which time a very pale yellow colour developed. Some solvent was removed, and a white crystalline solid gradually formed. The white solid was isolated and studied

(Found: Al, 7.89; N, 8.89%.

$(^tBu_2C{:}N)_2AlH$ ($C_{18}H_{37}AlN_2$) requires Al, 8.75; N, 9.08%).

ν_{max}(Nujol mull) 3384w, 3260s, 1889s, 1400s, 1356s, 1300m, 1380m, 1232m, 1221m, 1290sh, 1159w, 1085s, 1037m, 1021m, 951s, 942s, 935sh, 914m, 862m, 810s, 780s, 755sh, 738w, 722v.w, 686m, 650m, 586s, 529w, 512m, 493w, 453w, 430sh, 394w cm^{-1}.

The ^1H n.m.r. spectrum of this white solid recorded as a toluene solution showed a singlet absorption at 9.31τ.

Thus although the elemental analyses and ^1H n.m.r. spectrum of this material are consistent with its identity as $[(^tBu_2C{:}N)_2AlH]_n$, its I.R. spectrum clearly is not, as no peaks in the region appropriate for C=N stretching vibrations are present.

(iii) Reaction between di-t-butylmethyleneamine and trimethylamine-alane (mole ratio 1:1).

Trimethylamine-alane (5.23 g, 58.7 mmole) was dissolved in 40 ml diethyl ether and di-t-butylmethyleneamine (8.3 g, 58.7 mmole) was

added to this solution. Effervescence was observed during the exothermic reaction which occurred, and the solution became a pale yellow colour. The mixture was stirred at room temperature overnight then solvent was removed and replaced with hexane. The white needle-shaped crystals formed in this solution were identified as bis(di-t-butylmethyleneamino)alane with some coordinated trimethylamine, $(^tBu_2C{:}N)_2AlH.nNMe_3$ m.p. $\sim 110^o$ d.

(Found: Al, 7.73; N, 9.87%.

$(^tBu_2C{:}N)_2AlH$ requires Al, 8.75; N, 9.08%

$(^tBu_2C{:}N)_2AlH.^1/3NMe_3$ requires Al, 8.22; N, 9.96%

$(^tBu_2C{:}N)_2AlH.^1/2NMe_3$ requires Al, 7.98; N, 10.36%).

ν_{max}(Nujol mull) 1840w,br, 1712m, 1696sh, 1579w, 1478s, 1450sh, 1408m, 1396s, 1387s, 1363s, 1277m, 1238m, 1222m, 1190w, 1159w, 1085s, 1021s, 989s, 950sh, 940m, 916m, 858w, 821s, 805s, 763s, 747m, 728s, 640v.w, 571w, 538s, 490s, 450m, 418m cm^{-1}.

(iv) Reaction between di-t-butylmethyleneamine and trimethylamine-alane (mole ratio 1:1, second attempt).

To a solution of trimethylamine-alane (3.22 g, 36.1 mmole) in 40 ml diethyl ether was added di-t-butylmethyleneamine (5.04 g, 35.7 mmole). Effervescence was seen, and the solution became slightly cloudy. An I.R. spectrum of this solution showed the presence of unreacted di-t-butylmethyleneamine, so the solution was refluxed for ~ 3 hours, during which time a pale yellow colour developed, similar to that observed in the previous reaction. Solvent was removed and the pale yellow gelatinous residue was redissolved in fresh ether. A white apparently crystalline material was obtained from this solution.

The elemental analyses of this material were similar to those calculated for di-t-butylmethyleneaminoalane, $[^{t}Bu_2C{:}NAlH_2]_n$ (Found: Al, 12.36; N, 6.6%, N:Al ratio 1:1.04. $C_9H_{20}AlN$ requires Al, 15.94; N, 8.28% N:Al ratio 1:1) but its I.R. spectrum did not show peaks in the regions expected for Al-H and C=N stretching vibrations.

ν_{max}(Nujol mull) 3328m, 3294m, 3278m, 3245m, 1605sh, 1580s, 1480sh, 1462s, 1445s, 1409s, 1381sh, 1376s, 1262s, 1236w, 1222m, 1190m, 1159s, 1105s, 1070s, 1042s, 1020s, 986s, 962m, 944m, 918w, 841m, 818s, 800s,br, 772sh, 756w, 700sh, 639m, 593m, 562sh, 540w, 495s,br, 440m, 410sh, 392m cm^{-1}.

(v) Reaction between trimethylamine-alane and di-t-butylmethyleneamine (mole ratio 1:2).

To a solution of trimethylamine-alane (0.86 g, 9.6 mmole) in 50 ml diethyl ether was added di-t-butylmethyleneamine (2.73 g, 19.3 mmole). The mixture was stirred at room temperature overnight, during which time a pale yellow colour developed. An I.R. spectrum of this solution showed the presence of unreacted di-t-butylmethyleneamine. An I.R. spectrum recorded after the solution had been refluxed for ~8 hours still indicated the presence of excess ketimine. Ether was removed from the solution. Attempted recrystallisations of the residue from pentane and hexane were unsuccessful, and removal of solvent left an intractible yellow gelatinous material which could not be identified.

(d) Reactions carried out by Mr B. Hall.

The preliminary studies of several methyleneamino derivatives of

aluminium carried out by Mr B. Hall are summarised in table 4.1.

Hexane solutions of the reagents were mixed at -196°, allowed to reach room temperature then refluxed. Further experimental details and the azomethine stretching frequencies of the products obtained are given in the table. Their I.R. spectra are given below.

$[^tBu_2C{:}NAlMe_2]_2$ ν_{max}(Contact film) 2941s,br, 1724v.w, 1639v.w, 1610sh, 1580s, 1488sh, 1462s, 1372s, 1220sh, 1196s, 1047m, 972s, 939w,br, 881w, 841v.w, 810w, 799w, 769sh, 749w, 699v.s, v.br, 654sh, 614m, 549w, 497w cm^{-1}.

$LiAl(N{:}C^tBu_2)_2Me_2$ ν_{max}(Contact film) 2967s, 2941s, 2899sh, 1633s, 1605m, 1585w, 1495m, 1475m, 1403w, 1389m, 1372m, 1269m, 1233sh, 1212m, 1198sh, 1186sh, 1082m,br, 1043m, 1026sh, 966m, 957sh, 939sh, 886m, 800s,br, 704s,br, 651s,br cm^{-1}.

$^tBu_2C{:}NAl_2Me_5$ ν_{max}(Liquid film) 3278w, 2950s, 2849m, 2336w, 1586s, 1497m, 1471sh, 1429m, 1405m, 1377s, 1266m, 1221sh, 1205s, 1085m, 1053m, 934m, 939w, 878w, 847w, 813sh, 801m, 777m, 751m, 704v.s, v.br, 633m, 615w, 588w.br, 557m cm^{-1}.

$LiAl(N{:}C^tBu_2)Me_3$ ν_{max}(Liquid film) 2995sh, 2960s, 2918s, 2820m, 1633s, 1604m, 1486m, 1470m, 1400m, 1383m, 1365m, 1358sh, 1263w, 1228m, 1202m, 1180m, 1100w,br, 1060sh, 1039m, 1025w, 959m, 938sh, 880m, 844v.w, 700s,br, 590w, 510w cm^{-1}.

$[(^tBu_2C{:}N)_2AlMe]_2$ ν_{max}(Liquid film) 2967s, 2882sh, 1719s, 1609s, 1587sh, 1486s, 1475sh, 1464sh, 1397sh, 1389m, 1374s, 1326w, 1256m, 1221s, 1198s, 1064s, 980m, 952s, 943s, 877m, 852sh, 826br,sh, 800m, 775s, 749w, 725sh, 676s, 667s cm^{-1}.

Table 4.1

Reactions carried out by Mr B. Hall

Reagents	Experimental details	Product	ν(C=N)
$^tBu_2C{:}NLi + Me_2AlCl$ 20 mmole 20 mmole	Refluxed overnight. Product recrystallised from hexane solution	$[^tBu_2C{:}NAlMe_2]_2$ Colourless needle-shaped crystals.	1580
$2\,^tBu_2C{:}NLi + Me_2AlCl$ 18 mmole 9 mmole	Refluxed overnight. Product isolated from hexane solution	$LiAl(N{:}C^tBu_2)_2Me_2$ Pale yellow solid.	1633, 1605
$^tBu_2C{:}NLi + Me_5Al_2Cl$ 11.5 mmole 11.5 mmole	Refluxed for 3 hours. Product obtained on removal of solvent	$^tBu_2C{:}NAl_2Me_5$ Clear yellow liquid.	1586
$^tBu_2C{:}NH + LiAlMe_4$ 12 mmole 12 mmole	Refluxed for 6 hours. Product distilled at 53°, 0.8 mm Hg	$LiAl(N{:}C^tBu_2)Me_3$ Pale yellow opaque oil	1633, 1604
$2\,^tBu_2C{:}NLi + MeAlCl_2$ 40 mmole 20 mmole	Refluxed overnight. Product isolated from hexane solution	$[(^tBu_2C{:}N)_2AlMe]_2$ Pale yellow liquid	1719, 1609
$^tBu_2C{:}NLi + MeAlCl_2$ 20 mmole 20 mmole	Refluxed overnight. Intractible gelatinous material obtained on removal of solvent.	Probably impure $[(^tBu_2C{:}N)_2AlMe]_2$	1715, 1592
$^tBu_2C{:}NLi + MeAl_2Cl_5$ n = 1-5	Refluxed overnight	None isolated	
$n\,^tBu_2C{:}NLi + Me_3Al_2Cl_3$ n = 1-3	Refluxed overnight	None isolated	

2. Discussion.

(a) Preparation of methyleneamino derivatives of aluminium. Methyleneamino derivatives of aluminium have been prepared by all the general methods; nitrile insertion, alkane elimination and elimination of an insoluble or volatile halogen derivative (see Chapter 1).

The last general method has been used in the preparation of several methyleneaminoaluminium dihalides $[R_2C{:}NAlX_2]_2$, two tris(imino)alanes, $(R_2C{:}N)_3Al$ (R = Ph, ^tBu) (18), and lithium tetrakis(di-t-butylmethyleneamino) aluminate, $LiAl(N{:}C^tBu_2)_4$ (40).

(i) The preparation of $(^tBu_2C{:}N)_3Al$. In the present work a study of the co-ordinative properties of the tris(imino)alane $(^tBu_2C{:}N)_3Al$ was intended and the preparation of this compound from iminolithium and aluminium chloride by the method already described for its synthesis (18), was investigated.

The many attempts to prepare the required compound by this method (see experimental section) were all unsuccessful. In all cases the yellow solid obtained after the first recrystallisation was shown to contain both lithium and chlorine. Further recrystallisation afforded a yellow solid which contained lithium, but not chlorine, and was identified as lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C^tBu_2)_4$. Similar difficulties with this reaction have been reported elsewhere (39).

Thus although these experiments were carried out using the same technique as that described in the literature (18), different products were clearly being obtained. Lithium tetrakis(di-t-butylmethyleneamino)-aluminate might be formed from iminolithium and aluminium chloride in 3:1 mole ratio if the bis(imino)alane $(^tBu_2C{:}N)_2AlCl$ were produced simultaneously (Equation 4.1).

$$6.\ {}^{t}Bu_2C{:}NLi + 2AlCl_3 \rightarrow LiAl(N{:}C{}^{t}Bu_2)_4 + 5\ LiCl + [({}^{t}Bu_2C{:}N)_2AlCl]_n \qquad 4.1$$

However, it has been shown that bis(imino)aluminium chloride is unstable with respect to disproportion into iminoaluminium dichloride and tris-(imino)alane (Equation 4.2) (18).

$$2({}^{t}Bu_2C{:}N)_2AlCl \rightarrow \tfrac{1}{2}[{}^{t}Bu_2C{:}NAlCl_2]_2 + ({}^{t}Bu_2C{:}N)_3Al \qquad 4.2$$

The products of the reactions between aluminium chloride and three equivalents of iminolithium carried out in this work may therefore be $LiAl(N{:}C{}^{t}Bu_2)_4$, $({}^{t}Bu_2C{:}N)_3Al$, $[{}^{t}Bu_2C{:}NAlCl_2]_2$ and LiCl instead of just $({}^{t}Bu_2C{:}N)_3Al$ and LiCl as described previously (18). The properties of the solids obtained from the reaction are in agreement with this. The solid obtained after one recrystallisation, which contained lithium and chlorine was probably a mixture of all three aluminium-containing compounds. Recrystallisation of this mixture afforded only $LiAl(N{:}C{}^{t}Bu_2)_4$, presumably the least-soluble of the three compounds.

Repeated attempts at the preparation of tris(imino)alane always gave similar results. Some of the required material seemed to be present, but it could not be isolated as fractional recrystallisations always afforded lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C{}^{t}Bu_2)_4$.

According to the previous report, tris(di-t-butylmethyleneamino)alane, $({}^{t}Bu_2C{:}N)_3Al$, can be prepared from aluminium chloride and three equivalents of iminolithium (18). The yield of the required compound is not reported in this account, and it may be that fractional crystallisation of the material obtained from the reaction under slightly different conditions from those used in the present work (e.g. concentration of the solution, speed and temperature of crystallisation) afforded a small quantity of the

tris(imino)alane, $(^tBu_2C{:}N)_3Al$, rather than the aluminate, $LiAl(N{:}C^tBu_2)_4$ which was obtained during the present work although all the experimental details previously reported (18) were closely followed.

The work carried out in this thesis has cast some doubt on the purity of the tris(imino)alane obtained as reported previously. The reasons for this are discussed in this and later sections of this chapter.

It has already been shown that reaction between aluminium halides and two equivalents of methyleneamino-lithium or -trimethylsilane affords mono(imino)aluminium dihalides and tris(imino)alane, presumably as a result of disproportionation of initially-formed bis(imino)aluminium chloride (Equation 4.3.) (18).

$$4\ R_2C{:}NY + 2AlX_3 \rightarrow 2(R_2C{:}N)_2AlX \downarrow + 4XY' \qquad \tfrac{1}{2}[R_2C{:}NAlX_2]_2 + (R_2C{:}N)_3Al \qquad 4.3$$

(R = Ph, ^{t}Bu; X = Cl, Br; Y = Li, Me_3Si)

A similar disproportionation is observed for bis(diphenylmethyleneamino)chloroborane, $(Ph_2C{:}N)_2BCl$ (Equation 4.4.), but not for the related t-butyl compound, $(^tBu_2C{:}N)_2BCl$ (Equation 4.5), whose stability has been explained in terms of the potential disproportionation products. The iminodichloroborane, $^tBu_2C{:}NBCl_2$, is a liquid, so there is no lattice energy driving force for the reaction, and, as shown in this work, formation of the tris(imino)borane $(^tBu_2C{:}N)_3B$ requires several hours at high temperature.

$$2(Ph_2C{:}N)_2BCl \rightarrow Ph_2C{:}NBCl_2 + (Ph_2C{:}N)_3B \qquad 4.4$$

$$2(^tBu_2C{:}N)_2BCl \not\rightarrow {}^tBu_2C{:}NBCl_2 + (^tBu_2C{:}N)_3B \qquad 4.5$$

In the reactions between aluminium halides and three equivalents of iminolithium compounds there was no evidence for the presence of any lithium tetrakis(imino)aluminate. It was thought therefore that in a reaction between aluminium chloride and rather less than three equivalents of di-t-butylmethyleneaminolithium the formation of the tris(imino)alane $(^tBu_2C{:}N)_3Al$ might not be restricted by formation of the lithium aluminate $LiAl(N{:}C^tBu_2)_4$ as observed in reactions using the full stoichiometric quantity of iminolithium, and the impurities would instead be a small amount of di-t-butylmethyleneaminoaluminium dichloride (Equation 4.6)

$$\begin{array}{l} 2AlCl_3 + 4\,^tBu_2C{:}NLi \rightarrow 2(^tBu_2C{:}N)_2AlCl + 4LiCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad \tfrac{1}{2}[^tBu_2C{:}NAlCl_2]_2 + Al(N{:}C^tBu_2)_3 \\ \qquad\qquad\qquad\qquad \downarrow \; < 2LiN{:}C^tBu_2 \\ \qquad\qquad\qquad (^tBu_2C{:}N)_3Al + 2LiCl \end{array} \qquad 4.6$$

However, the reaction apparently did not proceed in this manner, as the ^1H n.m.r. and I.R. spectra of the yellow semi-solid obtained indicated that the two compounds $LiAl(N{:}C^tBu_2)_4$ and $[^tBu_2C{:}NAlCl_2]_2$ had been formed, possibly in the manner shown in equation 4.7.

$$\begin{array}{l} 2AlCl_3 + 4\,^tBu_2C{:}NLi \rightarrow 2(^tBu_2C{:}N)_2AlCl + 4LiCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad Al(N{:}C^tBu_2)_3 + \tfrac{1}{2}[^tBu_2C{:}NAlCl_2]_2 \\ \qquad\qquad\qquad\qquad \downarrow \; \sim 1LiN{:}C^tBu_2 \\ \qquad\qquad\qquad LiAl(N{:}C^tBu_2)_4 \end{array} \qquad 4.7$$

Again, lithium tetrakis(di-t-butylmethyleneamino)aluminate is formed in preference to tris(di-t-butylmethyleneamino)alane.

As it seems that the lithium aluminate $LiAl(N{:}C{:}^tBu_2)_4$ is always formed very readily in reactions between aluminium chloride and more than

two equivalents of di-t-butylmethyleneaminolithium, a preparative method not involving the lithium species would be a more suitable way of preparing tris(di-t-butylmethyleneamino)alane.

Preliminary studies of some trialkylaluminium-ketimine systems were made in an attempt to find a suitable route to the tris(imino)alane. Reactions using diphenylmethyleneamine were attempted first as this is more useful in the development of experimental procedures than di-t-butylmethyleneamine.

No reaction was observed between tri-i-butylaluminium and three equivalents of either diphenyl- or di-t-butylmethyleneamine, although it has been observed that di-t-butylmethyleneaminodi-i-butylaluminium has been formed by reaction between tri-i-butylaluminium and one equivalent of ketimine (143).

Reaction between trimethylaluminium and three equivalents of diphenylmethyleneamine afforded the mono(imino)dimethylaluminium compounds (Equation 3.8), which had previously been obtained from equimolar proportions of the reagents (Equation 4.9) (142).

$$Me_3Al + 3Ph_2C{:}NH \rightarrow Ph_2C{:}NAlMe_2 + CH_4 + 2Ph_2C{:}NH \qquad 4.8$$

$$Me_3Al + Ph_2C{:}NH \rightarrow Ph_2C{:}NAlMe_2 + CH_4 \qquad 4.9$$

Further substitution of the methyl groups by ketimine could not be achieved.

It seems therefore that iminodialkylalanes, $R^1_2C{:}NAlR^2_2$ are not reactive towards ketimines, and so not more than one methyleneamino group can be attached to aluminium in such reactions, even under forcing conditions.

The reaction between di-t-butylmethyleneamine and aluminium hydride, which is more reactive than the trialkylaluminium compounds was then investigated.

A solution of aluminium hydride was prepared from lithium aluminium hydride and aluminium chloride (Equation 4.10) (279).

$$3LiAlH_4 + AlCl_3 \rightarrow 3AlH_3 + 3LiCl \qquad 4.10$$

Careful checks were made that no lithium (probably as unreacted lithium aluminium hydride) was present in this solution.

Reaction between aluminium hydride and three equivalents of di-t-butylmethyleneamine afforded tris(di-t-butylmethyleneamino)alane (Equation 4.11).

$$3\,{}^{t}Bu_2C{:}NH + AlH_3 \rightarrow ({}^{t}Bu_2C{:}N)_3Al + 3H_2 \qquad 4.11$$

The reaction was complete after a few hours at room temperature, and the product was obtained as colourless, chunky crystals, rather similar in appearance to those of the related tris(imino)borane $({}^{t}Bu_2C{:}N)_3B$. This ease of reaction is a marked contrast to reactions between methyleneamines and trialkyl- or triaryl-aluminium compounds where an adduct is formed first and elimination of the alkane or phenyl compound is achieved only on heating (Equation 4.12).

$$R^1{}_2C{:}NH + R^2{}_3Al \rightarrow R^1{}_2C{:}NH.AlR^2{}_3$$
$$\xrightarrow{\Delta} {}^{1}/_{n}\,[R_2{}^{1}C{:}NAlR^2{}_2]_n + R^2H \qquad 4.12$$

(R^1 = Ph (142), Me_2N (69) ^{t}Bu (52); R^1 = Me (142, 69) Et (142, 69), Ph (69), ^{i}Bu (52))

The reaction described here for the preparation of tris(di-t-butylmethyleneamino)alane is analogous to the elimination reactions used to prepare tris(amino)alanes from secondary amines and aluminium hydride

(Equation 4.13) (264, 265).

$$AlH_3 + NR_2H \rightarrow AlH_3.NR_2H \xrightarrow{-H_2} 1/n[H_2AlNR_2]_n$$

$$\xrightarrow[-H_2]{R_2NH} HAl(NR_2)_2 \xrightarrow[-H_2]{R_2NH} Al(NR_2)_3 \qquad 4.13$$

The preparation of lithium tetrakis(di-t-butylmethyleneamino)-aluminate, $LiAl(N:C^tBu_2)_4$, is now well-established, but its preparation in good yield from tris(imino)alane and iminolithium (Equation 4.14) provided further confirmation of the identity of the previously-elusive tris(di-t-butylmethyleneamino)alane.

$$(^tBu_2C:N)_3Al + LiN:C^tBu_2 \rightarrow LiAl(N:C^tBu_2)_4 \qquad 4.14$$

(ii) Attempts to prepare the iminoalanes $[^tBu_2C:NAlH_2]_n$ and $[(^tBu_2C:N)_2AlH]_n$.

In view of the successful preparation of tris(di-t-butylmethyleneamino)alane from aluminium hydride and di-t-butylmethyleneamine (Equation 4.11), attempts were made to prepare the mono- and bis-(imino)alanes, $^tBu_2C:NAlH_2$ and $(^tBu_2C:N)_2AlH$, in a similar manner.

Reaction between aluminium hydride and one equivalent of di-t-butylmethyleneamine afforded a white, apparently crystalline solid which, although not fully identified, was clearly not the required iminoalane (Equation 4.15)

$$AlH_3 + {}^tBu_2C:NH \not\rightarrow {}^tBu_2C:NAlH_2 + H_2 \qquad 4.15$$

The I.R. spectrum of the product did not contain any peaks in the region appropriate for C=N stretching vibrations. Peaks were, however observed at frequencies appropriate for ν(N-H) and ν(Al-H).

A similar reaction between aluminium hydride and two equivalents of di-t-butylketimine afforded white crystals whose elemental analyses were fairly close to those calculated for the required product, $(^tBu_2C{:}N)_2AlH$, but their I.R. spectrum showed no ν(C=N) absorptions. Again, peaks in the regions appropriate for N-H and Al-H stretching vibrations were observed.

It may be therefore, that in reactions between aluminium hydride and di-t-butylketimine in mole ratios less than 1:3, initial attachment of the imino group is followed by a rearrangement, possibly via self-hydroalumination to give a species $[^tBu_2CHNAlH]_n$ (Equation 4.16). This may be particularly susceptible to hydrolysis by trace amounts of water to give $^tBu_2CHNH$- species (Equation 4.16) which give rise to the observed N-H stretching vibrations.

$$^tBu_2C{:}NAlH_2 \rightarrow [^tBu_2CHNAlH]_n \xrightarrow{\text{hydrolysis}} {}^tBu_2CHN\!\!\diagup\!\!\diagdown^{H} \qquad 4.16$$

In the preparation of aminoalanes from aluminium hydride and amines (264,265) aluminium hydride was used in the form of its trimethylamine adduct, $Me_3N.AlH_3$. Reactions between this compound and di-t-butylmethyleneamine in 1:1 and 1:2 mole ratios were therefore carried out in further attempts to prepare the iminoalanes $^tBu_2C{:}NAlH_2$ and $(^tBu_2C{:}N)_2AlH$.

Coordination to aluminium hydride of a strong donor such as trimethylamine will tend to increase the δ- charge on the aluminium-

attached hydrogens, and while this may encourage the unwanted hydroalumination reaction, it was hoped that the hydrogen elimination reactions to give the required products might have been sufficiently encouraged to occur preferentially (Equation 4.17).

$$Me_3N{\rightarrow}\overset{\delta+\ \delta-}{Al}\overset{H}{\underset{H_2}{}} + \overset{\delta+\ \delta-}{H}\text{-}N{=}C^tBu_2 \rightarrow {}^1/_n[H_2AlN{:}C^tBu_2]_n + H_2 + Me_3N \qquad 4.17$$

However, reaction between trimethylaminealane and two equivalents of di-t-butylketimine afforded an intractible yellow gelatinous material which was not the required product (Equation 4.18).

$$2\,{}^tBu_2C{:}NH + NMe_3.AlH_3 \not\rightarrow ({}^tBu_2C{:}N)_2AlH + H_2 + NMe_3 \qquad 4.18$$

Reaction between trimethylamine-alane and one equivalent of di-t-butylketimine afforded a white crystalline solid whose elemental analyses indicated that it might be the bis(imino)alane with some coordinated trimethylamine (Equation 4.19).

$${}^tBu_2C{:}NH + NMe_3.AlH_3 \rightarrow ({}^tBu_2C{:}N)_2AlH.nNMe_3 + H_2 \qquad 4.19$$

Attempts to isolate the uncoordinated species were unsuccessful, as the compound decomposed during removal of trimethylamine at $\sim 110^{o}$, 0.005 mm Hg.

However, when this experiment was repeated, in an attempt to obtain further information about its mechanism, the I.R. spectrum of the white crystals obtained showed absorptions in the region appropriate for N-H stretching vibrations, and no peaks at 1840 and 1712 cm^{-1}, characteristic of the product obtained from the previous reaction, were observed. This suggests that some hydroalumination, similar to

that observed in the other reactions had occurred in this system also.

The difficulties experienced both in obtaining good-quality starting materials and in isolating the rather poor-quality products from reactions which could not be satisfactorily repeated discouraged further investigations of these systems.

A useful comparison may be made between the iminoalanes and the series of aminoalanes, $(R_2N)_nAlH_{3-n}$. Tris- and bis-aminoalanes can be prepared in fairly good yield from trimethylaminealane and appropriate proportions of secondary amines (265), but monoaminoalanes can only be obtained in modest yield because of their thermal instability. A similar situation may obtain for the aminoalanes. Tris(imino)alanes are moderately stable; the bis(imino)alane-trimethylamine complex decomposed at its melting point during attempted removal under vacuum of the co-ordinated solvent. Mono(imino)alanes may be unstable at room temperature, and this would account for the facts that no such compounds could be isolated from what were originally considered suitable reaction mixtures, and that on one occasion a bis(imino)alane derivative was obtained from these reactions.

However, this still does not explain why bis(imino)alanes could not be prepared from reaction between aluminium hydride (co-ordinated or not) and two equivalents of methyleneamine.

(iii) Reactions carried out by Mr. B. Hall. Preliminary investigations of several methyleneamino derivatives of aluminium have been made by Mr. B. Hall.

Reactions between dimethylaluminium chloride and one and two equivalents of di-t-butylmethyleneaminolithium afforded iminodimethylalane and lithium bis(imino)dimethylaluminate respectively (Equations

4.20 and 4.21).

$$Me_2AlCl + {}^tBu_2C{:}NLi \rightarrow {}^1/2[{}^tBu_2C{:}NAlMe_2]_2 + LiCl \quad 4.20$$

$$Me_2AlCl + 2\,{}^tBu_2C{:}NLi \rightarrow Li({}^tBu_2C{:}N)_2AlMe_2 + LiCl \quad 4.21$$

These two compounds were isolated and fully characterised by elemental analyses.

Reactions between methylaluminium dichloride and two equivalents of iminolithium (Equation 4.22), between lithium tetramethylaluminate and ketimine (Equation 4.23) and between Me_5Al_2Cl and iminolithium (Equation 4.24) afforded compounds whose I.R. spectra were consistent with their identities as shown in the equation but whose elemental analyses were not entirely satisfactory

$$MeAlCl_2 + 2\,{}^tBu_2C{:}NLi \rightarrow \tfrac{1}{2}[({}^tBu_2C{:}N)_2AlMe]_2 + 2LiCl \quad 4.22$$

$$LiAlMe_4 + {}^tBu_2C{:}NH \rightarrow LiAl(N{:}C{}^tBu_2)Me_3 + CH_4 \quad 4.23$$

$$Me_3Al_2Cl + {}^tBu_2C{:}NLi \rightarrow Me_3Al_2N{:}C{}^tBu_2 + LiCl \quad 4.24$$

Reaction between methylaluminium dichloride and one equivalent of iminolithium did not afford imino(methyl)aluminium chloride but a solid, thoughton the basis of its I.R. spectrum, to contain iminodimethylaluminium, possibly obtained as a result of disproportionation as shown in equation 4.25.

$$MeAlCl_2 + {}^tBu_2C{:}NLi \rightarrow [{}^tBu_2C{:}NAlMeCl]_2 \downarrow \tfrac{1}{2}[({}^tBu_2C{:}N)_2AlMe]_2 + AlMeCl_2 \quad 4.25$$

However, in reactions between $MeAl_2Cl_5$ and $Me_3Al_2Cl_3$, and iminolithium in mole ratios 1:1 - 1:5 and 1:1 - 1:3 respectively, no products of formulae consistent with the stoichiometry of equations 4.26 and 4.27 were isolated.

$$MeAl_2Cl_5 + n\,{}^tBu_2C{:}NLi \not\rightarrow MeAl_2(N{:}C{}^tBu_2)_nCl_{5-n} + nLiCl \quad (n = 1\text{-}5) \qquad 4.26$$

$$Me_3Al_2Cl_3 + n\,{}^tBu_2C{:}NLi \not\rightarrow Me_3Al_2(N{:}C{}^tBu_2)_nCl_{3-n} + nLiCl \quad (n = 1\text{-}3) \qquad 4.27$$

Methylaluminium sesquichloride is not adequately described by its general formula, $Me_3Al_2Cl_3$, as some disproportionation into $Me_2Al_2Cl_4$ and $Me_4Al_2Cl_2$ occurs (Equation 4.28) (266)

$$2Me_3Al_2Cl_3 \rightleftharpoons Me_2Al_2Cl_4 + Me_4Al_2Cl_2 \qquad 4.28$$

Reaction between methylaluminium sesquichloride and iminolithium may therefore give several products as a result of reaction of the disproportionation species $Me_2Al_2Cl_4$ and $Me_4Al_2Cl_2$ as well as the parent compound $Me_3Al_2Cl_3$ with iminolithium. No compound of constant elemental analyses could be obtained from these reactions. The structures of the nine possible products of the reactions, $Me_nAl_2Cl_m(N{:}C{}^tBu_2)_{6-m-n}$, some or all of which may be present in any one reaction mixture, may be very similar, and fractional recrystallisation of the mixture would be almost impossible. It is hardly surprising therefore, that no single pure compound could be isolated.

Similar problems may arise in the $MeAl_2Cl_5/{}^tBu_2C{:}NLi$ system.

(iv) Preparation of tris- and tetrakis-methyleneamino derivatives of Group III elements.

Several interesting comparisons may be drawn between the preparations of related methyleneamino derivatives of boron, aluminium and gallium.

All three tris(diphenylmethyleneamino) derivatives, $(Ph_2C{:}N)_3M$ (M = B, Al, Ga) are readily prepared from stoichiometric proportions of metal trihalide and imino-lithium or -trimethylsilane (Equation 4.29).

$$3Ph_2C{:}NY + MX_3 \rightarrow (Ph_2C{:}N)_3M + 3XY \qquad 4.29$$

(M = B, X = Br, Y = Me_3Si (47), M = Al, X = Cl, Y = Li (18), M = Ga, X = Cl, Y = Li (45)).

The reactions affording tris(diphenylmethyleneamino)borane and -alane are complete after a few hours at room temperature, and although the reagents for the preparation of $(Ph_2C{:}N)_3Ga$ were heated to 70° for four hours, no evidence is presented that this was actually necessary (45).

This straightforward method was found to be unsuitable for the preparation of tris(di-t-butylmethyleneamino)borane, whose preparation from iminolithium and bis(imino)fluoroborane required 36 hours at 120° (Equation 4.30) (Chapter 2).

$$^tBu_2C{:}NLi + (^tBu_2C{:}N)_2BF \rightarrow (^tBu_2C{:}N)_3B + LiF \qquad 4.30$$

The studies described above suggest that, although reaction between aluminium chloride and three equivalents of di-t-butylmethyleneamino lithium may afford some tris(imino)alane (18), the product is likely

to be contaminated with $LiAl(N:C^tBu_2)_4$ and $[^tBu_2C:NAlCl_2]_2$; preparation of $(^tBu_2C:N)_3Al$ from aluminium hydride and three equivalents of di-t-butylmethyleneamine is much more reliable (Equation 4.31).

$$3\,^tBu_2C:NH + AlH_3 \rightarrow (^tBu_2C:N)_3Al + 3H_2 \qquad 4.31$$

Tris(di-t-butylmethyleneamino)gallium was easily prepared by reaction between gallium chloride and three equivalents of iminolithium during one hour at $\sim 70^o$ (Equation 4.32) (45).

$$3\,^tBu_2C:NLi + GaCl_3 \rightarrow (^tBu_2C:N)_3Ga + 3LiCl \qquad 4.32$$

The preparation of lithium metallates, $LiM(N:C^tBu_2)_4$ and $Li_2M(N:C^tBu_2)_5$, seems to bear some relation to the size of the metal. Lithium tetrakis(di-t-butylmethyleneamino)borate could not be prepared from tris(imino)borane and iminolithium, but the related lithium aluminate, $LiAl(N:C^tBu_2)_4$ is readily formed in reactions between aluminium chloride and more than two equivalents of iminolithium (Equation 4.33). The dilithium pentakis(imino)aluminate, $Li_2Al(N:C^tBu_2)_5$, has not been prepared. Lithium tetrakis(imino)gallate can be prepared from iminolithium and gallium chloride (4:1 mole ratio) and a similar reaction using five equivalents of iminolithium affords dilithium pentakis(di-t-butylmethyleneamino)gallium (Equation 4.34).

$$4\,^tBu_2C:NLi + MCl_3 \rightarrow LiM(N:C^tBu_2)_4 + 3LiCl \qquad 4.33$$

$(M = Al, Ga; \neq B)$

$$5\,^tBu_2C:NLi + MCl_3 \rightarrow Li_2M(N:C^tBu_2)_5 + 3LiCl \qquad 4.34$$

$(M = Ga; \neq B, Al)$

Steric effects seem to be important as the largest atom, gallium, can accommodate five methyleneamino groups, aluminium four, and boron only three (covalent radii Ga, 126 pm; Al 118 pm; B, 82 pm (49)).

The difference in stability to hydrolysis of the two tris(imino) derivatives, $(^tBu_2C{:}N)_3B$ >> $(^tBu_2C{:}N)_3Al$, is also thought to be due mainly to steric effects. Experiments with scale models show that, as expected, access to the central metal atom for approaching hydroxyl groups is considerably easier in the tris(imino)alane, with the larger central metal, than in tris(imino)borane, to which apparently such access is very limited. This hydrolytic sensitivity parallels the ease with which another methyleneamino group may be attached to the central metal.

Similar steric effects may also account for the properties of bis(imino)-borane and -alane. Bis(di-t-butylmethyleneamino)borane, $(^tBu_2C{:}N)_2BH$ is monomeric, stable at its melting point, and has no co-ordinated solvent molecules. Bis(di-t-butylmethyleneamino)alane, is also thought to be monomeric, but has some weakly-co-ordinated solvent $(^tBu_2C{:}N)_2AlH.nNMe_3$ and decomposes at its melting point. It seems that the larger metal in the latter compound allows solvent co-ordination, but not association, but even this co-ordination does not result in thermal stability of the compound.

b. Structure and spectroscopic properties of methyleneamino derivatives of aluminium.

(i) Structure. All the known mono(methyleneamino) derivatives of aluminium are thought to be dimeric, $[R^1R^2C{:}NAlXY]_2$, in solution (by cryoscopy, where solubility permits), in the vapour phase (by mass

spectrometry) and in the condensed phase (by I.R. spectroscopy). Four-membered $(AlN)_2$ ring structures (Figure 4.1.a) have been proposed for these dimeric species, and have been confirmed by X-ray crystallography for the compounds $[^tBu(Me)C:NAlMe_2]_2$ (Figure 4.1.b) (153) and $[p\text{-}BrC_6H_4(Ph)C:NAlPh_2]_2$ (Figure 4.1.c) (149). A similar structure is also proposed for $^tBu_2C:NAl_2Me_5$ (Figure 4.1.d).

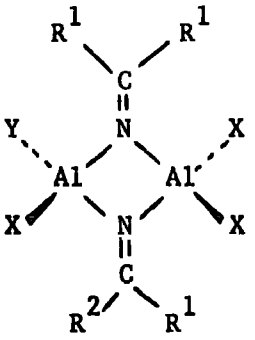
A trimeric structure for imino derivatives of aluminium $[R_2C:NAlX_2]_3$ (Figure 4.1.e) as found in related azide systems $[R_2AlN_3]_3$ (146), in some aminoalanes such as certain $[R_2NAlH_2]_3$ species (147), and in $[Me_2AlNHMe]_3$ (148) (Figure 4.1.f), would allow a greater Al-N-Al angle and hence less strain at the three-co-ordinate nitrogen atom. However, kinetic studies of nitrile - R_3Al reactions have shown that association of iminoaluminium compounds into dimers rather than trimers is favoured (145).

Even the compounds which the methyleneamino ligands contain bulky t-butyl groups (e.g. $[^tBu_2C:NAlCl_2]_2$ (18)) are dimeric. This is a marked contrast with similar derivatives of boron, as all the known di-t-butylmethyleneaminoboranes $^tBu_2C:NBXY$, and several other iminoboron compounds with bulky methyleneamino groups are monomeric because steric hindrance prevents association (see Chapter 2).

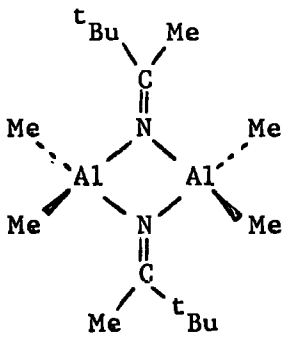
In the aluminium compounds however, the larger metal atom can accommodate even the bulky methyleneamino ligands in a dimeric structure. Similarly, monomethyleneamino derivatives of gallium are all dimeric, $[R^1R^2C:NGaXY]_2$ (Figure 4.1.b) (45, 154, 155)

Bis(di-t-butylmethyleneamino)methylaluminium $[(^tBu_2C:N)_2AlMe]_n$ and bis(di-t-butylmethyleneamino)alane-trimethylamine, $(^tBu_2C:N)_2AlH.nNMe_3$ are thought to be the first examples of bis(imino) derivatives of

Figure 4.1



(a)



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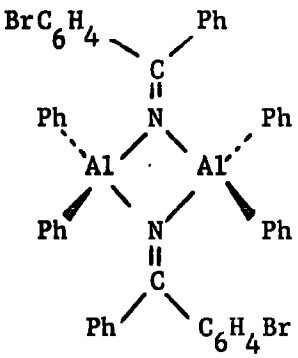

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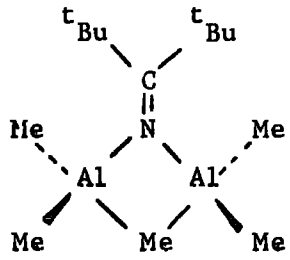

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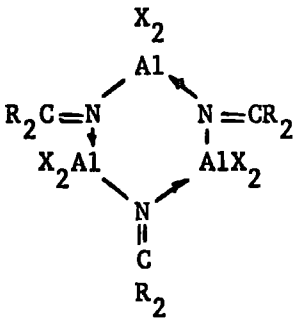

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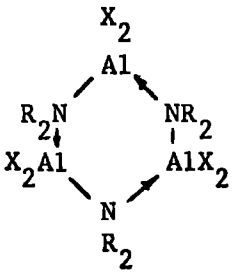

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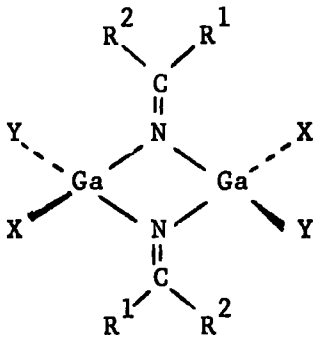


(g)

aluminium.

The iminomethylaluminium compound is believed to be dimeric, $[(^tBu_2C{:}N)_2AlMe]_2$, with two bridging and two terminal methyleneamino groups (Figure 4.2.a) rather than four terminal groups (Figure 4.2.b), as nitrogen is a better bridging atom than carbon. This again contrasts with the related boron compound, $(^tBu_2C{:}N)_2BMe$, which is monomeric (see Chapter 2).

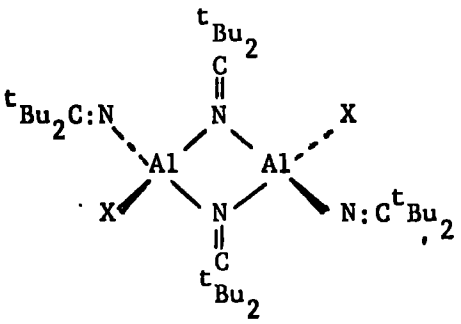
The bis(di-t-butylmethyleneamino)alane-trimethylamine complex $(^tBu_2C{:}N)_2AlH.nNMe_3$, is believed (on spectroscopic grounds, see later sections) to be monomeric, presumably because the complexed trimethylamine prevents association.

Unco-ordinated bis(di-t-butylmethyleneamino) derivatives of aluminium, $[(^tBu_2C{:}N)_2AlX]_n$ with groups X bulkier than hydrogen or methyl would be of particular interest as they might also be monomeric. Bis(imino)aluminium chlorides, $[(R_2C{:}N)_2AlCl]_n$ (R = Ph, ^{t}Bu), are unstable with respect to disproportionation to tris(imino)alane and iminoaluminium dichloride (18), but if stable monomeric bis(imino)aluminium compounds, perhaps with bulky organic groups X, could be prepared, a study of the influence of the group X on the properties of these compounds could be made.

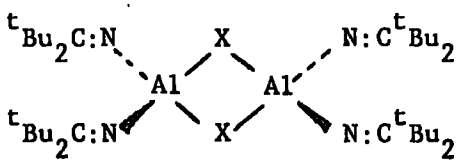
The two known tris(imino)aluminium compounds, $(Ph_2C{:}N)_3Al$ (18) and $(^tBu_2C{:}N)_3Al$, are monomeric as are their boron and gallium counterparts $(R_2C{:}N)_3M$ (M = B; R = Ph (62), ^{t}Bu; M = Ga; R = Ph, ^{t}Bu (45)).

Certain sterically-crowded tris(amino) derivatives of aluminium such as $(^iPr_2N)_3Al$ (147, 267) and $((Me_3Si)_2N_3Al$ (268, 269) are also monomeric, although derivatives with less-bulky substituents e.g. $[(Me_2N)_3Al]_2$ (147, 267) are associated.

Figure 4.2



(a)



(b)

A model of the hypothetical dimer $[(Ph_2C{:}N)_3Al]_2$ (Figure 4.3.a) indicates that this molecule would be quite strained, and the orientations of the phenyl groups could be severely limited, so it appears that lack of association of tris(diphenylmethyleneamino)aluminium is due to the bulk of the phenyl groups (18). Similar arguments apply to $(^tBu_2C{:}N)_3Al$ in which the t-butyl groups would afford even greater steric hindrance in an associated structure.

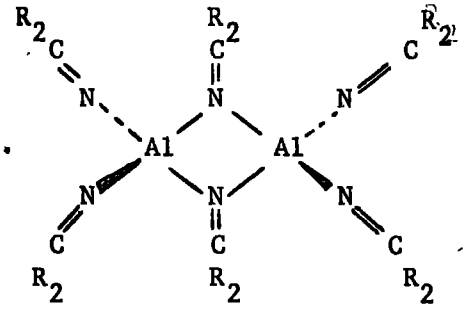
In the monomers $(Ph_2C{:}N)_3Al$ and $(^tBu_2C{:}N)_3Al$, the aluminium - nitrogen bond energy will be maximised if the C=N=Al units are linear as this condition allows greater overlap of the nitrogen 2p and aluminium 3p orbitals available for N → Al dative π-bonding. Linearity of the C=N=AL units would also cause the C-attached substituents to adopt a "paddle-wheel" orientation normal to the AlN_3 plane (Figure 4.3.b), the orientation which would allow most room for the substituents.

This structure is like that proposed for the related tris(imino)boranes $(R_2C{:}N)_3B$ (R = Ph (62), ^tBu) and tris(imino)gallanes $(R_2C{:}N)_3Ga$ (R = Ph, ^tBu (45)).

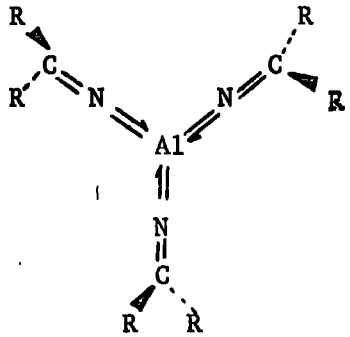
This "paddle-wheel" structure of monomeric tris(imino) derivatives of aluminium provides an interesting contrast to the related tris(amino)-aluminium monomer $(R_2N)_3Al$, for which the optimum orientation for N → Al dative π-bonding, with trigonal planar hybridisation of the amino-nitrogens, requires the substituents R to be coplanar with the AlN_3 skeleton (Figure (Figure 4.3.c), an orientation which is impossible when the groups R are bulky. In $((Me_3Si)_2N)_3Al$ for example, the dihedral angle between the AlN_3 and $NAlSi_2$ planes is 50^o, and the molecule is propeller-shaped (267).

The three methyleneaminoaluminates, $LiAl(N{:}C^tBu_2)_4$, $LiAl(N{:}C^tBu_2)_2Me_2$

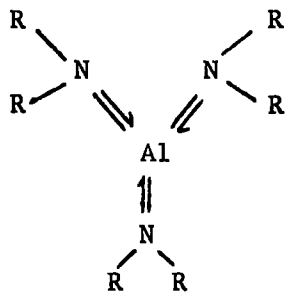
Figure 4.3



(a)



(b)



(c)

and $LiAl(N:C^tBu_2)Me_3$ are all thought to be monomeric. The crystal structure of lithium tetrakis(di-t-butylmethyleneamino)aluminate has been established by X-ray crystallography (Figure 4.4.a) (40), and shows the presence of both bridging and terminal di-t-butylmethyleneamino groups with near-linear C=N-Al units. The terminal ligands have short Al-N bonds (178 pm : compare Al-N single bond length of 194 pm (270)) and a C-N-Al angle of 167^o. A further point of interest is the orientation of one of the methyl groups (carbon atom C (4)) with respect to the lithium atom. Instead of rotating away from the lithium as would be expected to minimise steric hindrance, the methyl group leans towards it apparently developing a novel type of Li H C interaction.

The structures of lithium bis(di-t-butylmethyleneamino)dimethylaluminate $LiAl(N:C^tBu_2)_2Me_2$ (Figure 4.4.d) and lithium di-t-butylmethyleneaminotrimethylaluminate, $LiAl(N:C^tBu_2)Me_3$ (Figure 4.4.c), are also thought to involve a tetrahedral arrangement of the imino and methyl groups around aluminium. On the basis of their I.R. spectra they are thought to have bridging rather than terminal methyleneamino groups, and some Li H C interaction may occur in these compounds also.

Lithium tetrakis(di-t-butylmethyleneamino)gallate, $LiGa(N:C^tBu_2)_4$ is thought to be isostructural with its aluminium counterpart described above (Figure 4.5.d) (45).

Two possible structures have been proposed for dilithium pentakis-(di-t-butylmethyleneamino)gallate, $Li_2Ga(N:C^tBu_2)_5$. One involves two four-membered $GaLiN_2$ rings (Figure 4.5.b), the other a six-membered $GaLi_2N_3$ ring (Figure 4.5.c). The former structure is considered the more likely (45).

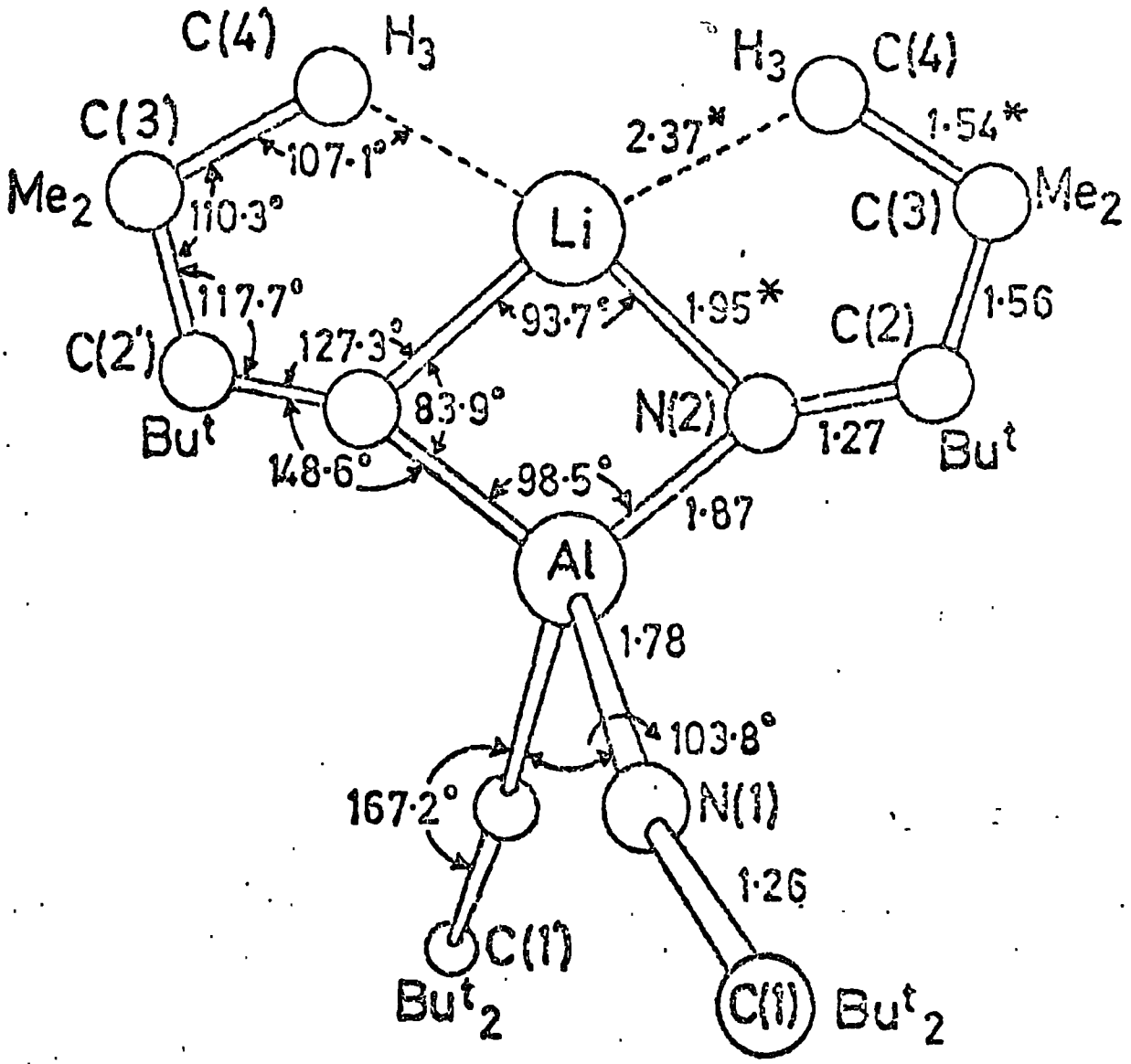
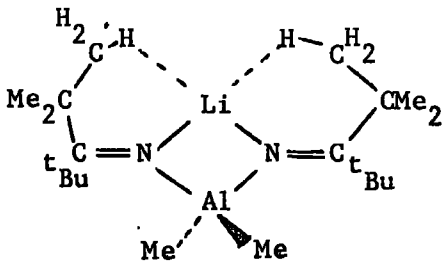


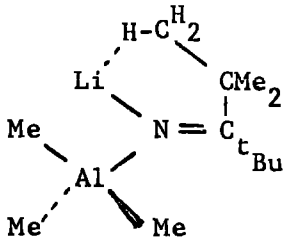
Figure 4.4.a

Crystal structure of $LiAl(N:C^tBu_2)_4$ (40).

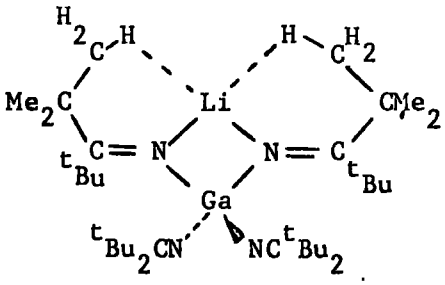
Figure 4.4. continued



(b)

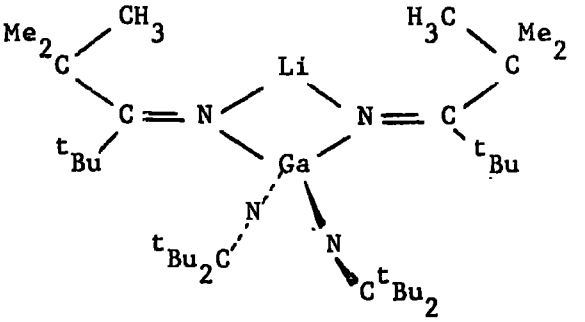


(c)

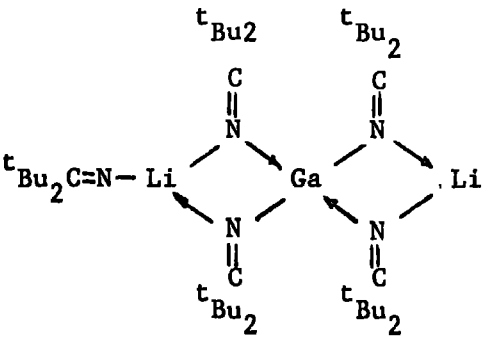


(d)

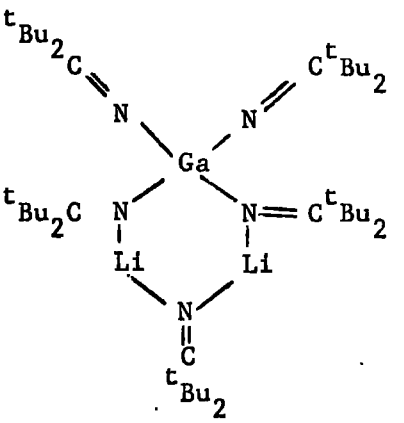
Figure 4.5



(a)



(b)



(c)

(ii) Azomethine stretching frequencies of methyleneamino derivatives of aluminium. The azomethine stretching frequencies of the new mono(di-t-butylmethyleneamino) derivatives of aluminium are given in table 4.2 together with those of some related compounds.

As observed for the bridging azomethine stretching frequencies of methyleneamino derivatives of magnesium (see Chapter 3) the bridging azomethine stretching frequencies of these methyleneamino derivatives do not seem to follow a simple pattern. Some absorptions are observed at higher frequency and some at lower frequency than the parent ketimine, and there is no simple correlation between these differences and the nature of the methyleneamino group or the other substituents on aluminium.

In the series of di-t-butylmethyleneaminoaluminium compounds (Table 4.2) the azomethine stretching frequency of the iminoaluminium dichloride compound $[^{t}Bu_2C{:}NAlCl_2]_2$ is considerably higher than those of the two iminomethylaluminiums, $[^{t}Bu_2C{:}NAlMe_2]_2$ and $^{t}Bu_2C{:}NAl_2Me_5$, which are rather similar.

However, the azomethine stretching frequencies of the two related diphenylmethyleneaminoaluminium derivatives $[Ph_2C{:}NAlCl_2]_2$ and $[Ph_2C{:}NAlMe_2]_2$ are in the opposite order, the chloro compound being rather lower than that of the methyl compound.

The I.R. spectrum of bis(di-t-butylmethyleneamino)methylaluminium, $[(^{t}Bu_2C{:}N)_2AlMe]_2$ shows two absorptions in the region appropriate for C = N stretching vibrations (table 4.3). These are assigned to terminal (higher frequency) and bridging (lower frequency) methyleneamino groups by analogy with other compounds known to have both bridging and terminal groups (e.g. $[(^{t}Bu_2C{:}N)_2Be]_2$ (39, 45)].

Table 4.2

Azomethine stretching frequencies (cm^{-1}) of some mono(methyleneamino) derivatives of aluminium.

Compound	ν(C=N)	Δν	Ref
$[^tBu_2C{:}NAlCl_2]_2$	1664	+54	18
$[^tBu_2C{:}NAlMe_2]_2$	1580	-30	a
$^tBu_2C{:}NAl_2Me_5$	1586	-24	a
$[Ph_2C{:}NAlCl_2]_2$	1593	-14	18
$[Ph_2C{:}NAlMe_2]_2$	1616	+9	18

(a) This work

$\Delta\nu = \nu(C{=}N)\ [R_2C{:}NAlX_2]_2 - \nu(C{=}N)\ R_2C{:}NH$

$\nu(C{=}N)\ R_2C{:}NH$: R = Ph, 1607 cm^{-1} (23), ^tBu, 1610 cm^{-1} (64).

Table 4.3

Azomethine stretching frequencies (cm^{-1}) of some bis(di-t-butylmethyleneamino) derivatives of aluminium and boron.

Compound	ν(C=N)	
	Terminal	Bridging
$(^tBu_2C{:}N)_2AlH.nNMe_3$	1712 (1696sh)	
$[(^tBu_2C{:}N)_2AlMe]_2$	1717	1609
$(^tBu_2C{:}N)_2BH$	1760	
$(^tBU_2C{:}N)_2BMe$	1745	

The azomethine stretching frequency ν(C=N) of the bis(imino)alane $(^tBu_2C{:}N)_2AlH.nNMe_3$ is observed at 1712 cm^{-1}, at a frequency similar to the terminal azomethine stretching frequency of $[(^tBu_2C{:}N)_2AlMe]_2$.

The terminal azomethine stretching frequencies of the related bis(di-t-butylmethyleneamino) derivatives of boron, $(^tBu_2C{:}N)_2BH$ and $(^tBu_2C{:}N)_2BMe$ are also rather similar, but are both rather higher than the corresponding mass of the central metal is less.

The azomethine stretching frequencies of the two tris(imino)aluminium compounds, $(^tBu_2C{:}N)_3Al$ and $(Ph_2C{:}N)_3Al$ are given in table 4.4 together with those of the related imino-boranes and -gallanes.

The variation in ν(C=N) with M for these tris(imino) derivatives $(R_2C{:}N)_3M$ can be expected to reflect both the varying mass of M and the varying strength of the N=M bond for the series of the di-t-butyl compounds $(^tBu_2C{:}N)_3M$, the observed sequence ν(C=N) for M = B > Al > Ga is consistent with the mass changes in this sequence. On the other hand, for the diphenyl compounds $(Ph_2C{:}N)_3M$, the observed sequence ν(C=N) for M = Al > B > Ga is consistent with the expected variation in N=M bond strength.

The azomethine stretching frequency of $(^tBu_2C{:}N)_3Al$ prepared as described in this thesis (1703 cm^{-1}) is rather higher than that reported previously (1690 cm^{-1}) (18).

Of the four lithium metallates shown in table 4.5, only the two lithium tetrakis(di-t-butylmethyleneamino) compounds $LiAl(N{:}C^tBu_2)_4$ and $LiGa(N{:}C^tBu_2)_4$ have an absorption in the region appropriate for C=N stretching vibration of terminally-attached methyleneamino groups (1700 and 1673 cm^{-1} respectively). That observed for $LiGa(N{:}C^tBu_2)_4$ is, as

Table 4.4

Azomethine stretching frequencies, ν(C=N) (cm^{-1}), of some tris(di-t-butylmethyleneamino) derivatives of boron, aluminium and gallium.

Compound	Ph	Ref	^{t}Bu	Ref
$(R_2C{:}N)_3B$	1667	62	1730	a
$(R_2C{:}N)_3Al$	1686	18	17	a
$(R_2C{:}N)_3Ga$	1645	45	1672	45

(a) This work

expected, at rather lower frequency than that for $LiAl(N:C^tBu_2)_4$. Peaks attributable to bridging methyleneamino groups are observed at lower frequencies (Table 4.5).

The two lithium (imino)methylaluminates, $Li(^tBu_2C:N)AlMe_3$ and $Li(^tBu_2C:N)_2AlMe_2$, have absorptions assignable to azomethine stretching vibrations in the region appropriate for bridging rather than terminal methyleneamino groups. Comparison of these spectra with that of $LiAl(N:C^tBu_2)_4$ whose structure is known (Figure 4.4.a) suggests that in the two compounds $Li(^tBu_2C:N)AlMe_3$ and $Li(^tBu_2C:N)_2AlMe_2$ the imino group or groups bridge between the aluminium and lithium atoms in a manner similar to that observed in $LiAl(N:C^tBu_2)_4$ (Figure 4.4.b and c)

(iii) ^1H n.m.r. spectra of methyleneamino derivatives of aluminium.

Details of the ^1H n.m.r. spectra of two of the new di-t-butylmethyleneamino derivatives and lithium tetrakis(di-t-butylmethyleneamino)aluminate are given in table 4.6. Unfortunately, the ^1H n.m.r. spectra of the new compounds prepared in exploratory studies by Mr. B. Hall were not recorded.

The ^1H n.m.r. spectrum of lithium tetrakis(di-t-butylmethyleneamino)-aluminate, $LiAl(N:C^tBu_2)_4$, is a multiplet (40, 56), but that of tris(di-t-butylmethyleneamino)aluminium, $(^tBu_2C:N)_3Al$, is a singlet probably because all the t-butyl groups are in magnetically-equivalent environments. Knowledge of this, used in conjugation with I.R. spectra, was used to identify the compounds obtained during attempted preparations of tris(di-t-butylmethyleneamino)aluminium. The presence of a complex multiplet in the appropriate region of the ^1H n.m.r. spectrum, together with the I.R. spectrum of the material obtained all too often provided good evidence for the formation of lithium tetrakis(di-t-butylmethyleneamino)aluminate in reactions explored as possible routes to tris(di-t-butylmethyleneamino)-

Table 4.5

Azomethine stretching frequencies (cm^{-1}) of some lithium di-t-butylmethyleneaminometallates

Compound	ν(C=N)		Ref
	Terminal	Bridging	
$LiAl(N:C^tBu_2)_4$	1700	1642, 1602	40
$LiAl(N:C^tBu_2)_2Me_2$		1633, 1605	a
$LiAl(N:C^tBu_2Me_3$		1633, 1604	a
$LiGa(N:C^tBu_2)_4$	1673	1649, 1629, 1616	45

(a) This work

Table 4.6

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

di-t-butylmethyleneamino derivatives of aluminium.

Compound	τ (p.p.m.)	Ref
$(^tBu_2C{:}N)_2AlH.nNMe_3$	9.22s (36), 8.32s (10)	a
$(^tBu_2C{:}N)_3Al$	9.35s	a
$LiAl(N{:}C^tBu_2)_4$	8.69c 9.02c	40, 52

Spectra recorded as ~ 20 wt. % solutions in toluene at +33°

s = singlet

c = complex

Relative intensities in brackets

(a) This work

aluminium (see section 4.2.a).

The ^1H n.m.r. spectrum of bis(di-t-butylmethyleneamino)alane-trimethylamine, $(^tBu_2C{:}N)_2AlH.nNMe_3$, showed a single absorption due to the t-butyl groups at 9.22 τ and a single absorption at 8.32 τ due to methyl groups in the co-ordinated amine. No peak due to the aluminium-attached proton was observed. The relative intensities of the two peaks ($\sim$10:36) respectively) suggests that there is approximately one molecule of trimethylamine per molecule of iminoalane (i.e. n = 1). This is rather more co-ordinated amine than was indicated by the elemental analyses of this compound, but as the trimethylamine is believed to be only weakly co-ordinated (the compound smelled very strongly of amine) this discrepancy is not surprising.

A study of the ^1H n.m.r. spectra of the compounds prepared by Mr. B. Hall would be of interest, as they may provide further structural information about these compounds, and the relative positions of peaks due to the methyl groups may afford interesting comparisons with related compounds.

(iv) Mass spectra of methyleneamino derivatives of aluminium. During attempts to obtain mass spectra of several of the new methyleneamino derivatives of aluminium the compounds broke down so extensively in the spectrometer that no ions with $^m/_e$ greater than 141 ($^tBu_2C{:}NH^+$) were observed.

Similar decomposition has been reported for diphenylmethyleneamino-aluminium dibromide $[Ph_2C{:}NAlBr_2]_2$ but not for the related chloro and methyl compounds $[Ph_2C{:}NAlCl_2]_2$ and $[Ph_2C{:}NAlMe_2]_2$ whose mass spectra have been discussed (18). No report has been made however of any attempts to

obtain the mass spectrum of di-t-butylmethyleneaminoaluminium chloride, $[^tBu_2C{:}NAlCl_2]_2$, although many of its other properties have been discussed (18).

The mass spectrum of the colourless tris(di-t-butylmethyleneamino)-alane prepared as described in this thesis showed only the fragmentation of the methyleneamino group even when recorded at low source temperature and low accelerating potential.

Aluminium-containing fragments were observed in the mass spectrum of the tris(di-t-butylmethyleneamino)alane obtained by previous workers (18). However, these may have arisen from fragmentation of lithium tetrakis(di-t-butylmethyleneamino)aluminate contaminating the sample.

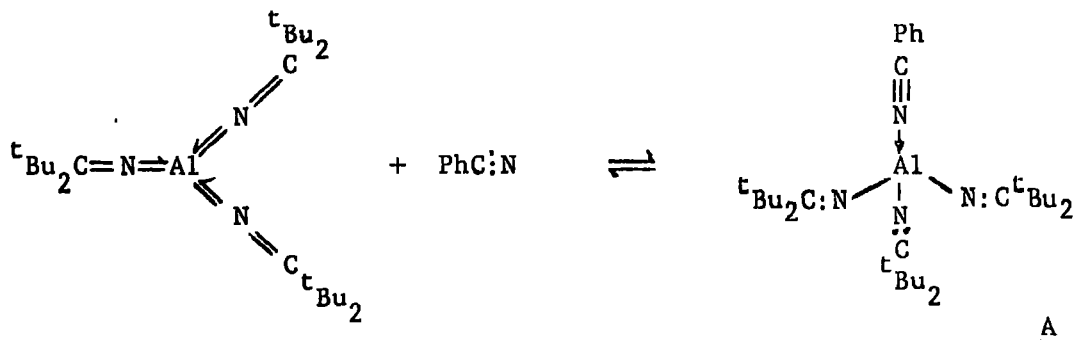
(c) Reaction of tris(di-t-butylmethyleneamino)aluminium with benzonitrile. The difference in behaviour towards di-t-butylmethyleneaminolithium, and susceptibility to hydrolysis by atmospheric moisture of tris(di-t-butyl methyleneamino)-borane and -alane suggested that while the tris(imino)-borane apparently will not co-ordinate with electron pair donor molecules (Chapter 2) the tris(imino)alane may well do so, and a preliminary study of the ^1H n.m.r. spectra of the tris(di-t-butylmethyleneamino)alane - benzonitrile system in toluene solution has been made.

The spectrum of the solution of tris(di-t-butylmethyleneamino)alane in toluene showed a single absorption due to the t-butyl groups at 9.35 τ. When one equivalent of benzonitrile was added, the solution became pale yellow in colour, and its ^1H n.m.r. spectrum showed a complex multiplet with main peaks at 9.22, 9.34, 9.55 and 9.60 τ. Addition of a little more benzonitrile caused the colour of the solution to deepen, and its ^1H n.m.r. spectrum showed two peaks at 9.26 and 9.52 τ. When excess

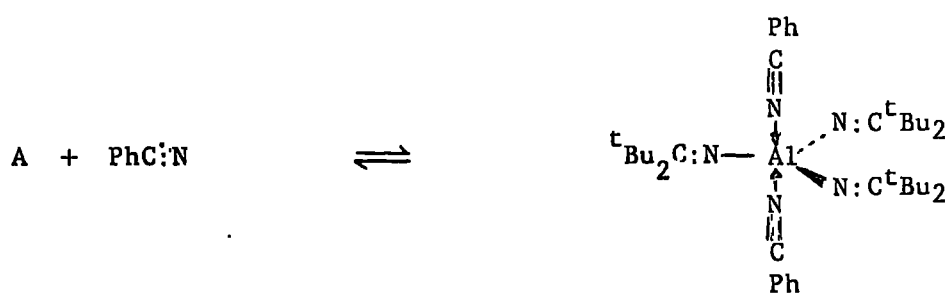
benzonitrile was added, the yellow colour was discharged, and the solution became rather gelatinous. Its ^1H n.m.r. spectrum showed only one peak, at 9.54 τ.

Comparison of these spectra suggests that in the solution prepared from equimolar proportions of tris(imino)alane and benzonitrile, three distinct species are present: unco-ordinated tris(imino)alane (9.34 τ), a tris(imino)alane - benzonitrile complex in which all the t-butyl groups are equivalent (9.55 τ), and a complex in which there is more than one environment for the t-butyl groups (9.34 and 9.60 τ) (Equation 4.35).

The structures of the two complexes probably involve four- and five-co-ordinate aluminium as shown in equation 4.35.



Three-co-ordinate aluminium Four-co-ordinate aluminium



Five-co-ordinate aluminium

4.35

In the spectrum of tris(imino)alane and slightly more than one equivalent of benzonitrile, no peak due to unco-ordinated tris(imino)alane is present at ~ 9.38 τ. This, together with the increase in colour intensity of the solution suggests that more of the complex $(^tBu_2C{:}N)_3Al.N{:}CPh$ is being formed. However, only one peak attributable to t-butyl groups in this species is observed (9.26 τ), and by comparison with the previous spectrum, a second peak at 9.60 τ would also be expected. A peak attributable to t-butyl groups in the complex $(^tBu_2C{:}N)_3Al.2N{:}CPh$ is also present in this spectrum (9.52 τ).

This suggests that in the solution with rather more than one equivalent of benzonitrile, only the two species $(^tBu_2C{:}N)_3Al.NC{:}Ph$ and $(^tBu_2C{:}N)_3Al.2N{:}CPh$ are in equilibrium (Equation 4.35).

$$(^tBu_2C{:}N)_3Al.N{:}CPh + N{:}CPh \rightleftharpoons (^tBu_2C{:}N)_3Al.2N{:}CPh \qquad 4.35$$

3. Summary of the new methyleneaminoaluminium compounds. The preparation of tris(di-t-butylmethyleneamino)alane, $(^tBu_2C{:}N)_3Al$, from aluminium hydride and di-t-butylmethyleneamine has been shown to be more reliable than the reaction between aluminium chloride and three equivalents of iminolithium, in which the compounds $LiAl(N{:}C^tBu_2)_4$ and $[^tBu_2C{:}NAlCl_2]_2$ are apparently more readily formed. Reactions between aluminium hydride or its trimethylamine adduct, $AlH_3.NMe_3$, and one or two equivalents of di-t-butylmethyleneamine were less successful, and only once could a bis(imino) be isolated, as its trimethylamine adducts $(^tBu_2C{:}N)_2AlH.nNMe_3$. The preliminary studies of some di-t-butylmethyleneamino derivatives of some methylaluminium compounds, $LiAl(N{:}C^tBu_2)_nMe_{4-n}$ and $[(^tBu_2C{:}N)_nAlMe_mCl_{3-m-n}]_2$ have indicated that further work in this area may be of interest.

Appendix 1

Di-t-butylmethyleneaminodimethylamine, $^{t}Bu_2C{:}NNMe_2$.

1. Introduction. An important feature of this thesis and other studies of di-t-butylmethyleneamino derivatives of metals and metalloids, $^{t}Bu_2C{:}NMX_n$, has been the interpretation of singlet absorptions in their ^{1}H n.m.r. spectra due to the t-butyl groups in terminal $^{t}Bu_2C{:}N$-ligands. These singlets can arise either from t-butyl groups in the magnetically-equivalent environments afforded by a linear $\rangle C{=}N{=}M$ skeleton, or from t-butyl groups in non-equivalent environments in a bent $\rangle C{=}N{-}M$ unit in which inversion at nitrogen is more rapid than the ^{1}H n.m.r. timescale.

These spectra have usually been interpreted in terms of an effectively linear $\rangle C{=}N{=}M$ structure as no change in the width of the peaks was observed when the spectra were recorded at low temperature.

In order to show that a bent $\rangle C{=}N{-}Y$ skeleton would give rise to a doublet t-butyl signal in the ^{1}H n.m.r., the compound $^{t}Bu_2C{:}NNMe_2$ was prepared and its ^{1}H n.m.r. spectrum was recorded.

Before this work the only compound $^{t}Bu_2C{:}NY$ to have been shown by ^{1}H n.m.r. to have a bent $\rangle C{=}N{-}Y$ skeleton was di-t-butylmethyleneamine (52), which at $+33^{o}$ gave a single absorption due to the t-butyl groups at 8.83 τ, though at -30^{o} two signals, at 8.74 and 8.88 τ, were seen.

From these observations, an approximate minimum value of the activation energy for the inversion at nitrogen of $^{t}Bu_2C{:}NH$ of ~ 5.5 kcals $mole^{-1}$ may be calculated (284). (Further work on the temperature-dependence of the chemical shift and width of these

peaks would be necessary for a more accurate value of the activation energy to be obtained).

Further examples of such systems with bent $\rangle C=N-Y$ systems were required to show that such a system could be adequately detected, otherwise singlet absorptions in the ^1H n.m.r. of derivatives $^tBu_2C:NMX_n$ could always arise from bent $\rangle C=N-M$ units in which inversion at nitrogen was rapid.

Recent attempts to prepare N-methyl-di-t-butylmethyleneamine $^tBu_2C:NMe$, from iminolithium and either dimethylsulphate or methyl bromide were unsuccessful (46), so the preparation of an N-amino derivative of di-t-butylmethyleneamine was attempted.

2. Preparation of di-t-butylmethyleneaminodimethylamine, $^tBu_2C:NNMe_2$

N-chlorodimethylamine, prepared as described in the literature from N-chlorosuccinimide and trimethylamine (280), was kindly given by Mr N.D. Cowan. A solution of di-t-butylmethyleneaminolithium (30.4 mmole) in 60 ml ether was added slowly to a solution of 30 mmole N-chloromethylamine in 60 ml ether at -196°, then the mixture was allowed to warm up. As the mixture melted, a very bright blue colour developed. This gradually changed to clear yellow as the mixture continued to warm up. At ~ -5° a white precipitate was formed, and at ~ 0° the yellow colour of the solution faded. The mixture was stirred at room temperature overnight, then all the volatile material was removed and collected. Ether was pumped off and the remaining pale yellow liquid was distilled at 36-38°, 0.01 mm Hg, to give a clear colourless liquid identified as di-t-butylmethyleneamino-dimethylamine, $^tBu_2C:NNMe_2$.

(Found: C, 71.38; H, 13.17; N, 15.45%; M, 191.

$C_{11}H_{24}N_2$ requires C, 71.68; H, 13.13; N, 15.20% M, 184.33.)

ν_{max} (liquid film) 3005sh, 2980sh, 2952s, 2920s, 2855s, 2816s, 2774m, 2762m, 1605m, 1590m, 1492sh, 1483s, 1469m, 1458sh, 1447sh, 1431m, 1416m, 1390s, 1364s, 1353m, 1322m, 1262w, 1233sh, 1222s, 1210s, 1196s, 1178sh, 1167w, 1117w, 1089w, 1064m, 1020m, 997m, 952s, 930w, 916w, 876m, 863w, 784w, 721w, 677w, 538m, 428 cm^{-1}.

3. Discussion. Hydrazones are usually prepared by acid-catalysed reactions between the appropriate aldehyde or ketone and hydrazine (Equation A1.1).

$$R^1R^2C{:}O + R^3R^4N\text{-}NR^5R^6 \rightarrow R^1R^2C{:}NNR^3R'^4 \qquad A1.1$$

Di-t-butylketone hydrazone has been prepared from the ketimine and hydrazine (Equation A1.2) (281).

$$^tBu_2C{:}NH + H_2N\text{-}NH_2 \rightarrow {}^tBu_2C{:}NNH_2 \qquad A1.2$$

The preparation of di-t-butylketone dimethylhydrazone from iminolithium and N-chlorodimethylamine (Equation A1.3) described here is believed to be the first example of the use of this type of reaction for hydrazone synthesis.

$$^tBu_2C{:}NLi + Me_2NCl \rightarrow {}^tBu_2C{:}NNMe_2 + LiCl \qquad A1.3$$

The success of this reaction contrasts with the failure to prepare tetramethyhydrazine from N-chlorodimethylamine and lithium dimethylamide by a similar method (Equation A1.4) (282).

$$Me_2NCl + Me_2NLi \rightarrow Me_2N.NMe_2 + LiCl \qquad A1.4$$

The azomethine stretching frequency of $^{t}Bu_2C{:}NNMe_2$ occurs at 1605 cm^{-1}, in the region appropriate for hydrazone compounds (Table A1.1) (283) but rather lower than that of the closely-related compound $^{i}Bu_2C{:}NNMe_2$.

Table A1.1

C=N stretching frequencies (cm^{-1}) of some compounds containing the >C=N- group.

Compound	ν(C=N)
$^{t}Bu_2C{:}NNMe_2$ (a)	1605
$^{i}Bu_2C{:}NNMe_2$	1640
$^{t}BuMeC{:}NNMe_2$	1630
$Me_2C{:}NNMe_2$	1640
$H_2C{:}NNMe_2$	1590
$Ph_2C{:}NNMe_2$	1588

(a) This work. All others, reference 283.

The ^{1}H n.m.r. spectrum of $^{t}Bu_2C{:}NNMe_2$ at temperatures between 33 and 136° show a singlet at 7.93 τ due to the methyl groups and a doublet with peaks at 8.75 and 8.93 τ due to the t-butyl groups in magnetically non-equivalent environments. This indicates that even at 136°, inversion about the azomethine nitrogen is not sufficiently rapid for the two t-butyl groups to appear equivalent in the ^{1}H n.m.r. spectrum.

Table A1.2

$\Delta G^{\ddagger}$ values (activation energies for inversion at the azomethine nitrogen) (kcal. $mole^{-1}$) for some compounds containing the $>C{=}N-$ group

Compound	$\Delta G^{\ddagger}$	Reference
$Me_2C{:}NPh$	20.3	287
$Ph_2C{:}NH$	~ 14	286
Ph(sec-Bu)C:NH	~ 6.5	286
$PhMeC{:}NCH_2Ph$	23-24	16
$(CF_3)_2C{:}NCF(CF_3)_2$	~ 13	285
$Me_2C{:}NC{:}N$	18.9	287
$(NMe_2)_2C{:}NC{:}N$	< 10	287

From the separation of these two peaks (0.18 p.p.m., or 10.8 c.p.s) it can be shown that inversion at the azomethine nitrogen is occurring less than ~ 7 times per second (284) throughout the temperature range studied. However, the rate of change of the rate of inversion could not be measured - no change in the widths of the peaks was observed - so the activation energy of the inversion process could not be determined.

Activation energies for inversion at the azomethine nitrogen for some other compounds containing the $>C{=}N-$ group are given in table A1.2.

The main peaks in the mass spectrum of di-t-butylmethyleneamino-dimethylamine, $^{t}Bu_2C{:}NNMe_2$, are given in table A1.3

Table A1.3

Main peaks in the mass spectrum of $^{t}Bu_2C{:}NNMe_2$.

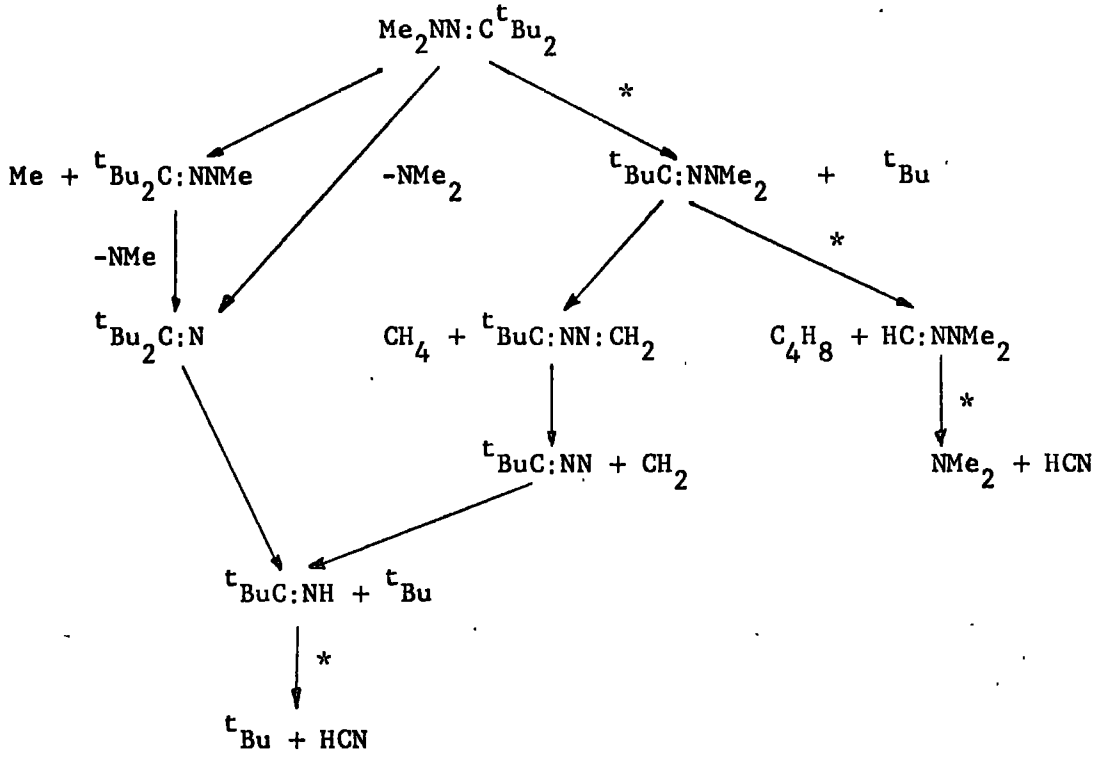
m/e	Relative Intensity	Assignment
184	34	$^{t}Bu_2C{:}NNMe_2$
169	7	$^{t}BuC{:}NNMe$
140	< 1	$^{t}Bu_2C{:}N$
127	68	$^{t}BuC{:}NNMe_2$
111	7	$^{t}BuC{:}NNiCH_2$
97	2	$^{t}BuC{:}NN$
84	31	$^{t}BuC{:}NH$
71	79	$HC{:}NNMe_2$
57	68	^{t}Bu
44	100	NMe_2

The suggested fragmentation pattern for this compound is shown in figure A1.1.

There seem to be two main fragmentation pathways. One is the fragmentation of the species $^{t}Bu_2C{:}NNMe$ and $^{t}Bu_2C{:}N$ obtained by loss of a methyl or Me_2N- group respectively from the parent compound, and the other is the breakdown of the species $^{t}BuC{:}NNMe_2$ which results from loss of a t-butyl group from the parent compound. Some of the fragmentations in this latter pathway are supported by the presence of metastable peaks.

Figure A1.1

Fragmentation pattern of $^{t}Bu_2C{:}NNMe_2$



* Fragmentation confirmed by metastable peak.

Appendix 2.

Preliminary studies of reactions between boron trifluoride and 1,1,3,3-tetramethylguanidinolithium, and between triethylborane and 1,1,3,3-tetramethylguanidine.

1. Experimental.

(a) Reaction between triethylborane and 1,1,3,3-tetramethylguanidine.

Triethylborane (26.7 ml of a 1.0 M solution in THF, 26.7 mmole) was added to a solution of tetramethylguanidine (3.08 g, 26.7 mmole) in 20 ml hexane at -196°. The mixture was stirred at room temperature overnight, during which time a pale yellow colour developed. Removal of solvent left a waxy yellow solid which could not be crystallised. Vacuum sublimation at room temperature of this material afforded colourless crystals identified as the tetramethylguanidine-triethylborane adduct, $(Me_2N)_2C{:}NH.BEt_3$

(Found: B, 5.0; N, 18.75%, M, 206.

$C_{11}H_{28}B\,N_3$ requires B, 5.1; N, 19.71%; M, 213.19)

ν_{max}(Nujol mull) 3375s, 1589s, 1554s, 1475sh, 1456s, 1431s, 1418s, 1409s, 1378w, 1365sh, 1350s, 1264m, 1250m, 1235m, 1139s, 1110?, 1063s, 1046s, 997w, 952w, 916w, 882s, 825sh, 808s, 758w, 735m, 650m, 630sh, 566w, 499w, 470v.w cm^{-1}.

(b) Reaction between boron trifluoride diethyl etherate and tetramethylguanidinolithium (mole ratio 1:2).

Tetramethylguanidinolithium was prepared by adding a solution of n-butyl lithium (37.1 ml of a 1.64M solution, 60.8 mmole) to a solution of 1,1,3,3-tetramethylguanidine (7.03 g, 61 mmole) in 20 ml diethyl ether

at -196° and allowing the mixture to warm to room temperature (69). This solution was added to a solution of boron trifluoride diethyl etherate (4.33 g, 30.5 mmole) in 20 ml diethyl ether frozen to -196°. The mixture was warmed to room temperature and stirred overnight. Solvent was removed from the brown suspension to leave a brown viscous liquid. This was extracted with hexane/diethyl ether. Solvent was removed from the solution so obtained to leave a brown liquid which was only tentatively identified as bis(tetramethylguanidino)-fluoroborane, $((Me_2N)_2C{:}N)_2BF$, as consistent elemental analyses could not be obtained.

ν_{max}(liquid film) 2995sh, 2930s, 2868s, 2790s, 1665s,br, 1603s, 1484m, 1456m, 1424w, 1416w, 1377m, 1342m, 1256w, 1220sh, 1200m, 1167w, 1144w, 1117m, 1073m, 1057m, 1010w, 980m, 912w, 891w, 790w,br, 750w, 730w, 703w, 662w, 565w, cm^{-1}.

Attempted distillation of this brown liquid caused its decomposition.

(c) Reaction between boron trifluoride diethyl etherate and tetramethylguanidinolithium (mole ratio 1:1).

A solution of tetramethylguanidinolithium (13.8 mmole) in 40 ml diethyl ether was prepared from n-butyl lithium and tetramethylguanidine as described in the previous experiment and added to a solution of boron trifluoride diethyl etherate (1.89 g, 13.3 mmole) in 20 ml diethyl ether at -196°. The mixture was stirred at room temperature overnight, then solvent was removed from the off-white cloudy suspension. The residue was extracted with diethyl ether to give a yellow solution, and a white residue thought

to contain lithium tetrafluoroborate. Removal of solvent from the yellow solution left a slightly cloudy yellow liquid for which consistent elemental analyses could not be obtained. The I.R. spectrum of this liquid (see below) was similar to that of the product of the previous experiment, especially the two peaks at 1665 and $\sim$ 1600 cm^{-1}, so this yellow liquid was also tentatively identified as bis(tetramethylguanidino)fluoroborane, $((Me_2N)_2C{:}N)_2BF$.

ν_{max}(liquid film) 3336v.w, 3000sh, 2930s, 2872s, 2840sh, 1665s,br, 1600s, 1527w, 1508sh, 1490s, 1458, 1426w, 1408w, 1379s, 1350m, 1260m, 1227w,br, 1200w, 1166w, 1144m, 1121s, 1074s, 1058s, 1010s, 987s, 940w, 913m, 893s, 786s, 752w, 736m, 677w, 564s, 545w cm^{-1}.

When distillation of this yellow liquid was attempted, extensive decomposition occurred.

2. Discussion. A series of tetramethylguanidine adducts, $(Me_2N)_2C{:}NH.MX_n$, of Group 111 Lewis acids has been prepared by other workers (69). The triethylborane-tetramethylguanidine adduct extends this series.

The structure shown in figure A2.1.a for these 1:1 monomeric adducts appears more likely on steric grounds than the structures shown in figures A2.2b and c, in which coordination is through one or both amino nitrogens (69). Coordination through the amino nitrogen might be expected to be accompanied by marked changes in the C=N and N-H I.R. stretching frequencies.

In a study of some transition-metal complexes of tetramethylguanidine it was found that the absorption attributable to the azomethine stretching vibration (ν(C=N) (the only band between 1500 and 1800 cm^{-1})

shifted 40-60cm^{-1} to lower frequency on coordination (288). This contrasts with the observed increase in ν(C=N) on coordination of substituted methyleneamines $R^1_2C{:}NR^2$ to boron trifluoride (64).

The azomethine stretching frequencies of the two aluminium complexes $(Me_2N)_2C{:}NH.AlX_3$ (X = Me, Et) could not be assigned, as three bands were observed in the region 1540-1660 cm^{-1} in both spectra, one at higher and two at lower frequency than the parent methyleneamine (69) (Table A2.1). The I.R. spectrum of the triethylborane complex $(Me_2N)_2C{:}NH.BEt_3$ however, showed only two peaks in the region appropriate for ν(C=N), both at lower frequency than the parent methyleneamine. Although it is not certain which of the two peaks is due to the C=N stretching vibration, coordination of tetramethylguanidine to triethylborane clearly results in a lowering of its C=N stretching frequency.

In all cases however, the readily-identified N-H stretching vibration was observed at higher frequency than that of the parent methyleneamine (Table A2.1).

The ^{1}H n.m.r. spectra of these complexes and that of the parent ketimine are given in table A2.2.

The values of τ(NH) and $\tau(NMe_2)$ of the complexes are observed at higher field than those of the free methyleneamine, and these changes, particularly those of τ(NH) values, are evidence for the structure of the complexes being that shown in figure A2.1.a, as coordination through the amino nitrogens (Figures A2.1.b and c) would not be expected to result in such large changes in τ(NH).

It is interesting to note that in the ^{1}H n.m.r. spectra of all the complexes the NMe_2 resonance is a singlet. All three structures

Table A2.1

Skeletal stretching frequencies ν(C=N) and ν(N-H) (cm^{-1}) of 1,1,3,3-tetramethylguanidine and some of its complexes.

Compound	ν(C=N)	ν(N-H)
$(Me_2N)_2C{:}NH$	1592s	3330
$(Me_2N)_2C{:}NH.AlMe_3$	1612s, 1579s, 1553s	3356
$(Me_2N)_2C{:}NH.AlEt_3$	1603m,sh,1572s,1548s	3350
$(Me_2N)_2C{:}NH.BEt_3$ (a)	1589s, 1554s	3375

(a) This work: all others, reference 69.

Table A2.2.

^1H n.m.r. spectroscopic results for 1,1,3,3-tetramethylguanidine and some of its complexes.

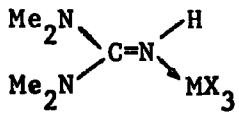
Compound	τ(NH) ppm	$\tau(NMe_2)$ ppm
$(Me_2N)_2C{:}NH$	4.73 (1)	7.36 (12)
$(Me_2N)_2C{:}NH.AlMe_3$	5.58 (1)	7.69 (12)
$(Me_2N)_2C{:}NH.AlEt_3$	4.82 (1)	7.50 (12)
$(Me_2N)_2C{:}NH.BEt_3$ (a)	6.46 (1)	8.11 (12)

(a) This work: all others, reference 69.

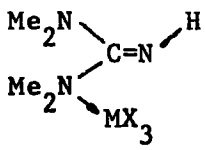
All peaks are singlets. Relative intensities are given in brackets. Samples were in the form of ~ 20 wt.% solutions in benzene

$\tau(Me_4Si)$ = 10 ppm

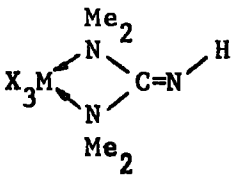
Figure A2.1



(a)



(b)



(c)

described for these compounds (Figures A2.1.a - c) might be expected to give rise to two distinct NMe_2 absorptions arising from the magnetically-distinct amino-groups in these adducts unless rapid exchange occurred, or unless the orientation of the amino-groups in figure A2.1.a was such as to minimise their magnetic difference. The spectrum of uncoordinated $(Me_2N)_2C{:}NH$ at 33° likewise contains a singlet attributable to the dimethylamino-protons.

Much greater differences in the I.R. and ^1H n.m.r. spectra were observed for the boron than the aluminium compounds, so further work on tetramethylguanidine adducts of boron derivatives may be of interest.

It seems that reactions between boron trifluoride and both one and two equivalents of tetramethylquanidinolithium may afford the bis(imino)fluoroborane $((Me_2N)_2C{:}N)_2BF$ (Equations A2.1 and A2.2) in a manner similar to the preparation of bis(di-t-butylmethyleneamino) fluoroborane, $(^tBu_2C{:}N)_2BF$ (see Chapter 2).

$$2(Me_2N)_2C{:}NLi + 2BF_3 \rightarrow ((Me_2N)_2C{:}N)_2BF + LiBF_4 + LiF \qquad A2.1$$

$$2(Me_2N)_2C{:}NLi + BF_3 \rightarrow ((Me_2N)_2C{:}N)_2BF + 2LiF \qquad A2.2$$

Cryoscopic molecular weight determinations were not carried out as the products of these reactions could not be adequately purified, but an ^{11}B n.m.r. spectrum showed a single broad absorption at ~ 0 p.p.m. relative to $B(OMe)_3$ which indicates that the boron atom is three- rather than four-coordinate, and this is consistent with

the compound being monomeric rather than dimeric.

The ^1H n.m.r. spectrum of $((Me_2N)_2C{:}N)_2BF$ showed a single absorption due to the methyl groups at 7.76 τ. This indicates either that the methyl groups are in magnetically-equivalent environments, or that they are inverting rapidly between non-equivalent ones.

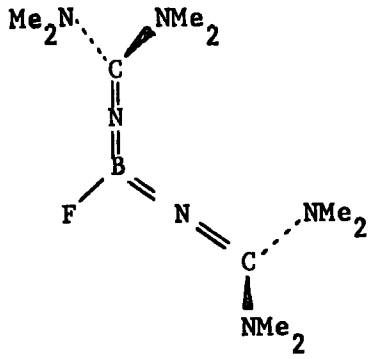
The I.R. spectrum of $((Me_2N)_2C{:}N)_2BF$ has two peaks in the region appropriate for C=N stretching vibrations, at 1665 and ~ 1600 cm^{-1}. It is not clear which of these is attributable to ν(C=N), but even the peak at 1665 cm^{-1} is at rather lower frequency than would be anticipated if the compound has the expected structure (Figure A2.2.a) similar to that postulated for $(^tBu_2C{:}N)_2BF$.

Tetramethylguanidino derivatives of boron may perhaps be more readily prepared from chloroboranes than fluoroboranes, as their reactions with other iminolithium compounds are more straightforward (see Chapter 2).

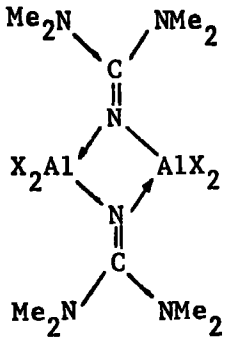
Some tetramethylguanidino derivatives of aluminium, $[(Me_2N)_2C{:}NAlX_2]_n$ (X = Cl,Me,Et), have been prepared and found to be dimeric (n = 2). They are thought to have the structure shown in figure A2.2.b (69).

Further work on these related boron and aluminium compounds would be of interest.

Figure A2.2



(a)



(b)

Appendix 3

Experimental Details

1. General techniques.

Most of the reactions described in this thesis involved handling compounds sensitive to hydrolysis by atmospheric moisture. Reactions were normally carried out in an atmosphere of pure dry nitrogen in a two-necked round-bottomed flask. Air-sensitive solids were handled in a glove box. Liquids and solutions were transferred as required by syringe against a counter current of nitrogen.

2. Glove box.

The purity of the nitrogen atmosphere in the glove box was maintained by continuously recycling it through a trap at -196° to remove any volatile material, and a furnace at 400° containing copper wire to remove traces of oxygen. All external tubing was of polythene, and the gloves used were made of "Butasol" rubber.

3. Nitrogen supply.

Nitrogen drawn off from a tank containing liquid nitrogen. Traces of oxygen were removed by passing the gas through a furnace at 400° containing copper wire, then delivered to a multiple outlet system.

4. Solvents.

Hydrocarbon solvents and diethyl ether were dried and stored over extruded sodium wire. THF was freshly-distilled before use.

5. Starting materials.

Boron trichloride, boron trifluoride and boron trifluoride diethyl etherate were vacuum distilled before use. Aluminium chloride was sublimed at $\sim 90^{\circ}$ ~ 0.005 mm Hg before use.

Solutions of alkyl lithium compounds were standardised against a 0.1 M solution of sec-butanol in xylene using 1,10-phenanthroline as indicator (279).

Solutions of di-t-butylmethyleneaminolithium were prepared by mixing hydrocarbon or ether solutions of t-butyl cyanide and t-butyl lithium at -196°, then stirring the mixture at room temperature for ~ 20 minutes (64).

Solutions of diphenyl- and di-p-tolyl-methyleneaminolithium were prepared by adding a solution of n-butyl lithium to a solution of the appropriate ketimine at -196°. The mixtures were stirred at room temperature for ~ 20 minutes before use.

The methyleneamines used were prepared as described in the literature (220, 265).

6. Instrumentation.

(a) Infra-Red Spectra.

I.R. spectra in the range 4000-250 cm^{-1} were recorded on a Perkin-Elmer 457 grating spectrometer. Samples were in the form of Nujol mulls, KBr discs, thin films or solutions in a suitable solvent, as appropriate.

(b) Nuclear magnetic resonance spectra.

These were recorded on a Varian A56/60D spectrometer operating at 60 MHz/sec (^{1}H) or a Perkin-Elmer R10 instrument operating at

19.25 MHz/sec (^{11}B). Samples were either neat liquids or solutions in benzene, toluene or deuterobenzene as appropriate. External reference standards were tetramethylsilane (for ^{1}H n.m.r. spectra) and trimethoxyborane (for ^{11}B n.m.r. spectra).

(c) Mass spectra.

Mass spectra were recorded on an A.E.I. MS 9 mass spectrometer at 70 eV and an accelerating potential of 8 kV, with a source temperature of 150-250° and electromagnetic scanning. Samples were introduced by direct insertion into the ion source.

(d) Molecular weights.

These were determined cryoscopically in benzene where solubility permitted using a conventional Beckmann apparatus. The benzene was calibrated (in respect of its freezing point constant) using freshly-sublimed biphenyl.

7. Analytical methods.

Carbon hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Nitrogen was also determined by the Kjeldhal method.

Halogens were determined by fusion of the compound with potassium followed by volumetric determination of the halide ions.

Lithium was determined by flame photometry.

Boron, aluminium and magnesium were determined using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer.

Boron compounds were decomposed by combustion in oxygen. An aqueous solution of the residue was prepared and its boron content determined.

Aluminium and magnesium compounds were decomposed using a mixture of concentrated nitric and perchloric acids. The liquid was heated until it was clear then diluted with water and the metal content of the solution determined.

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