# Azomethine derivatives of some metals and metalloids

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# AZOMETHINE DERIVATIVES OF SOME METALS AND METALLOIDS

by

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A thesis submitted for the degree of Doctor of Philosophy

University of Durham

June 1973

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## ACKNOWLEDGEMENTS

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I am indebted to the Science Research Council for a maintenance grant.

J.B. Farmer
Durham 1973.

# MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1969 and September 1972. It has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of the work in this thesis has formed the subject matter of the following publications:

Di-t-butylmethyleneamino derivatives of Group III metals.
J.B. Farmer, R. Snaith and K. Wade, Autumn Meeting of the Chemical Society, Imperial College, London, 1970, B14. (Ref.36)

Azomethine Derivatives. Part XVI. Some Diphenylmethyleneaminosilanes and Di-t-butylmethyleneaminosilanes.
J.B. Farmer, R. Snaith and K. Wade, J.C.S. Dalton, 1972, 1501. (Ref.39).

## ABSTRACT

This thesis describes the preparation of some methyleneamino derivatives of beryllium, zinc, gallium and silicon. The structural implications of their infra-red spectra and nuclear magnetic resonance spectra are discussed. As a background to the work, the characteristics of such compounds are discussed in the Introduction, and in greater detail in each Chapter.

Di-t-butylmethyleneaminolithium reacts with beryllium chloride giving dimeric di-t-butylmethyleneaminoberyllium chloride, $(Bu^t_2C:NBeCl)_2$, and the lithium beryllates $Li_nBe(N:CBu^t_2)_{2+n}$ (n = 1,2). Bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t_2C:N)_2Be]_2$ was inaccessible by this route but was prepared by reacting di-t-butylmethyleneamine with di-isobutylberyllium (2:1). The crystal structure of this compound shows that the terminal CNBe unit is nearly linear and that the Be-N bond is relatively short, appropriate for $N \rightarrow Be$ $(p \rightarrow p)$ $\pi$-bonding. The structure determination supports the postulate that a high azomethine stretching frequency, $\nu(C{=}N)$ is indicative of a linear CNBe unit and Be-N multiple bonding. Attempts to prepare adducts with trimethylamine and tetramethylethylenediamine were unsuccessful.

Reaction between methyleneamines and dialkylberylliums afford the derivatives $(R_2C:NBeR')_2$ ($R = Bu^t$, Ph; $R' = Bu^i$ and $R = Ph$; $R' = Bu^t$). A new monomeric compound, di-t-butylmethyleneamino-bis(trimethylsilyl)-aminoberyllium, $Bu^t_2C:NBeN(SiMe_3)_2$ was prepared and characterised.

Reactions of zinc chloride with one or two moles of di-t-butylmethyleneaminolithium give dimeric iminozinc compounds, $(Bu^t_2C:NZnCl)_2$ and

$[(Bu^t{}_2C:N)_2Zn]_2$. A high azomethine stretching frequency in the latter compound is attributed to significant $p_\pi$-$p_\pi$ interaction between zinc and nitrogen. Dimethylzinc reacts with one or two moles of di-t-butylmethyleneamine giving $[(Bu^t{}_2C:N)_nZnMe_{2-n}]_2$ (n = 1,2).

Reaction between di-t-butylmethyleneaminolithium and gallium trichloride affords the compounds $Li_nGa(N:CBu^t{}_2)_{3+n}$ (n = 0,1,2). Bis(di-t-butylmethyleneamino)gallium chloride could not be isolated, presumably through disproportionation to the mono- and tris-derivatives. A high azomethine stretching frequency, $\nu(C{=}N)$, for $(Bu^t{}_2C:N)_3Ga$, is taken as evidence for a linear C=N-Ga skeleton with appreciable $N \rightleftharpoons Ga$ π-bonding. The phenyl analogue $(Ph_2C:N)_3Ga$ was prepared by a similar method.

Equimolar proportions of diphenylmethyleneaminolithium and chlorosilanes $Me_nSiCl_{4-n}$ (n = 0,1,2) afford the diphenylmethyleneaminosilanes $(Ph_2C:N)_2SiMe_nCl_{2-n}$, apparently through disproportionation of the mono-substituted compounds $Ph_2C:NSiMe_nCl_{3-n}$, which could only be isolated when n = 2. The spectra of these compounds show that these may have bent C:NSi skeletons.

Preliminary investigations into transition metal systems $(R_2C:N)_3M$ (M = Fe; R = $Bu^t$,Ph and M = Cr; R = $Bu^t$) are discussed in an appendix.

# CHAPTER 1

# INTRODUCTION

## Nomenclature

For many years the naming of compounds containing the C=N- group has been variable. In order to avoid ambiguity the Chemical Society have ruled that such compounds should be named as derivatives of the (unknown) parent compound methyleneamine, $CH_2=NH$. Hence diphenylketimine, $Ph_2C:NH$, is diphenylmethyleneamine and $Ph_2C:N\cdot MX_n$ is a diphenylmethyleneamino derivative of the metal M. In a similar manner, "aldimines" RCH:NH are designated as alkyl(or aryl)methyleneamines.

In this introduction, the terms ketimine, aldimine and azomethine are used for simplicity when generalisations are made about a class of compounds but in subsequent chapters the systematic nomenclature is employed.

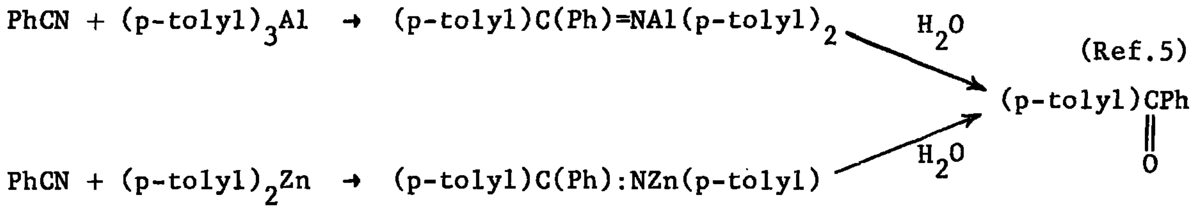
## History

The most widely used route to the synthesis of ketimines has been the reaction between a nitrile and a Grignard reagent followed by hydrolysis:

$$RC\equiv N + R'MgX \rightarrow RR'C{=}NMgX \xrightarrow{\text{hydrolysis}} RR'C{=}NH$$

Blaise,[1] in 1901, was not able to stop the hydrolysis at this stage and his products were ketones, RR'C=O. However, Moureau and Mignonac[2] found that by careful hydrolysis using hydrogen chloride and then ammonia at -15°, diphenylmethyleneamine, $Ph_2C{=}NH$, could be prepared in 70% yield. Pickard[3] was the first to report the successful preparation of dialkylmethyleneamines by the Grignard method.

This addition of a nitrile to a Grignard reagent was extended to organolithium,[4] organoaluminium[5] and organozinc[5] compounds:



$$\mathrm{PhCN + (p\text{-}tolyl)_3Al \rightarrow (p\text{-}tolyl)C(Ph){=}NAl(p\text{-}tolyl)_2 \xrightarrow{H_2O} (p\text{-}tolyl)\underset{\underset{O}{\|}}{C}Ph}$$

$$\mathrm{PhCN + (p\text{-}tolyl)_2Zn \rightarrow (p\text{-}tolyl)C(Ph){:}NZn(p\text{-}tolyl) \xrightarrow{H_2O} (p\text{-}tolyl)\underset{\underset{O}{\|}}{C}Ph}$$

(Ref.5)

For Al Yield 17%
Zn Yield 22%

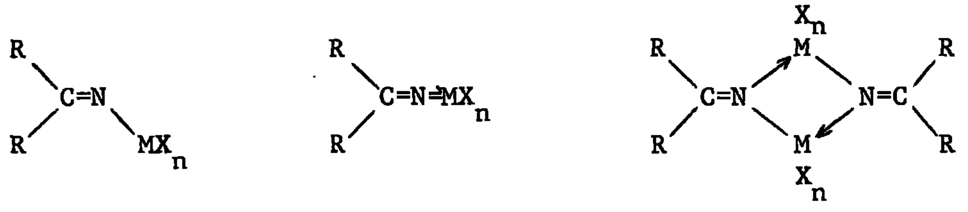
It was not until 1934 that a metal containing ketimino derivative was prepared and separated. By reacting diphenylmethyleneamine with sodamide in liquid ammonia, Smith and Bergstrom[6] were able to prepare diphenylmethyleneaminosodium in a somewhat impure state. The preparation of propylmethyleneaminodi-i-butylaluminium $(PrCH{:}NAlBu^i{}_2)_n$ was the first ketimino derivative of a metal to be isolated in a pure form[7] but it was some 20 years later before an investigation into the structural and spectroscopic aspects of this metal-nitrogen chemistry was begun.

Mode of Bonding

Much attention has centred on the nature of the bonding of ketimino groups to metals and metalloids, particularly with respect to the possibility of dative $\pi$-bonding. The most likely geometrical arrangements of the atoms are shown in Fig.I.1.

Examples of the non-linear C=N-M unit of Fig.I.1.a appear to occur only in systems where the metal M is co-ordinatively saturated, and would be expected to exhibit syn-anti isomerisation. This latter aspect was observed in the low temperature $^1H$ n.m.r. of the unsymmetrical germanium compound $p\text{-}CF_3C_6H_4(Ph)C{=}NGeMe_3$.[8] Other evidence in support of the non-linear conformation arose from the ultra-violet spectra of some twenty-

FIGURE I.1



(a) (b) (c)

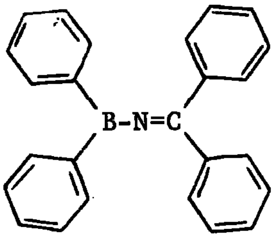
eight silyl ketimines,[9] in which the n → $\pi^*$ transition had been investigated to study the $d_\pi$-$p_\pi$ interaction between the silicon and nitrogen. The validity of these two spectroscopic techniques will be discussed later.

In compounds where the metal is co-ordinatively unsaturated, there is a possibility of $N \rightleftharpoons M$ dative π-bonding, which is expected to be at a maximum for a linear C=N-M group (Fig.I.1b). In this case, the nitrogen would be sp hybridised with one hybrid orbital being used to σ-bond to the metal, the other to the carbon nitrogen, and a pure nitrogen p-orbital used for the C-N π system. A nitrogen lone pair lying in the plane of the $R_2C{=}N$ group then has the correct symmetry for overlap with a p- or d-orbital of the metal. However, Ebsworth,[10] using silyl compounds as an example, has noted that even in non-linear systems, substantial π-bonding is still possible. Structural information that supports a pseudo-allene geometry is provided by the X-ray crystal structure of $Ph_2C{=}N \rightleftharpoons B(mesityl)_2$[11] where the C-N-B skeleton is almost linear (170°), the C-N and N-B distances are short as appropriate for multiple bonds and the $BC_2$ and $C(Ph)_2$ planes are almost perpendicular. Boron-nitrogen multiple bonding is not uncommon; from the Raman spectrum[12] of monomeric $Me_2NBMe_2$[13] the calculated B-N force constant indicates a double B-N bond.

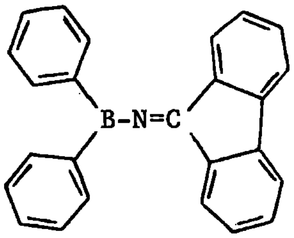
The third type of bonding shown in Fig.I.1.c, involving association of molecules, is another possible way in which co-ordination saturation is achieved. The ability of the nitrogen to donate its lone pair of electrons to a metal atom should be linked to the basicity of the free ketimine. Unfortunately, few data have been collected in this area but work by Culbertson[14] has shown that ketimines, whose $pK_a$ values lie between 5 and 8, are generally weaker bases than amines ($pK_a$ for primary and secondary amines are approximately 10-11). The degree of association of the ketimino derivatives $R_2C{=}NMX_n$ is also influenced by steric factors. A cyclic trimer would be preferred to dimers containing the $(MN)_2$ four membered ring on account of the valency angle distortion from 109° to about 90° in the dimer. However, as the size of R and X increase the steric interference between them is more acute in the trimer, and in the extreme the monomeric linear structure of Fig.I.1.b. is realised. Derivatives of boron clearly show this factor:[15,16] $Ph_2C{:}NBPh_2$, $(p\text{-tolyl})_2C{:}NBPh_2$, $(p\text{-}ClC_6H_4)_2C{:}NBPh_2$, $p\text{-}BrC_6H_4(Ph)C{:}NBPh_2$ are all monomeric whereas $(PhCH{:}NBPh_2)_2$ is a dimer; also all the di-t-butylmethyleneaminoboron compounds are monomeric owing to the bulk of the ketimine group.[16] The fluorenylideneamino derivative $C_{12}H_8C{:}NBPh_2$ is monomeric but when the phenyl substituents on the boron are linked together a dimer is formed, as in $(Ph_2C{:}NBC_{12}H_8)_2$, indicating that the groups on the boron seem to have more effect on the association of the species than those on the ketimine carbon atom. (Compare Fig.1.2 (a),(b) and (c)).[15]

Four X-ray structures of imino derivatives have recently been determined showing the four membered $(MN)_2$ ring: $(MeCH{:}NBMe_2)_2$,[17] $(Bu^tMeC{:}NAlMe_2)_2$,[17] $[p\text{-}BrC_6H_4(Ph)C{:}NAlPh_2]_2.2C_6H_6$,[18] (Fig.I.2(d)) and $[(Bu^t{}_2C{:}N)_2Be]_2$ (Fig.I.2(e)) which will be discussed in Chapter II.

# FIGURE I.2



(a)



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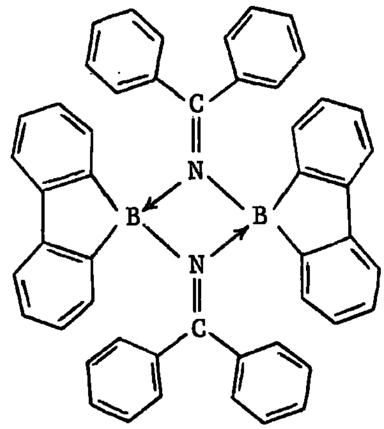
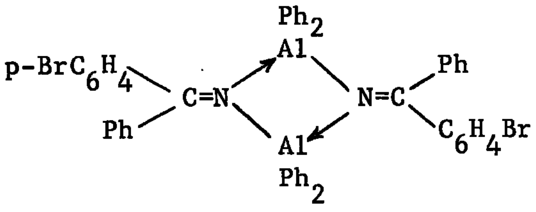
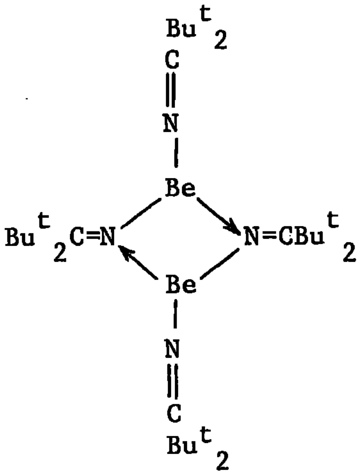


(c)



(d)



(e)

Association is not limited to the formation of dimers, as evidenced by the existence of $[(Ph_2C:N)_2Be]_n$[19] and $[\{(p\text{-tolyl})_2C:N\}_2Be]_3$.[19]

Several methods for determining the linearity of the C-N-M skeleton have been explored. The most conclusive technique is that of X-ray crystal structure analysis but as this is not the easiest to perform, various spectroscopic means have been employed, namely infra-red, n.m.r., and ultra-violet.

## Infra-red Spectra

There has been no comprehensive spectroscopic study of methyleneamines, RR'C:NH and information available is, as yet, rather sparse. Pickard and Polly[20] reported C:N and NH stretching frequencies and these, with recent data,[21,22] are given in Table I.1.

For a metal containing ketimine $(RR'C:NMX_n)_y$ there are two main factors involved. An electronic effect will operate which would be expected to reduce the electron density in the azomethine link, causing a corresponding reduction in $\nu(C:N)$. However, the mechanical constraint imposed on the vibration of the azomethine group by the $MX_n$ unit may offset the electronic effect. The latter aspect appears to be more important as in nearly all cases, the $\nu(C:N)$ stretching frequency is higher than the parent ketimine. Notable exceptions are shown in Table I.2.

In these examples the ketimine ligand acts as a bridging unit and necessarily has a bent C-N-M group. However, if these three atoms attain a linear conformation, it would be expected to show a skeletal asymmetric vibration $\nu(C{=}N{-}M)$ at a higher frequency than the non-linear unit by comparison with other cumulatively $\pi$-bonded systems (see Table I.3).

## TABLE I.1

Stretching Frequencies $\nu_{(C:N)}$ and $\nu_{(NH)}$ for some methyleneamines RR'C:NH

| R | R' | ν(C:N) $cm^{-1}$ | ν(N-H) $cm^{-1}$ | Reference |
|---|---|---|---|---|
| Ph | Ph | 1603 | 3236 | 20 |
| p-$ClC_6H_4$ | p-$ClC_6H_4$ | 1590,[21] 1653 | 3247 | 20 |
| p-$BrC_6H_4$ | Ph | 1607 | | 21 |
| p-tolyl | p-tolyl | 1610 | | 21 |
| Ph | $Bu^t$ | 1618 | 3226 | 20 |
| p-tolyl | Et | 1631 | 3205 | 20 |
| o-tolyl | $Bu^n$ | 1629 | 3205 | 20 |
| o-tolyl | $Pr^n$ | 1629 | 3226 | 20 |
| Et | $Bu^n$ | 1645 | 3226 | 20 |
| $Pr^n$ | $Pr^n$ | 1645 | 3226 | 20 |
| $Bu^t$ | $Bu^t$ | 1610 | | 21 |
| $CF_3$ | $CF_3$ | 1672 | | 22 |
| $C_2F_5$ | $C_2F_5$ | 1669 | 3289 | 22 |

## TABLE I.2

## Stretching frequencies $\nu_{(C:N)}$ for some diphenylmethyleneamino derivatives of Group III elements

| Compound | $\nu(C:N)$ $cm^{-1}$ | Reference |
|---|---|---|
| $(Ph_2C:NBCl_2)_2$ | 1590 | 23 |
| $(Ph_2C:NAlCl_2)_2$ | 1593 | 24 |
| $(Ph_2C:NGaCl_2)_2$ | 1591 | 25 |
| $(Ph_2C:NBBr_2)_2$ | 1586 | 23 |
| $(Ph_2C:NAlBr_2)_n$ | 1587 | 24 |

## TABLE I.3

## Skeletal stretching frequencies of some cumulatively π-bonded systems

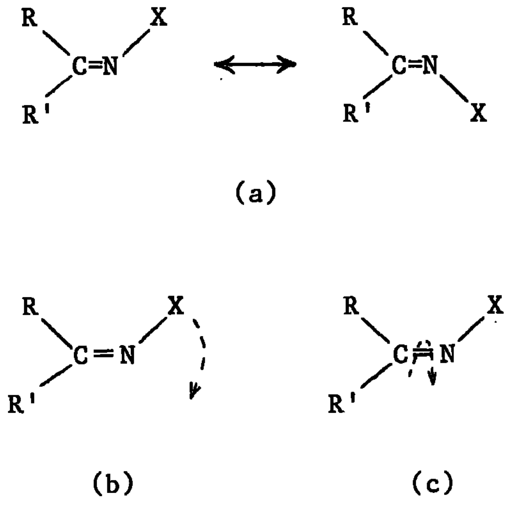
| Compound | $\nu(X:Y:Z)$ $cm^{-1}$ | X=Y=Z | Reference |
|---|---|---|---|
| RN:C:NR | ca.2140 | N=C=N | 26 |
| $Ph_2C:C:NMe$ | 1998 | C=C=N | 27 |
| $R_2C:C:CR_2$ | ca.1950 | C=C=C | 28 |
| $Ph_2C:N:CPh_2{}^{+}MX_n{}^{-}$ | ca.1845 | C=N=C | 29 |
| $Ph_2C:NBPh_2$ | 1786 | $C{=}N\overset{\rightharpoonup}{=}B$ | 15,30 |
| $[(Ph_2C:N)_2Be]_n$ | 1732 (terminal) | $C{=}N\overset{\rightharpoonup}{=}Be$ | 19 |

It is interesting to note the large difference (200 $cm^{-1}$) between the azomethine stretching frequencies of $(Ph_2C{:}NBBr_2)_2$ and that of $Ph_2C{:}NBPh_2$. Other comparisons can be drawn from the bis-ketimino compounds of beryllium which exist as oligomers with both bridging and terminal ligands. Two absorptions may be expected, one for the bridging group which has a non-linear CNBe unit and the other for the terminal group. Accordingly it was found[19] that for $[(Ph_2C{:}N)_2Be]_n$, $[\{(p\text{-tolyl})_2C{:}N\}_2Be]_3$ and $[\{(p\text{-tolyl})Bu^tC{:}N\}_2Be]_2$ there were two distinct sets of azomethine stretching frequencies at 1627, 1626 and 1637 $cm^{-1}$, and 1732, 1731 and 1739 $cm^{-1}$ respectively. The latter absorptions were attributed to the terminal ketimine groups possessing a linear $C{=}N{\Rightarrow}Be$ skeleton.

Nuclear Magnetic Resonance

Considerable attention has been paid to the n.m.r. of azomethine compounds, mainly with respect to the possibility of syn-anti isomerism (Fig.1.3(a)).

FIGURE I.3



Considering the case when R' = R, if the activation energy of inversion of X about the nitrogen is high then the rate of inversion may be slow enough compared with the n.m.r. time scale for the non-equivalence of the R groups to be observed as two peaks of equal intensity on the n.m.r. spectrum. At room temperature this rate of inversion may be high and one peak is observed (showing that the R groups are magnetically equivalent) but at lower temperatures, the resonances may split as the rate of inversion decreases. Di-t-butylmethyleneamine, $Bu^tC:NH$, for example, shows a singlet for the butyl protons at 8.83τ at 33° and a doublet (8.73, 8.90τ) at -60°.[24,35]

The topic of syn-anti isomerisation in methyleneamines has been recently reviewed by McCarty[31] although there is very little information on the metallo derivatives. It appears as though steric effects play a prominent part in the isomerisation process of RR'C:NR". Staab and co-workers[32,33] found that for the series MeCR:N.CH(Me)Ph where R = Et, $Pr^i$, $Bu^t$ the syn-anti isomer ratios were 17:83, 7:93 and 0:100 respectively. For the less sterically hindered $Me_2C:NCH_2Ph$, the methyl resonances were observed as separate peaks (τ = 7.98, 8.14) even at 170° which permits a calculation of the lower limit of 23 $kcal.mole^{-1}$ for the free energy of activation.[33] Recent investigations have centred on the use of fluorocarbon compounds in order to create substituents with a strong inductive effect but little resonance interaction.[34] Para-substituted N-phenylimines $(CF_3)_2C:NC_6H_4X$ were studied in an attempt to rationalise the mode of isomerisation about the nitrogen (X = H, Cl, F, OMe, $NO_2$, Me). At 56.4 MHz the difference in chemical shifts corrected to 0° was of the order 360 to 430 Hz and the free energies of activation of isomerisation 14.35 to 15.53 $kcal.mole^{-1}$ at 25°. The calculated rate constants gave a Hammett plot with a linear correlation coefficient of 0.989, using $\sigma^+$ substituent constants, in all cases except for X = $NO_2$. These results were interpreted in there being two mechanisms: For X = $NO_2$ the in-plane inversion (lateral) mechanism operates as in $R_3N$ (see Fig.I.3b) and for the other examples, rotation about the C=N takes place (Fig.I.3c).

N.m.r. spectroscopy has been successfully used in elucidating the molecular structures of various metal and metalloid containing ketimino derivatives (e.g. Li,[35] Be,[19] B,[16,36] Al,[24,36,37] Ga,[38] Si,[39] Mo,[40]). Mislow has quantitatively measured the energy of activation for the inversion at nitrogen[8] and phosphorus[41] of compounds containing Group IVa atoms. A study of $Ph(R)P\text{-}MMe_3$[41] where R = Me, $Me_2CH$ and M = C, Si, Ge, Sn revealed that the barrier to pyramidal inversion at the phosphorus can be related to the electronegativity of the metal M - the higher the electronegativity, the higher the energy barrier. Subsequent work on $(p\text{-}CF_3C_6H_4)PhC{:}NGeMe_3$[8] showed that at temperatures below -110° the $Me_3Ge$ $^1H$ n.m.r. spectrum consisted of two overlapping singlets (limiting $\Delta_{\nu AB}$ = 1.1 Hz at 60 MHz), representing the syn and anti forms of the imine, which coalesced at -108°. A first order rate constant of $k_{-108^o} = 2.4\ sec^{-1}$ was calculated giving a $\Delta G^{\ddagger}_{-108}$ value of 9.2 $kcal.mole^{-1}$.

The scope of n.m.r. spectroscopy as a probe for determining the linearity of the CNM skeleton in the ketimine $R_2C{:}NMX_n$ is in principle restricted by the limiting temperature for inversion. If a singlet is observed at the lowest temperature attainable for the sample then it may imply either that the CNM unit is linear or that inversion at the nitrogen of a non-linear CNM unit is still occurring at a high rate despite the low temperature. However, through such investigations, predictions have been made concerning the nature of the bonding about the ketimino nitrogen that have been shown to be correct by other analytical techniques.

## Ultra Violet Spectroscopy

The only study of the UV spectra of metal containing ketimino derivatives has been by Chan and Rochow[9] who looked at the spectra of a comprehensive range of diarylmethyleneamino compounds of Group IV metals and metalloids in the wavelength range 200-400 mμ. Their results showed that for each spectrum there were two absorptions: a low energy absorption at a wavelength of about 350 mμ attributed to the $n \rightarrow \pi^*$ transition of a non-bonding electron on nitrogen and the other (ca. 250 mμ) to the $\pi \rightarrow \pi^*$ transition of the conjugate system. These two electronic transitions can be simply represented by an energy level diagram proposed by West[42] and shown in Fig.I.4.

Silicon substituents on the nitrogen lower the energy for the $n \rightarrow \pi^*$ transition both by their electropositive nature and by the $d_\pi$-$p_\pi$ interaction with the orbitals in the group. This latter effect is at its maximum when the C-N-Si linkage is linear (see Fig.I.5). Under these circumstances there is a large interaction between the nitrogen lone pair and the silicon 3d orbitals leading to a lowering of both n and $\pi^*$ energy levels. The lowering of the energy level of n will be less if the C-N-Si skeleton were bent as the $d_\pi$-$p_\pi$ interaction would be relatively small. Thus Chan and Rochow concluded that the $n \rightarrow \pi^*$ transition for a bent structure would be at a longer wavelength than for the linear structure.

By varying the silicon substituents to contain π-donating species such as phenyl, alkoxy and vinyl groups, it was found that the $n \rightarrow \pi^*$ transition did not vary significantly in energy, implying that if there was N-Si multiple bonding, then the presence of competing electron donors to the silicon should markedly affect any nitrogen-silicon $p_\pi$-$d_\pi$ bonding. The absence of any change in wavelength was interpreted in there being no Si-N

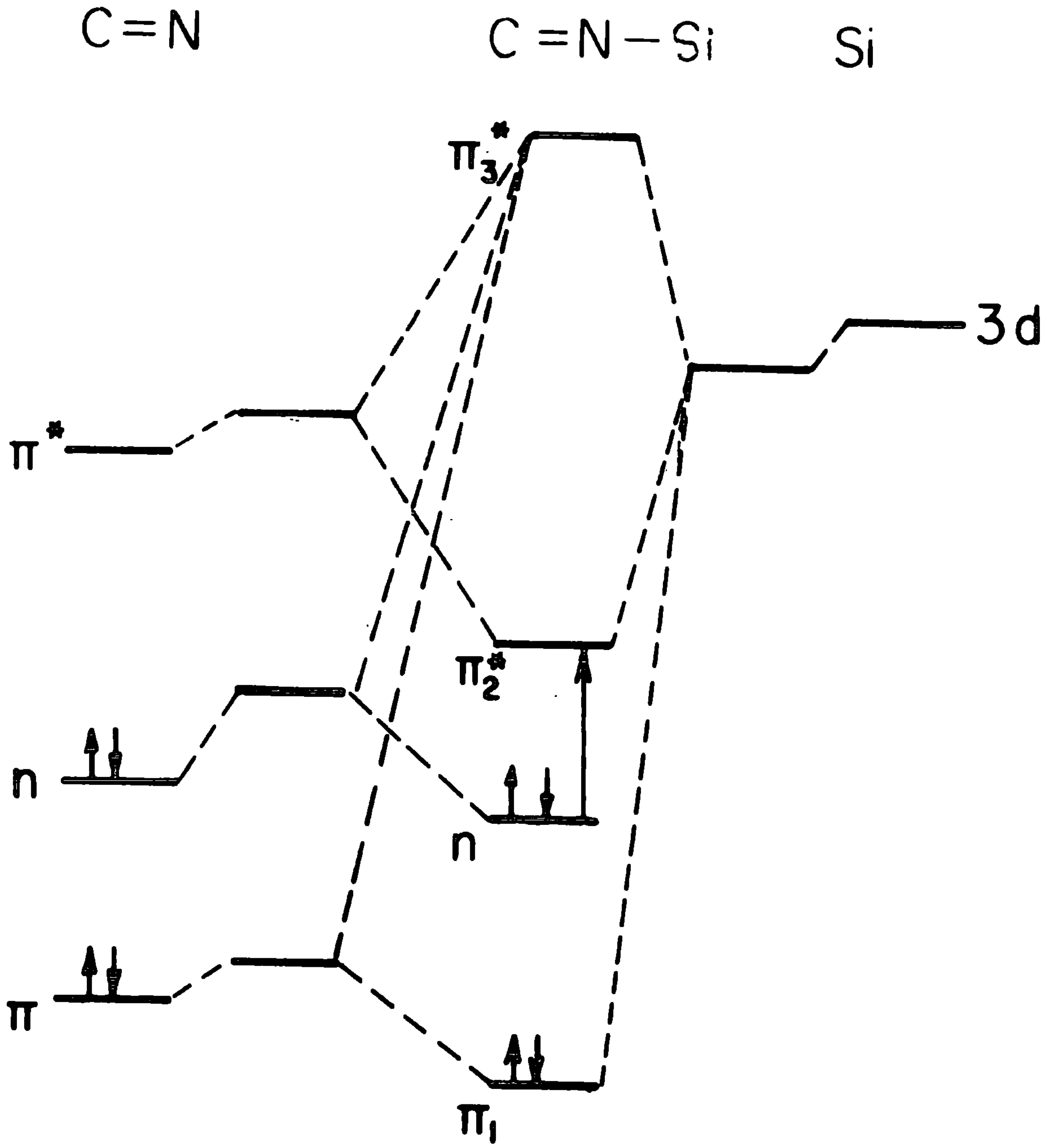


FIGURE I.4

Energy levels and transitions for the C=N-M group

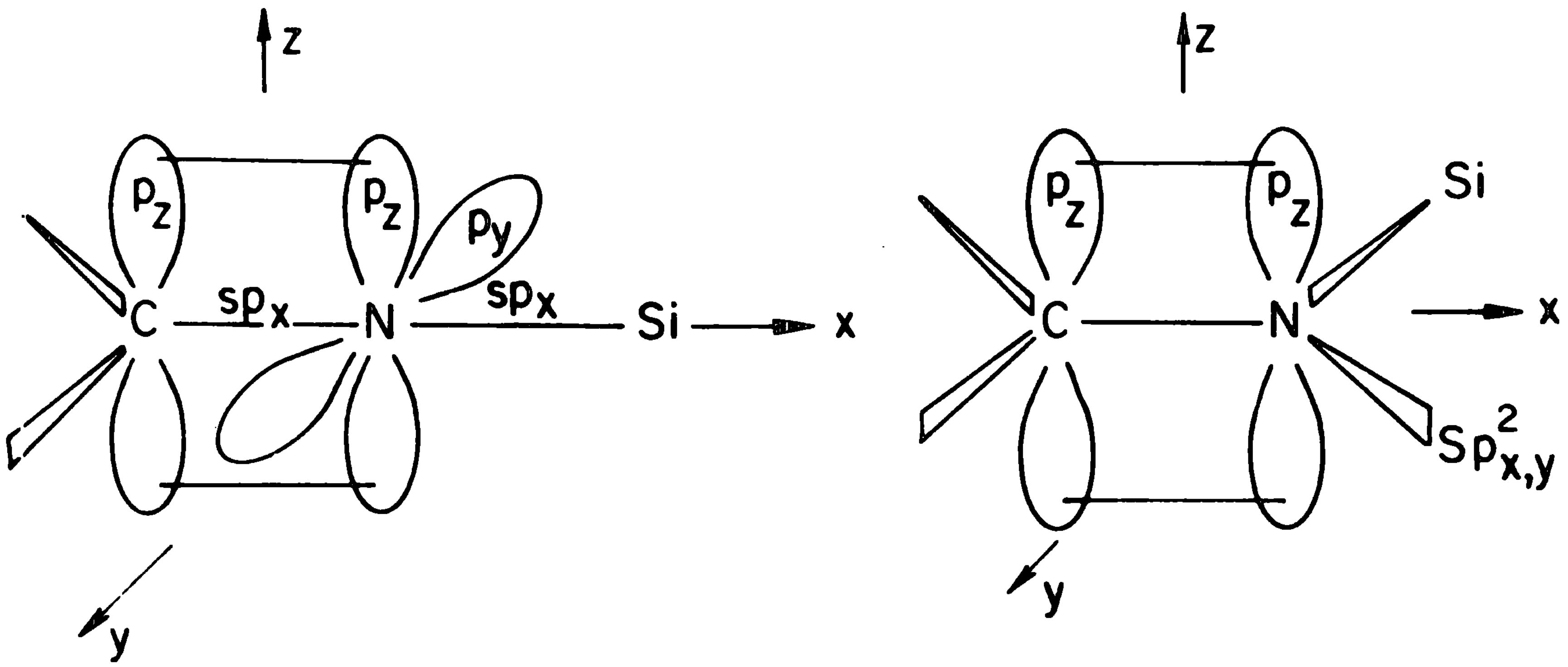


FIGURE I.5

Linear and Bent C=N-Si linkages

$p_{\pi}$-$d_{\pi}$ bonding and hence a bent C-N-Si group. However, one factor was omitted from the discussion, namely that if both the $\pi^*$ and n energy levels were lowered by the same quantity of energy, then the observed results could accommodate both a linear or bent C-N-Si structure.

X-ray Crystallographic Analysis

Only in recent years has X-ray crystallography been employed to determine the structures of metal-containing ketimine derivatives. Of interest is the angle at the nitrogen atom and the length of the C=N bond; Table I.4 shows data for oximes and Table I.5 lists the metal containing derivatives with appropriately assigned i.r. stretching frequencies.

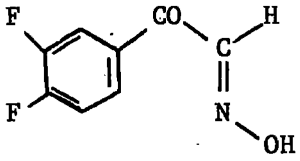
Pauling[52] has found that the C=N bond length is of the order 1.29Å to 1.31Å compared with the single C-N bond length of about 1.47Å. Oximes[43-47] show great consistency in the C=N bond length (1.27-1.29Å) and a C=N-O bond angle of 110°-112°.

For metal substituted ketimines there is also a remarkable similarity between the C=N bond lengths (1.26-1.29Å) despite a variation in the C=N-M bond angle. The structure of $Ph_2C{:}NB(mesityl)_2$ is shown in Fig.I.6. The B-N bond length (1.38Å) is very short compared with other boron nitrogen compounds (ca. 1.58Å[53]) and this was attributed[11] to multiple B-N bonding since a BN double bond is expected to have a length of ca. 1.35Å.[52] Furthermore, molecular orbital calculations show that the bond orders of B⇌N and C=N are 1.6 and 1.8 respectively.

The results of the X-ray structure determination of $(BuCMe{:}NAlMe_2)_2$[17] are shown in Fig.I.7. In this example of a four membered $(AlN)_2$ ring, co-ordination saturation of the aluminium is achieved and apart from the distortion from a tetrahedral arrangement of orbitals about the aluminium,

## TABLE I.4

### Carbon-nitrogen bond lengths and C-N-O bond angles in some oximes

| Compound | C═N bond length (Å) | C-N-O bond angle | Reference |
|---|---|---|---|
| $Me_2C:NOH$ | 1.29 | 111° | 43 |
| HON:CH-CH:NOH | 1.28 | 111° | 44 |
| HON:C(Me)-(Me)C:NOH | 1.27 | 111° | 45 |
| $H_2N.CH:NOH$ | 1.29 | 110° | 46 |
|  | 1.27 | 112° | 47 |

## TABLE I.5

### Crystallographic data for metal containing ketimine derivatives

| Compound | C=N bond length Å | C-N-X bond angle | $\nu(C=N)\ cm^{-1}$ | Reference |
|---|---|---|---|---|
| trans $(Me_2BNCHMe)_2$ | 1.27 | 138 | $1700^{a\ 49}$ | 17 |
| $Ph_2C:NB(mesityl)_2$ | 1.29 | 173 | $1792^{15}$ | 11 |
| $[C_6H_4Br(Ph)C:NAlPh_2]_2$ | 1.28 | 129,134 | | 18 |
| $(Bu^tMeC:NAlMe_2)_2$ | 1.27 | 125,140 | $1629^{50}$ | 17 |
| $LiAl(N:CBu^t_2)_4$ | 1.26 | $167^b$ | $1700^{35}$ | 48 |
| | 1.27 | $149^b$ | $1642,1602^{35}$ | |
| $[(Bu^t_2C:N)_2Be]_2$ | 1.27 | 161 | $1721^c$ | 51 |
| | 1.28 | 139 | $1631^c$ | |

a. As vapour. b. C=N-Al bond angles. c. This work.

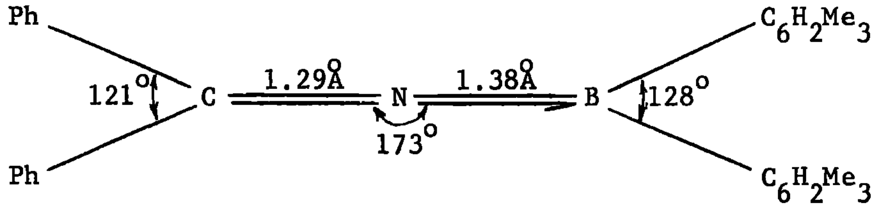


FIGURE I.6

Structure of $Ph_2C{:}NB(mesityl)_2$

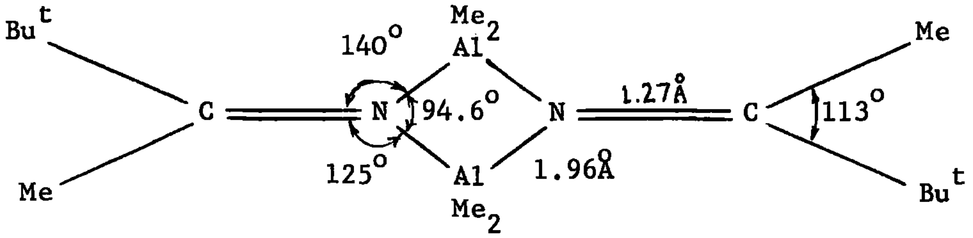


FIGURE I.7

Structure of $(Bu^tMeC{:}NAlMe_2)_2$

bond lengths and bond angles are consistent with other carbon-aluminium-nitrogen compounds: The C=N bond length of 1.27Å is comparable with oximes[43-47]; the Al-N bond length of 1.94Å falls within the range 1.91-1.96Å found for many bridging aluminium-nitrogen compounds, for example 1.91Å in $[Me_2AlN(CH_2)_2]_3$[54] and $(PhAlNPh)_4$,[55] 1.92Å in $[C_6H_4Br(Ph)C{:}NAlPh_2]_2$,[18] 1.94Å in $Al_4Cl_4(NMe_2)_4(NMe)_2$[56] and $(Me_2Al.OCPh.NPh)_2$,[57] 1.95Å in $(Me_2AlNHMe)_3$[58] and 1.96Å in $(Me_2AlNMe_2)_2$.[59] The distortion of the Al-N=C bond angles presumably occurs to accommodate the bulky Bu$^t$ groups.

The correlation between the linearity of the C=N-M skeleton and the stretching frequency ν(C=N) is evident from Table I.5. The relatively high values for $Ph_2C{:}NB(mesityl)_2$ (1792 cm$^{-1}$, $Ph_2CNH$ is at 1603 cm$^{-1}$,[20]), $LiAl(N{:}CBu^t_2)_4$ (1700 cm$^{-1}$, $Bu^t_2CNH$ is at 1610 cm$^{-1}$ [21]) and $[(Bu^t_2C{:}N)_2Be]_2$ (1721 cm$^{-1}$) are assigned to the near linear conformations of C=N-M in accordance with the postulates previously discussed.

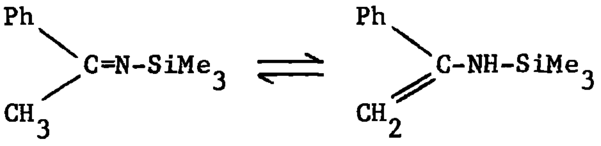
## Enamine Tautomerism

Ketimines having a hydrogen atom in the α position to the azomethine unit carbon atom often exhibit enamine tautomerism:

$$\text{-CH-C=NH} \quad \text{——} \quad \text{-C=C-NH}_2$$

enamine

The presence of the enamine form of the N-organosilylmethyleneamine $PhMeC{:}NSiMe_3$ was detected by the presence of olefinic protons in the $^1H$ n.m.r. spectrum:[9]



However, work on the reactions of organoaluminium compounds with nitriles[50] has shown that derivatives of the type $(RCMe{:}NAlX_1X_2)_2$ can be isolated and characterised.

In the following work, any possibility of such tautomerism has been eliminated by preparing compounds in which the ketimine ligands are di-t-butylmethyleneamino, $Bu^t{}_2C{:}N$-, and diphenylmethyleneamino, $Ph_2C{:}N$-, neither of which possess an α-hydrogen atom.

# CHAPTER II

# METHYLENEAMINO DERIVATIVES OF BERYLLIUM

This chapter describes the preparation and spectroscopic properties of dimeric di-t-butylmethyleneaminoberyllium chloride, $(Bu^t_2C:NBeCl)_2$, dimeric bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t_2C:N)_2Be]_2$, monomeric lithium tris(di-t-butylmethyleneamino)beryllate, $LiBe(N:CBu^t_2)_3$, monomeric dilithium tetrakis(di-t-butylmethyleneamino)beryllate, $Li_2Be(N:CBu^t_2)_4$, the methyleneamino derivatives $(R_2C:NBeR')_x$ where R = $Bu^t$, Ph and R' = $Bu^i$, $Bu^t$, and di-t-butylmethyleneamino-bis(trimethylsilyl)aminoberyllium, $Bu^t_2C:NBeN(SiMe_3)_2$. Aspects of their i.r. and $^1H$ n.m.r. spectra are discussed in relation to the possibility of N → Be (p → p) multiple π-bonding, with details of a recent X-ray crystallographic study of $[(Bu^t_2C:N)_2Be]_2$. Attempts to prepare complexes with trimethylamine and tetramethylethylenediamine (TMED) are also described.

## EXPERIMENTAL SECTION

### Starting Materials

Beryllium chloride was prepared by heating finely divided beryllium in a stream of chlorine gas followed by resublimation. Di-iso-butylberyllium and di-t-butylberyllium in ether solution were gifts from Professor G.E. Coates, prepared from Grignard reactions.[60] The beryllium content of these solutions was determined by titrating the alkaline solution formed by adding an excess of potassium fluoride to the beryllium hydrolysate (organic matter having previously been destroyed by repeated evaporation to dryness with nitric acid) to a green end-point using bromothymol blue indicator.

Diphenylmethyleneamine was prepared by methanolysis of the product of the reaction between phenyl cyanide and phenylmagnesium bromide.[61] t-Butyl cyanide, n- and t-butyl-lithium (approx. 2M in hexane or pentane) were obtained commercially, the two alkyl-lithiums being standardised by titration with sec-butanol in dry xylene, using 1,10-phenanthroline as indicator.[62] Di-t-butylmethyleneamine was prepared by the methanolysis of di-t-butylmethyleneaminolithium, followed by fractional distillation.[21]

Bis(trimethylsilyl)amine, trimethylamine and tetramethylethylenediamine were all freshly distilled from suitable drying reagents before use.

All materials throughout were handled under dry nitrogen or in vacuo.

### Preparation of Di-t-butylmethyleneaminoberyllium chloride, $[Bu^t_2C{:}NBeCl]_2$

A solution of di-t-butylmethyleneaminolithium was prepared by adding t-butyl-lithium (11.6 ml. of a 2.18M solution in hexane, 25 mmole) by syringe to a frozen (-196°) solution of t-butyl cyanide (2.0 g., 25 mmole) in hexane (40 ml.). The mixture was allowed to attain room temperature and stirred for 40 min. before being added to a frozen solution of beryllium chloride (2 g., 25 mmole) in ether (40 ml.). The solution was then stirred at room temperature for 4 hr. during which time a white solid precipitated out. Solvent was removed under vacuum and replaced with toluene (20 ml.) in which the solid residue was boiled for 20 min. Solvent was again pumped off and the precipitated lithium chloride separated by filtration with hot toluene. Crystallisation of the yellow filtrate yielded dimeric di-t-butylmethyleneaminoberyllium chloride, $(Bu^t_2C{:}NBeCl)_2$, m.p. 88-90° decomp. (Found: C,56.6; H,9.3; Be,4.9; Cl,19.0; N,7.4%; M,343. $C_{18}H_{36}Be_2Cl_2N_2$ requires C,58.5; H,9.8; Be,4.9; Cl,19.2; N,7.6%; M,369); $\nu_{max}$ (Nujol mull) 1668sh, 1626vs, 1610vs, 1543w, 1309vw, 1266w, 1250vw, 1222m, 1205sh, 1183vw, 1155vw, 1094sh, 1056vs, 1037w, 1014w, 977vs, 937m, 897s, 864w, 835w, 809vs, 749w, 735w, 695sh, 667w, 643w,br, 619m,br, 593s,br, 501s,br and 441m,br $cm^{-1}$.

Reaction of Beryllium Chloride with Di-t-butylmethyleneaminolithium (2 molar equivalents - attempted synthesis of $(Bu^t{}_2C:N)_2Be$)

A solution of di-t-butylmethyleneaminolithium (2.94 g., 20 mmole) in hexane (30 ml.) was added to a frozen solution of beryllium chloride (0.8 g., 10 mmole) in ether (20 ml.) and subsequently stirred at 19° for 6 hr. Solvent was pumped off and the pale yellow solid residue boiled with toluene for 1 hr. After removal of solvent, extraction of the residue with hexane afforded pale yellow crystals of lithium tris(di-t-butylmethyleneamino) beryllate, $LiBe(N:CBu^t{}_2)_3$, m.p. 141-142°. (Found: C,74.6; H,12.6; Be,2.03; Li,1.59; N,9.4%; M,453. $C_{27}H_{54}BeLiN_3$ requires C,74.3; H,12.4; Be,2.06; Li,1.60; N,9.6%; M,436); $\nu_{max}$ (Nujol mull) 1663vs, 1656sh, 1605s, 1325w, 1263vw, 1227s, 1208s, 1172m, 1159sh, 1094w, 1037s, 1005m, 966sh, 949vs, 936sh, 928sh, 913vs, 877vs, 831s, 818vs, 797sh, 789sh, 728m, 722sh, 667w, 654w, 604m, 583vw, 566w, 551m, 526w,br, 500m,br, 470m,br and 443w,br $cm^{-1}$.

Preparation of Bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t{}_2C:N)_2Be]_2$

Di-iso-butylberyllium (3 ml. of a 3.66M solution in ether, 10.8 mmole) was added by syringe to a solution of di-t-butylmethyleneamine (3.1 g., 22 mmole) in ether (40 ml.) at -196°. The initially colourless solution gradually turned yellow as it was allowed to warm up to room temperature. There was no visible evolution of gas even when refluxed for 2 days in ether. On crystallisation from the solvent ether, a yellow solid separated and was identified as dimeric bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t{}_2C:N)_2Be]_2$, m.p. 220-230° decomp. (Found: C,74.5; H,12.3; Be,3.25; N,10.0%; M,548. $C_{36}H_{72}Be_2N_4$ requires C,74.8; H,12.4; Be,3.11; N,9.7%; M,578); $\nu_{max}$ (Nujol mull) 1746sh, 1721vs, 1631vs, 1366vs, 1325sh, 1266vw, 1225s, 1209m, 1186sh, 1064vs, 1050sh, 1040s, 1007s, 971s, 948s, 930m, 891s, 827m, 805vs, 725w, 671sh, 668m, 602m, 592sh, 549w, 519m, 499m and 452w $cm^{-1}$.

<u>Reaction of Bis(di-t-butylmethyleneamino)beryllium with Di-t-butylmethyleneaminolithium</u> (2 molar equivalents - attempted synthesis of $Li_2Be(N:CBu^t_2)_4$)

Di-t-butylmethyleneaminolithium (2.65 g., 18 mmole) in hexane (40 ml.) was slowly added to bis(di-t-butylmethyleneamino)beryllium (2.6 g., prepared as above, 9 mmole of monomer) also in hexane (40 ml.). Almost immediately a white solid was precipitated leaving a virtually colourless solution. Addition of 40 ml. toluene dissolved most of the precipitate. After stirring for 10 hr. at 60°, the solvent was pumped off and the residue extracted with hot toluene. Crystallisation yielded a fine white compound with a melting point of 140-142°. Analysis of a sample gave the ratio $Li:Be:NCBu^t_2$ as 1.8:1:3.8, and a molecular weight in benzene of 502. $\nu_{max}$ (Nujol mull) 1709m, 1660m, 1606vs, 1326w, 1265w, 1227sh, 1208s, 1082m, 1036s, 1022w, 1010w, 1000w, 930vs, 894w, 877sh, 833sh, 816m, 794sh, 781sh, 769w, 727m, 701w, 667w, 639s,br, 559vs,br, 490s,br and 417w,br $cm^{-1}$.

<u>Preparation of Di-t-butylmethyleneaminoiso-butylberyllium</u>, $(Bu^t_2C:NBeBu^i)_2$

Di-iso-butylberyllium (7.8 ml. of a 3.66M solution in ether, 28.8 mmole) was added by syringe to a solution of di-t-butylmethyleneamine (4.06 g., 28.8 mmole) in hexane (40 ml.) at -196°. The solution was allowed to warm up to room temperature and then stirred for 24 hr. Solvent was pumped off and the residue recrystallised from hexane to yield long, bulky, pale yellow crystals identified as dimeric <u>di-t-butylmethyleneaminoiso-butylberyllium</u>, $(Bu^t_2C:NBeBu^i)_2$, m.p. 139-141°. (Found: C,75.7; H,12.5; Be,4.41; N,6.9%; M,395. $C_{26}H_{54}Be_2N_2$ requires C,75.7; H,13.1; Be,4.4; N,6.8%; M,412); $\nu_{max}$ (Nujol mull) 1646sh, 1635vs, 1610sh, 1563vw, 1543vw, 1524vw, 1323sh, 1312m, 1266w, 1224m, 1211sh, 1178m, 1161m, 1063s, 1052vs, 1035s, 1014s, 973vs, 957s, 943sh, 931w, 889vs, 812vs, 801vs, 789s, 742m, 722w, 671s, 634vw, 591m,br, 555w, 543s, 525vw, 508s, 485m,br, 472vw and 456vw cm$^{-1}$.

Preparation of diphenylmethyleneaminoiso-butylberyllium, $(Ph_2C{:}NBeBu^i)_2$

Diphenylmethyleneamine (3.62 g., 20 mmole) was syringed into a solution of di-iso-butylberyllium (5.45 ml. of a 3.66M solution in ether, 20 mmole) in ether (30 ml.) at -196°. On warming to room temperature, a blood red solution formed. After stirring at 20° for 12 hr., the solution was refluxed for 1 hr. before the solvent was pumped off. Subsequent crystallisation from hexane afforded deep red crystals of dimeric diphenylmethyleneaminoiso-butylberyllium, $(Ph_2C{:}NBeBu^i)_2$, m.p. 133-135° (Found: C,83.0; H,7.8; Be,3.6; N,5.5%; M,480. $C_{34}H_{38}Be_2N_2$ requires C,82.9; H,7.7; Be,3.7; N,5.7%; M,492); $\nu_{max}$ (Nujol mull) 1961w, 1896w, 1818w, 1777w, 1739vw, 1722vw, 1691vw, 1677vw, 1610vs, 1578vs, 1513w, 1323s, 1294m, 1274s, 1208w, 1178m, 1161m, 1076sh, 1067s, 1030m, 1014m, 1002m, 984w, 966vs, 954s, 952sh, 921s, 885s, 836vs, 800w, 794sh, 787s, 760m, 737w, 719vs, 704vs, 699vs, 671m,br, 656w, 640w, 630w, 621m, 615w,br, 580m, 554sh, 548m and 534w cm$^{-1}$.

Preparation of diphenylmethyleneamino-t-butylberyllium, $(Ph_2C{:}NBeBu^t)_2$

Diphenylmethyleneamine (1.76 g., 9.76 mmole) was added to a solution of di-t-butylberyllium (4 ml. of a 2.44M solution in ether, 9.76 mmole) at -196° in ether (30 ml.). At room temperature this solution was cherry red in colour but within 4 hr. an orange solid was precipitated which dissolved on adding benzene (30 ml.). The ether was slowly pumped off to leave a dark red solution from which was crystallised an orange solid identified as diphenylmethyleneamino-t-butylberyllium dimer, $(Ph_2C{=}NBeBu^t)_2$, m.p. 185-187°. (Found: C,82.9; H,7.4; N,5.7%; M,472. $C_{34}H_{38}Be_2N_2$ requires C,82.9; H,7.7; N,5.7%; M,492); $\nu_{max}$ (Nujol mull) 1648m, 1605m, 1581w, 1544vw, 1316vw, 1266m, 1199w, 1172vw, 1105m, 1082w, 1020m, 947m, 917w, 896vw, 886vw, 852w, 826m, 809w, 800m, 763m, 749m, 729w, 701s, 668w, 655w, 637w, 633vw, 622w, 600w, 575w and 491vw cm$^{-1}$.

Attempts to prepare Di-t-butylmethyleneamino-t-butylberyllium, $Bu^t_2C{:}NBeBu^t$

(a) A solution of di-t-butylberyllium (5 ml. of a 2.44 M solution, 12.2 mmole) in ether (30 ml.) was treated with di-t-butylmethyleneamine (1.70 g., 12.2 mmole) at -196°. After stirring at room temperature for 6 hr., the ether was pumped off and replaced by hexane which was kept under reflux for a further 6 hr. Crystallisation was found to be impossible using several solvents and removal of solvents under reduced pressure left a translucent oil which gave inconsistent analytical data. The i.r. spectrum showed $\nu_{max}$ (contact film) 1720w, 1663vs and 1608m cm$^{-1}$.

(b) The addition of t-butyl cyanide (0.83 g., 10 mmole) to di-t-butylberyllium (4.1 ml. of a 2.44M solution in ether, 10 mmole) under similar conditions to method (a) also failed to produce the required product, $(Bu^t_2C{:}NBeBu^t)_n$, and the analytical results of the oil obtained did not fit any meaningful formula. The i.r. spectrum showed $\nu_{max}$ (contact film) 1652 vw and 2272s cm$^{-1}$.

(c) A solution of di-t-butylmethyleneaminolithium (1.59 g., 10.8 mmole) in hexane (20 ml.) was added to a frozen solution of beryllium chloride (0.86 g., 10.8 mmole) in ether (20 ml.) and then stirred at room temperature for 6 hr. To the resulting mixture of di-t-butylmethyleneamino-beryllium chloride, $(Bu^t_2C{:}NBeCl)_2$, and precipitated lithium chloride, was added di-t-butyl-lithium (5.0 ml. of a 2.18M solution in hexane, 10.8 mmole) at -196°. After stirring at room temperature for 4 hr. solvent was pumped off and replaced by toluene. Further stirring at 70° for 16 hr.

followed by filtration gave a colourless solution which eventually afforded pale yellow crystals. The product was identified as di-t-butylmethyleneaminoberyllium chloride, $(Bu^t{}_2C{:}NBeCl)_2$, by its i.r. spectrum.

(d) Di-t-butyl-lithium (5.5 ml. of a 2.18M solution in hexane, 12 mmole) was added to a frozen solution of beryllium chloride (0.96 g., 12 mmole) in ether (30 ml.). On allowing to warm to room temperature followed by stirring for 6 hr. a white suspension of lithium chloride appeared. A solution of di-t-butylmethyleneaminolithium (1.76 g., 12 mmole) was then slowly added to this solution of t-butylberyllium chloride, $(Bu^tBeCl)_x$ at $-196^o$. Subsequent stirring at room temperature for 6 hr., followed by a further period of 6 hr. in toluene at $70^o$ and filtration, yielded a colourless solution. Removal of solvent left an oil which gave inconsistent analytical data. The i.r. spectrum showed $\nu_{max}$ (contact film) 1718sh, 1701vs, 1619vs and 1608sh $cm^{-1}$.

<u>Preparation of Di-t-butylmethyleneamino-bis(trimethylsilyl)aminoberyllium,</u>
$Bu^t{}_2C{:}NBeN(SiMe_3)_2$

A solution of bis(trimethylsilyl)aminolithium, $(Me_3Si)_2NLi$, was prepared by adding n-butyl-lithium (10 ml. of a 2.0M solution in pentane, 20 mmole) to bis(trimethylsilyl)amine (3.22 g., 20 mmole) in ether (30 ml.) at $-196^o$ and allowing the mixture to attain room temperature. To this solution was added di-t-butylmethyleneaminoberyllium chloride, $(Bu^t{}_2C{:}NBeCl)_2$, (3.69 g., prepared as above, 10 mmole of dimer) in toluene (20 ml.) at liquid nitrogen temperature. On allowing to warm to room temperature, lithium chloride separated as a fine suspension which was filtered off after stirring for 6 hr. Removal of solvent from the almost colourless filtrate left a pale yellow oil whose i.r. spectrum showed $\nu_{max}$

1720 and 1659 cm$^{-1}$. Distillation of this oil under reduced pressure yielded an oil which gradually solidified and was identified as monomeric di-t-butylmethyleneamino-bis(trimethylsilyl)aminoberyllium, $Bu^t_2C:NBeN(SiMe_3)_2$, b.p. 120°/0.1 mm.Hg. (Found: C,58.5; H,11.8; N,8.9; Be,2.92%; M,307 (by cryoscopy), 330 (by osmometry). $C_{15}H_{36}N_2BeSi_2$ requires C,58.3; H,11.7; N,9.1; Be,2.91%; M,309); $\nu_{max}$ (Nujol mull) 1747s, 1734s, 1608w, 1253vs, 1196s, 1142w, 1065vs, 980vs,br, 889vs, 833vs,br, 753s, 712m, 674s, 630w, 614w, 544vw,br, 531vw,br, 507m, 440vw,br and 419w,br cm$^{-1}$.

Attempted Syntheses of the complexes $Bu^t_2C:NBeCl.NMe_3$ and $(Bu^t_2C:N)_2Be.TMED$

(a) $Bu^t_2C:NBeCl.NMe_3$: Trimethylamine (0.71 g., 12 mmole) was condensed into a flask containing di-t-butylmethyleneaminoberyllium chloride (2.22 g., 6 mmole of the dimer) in toluene (30 ml.) at -196° and the mixture slowly allowed to warm to room temperature. After stirring for 6 hr. solvent was removed under reduced pressure to yield a viscous oil which was identified by its i.r. spectrum as $(Bu^t_2C:NBeCl)_2$. Analysis of the solvent pumped off showed it to contain unreacted trimethylamine.

The experiment was repeated with a two fold excess of trimethylamine over the di-t-butylmethyleneaminoberyllium chloride, only to give the same result as above.

(b) $(Bu^t_2C:N)_2Be.TMED$: Equimolar proportions of tetramethylethylenediamine (TMED) and bis(di-t-butylmethyleneamino)beryllium were mixed at room temperature and stirred for several hours. No evidence of adduct formation was found, but after heating in toluene at 80° for 24 hr. the product not only showed absorptions in the i.r. characteristic for the starting materials but also a weak absorption at 1727 cm$^{-1}$.

## DISCUSSION

Very little attention has been paid to organoberyllium chemistry compared to other fields of organometallic chemistry, as evidenced by the relatively few workers in the area. Recent reviews discussing organo derivatives of beryllium have been written by Seyferth,[63] Coates and Morgan,[64] and Fetter.[65]

Organoberyllium compounds, in particular the alkyls, are very strong Lewis acids and it is not surprising that the majority of reactions begin with co-ordination of a Lewis base to the beryllium atom. The strongest dative bonded complexes are generally formed when the atom is nitrogen and decrease in the order $N > P > O > S$ as is also found in organo-aluminium and -gallium chemistry (for example $Me_2Be$,[66] $Me_3Al$,[67-69] and $Me_3Ga$.[70,71] If the donor has an acidic hydrogen, then cleavage of the beryllium-carbon bond may occur:

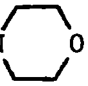
e.g. $$Pr^i_2Be + HNMe_2 \rightarrow [Pr^i_2Be,NHMe_2] \xrightarrow{25^o} Pr^iBeNMe_2 + C_3H_8$$

(Ref.72)

or if the donor molecule is unsaturated, an addition reaction may follow:

e.g. $$MeBeH + PhCHO \rightarrow [MeBeH,PhCHO] \rightarrow (PhCH_2OBeMe)_4$$ (Ref.73)

Intermediates in certain reactions of this type have been isolated although they are generally somewhat unstable: $Me_2Be.NH_3$ is stable at $-80^o$ but begins to eliminate methane between $-70^o$ and $-50^o$;[74] the presence of $Me_2Be.NH_2Me$ has been shown at $-90^o$ but no attempts were made to separate it; $Me_2Be.NMe_2H$ decomposes slowly at room temperature but rapidly at its melting point of $44^o$;[75] the reactions of piperidine and morpholine with

Me$_2$Be yield complexes Me$_2$Be.HN and Me$_2$Be.HN respectively at -20$^o$ but decompose at room temperature.[76] In contrast, several stable adducts of acetylenic derivatives of beryllium have been isolated that do not readily lose organo groups. For example (PhC⋮C)$_2$Be.2NHMe$_2$ m.p. 151-153$^o$, (PhC⋮C)$_2$Be.2NH$_2$Me m.p.86-87$^o$ and (PhC⋮C)$_2$Be.PhNH$_2$ m.p. above 310$^o$.[77] The reason for the stability of these compounds is doubtless due to the decrease of nucleophilic reactivity of alkynyl-beryllium relative to alkyl-beryllium bonds.

The first reported preparation of an organoberyllium nitrogen compound was by Gilman and Schulze in 1929; when they reacted azobenzene with dimethylberyllium, (MePhN.NPh)$_2$Be was formed.[78] It was many years later before the subject was more fully investigated. Trimeric MeBe.NMe$_2$ was prepared from the decomposition of Me$_2$Be.NMe$_2$H,[75] (Pr$^i$Be.NMe$_2$)$_n$ and [(Me$_2$N)$_2$Be]$_3$ from successive additions of Me$_2$NH to Pr$^i{}_2$Be,[72] the latter trimeric compound from the addition of Me$_2$NH to BeH$_2$[60a] and [(Ph$_2$N)$_2$Be]$_2$ from Et$_2$Be and Ph$_2$NH.[79] Nearly all the aminoberyllium alkyls have been prepared from the reaction between a beryllium dialkyl and a secondary amine,

$$R_2Be + R'_2NH \rightarrow RH + \frac{1}{n}(RBeNR'_2)_n \xrightarrow{R'_2NH} (R'_2N)_2Be$$

The use of beryllium chloride for preparing bisamino derivatives, or indeed aminoberyllium chlorides, does not appear to have been investigated:

viz.

$$BeCl_2 + R_2NLi \rightarrow \frac{1}{n}(R_2NBeCl)_n + LiCl\downarrow \xrightarrow{R_2NLi} (R_2N)_2Be$$

The first systematic study of aminoberyllium compounds was made by Coates and Fishwick.[80] This key paper reveals several important factors that are relevant to the chemistry of beryllium. Ten aminoberyllium alkyls were prepared (see Table II.1) by reacting the appropriate beryllium

TABLE II.1

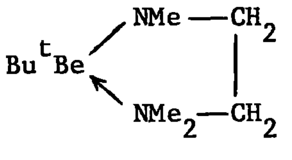
Aminoberyllium Dimers and Trimers

| | | | |
|---|---|---|---|
| Trimers | $(MeBeNMe_2)_3$<br>$(EtBeNMe_2)_3$ | $(MeBeNEt_2)_3$<br>$(Pr^iBeNMe_2)_3$ | $(PhBeNMe_2)_3$ |
| Dimers | $(MeBeNPr^n{}_2)_2$<br>$(PhBeNPh_2)_2$ | $(MeBeNPh_2)_2$<br>$(EtBeNPh_2)_2$ | $(EtBeNEt_2)_2$<br>$[MeBeN(CH_2Ph)Ph]_2$ |

alkyl and secondary amine. The eleventh compound in Table II.1, $[MeBeN(CH_2Ph)Ph]_2$, was obtained from methylberyllium hydride:

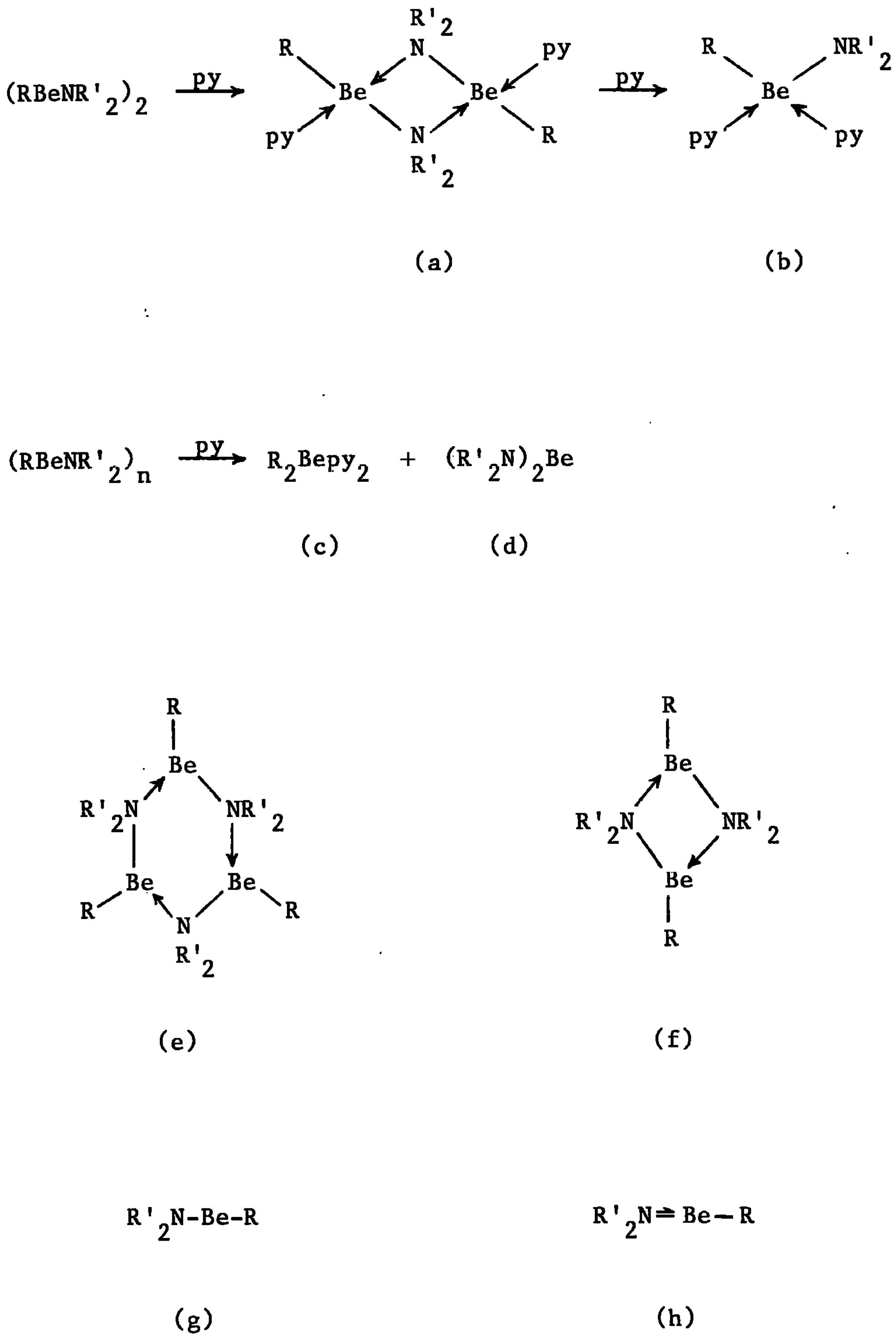
$$MeBeH + PhCH{=}NPh \rightarrow [MeBeN(CH_2Ph)Ph]_2 \quad \text{(Ref.73)}$$

Di-t-butylberyllium formed a 1:1 complex with dimethylamine which did not eliminate isobutane completely. On the other hand trimethylethylenediamine reacted with di-t-butylberyllium-diethyl ether complex completely at room temperature to form the only aminoberyllium alkyl known to be monomeric in benzene:



The complexes formed between these amino compounds and pyridine and 2,2'-bipyridyl were also described. The reactions are sometimes complicated by disproportionation processes as shown in Figure II.1. When R = R' = Me,

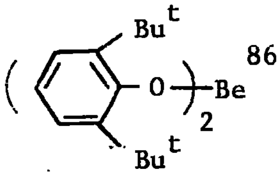
FIGURE II.1


(RBeNR'2)2
py
R
R'2
N
py
Be
Be
py
N
R'2
R
py
R
NR'2
Be
py
py
(a)
(b)
(RBeNR'2)n
py
R2Bepy2
+
(R'2N)2Be
(c)
(d)
R
Be
R'2N
NR'2
Be
Be
R
N
R'2
R
R
Be
R'2N
NR'2
Be
R
(e)
(f)
R'2N-Be-R
R'2N=Be—R
(g)
(h)

one equivalent of pyridine gives a colourless product ((a); R = R' = Me) and with excess pyridine, a pale cream coloured product ((b); R = R' = Me) is formed. Similarly, $(MeBeNPh_2)_2$ gives yellow products (a) and (b). Interestingly, $(MeBeNPh_2py)_2$ was the first methylberyllium compound prepared that was not decomposed by cold water. For $(EtBeNPh_2)_2$, no product corresponding to type (a) could be isolated and with $(MeBeNPr_2{}^n)_2$ products of types (c) and (d) were obtained. The addition of 2,2' bipyridyl produced highly coloured products of types (a), (b), (c) and $(R'_2N)_2Be.bipy$.

Of interest in this work is the colour, state of association, molecular structure and possibility of $\pi$ bonding in these compounds. The absorption spectra of the coloured 1:1 complexes of bipyridyl with beryllium alkyls or aryls, $R_2Bebipy$, were interpreted in terms of the transfer of an electron from the Be-C bonds to the lowest unoccupied $\pi$ orbital of the bipyridyl. This transition was believed to be responsible for the intense colours.[81] By replacing an alkyl group with an amino group, there is an additional possibility that the presence of a lone pair of electrons on the nitrogen will promote such a charge transfer transition.

With regard to the state of association, the compounds $(RBeNR'_2)_{2,3}$ are believed to exist as four or six membered ring species (Fig.II.1(e) and (f)). Entropy factors would favour the formation of dimers but opposing this is the increased ring strain of $Be_2N_2$ compared to $Be_3N_3$. By far the most important factor is the size of the substituents on the beryllium and nitrogen atoms. All the dimethylaminoberyllium alkyls are trimers and with the exception of $(MeBeNEt_2)_3$, any group larger than methyl on the nitrogen leads to a dimeric state of association. Molecular models show that the steric interference between neighbouring beryllium and nitrogen substituents is far less in the case of the dimers. In the extreme, with very large R and R' groups, a monomeric state can be envisaged (Fig.II.1(g)) but there are no known examples of this. The beryllium atom in (g), being a strong Lewis acid, would be electronically unstable and would have to satisfy its co-ordination unsaturation by accepting the lone pair of electrons from the nitrogen, as in (h). $Bu^tBeNMe.CH_2.CH_2.NMe_2$ is monomeric but in this case the beryllium is three co-ordinate by virtue of the lone electron pair donation from the $-NMe_2$ nitrogen atom. Two co-ordinate beryllium does exist, however, in compounds where the ligands are too bulky to permit association as in $Bu^t{}_2Be$,[82,83] $[(Me_3Si)_2N]_2Be$,[84,85]



[86] (this is probably the first example of a linear O-Be-O skeleton) and $(Me_3C.CH_2)_2Be$[87] is partially associated. The monomeric nature of MeBeCp and CpBeCl[88] is believed to arise from the beryllium atom being bonded to the five-electron cyclopentadienyl ligand and, having formed $\sigma$ bonds to chlorine or carbon (methyl), is thus surrounded by an octet of electrons. $Cp_2Be$ has been studied and found to be monomeric both in the gas phase and at $-120^{o}$.[89-92]

An electron diffraction investigation of the monomeric $[(Me_3Si)_2N]_2Be$ revealed that the N-Be-N unit is linear and the Be-N bond distance (1.56Å) was consistent with $p_{\pi}$-$p_{\pi}$ dative bonding.[85] The parameters were compared to those found in the trimer $[(Me_2N)_2Be]_3$ which was originally thought to contain a $(BeN)_3$ six membered ring[72] but was later shown, on the basis of its $^1H$[93] and $^9Be$[94] n.m.r. spectra, to have a linear $Be_3$ arrangement with four bridging amino groups (see Fig.II.2). The crystal structure of this

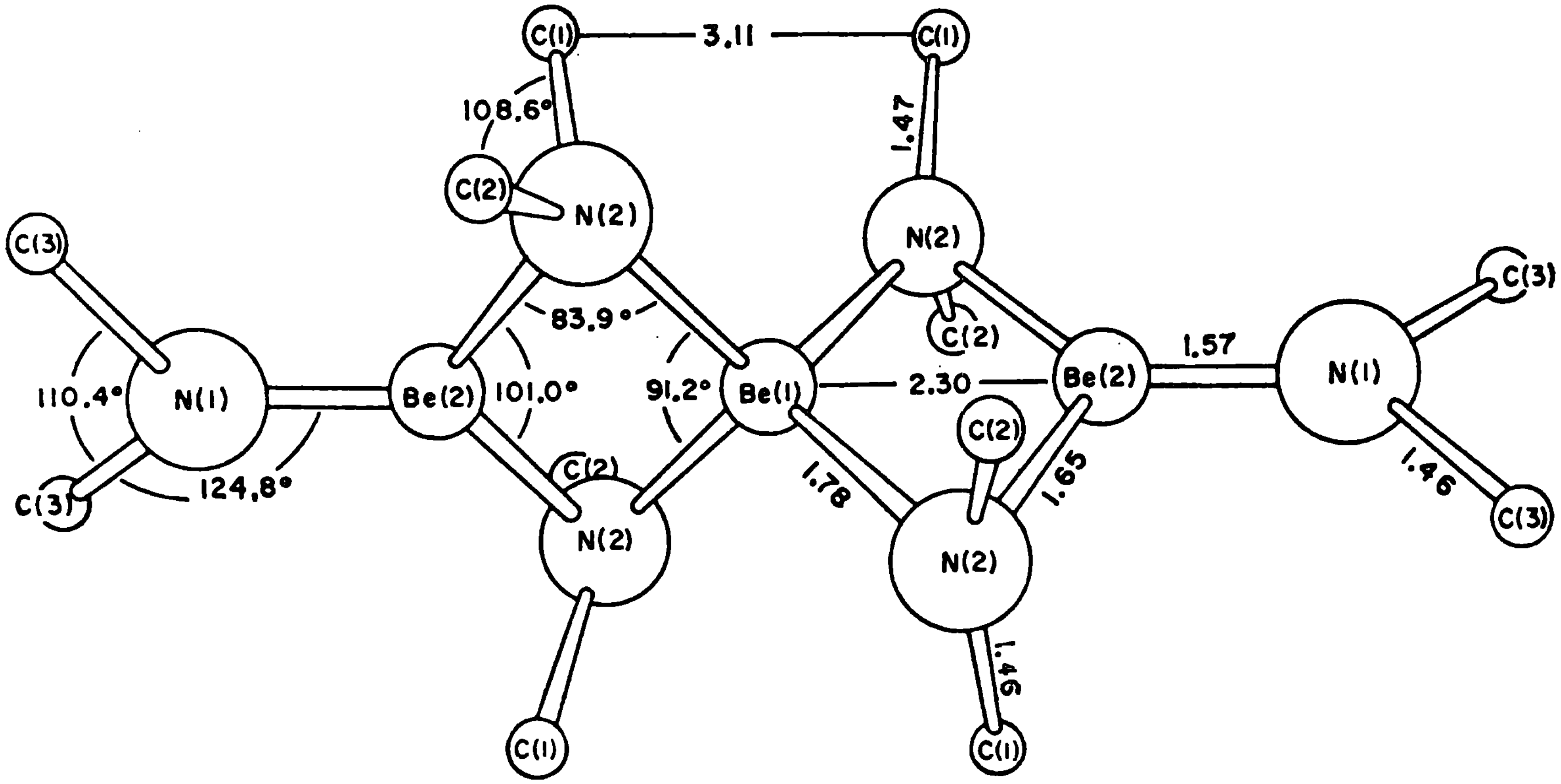


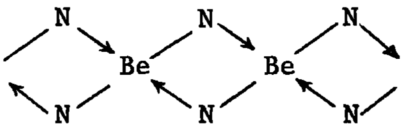
FIGURE II.2.

Trimeric Bis(dimethylamino)beryllium $[(Me_2N)_2Be]_3$

compound showed that the terminal Be-N distance was 1.57Å, the Be(terminal)-N distance 1.65Å and Be(central)-N distance 1.78Å,[95] the expected sequence if π-bonding effects are considered. Furthermore, the three co-ordinate terminal beryllium atom is coplanar with the terminal nitrogen atom and the attached methyl carbon atoms.

The authors of both papers discussing these two structures (Refs. 85 and 95 respectively) claim that polymerisation of these compounds to achieve complete valence saturation,

viz.



is prevented by the bulk of the substituents involved and consequently dative π-bonding of the terminal Be-N units has to satisfy the resulting co-ordination deficiency. In support of this, the existence of polymeric $(Me_2N)_2Mg$[96] is explained by the fact that the non-bonded methyl-methyl distances would be relatively large enough to permit an infinite polymer. Opposing this point of view is a recent report on the crystal structure of potassium amidoberyllate, $K^+[Be(NH_2)_3]^-$, which is monomeric with approximately $D_{3h}$ symmetry for the $BeN_3$ unit.[97] The Be-N bond length of 1.59Å is consistent with dative $p_\pi$-$p_\pi$ Be ← N bonding but the authors claim that the alternative polymeric tetrahedral structure would be sterically stable. The amide with the smallest substituents, $Be(NH_2)_2$, has been prepared (Ref.98 and references therein) and is probably an infinite polymer.

In view of the structural information reported to date, it is interesting to note Goubeau's comments on the bond orders between main group first row elements.[99] His predictions are based on three postulated conditions for π-bonding: Electron deficiency on both bonding partners, the sum of the Pauling electronegativity must be at least five, and third, the difference of electronegativities must be small. He concludes that bonding of the type $\mathrm{B}_{e}\overset{\leftarrow}{=}\mathrm{N}$ is not significant compared to say analogous boron compounds.

It was the growing interest in this field of beryllium-nitrogen chemistry that prompted an investigation into the structural and spectroscopic properties of methyleneamino derivatives of beryllium. The first report of such derivatives was made in 1970[19] when some six compounds of the type $[R_1R_2C{:}NBeCl]_2$ and $[(R_1R_2C{:}N)_2Be]_x$ were described. They were synthesised from the reaction between $BeCl_2$ and the appropriate methyleneaminolithium in the required proportions, except for $[Ph_2C{:}NBeCl]_2$ for which $Ph_2C{:}NSiMe_3$ was used. This latter reagent had been successfully employed in the preparation of methyleneaminoboron compounds[100] but it was found that substitution of the second beryllium chlorine atom was not possible. viz.

$$BeCl_2 + Ph_2C{:}NSiMe_3 \longrightarrow \tfrac{1}{2}(Ph_2C{:}NBeCl)_2 + Me_3SiCl\uparrow$$

$$BeCl_2 + 2Ph_2C{:}NSiMe_3 \not\longrightarrow \frac{1}{n}[(Ph_2C{:}N)_2Be]_n + 2Me_3SiCl\uparrow$$

otherwise,

$$BeCl_2 + R_2C{:}NLi \rightarrow \tfrac{1}{2}(R_2C{:}NBeCl)_2 + LiCl\downarrow$$

$$BeCl_2 + 2R_2C{:}NLi \rightarrow \frac{1}{x}[(R_2C{:}N)_2Be]_x + 2LiCl\downarrow \qquad x = 2,3 \text{ or } n$$

The azomethine stretching absorptions, $\nu(C{=}N)$, of the compounds are given in Table II.2. The difference between the terminal and bridging azomethine frequencies of about 100 $cm^{-1}$ is clearly shown.

The association and molecular structures of these six compounds demonstrate the similarity between amino and methyleneamino chemistry. The proposed structure of the methyleneaminoberyllium chlorides involves a four

## TABLE II.2

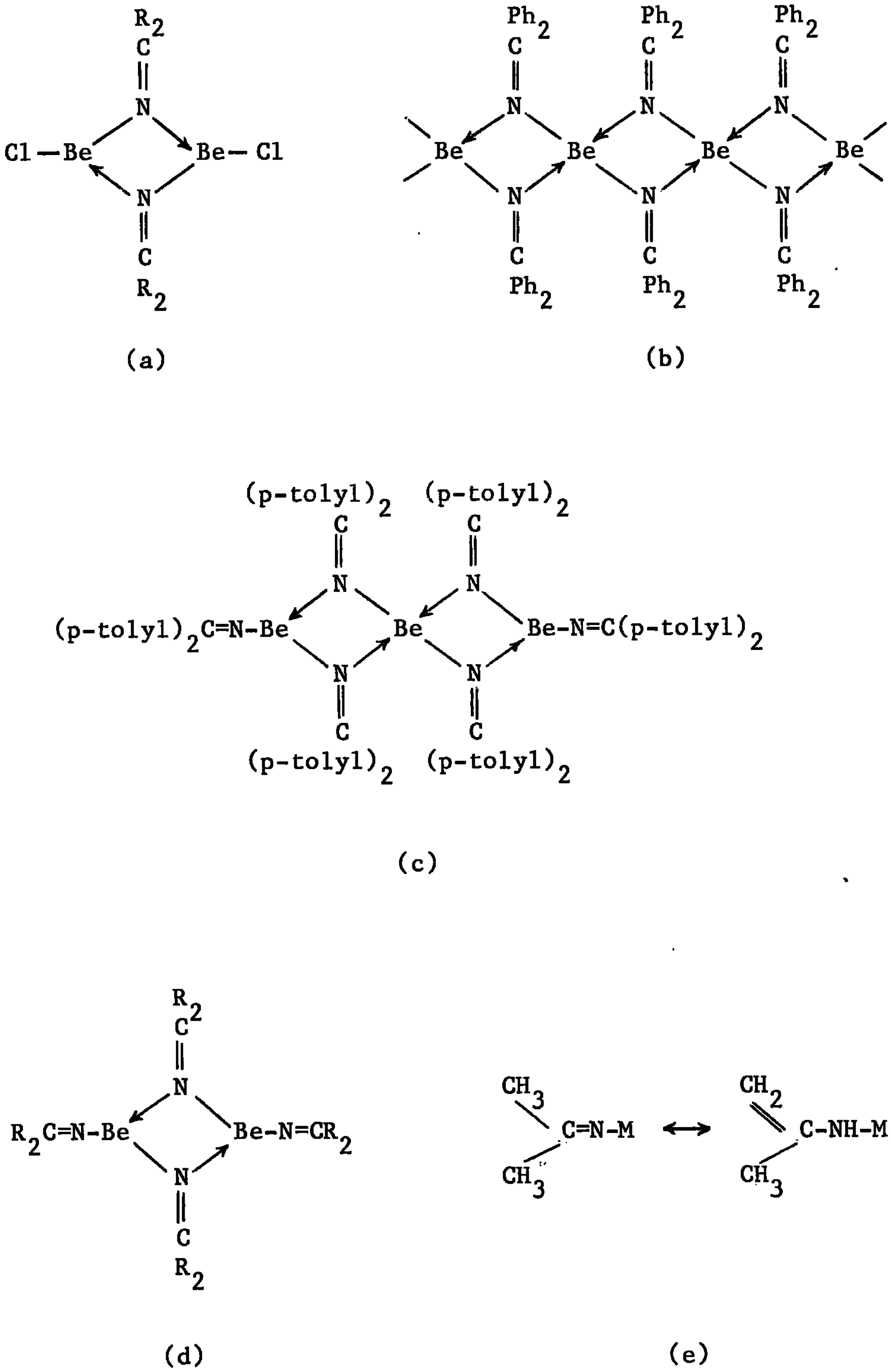
Infra-red azomethine stretching frequencies (Nujol mulls)

| Compound | $\nu(C{=}N)$ (bridging) ($cm^{-1}$) | $\nu(C{=}N \mathrel{\overset{\rightharpoonup}{=}} Be)$ (terminal) ($cm^{-1}$) |
|---|---|---|
| $(Ph_2C{:}NBeCl)_2$ | 1608 | - |
| $[(p\text{-tolyl})_2C{:}NBeCl]_2$ | 1610 | - |
| $[(p\text{-tolyl})Bu^tC{:}NBeCl]_2$ | 1614 | - |
| $[(Ph_2C{:}N)_2Be]_n$ | 1627 | 1732 |
| $[\{(p\text{-tolyl})_2C{:}N\}_2Be]_3$ | 1626 | 1731 |
| $[\{(p\text{-tolyl})Bu^tC{:}N\}_2Be]_2$ | 1637 | 1739 |

membered $(BeN)_2$ ring, shown in Fig.II.3(a), as has been found for boron, aluminium and gallium compounds $(R_2C{:}NMCl_2)_2$.[23-25] $[(Ph_2C{:}N)_2Be]_n$ may be a linear polymer (Fig.(b)). The trimer $[\{(p\text{-tolyl})_2C{:}N\}_2Be]_3$ is believed to have a linear arrangement of beryllium atoms as in (c) on the basis of its $^1H$ n.m.r. spectrum, similar to the structures of $[(Me_2N)_2Be]_3$,[93-95] $[(Bu^tO)_2Be]_3$,[94,101] $Cl_2Be_3(OBu^t)_4$[102] and $(PhC{\equiv}C)_2Be_3(OBu^t)_4$,[77] the latter two compounds having bridging butoxy groups. $[\{(p\text{-tolyl})Bu^tC{:}N\}_2Be]_2$ probably has structure (d) in agreement with the two azomethine stretching frequencies.

It can be seen that as the size of the ketimino group is increased, $Ph_2C{:}N\text{-}$, $(p\text{-tolyl})_2C{:}N\text{-}$, $(p\text{-tolyl})Bu^tC{:}N\text{-}$, the association number of the fully substituted derivatives decreases. Thus if it were not for the expected enamine tautomerism (Fig.II.3(e)) in $Me_2C{:}N\text{-}$ derivatives, then $(Me_2C{:}N)_2Be$ would no doubt be polymeric. Of more interest is to study the

## FIGURE II.3


(a)
(b)
(c)
(d)
(e)
Cl — Be
Be — Cl
R2
Ph2
(p-tolyl)2
(p-tolyl)2C=N-Be
Be-N=C(p-tolyl)2
R2C=N-Be
Be-N=CR2
CH3
C=N-M
CH2
C-NH-M

effect of increasing the size of $R_2C{:}N$ and with this in mind, di-t-butylmethyleneamino derivatives of beryllium were prepared in this more recent investigation.

Di-t-butylmethyleneaminoberyllium chloride, $(Bu^t_2C{:}NBeCl)_2$, was prepared by the reaction between beryllium chloride and di-t-butylmethyleneaminolithium in equimolar proportions and found to be a yellow, air-sensitive solid. Attempts to replace the chlorine by a further ketimino group resulted in the unexpected formation of the beryllate $LiBe(N{:}CBu^t_2)_3$:

$$\begin{tikzcd} & \tfrac{1}{2}LiBe(N{:}CBu^t_2)_3 + \tfrac{1}{4}(Bu^t_2C{:}NBeCl)_2 + \tfrac{3}{2}LiCl \\ BeCl_2 + 2Bu^t_2C{:}NLi \arrow[ur] \arrow[dr, "\times" marking] & \\ & \tfrac{1}{2}[(Bu^t_2C{:}N)_2Be]_2 + 2LiCl \end{tikzcd}$$

Separation of the lithium beryllate was effected by extraction with hexane in which $(Bu^t_2C{:}NBeCl)_2$ is virtually insoluble. The same pale yellow solid could also be prepared by the reaction between $BeCl_2$ and $Bu^t_2C{:}NLi$ in 1:3 molar proportions. Bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t_2C{:}N)_2Be]_2$, was synthesised from the reaction of the free ketimine $Bu^t_2C{:}NH$ with an ether solution of di-isobutylberyllium,

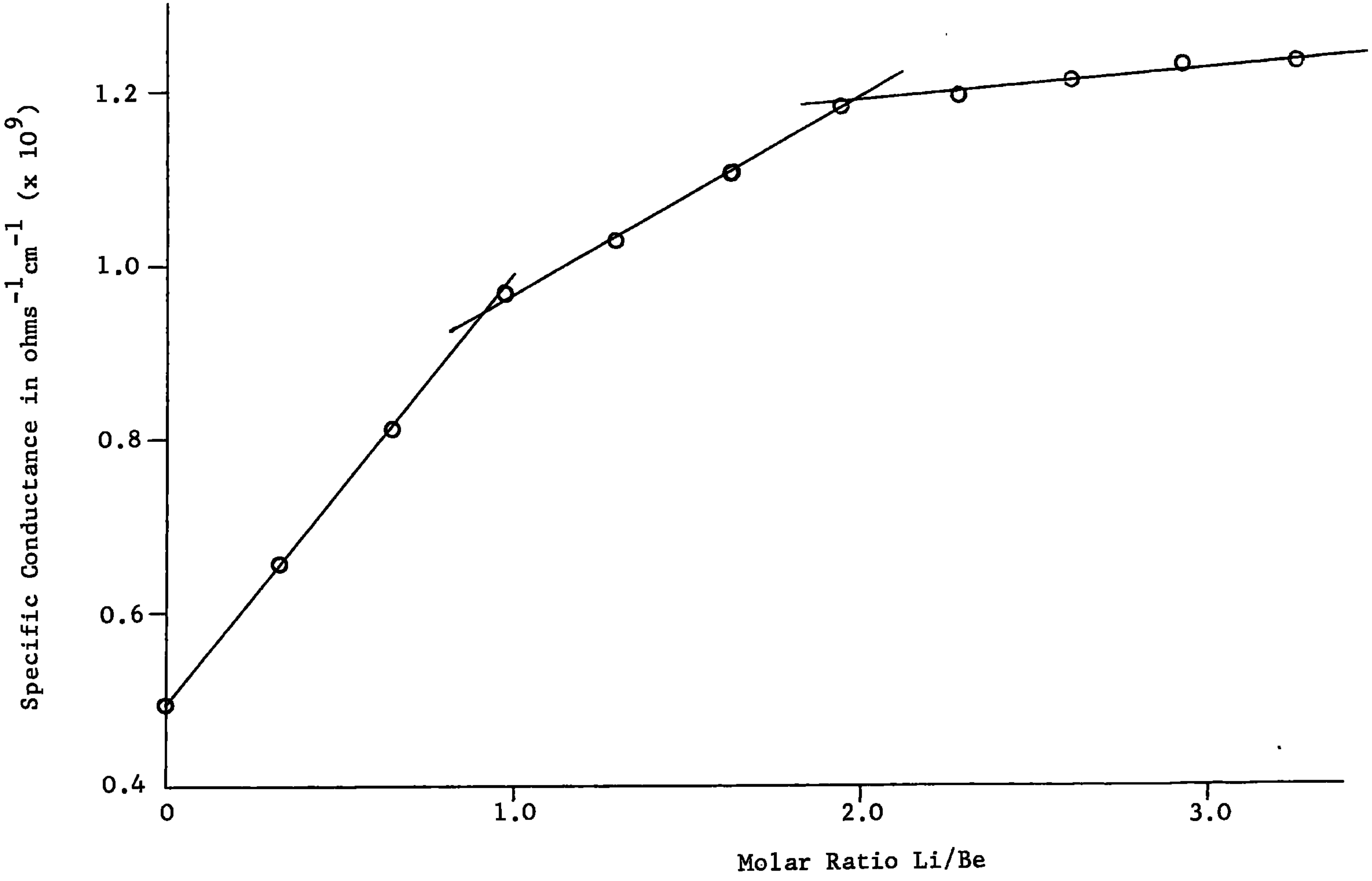
$$2Bu^t_2C{:}NH + Bu^i_2Be \rightarrow \tfrac{1}{2}[(Bu^t_2C{:}N)_2Be]_2 + 2C_4H_{10}$$

similar to the method used for preparing aminoberyllium compounds.[80] The reaction proceeded smoothly when allowed to warm up from $-196^\circ$ and there was no visible evolution of gas. Crystallisation of the ether solution yielded yellow crystals of the dimer which were later used for an X-ray structure determination.

In view of the existence of the acetylenic compound $Li_2Be(C{:}CH)_4$,[77] an attempt was made to prepare the corresponding imino derivative $Li_2Be(N{:}CBu^t_2)_4$ by reacting $LiN{:}CBu^t_2$ with $[(Bu^t_2C{:}N)_2Be]_2$ in the required proportions. The product obtained analysed as $Li_{1.8}Be(N{:}CBu^t_2)_{3.8}$. There are numerous examples of anionic organoberyllium complexes (reviewed in Ref.64) but structural information is available only for one compound, namely $Li_2BeMe_4$, in which the beryllium atom is surrounded by a distorted tetrahedron of methyl groups.[103]

In order to try and clarify the question of whether these unique LiBe and $Li_2Be$ species exist in solution, it was assumed that if $LiBe(N{:}CBu^t_2)_3$ and $Li_2Be(N{:}CBu^t_2)_4$ showed some ionic character then a conductometric titration of $Bu^t_2C{:}NLi$ against $[(Bu^t_2C{:}N)_2Be]_2$ should indicate the formation of the lithium compounds. The main difficulty encountered was the reactivity of the reagents to certain solvents (e.g. unsaturated systems like nitrobenzene) and also how to obtain a solution of $Bu^t_2C{:}NLi$ in the chosen solvent. It has been reported[35] that once $Bu^t_2C{:}NLi$ has been separated from its solvent it is somewhat difficult to redissolve. Thus the solvent was limited to hexane or pentane, the solvents in which it was prepared.

A solution of $Bu^t_2C{:}NLi$ (0.2 mmole per ml. hexane) was added in 0.5 ml. aliquots to a solution of $[(Bu^t_2C{:}N)_2Be]_2$ (0.306 mmole of monomer in 5 ml. hexane) in a conductivity cell with two platinum electrodes of 1 $cm^2$ area each, held parallel to each other 0.5 cm. apart. The titration was conducted under nitrogen and the cell immersed in a water bath to maintain a constant temperature of 22°C throughout the experiment. The conductivity of the solution was measured on a Wayne Kerr B224 Universal Bridge.



Discontinuities at Li/Be =
0.92 and 1.98

FIGURE II.4

Conductometric titration of $Bu^t_2C{:}NLi$ and $[(Bu^t_2C{:}N)_2Be]_2$

The titration results are shown graphically in Figure II.4 (calculations in detail are given in Appendix II). In view of the solvent used it is not surprising to see the extremely low specific conductnace throughout the titration. However, after corrections for the conductivity of the hexane, the plot of specific conductance against the molar ratio Li/Be does reveal two breaks in the curve at about the compositions $\mathrm{LiBe(N{:}CBu^t_2)_3}$ and $\mathrm{Li_2Be(N{:}CBu^t_2)_4}$.

None of the compounds mentioned to date contained imino groups attached to two co-ordinate beryllium so an attempt was made to prepare methyleneaminoberyllium alkyls, $\mathrm{R_2C{:}NBeR'}$, in which the R' group was sufficiently large to prevent association. Compounds were prepared by adding the methyleneamine, $\mathrm{R_2C{:}NH}$, to an ethereal solution of the beryllium dialkyl at a low temperature. When R = phenyl and R' = $\mathrm{Bu^i}$ and $\mathrm{Bu^t}$, two dimeric red solids were obtained. For R = $\mathrm{Bu^t}$ and R' = $\mathrm{Bu^i}$ long, bulky pale yellow crystals of the dimer $\mathrm{(Bu^t_2C{:}NBeBu^i)_2}$ were extracted. The reaction between $\mathrm{Bu^t_2C{:}NH}$ and $\mathrm{Bu^t_2Be}$ gave a product of inconsistent composition. Accordingly three other methods to prepare $\mathrm{Bu^t_2C{:}NBeBu^t}$ were tried:

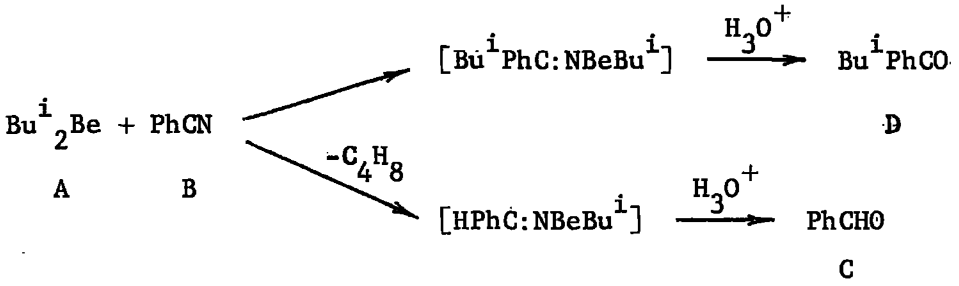
i) $\mathrm{Bu^t_2Be + Bu^tC{\vdots}N \rightarrow Bu^t_2C{:}NBeBu^t}$

ii) $\mathrm{Bu^t_2C{:}NLi + BeCl_2 \rightarrow \tfrac{1}{2}(Bu^t_2C{:}NBeCl)_2 \xrightarrow{Bu^tLi} Bu^t_2C{:}NBeBu^t + 2LiCl}$

iii) $\mathrm{Bu^tLi + BeCl_2 \rightarrow \frac{1}{x}(Bu^tBeCl)_x \xrightarrow{Bu^t_2C{:}NLi} Bu^t_2C{:}NBeBu^t + 2LiCl}$

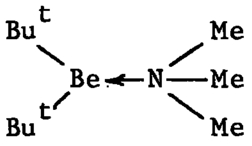
Reactions between organoberyllium compounds and cyanides have not been systematically investigated. A recent report suggests that such addition reactions are preceeded by co-ordination of the cyanide to the beryllium.[104]

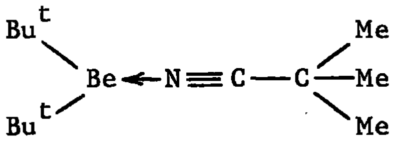
The authors of this paper reacted $Bu^i_2Be$ with PhC$\vdots$N followed by hydrolysis to give PhCHO and $PhBu^iCO$ in proportions depending on the temperature of the experiment. This process can be represented in the following scheme (the intermediate co-ordination state is not shown):



When the reactants are in equimolar proportions, at 0° the ratio of C:D is 7:93 and at 67° the same ratio is 86:14, the respective conversion rates being 40% and 84%. These ratios are not unexpected as $Bu^i_2Be$ eliminates isobutene at about 80° to give isobutylberyllium hydride.[105]

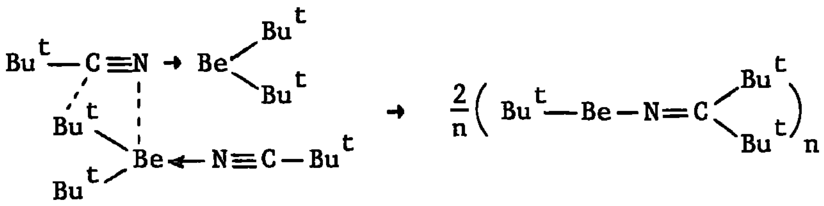
The product obtained from the reaction between $Bu^t_2Be$ and $Bu^tC\vdots N$ was a pale coloured oil with indefinite composition; in air the oil immediately inflamed. The adduct $Bu^t_2Be.NMe_3$ has been prepared[106] and so it seems probable that the reaction formed $Bu^t_2Be.N\vdots CBu^t$ when a comparison is made of the molecular structures:



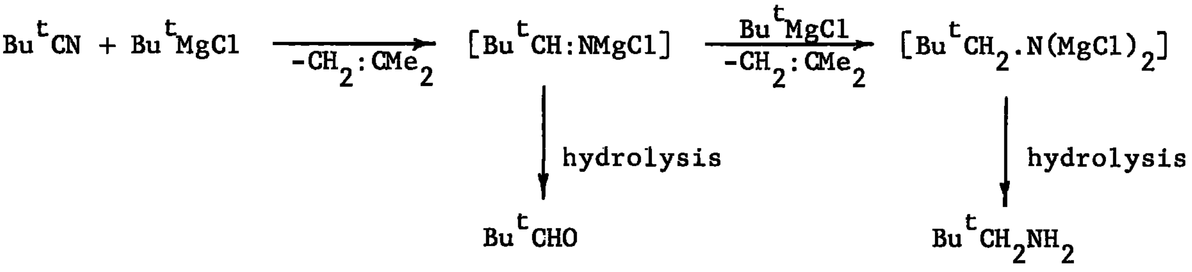


Migration of one of the beryllium $Bu^t$ groups to the nitrile carbon atom should then give $Bu^tBeN{:}CBu^t_2$ in a manner similar to that postulated for aluminium rearrangements, $RC\vdots N.AlR'_3$.[50]

viz.



The lack of rearrangement of the above system can be contrasted with the reaction between t-butylcyanide and t-butyllithium in which the insertion reaction takes place below room temperature to give $Bu^t_2C:NLi$.[21] In the Grignard reaction between $Bu^tCN$ and $Bu^tMgCl$, the hydrolysis products showed no signs of $Bu^t_2C:NMgCl$ being formed as an intermediate.[107] Instead, reduction products were obtained corresponding to the reaction,



The difference between the reactions may be explained in the following way: Nucleophilic attack on the carbon of the co-ordinated nitrile would be expected to occur less readily if the migrating group is attached to a more electronegative metal, thus carrying a lower negative charge (electronegativities Li, 0.97; Mg, 1.23; Be, 1.47[108]).

The following two attempts to prepare $Bu^t_2C:NBeBu^t$ by metathetical reactions both failed presumably due to the steric congestion of the intermediates. The infra-red data for the product resulting from the reaction between $[(Bu^tBeCl)_x]$ and $Bu^t_2C:NLi$ (equation (iii)) indicates that some reaction may have occurred.

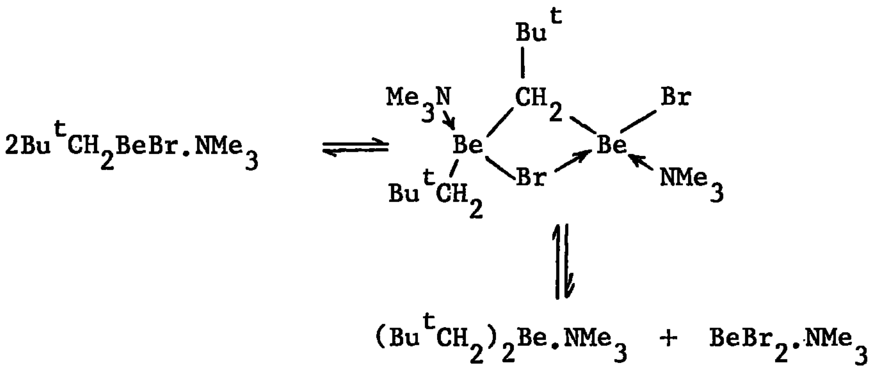
The first apparently monomeric ketiminoberyllium compound prepared with two co-ordinate beryllium was di-t-butylmethyleneamino-bis(trimethylsilyl)amino beryllium, $\mathrm{Bu^t{}_2C{:}NBeN(SiMe_3)_2}$. Its synthesis consisted of two metathetical reactions using $\mathrm{(Me_3Si)_2NLi}$ and $\mathrm{Bu^t{}_2C{:}NLi}$ on $\mathrm{BeCl_2}$:

$$\begin{tikzcd}
\mathrm{(Me_3Si)_2NH + Bu^nLi} \arrow[r] & \mathrm{(Me_3Si)_2NLi} \arrow[r, "\mathrm{BeCl_2}"] & \mathrm{(Me_3Si)_2NBeCl} \arrow[d, "\mathrm{Bu^t{}_2C{:}NLi}"] \\
 & & \mathrm{Bu^t{}_2C{:}NBeN(SiMe_3)_2}
\end{tikzcd}$$

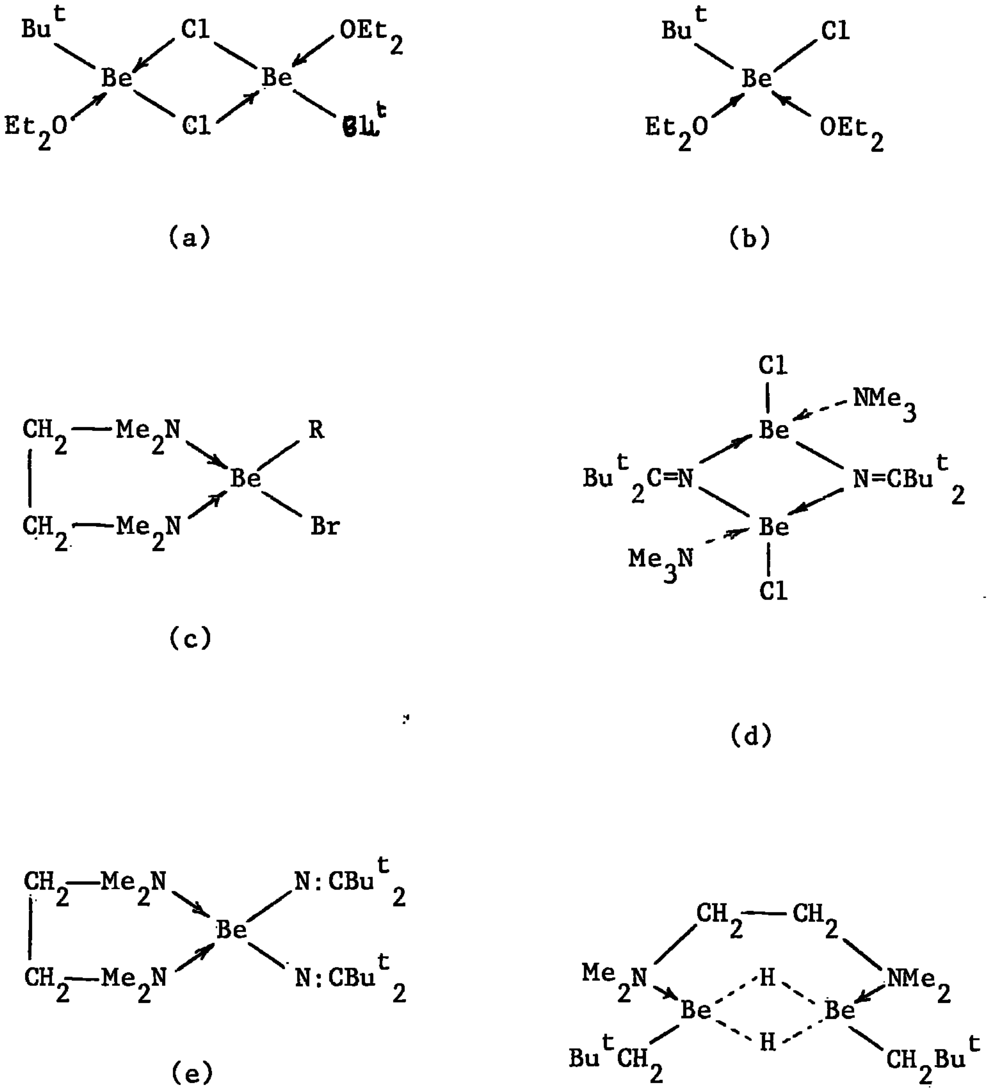
Distillation under reduced pressure yielded a yellow oil, b.p. 120°/0.1 mm.Hg, which gradually solidified; its monomeric nature was determined by both cryoscopy and osmometry. That it is monomeric is not very surprising; bis[di(trimethylsilyl)amino]beryllium, $\mathrm{[(Me_3Si)_2N]_2Be}$, is monomeric[85] whereas the bis(di-t-butylmethyleneamino)beryllium, $\mathrm{[\{(Me_3C)_2C{:}N\}_2Be]_2}$ is dimeric, a combination of the two ligands on one beryllium atom thus leading to either a monomeric or dimeric state of association. Another beryllium system in which the state of association is influenced by the distance of the bulky ligand from the beryllium atom is the series $\mathrm{(Me_3C)_2Be}$, $\mathrm{(Me_3C.CH_2)_2Be}$ and $\mathrm{(Me_3SiCH_2)_2Be}$ which exist as monomer,[83] monomer-dimer mixture[87] and dimer[87] respectively. In this example the trimethyl group is increasingly further from the beryllium, hence allowing dimerisation (compare the stabilities of $\mathrm{Ph_2Be(NMe_3)_2}$ and $\mathrm{Ph_2Be(PMe_3)_2}$; the latter has a negligible dissociation pressure whilst that for the trimethylamine complex is 0.5 mm[109]).

Two attempts were made to prepare complexes in which the beryllium atom was co-ordinatively saturated so as to convert bridging methyleneamino groups into terminal ligands. Two donor molecules were used, namely trimethylamine and tetramethylethylenediamine (TMED), $Me_2N.CH_2.CH_2.NMe_2$, and were reacted with $(Bu^t_2C{:}NBeCl)_2$ and $[(Bu^t_2C{:}N)_2Be]_2$ respectively. Trimethylamine with all alkyl-, aryl- and alkynyl-beryllium compounds so far prepared form 1:1 or 2:1 complexes. With dimethylberyllium, $Me_2Be.NMe_3$ is formed which is monomeric as vapour and in benzene.[81] A further trimethylamine molecule can be added with difficulty, giving $Me_2Be.(NMe_3)_2$ which rapidly dissociates to the 1:1 complex.[110] It is interesting to note that although monomeric $Me_2Be.NEt_3$ and $(PhC{\vdots}C)_2Be.NEt_3$[77] can be prepared, a second triethylamine molecule cannot be added, doubtless for steric reasons. The complex formed between di-t-butylberyllium and trimethylamine, $Bu^t_2Be.NMe_3$[106], has a melting point ($45^o$-$46^o$) expected for a near symmetrical molecule (c.f. the liquids $Et_2Be.NMe_3$[128] and $Pr^i_2Be.NMe_3$[72]), as has the trimethylphosphine analogue, $Bu^t{}_2Be.PMe_3$ (m.p. $46^o$). Neither of these two compounds, nor $Pr^i_2Be.NMe_3$ will add a second donor molecule. Likewise, when the tertiary butyl group is further away from the beryllium atom, as in di-neopentylberyllium, $(Bu^tCH_2)_2Be$, only one molecule of trimethylamine will attach itself to the metal.[111] However, in $(Bu^tC{\vdots}C)_2Be$ where the bulk of the ligand is far removed from the beryllium atom, both 1:1 and 1:2 complexes have been reported with trimethylamine as the donor molecule.[112]

The reaction between trimethylamine and di-t-butylmethyleneaminoberyllium chloride, $(Bu^t{}_2C{:}NBeCl)_2$, was tried in order to determine whether the complexes $Bu^t{}_2C{:}NBeCl.NMe_3$ and $Bu^t{}_2C{:}NBeCl(NMe_3)_2$ could be prepared. Since $Bu^t{}_2C{:}NBeCl.NMe_3$ is isoelectronic with $Bu^t{}_2C{:}NBeCMe_3Cl^-$ and attempts to prepare $Bu^t{}_2C{:}NBeCMe_3$ failed, the synthesis of $Bu^t{}_2C{:}NBeCl.NMe_3$ would throw more light on the steric factors involved in the $Bu^t{}_2C{:}NBeX$ systems. Little research has been done on organoberyllium halides; the preparation of such compounds is reviewed in Reference 64. Of those with bulky organic ligands, $Bu^tBeCl$ has been studied most. The ether complex in benzene is dimeric but in ether, the chloride bridges (see Figure II.5 (a) and (b)) are cleaved by ether to give a monomeric 1:2 complex.[106] Four co-ordinate beryllium has also been achieved by complexing TMED with RBeBr (R = Et, $CH_2Bu^t$. Figure II.5 (c)). In contrast, neopentylberyllium bromide and trimethylamine reacted to give the disproportionation product $BeBr_2.NMe_3$.[111]



Surprisingly, when trimethylamine was reacted with $(Bu^t{}_2C{:}NBeCl)_2$ there were no signs of adduct formation. A possible reason for this may be that because of the dimeric state of association of the beryllium compound, approach of a trimethylamine molecule is inhibited by the congestion about the beryllium atom (Figure II.5 (d)), whereas the beryllium atom in $Bu^t{}_2Be$ is two co-ordinate and perhaps allows an easier approach for donor molecules, despite the bulk of $Bu^t$.



(a)

(b)

(c)

(d)

(e)

(f)

FIGURE II.5

Tetramethylethylenediamine can bond to organoberyllium compounds in three ways. The most common way is shown in Figure II.5.c) where the TMED is acting as a chelating amine e.g. $Me_2Be(TMED)$.[81] Necessarily, the beryllium atom is co-ordinatively saturated. When the organo ligands are large, then it becomes impossible for $R_2Be(TMED)$ to be a chelate complex. Thus in $Bu^t{}_2Be(TMED)$ there is only one nitrogen atom co-ordinated at a time and $^1H$ n.mr. studies show that there is rapid exchange between free and complexed nitrogen.[106] This effect is not observed for the magnesium analogue $Bu^t{}_2Mg(TMED)$[113] which presumably has the structure of $Me_2Be.(TMED)$. The third type of bonding is shown in Figure II.5.f) in which the diamine co-ordinates to the dimeric species to form a third bridging group. Such a structure has been postulated for alkylberyllium hydrides $(RBeH)_2.(TMED)$ in benzene where R = $Bu^i$,[105] $Bu^tCH_2$,[111] Et,$Bu^s$, $Bu^t$,n-$C_5H_{11}$.[114]

The reaction between TMED and the dimer $[(Bu^t{}_2C{:}N)_2Be]_2$ was tried with a view to synthesise $(Bu^t{}_2C{:}N)_2Be(TMED)$ as shown in Figure II.5(e). Such a structure would eliminate the need for a bridging ketimine group and would allow the two ligands to adopt either a linear or bent C=N-Be conformation. With four nitrogens surrounding the beryllium, valence saturation of the beryllium atom is achieved and there would be no possibility of $(p_\pi - p_\pi)$ Be $\leftarrow$ N multiple bonding. Any linearity found (spectroscopically) for the C=N-Be linkage can then be attributed only to steric effects. When an attempt was made to prepare the complex, only starting materials were recovered. However the i.r. spectrum showed not only the reagent absorptions but also a weak peak appropriate for a linear C=N-Be unit (1727 cm.$^{-1}$).

All the beryllium compounds prepared are very air and moisture sensitive, particularly in the case of the alkylberyllium derivatives. Thermal decomposition of these derivatives was not investigated but in the case of $[(Bu^t{}_2C:N)_2Be]_2$ a red sublimate was observed at its melting point (220-230$^o$). During a study of nitrile adducts,[115] it was found that when heated in closed vessels, $PhCN.GaEt_3$ gave $(PhCH:NGaEt_2)_2$, $Bu^tCN.GaEt_3$ gave $(Bu^tCH:NGaEt_2)_2$ and $PhCN.GaMe_3$ gave 2,4,6-triphenyltriazine $Ph_3C_3N_3$. The mechanism proposed involved a methyleneamino intermediate and it seems likely that the red sublimate in this beryllium example may well have been an organic polymerisation product.

The physical properties of the new beryllium compounds are listed in Table II.3.

## Spectroscopic Data for the new methyleneaminoberyllium compounds

Frequencies of characteristic absorptions in the i.r. spectra of these compounds are shown in Table II.4, and the absorptions in the azomethine stretching region ν(C=N) have been assigned to bridging and terminal methyleneamino groups. This assignment of absorptions can be rationalised by first considering the methyleneaminoberyllium alkyls which, being dimers, can adopt three possible structures (Figure II.6(a),(b) and (c)). Structure (c) can be ruled out on the grounds that with both bridging and terminal methyleneamino groups two azomethine absorptions

## TABLE II.3

### Physical Properties of the New Beryllium Compounds

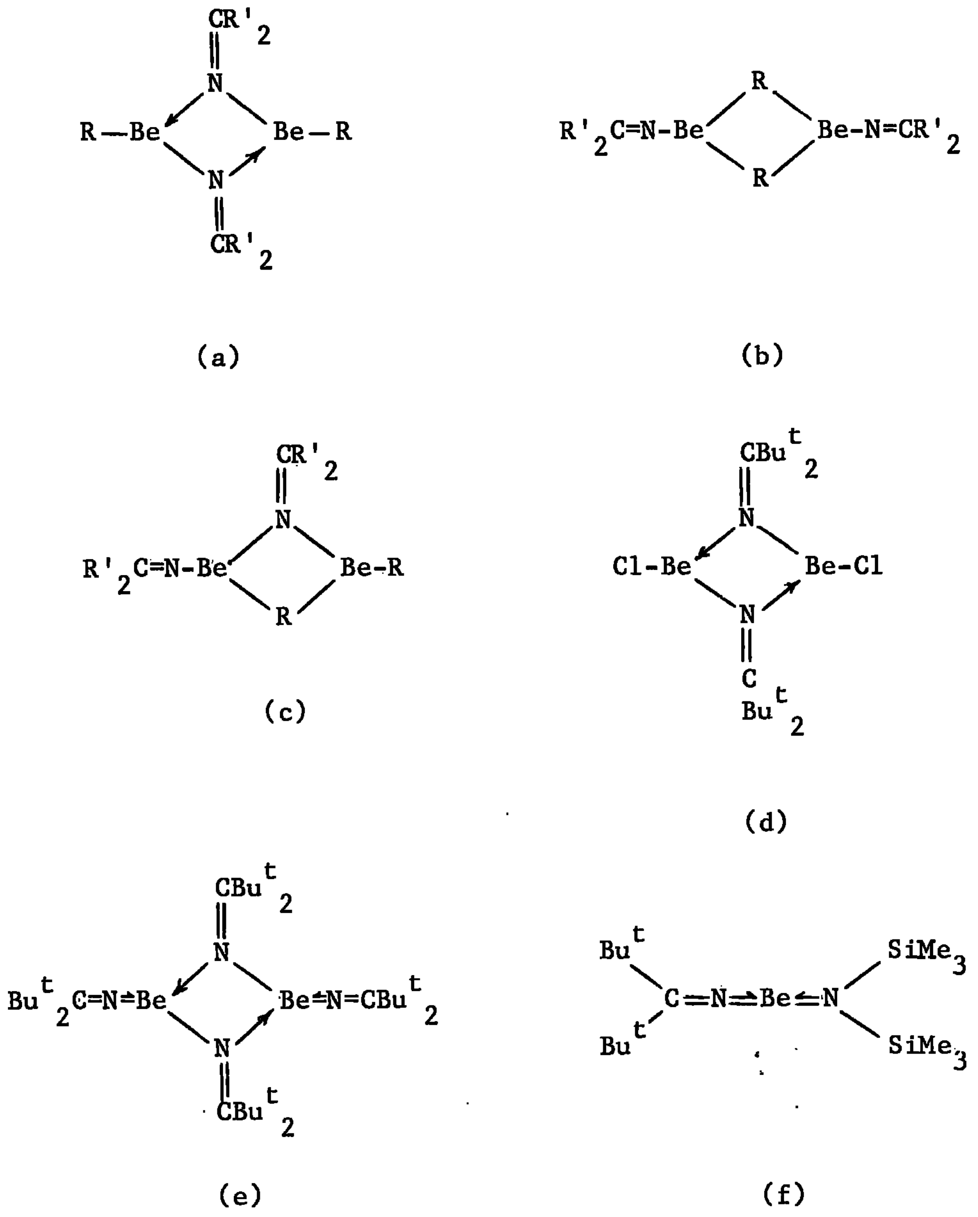
| Compound | Appearance | M.p.(B.p.) | Solubility |
|---|---|---|---|
| $(Bu^t{}_2C:NBeCl)_2$ | Yellow solid | 88-90° decomp. | Sol. toluene<br>Insol. hexane |
| $[(Bu^t{}_2C:N)_2Be]_2$ | Yellow crystalline solid | 220-230° decomp | Sol. ether, hexane, toluene |
| $LiBe(N:CBu^t{}_2)_3$ | Pale yellow crystalline solid | 141-142° | Sol. hexane, toluene |
| $Li_2Be(N:CBu^t{}_2)_4$ | White Powder | 140-142° | Sol. toluene |
| $(Bu^t{}_2C:NBeBu^i)_2$ | Pale yellow crystalline solid | 139-141° | Sol. ether, hexane |
| $(Ph_2C:NBeBu^i)_2$ | Deep red solid | 133-135° | v.sol. ether |
| $(Ph_2C:NBeBu^t)_2$ | Orange solid | 185-187 | sol. ether<br>v.sol. benzene |
| $Bu^t{}_2C:NBeN(SiMe_3)_2$ | Pale yellow oil which gradually solidifies | b.p.120°/0.1 mm.Hg | sol. toluene |

## TABLE II.4

## Characteristic i.r. azomethine stretching frequencies (Nujol mulls)

<table>
<tr><th>Compound</th><th>$\nu$(C=N) bridging ($cm^{-1}$)</th><th>$\nu$(C=N=Be) terminal ($cm^{-1}$)</th></tr>
<tr><td>$(Bu^t{}_2C{:}NBeCl)_2$</td><td>1626</td><td>-</td></tr>
<tr><td>$[(Bu^t{}_2C{:}N)_2Be]_2$</td><td>1631</td><td>1721</td></tr>
<tr><td>$(Bu^t{}_2C{:}NBeBu^i)_2$</td><td>1635</td><td>-</td></tr>
<tr><td>$(Ph_2C{:}NBeBu^i)_2$</td><td>1610</td><td>-</td></tr>
<tr><td>$(Ph_2C{:}NBeBu^t)_2$</td><td>1648</td><td>-</td></tr>
<tr><td>$Bu^t{}_2C{:}NBeN(SiMe_3)_2$</td><td></td><td>1734,1747</td></tr>
<tr><td>$LiBe(N{:}CBu^t{}_2)_3$</td><td colspan="2">1663</td></tr>
<tr><td>$Li_2Be(N{:}CBu^t{}_2)_4$</td><td colspan="2">1660, 1709</td></tr>
</table>

should be observed. For (b) it must be assumed that alkyl groups are better at bridging two beryllium atoms than nitrogen. This is extremely unlikely when R=$Bu^t$ since no beryllium compounds prepared to date have bridging tertiary butyl groups, owing to their bulk; dimeric ether adducts of t-butylberyllium halides, $(Bu^tBeX,Et_2O)_2$, (X = Cl,Br), have halogen bridges.[106] Thus it can be concluded that the dimeric methyleneaminoberyllium alkyls prepared have structure (a) with bridging methyleneamino groups, and that beryllium derivatives with similar i.r. absorptions also have bridging methyleneamino groups.


(a)

(b)

(c)

(d)

(e)

(f)

FIGURE II.6

The new chloro derivative, $(Bu^t{}_2C{:}NBeCl)_2$ has an azomethine stretching frequency of 1626cm.$^{-1}$ which can be attributed to ν(C=N) of the two bridging methyleneamino groups. This is in accord with previous work on related beryllium, boron, aluminium and gallium compounds[19,23-25] when it was similarly predicted that derivatives of the type $(R_2C{:}NBeCl)_2$ or $(R_2C{:}NMCl_2)_2$ would have bridging methyleneamino groups (Figure II.6(d) for beryllium).

Bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t{}_2C{:}N)_2Be]_2$, necessarily must have structure (e) with both bridging and terminal groups and consequently there are two azomethine stretching absorptions of 1631cm$^{-1}$ and 1721cm.$^{-1}$ Clearly the former is that for the bridging ligands as it falls within the range 1608-1648cm$^{-1}$ (results for Table II.2 and Table II.4) appropriate for a non-linear Be-N-C skeleton. The second absorption (1721cm$^{-1}$) can be assigned to the asymmetric stretching vibration ν(C=N$\doteq$Be) resulting from a linear C-N-Be configuration. Such a linear unit would allow most room for the bulky substituents and also maximise the overlap of the lone pair of electrons on the nitrogen with the vacant beryllium orbitals available for dative N $\rightleftharpoons$ Be π-bonding.

With the data collected so far, the two categories can be assigned frequency ranges; 1608-1648cm$^{-1}$ for bridging methyleneamino groups and 1721-1739cm$^{-1}$ for terminal groups. When the silyl compound $Bu^t{}_2C{:}NBeN(SiMe_3)_2$ was analysed, it was found to be monomeric with i.r. absorptions at 1734 cm$^{-1}$. and 1747 cm$^{-1}$ (more of a doublet than two distinct peaks) but none in the region 1600-1730cm$^{-1}$, except for a somewhat weak peak at 1608 $cm^{-1}$ resulting from slight hydrolysis. A crystallographic study of this compound would be of particular interest as it is one of the few monomeric two-co-ordinate beryllium species and is the first methyleneaminoberyllium derivative to have just a terminal ligand. Molecular structures have been determined for $[(Me_3Si)_2N]_2Be$[85] and $[(Bu^t{}_2C:N)_2Be]_2$[51] and in both cases the Be-N bond lengths (Be-N terminal for the second compound) are appropriate for $Be \stackrel{\leftarrow}{=} N$ π-bonding. Hence if the bulk of the substituents would permit it, the butyl and silyl groups would be in the same plane for $Bu^t{}_2C:NBeN(SiMe_3)_2$ (Figure II.6 (f)).

The two lithium compounds $LiBe(N:CBu^t{}_2)_3$ and $Li_2Be(N:CBu^t{}_2)_4$ both have absorptions at intermediate frequencies (1663 $cm^{-1}$ and 1660, 1709 $cm^{-1}$ respectively) which fall into neither of the above categories. A possible reason is that steric requirements have forced the methyleneamino unit into a position in which the Be-N-C skeleton is slightly bent. Of interest is the high frequency absorption (1709 $cm^{-1}$) of $Li_2Be(N:CBu^t{}_2)_4$. This implies that there is a linear Be-N-C group with $Be \stackrel{\leftarrow}{=} N$ π-bonding which is impossible if the beryllium atom is surrounded by four nitrogen atoms, thus achieving valence saturation. Possible structures of these compounds will be discussed in connection with the n.m.r. data.

The frequency of the bands due to $Be \stackrel{\leftarrow}{=} N = C$ is about 50 $cm^{-1}$ lower than the corresponding absorptions due to $B \stackrel{\leftarrow}{=} N = C$ asymmetric stretching vibrations for boron compounds $R_2C{=}N \stackrel{\leftarrow}{=} BPh_2$[15] and when compared with $\nu(C{=}N{=}C)$ for the dialkylideneammonium cation, $[Ph_2C:N:CPh_2]^+$, at 1845 $cm^{-1}$,[29] reflects the decreasing $N \stackrel{\leftarrow}{=} M$ bond order in the sequence

M = C > B > Be.

Details of the $^1H$ n.m.r. spectra of these methyleneaminoberyllium derivatives are given in Table II.5. The compounds $Li_2Be(N{:}CBu^t_2)_4$ and $(Ph_2C{:}NBeBu^i)_2$ gave no n.m.r. signal in toluene, probably because of their relative insolubility. It is surprising to note that di-t-butylmethyleneaminoiso-butylberyllium, $(Bu^t_2C{:}NBeBu^i)_2$, has two peaks in the region when the t-butylmethyleneamino protons of di-t-butylmethyleneamino derivatives are found (at +33°, the parent ketimine, $Bu^t_2C{:}NH$ absorbs at $\tau = 8.83$,[35] $Bu^t_2C{:}NLi$ at $\tau = 9.15$,[35] $Bu^t_2C{:}NSiX_3$ at $\tau = 8.84 - 8.92$,[39] $Bu^t_2C{:}NBXY$ at $\tau = 8.85 - 8.95$[16] etc.). This may arise from a combination of tertiary-butyl and iso-butyl signals since the n.m.r. signals for di-isobutylberyllium, $Bu^i_2Be$, are in the regions $\tau = 9.33$, $9.44$ ($CH_2$), $\tau = 8.75$, $8.85$ (Me) and $\tau = 7.80$ (CH)[116] although such a simple spectrum for $(Bu^t_2C{:}NBeBu^i)_2$ with relative intensities for the two peaks of 1:1 would be unexpected under such circumstances. The n.m.r. spectrum for the chloro derivative $(Bu^t_2C{:}NBeCl)_2$ is in accord with the proposed structure (Figure II.6(d)) of a symmetrical molecule having bridging methyleneamino groups.

For bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t_2C{:}N)_2Be]_2$ there are three n.m.r. signals, two of which have the appearance of an ill-resolved doublet ($\tau = 8.69$, $8.71$) and the other at $\tau = 8.77$, in relative intensities 1:1:2 respectively. None of these absorptions change position appreciably when the temperature is lowered from +40° to -60°

## TABLE II.5

### $^{1}$H n.m.r. spectra of the methyleneamino derivatives of beryllium

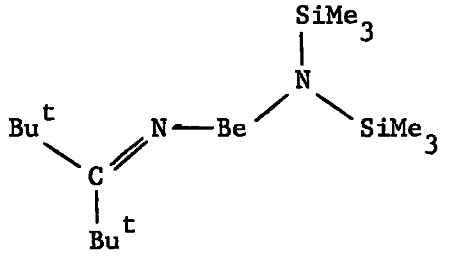
| Compound | Temperature | $\tau$ |
|---|---|---|
| $(Bu^t{}_2C{:}NBeCl)_2$ | +40° | 9.10 |
| $[(Bu^t{}_2C{:}N)_2Be]_2$ | +40° | 8.69(1), 8.71(1), 8.77(2) |
| | -60° | 8.68(1), 8.70(1), 8.77(2) |
| $LiBe(N{:}CBu^t{}_2)_3$ | +33° | 8.69(1), 8.99(1) |
| | -50° | 8.75(1), 9.13(1) both doublets |
| $(Bu^t{}_2C{:}NBeBu^i)_2$ | +33° | 8.69(1), 9.0(1) |
| $(Ph_2C{:}NBeBu^t)_2$ | +33° | 8.93 for Me in $Bu^t$ |
| $Bu^t{}_2C{:}NBeN(SiMe_3)_2$ | +40° | 8.60(2), 8.70(1), 8.75(1), 8.85(1), 9.0(1) for $Bu^t$<br>9.68(1), 9.73(2), 9.77(1), 9.80(1), 9.94(1) for $SiMe_3$ |

Spectra were recorded for saturated solutions in toluene using T.M.S. as internal reference

$\tau(Me_4Si)$ = 10.00 p.p.m. Relative intensities in parentheses.

which implies that either the methyleneamino groups arepermanently non-linear in a symmetrical molecule or that they are near linear, consistent with the i.r. data (see Chapter I for discussion). However, there must be some distortion in the dimer to give three peaks; the crystal structure, discussed later (see p.71), shows that the butyl groups on the terminal ligands are non-equivalent giving rise to the observed relative intensities.

The silyl derivative $Bu^t_2C{:}NBeN(SiMe_3)_2$ has a rather complex n.m.r. spectrum. The five signals between $\tau = 8.60$ and $9.00$ are quite separate from the other absorption region, $\tau = 9.68$ to $9.94$, and can be attributed to the methyl groups of the methyleneamino ligand. The spectrum is inconsistent with the structure (f) (Figure II.6) since with a linear C-N-Be-N skeleton only two signals would be observed, one for $Me(Bu^t)$ and the other $Me(SiMe_3)$. A structure that would produce such a complex spectrum could be as shown:-



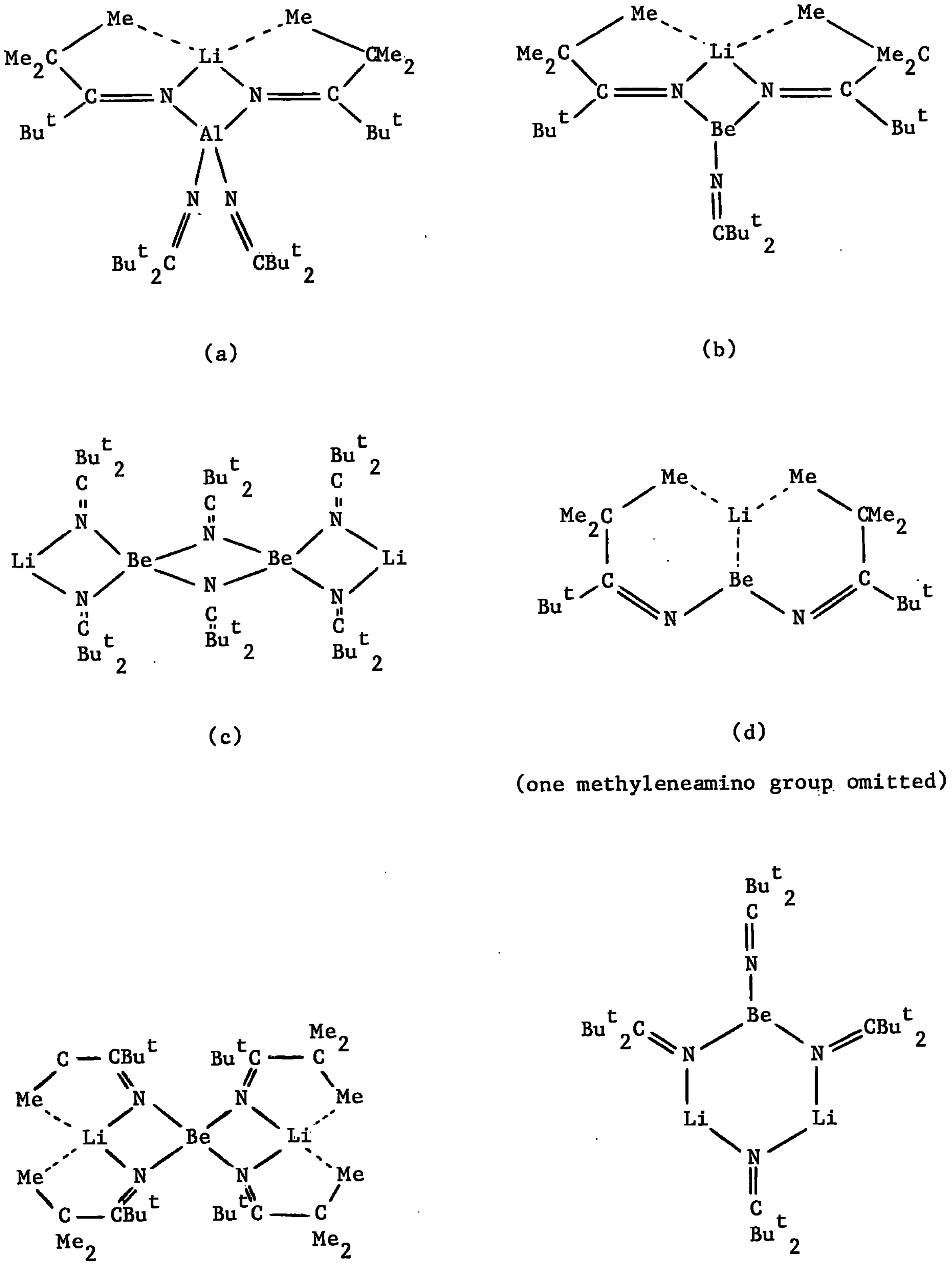
with either or both butyl and trimethylsilyl groups twisted out of the plane of the paper. Although this structure shows a non-linear C-N-Be skeleton, it is quite possible that only a slight deviation from linearity will produce the complex n.m.r. spectrum. Alternatively the total of ten signals may have arisen from a disproportionation reaction,

$$2Bu^t_2C{:}NBeN(SiMe_3)_2 \rightarrow \tfrac{1}{2}\,[(Bu^t_2C{:}N)_2Be]_2 \;+\; [(Me_3Si)_2N]_2Be$$

although this is rather unlikely when the $\tau$ values and relative intensities of the signals for the two methyleneamino compounds are compared.

Structures and reactions of organic ate-complexes, $M'_xM''R_y$ (M',M" are metals, R is the organic ligand) have been reviewed by Tochtermann[117] and more recent developments in lithio-beryllium chemistry by Coates and Morgan.[64] Only one metallate containing methyleneamino groups, namely lithium tetrakis(di-t-butylmethyleneamino) aluminate, $LiAl(N{:}CBu^t_2)_4$, has had its structure determined.[48] It contains an aluminium atom surrounded by a tetrahedral arrangement of methyleneamino groups, with two of these groups bridging the aluminium to the lithium. The structural data also show that there is probably Li•••H-C interaction (Figure II.7(a)). A similar structure can also be envisaged for $LiBe(N{:}CBu^t_2)_3$, with there being three co-ordinate beryllium, (Figure II.7(b)). This structure is somewhat inconsistent with the i.r. stretching frequencies of the azomethine group; by analogy with $[(Bu^t_2C{:}N)_2Be]_2$ which contains both bridging and terminal methyleneamino groups, then instead of one ν(C=N) absorption (at 1663cm$^{-1}$) there should be two at approximately 1630cm$^{-1}$ and 1720cm$^{-1}$. An alternative structure is shown in (c) which is similar to that proposed[64] for lithium triphenylberyllate, $LiBePh_3$.[118,119] Again, the i.r. spectrum shows only one ν(C=N) absorption where two are expected. Also, the n.m.r.

FIGURE II.7



(a)

(b)

(c)

(d)

(one methyleneamino group omitted)

(e)

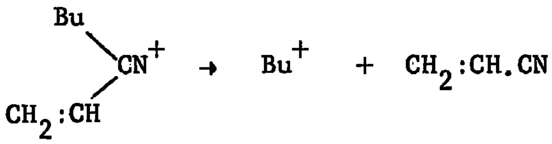
(f)

spectrum should have two signals of relative intensity 2:1 instead of the found ratio of 1:1 and lastly, the molecular weight measurements do not support such a structure. The structure shown in Figure II.7(d) with three nitrogen atoms and one lithium atom forming a tetrahedron about the beryllium would be appropriate for the spectroscopic data but the chance of the lithium being far from the electron rich set of three nitrogen atoms is exceedingly remote.

The dilithio beryllate derivative, $Li_2Be(N:CBu^t{}_2)_4$, probably has structure (e) (Figure II.7) which is seen to have a very similar structure to $LiAl(N:CBu^t{}_2)_4$. This tetrahedral array of ligands about the beryllium has also been observed in $Li_2BeMe_4$[103] and also its counterpart $Li_2ZnMe_4$.[120] In both examples the two lithium atoms can occupy two sets of positions but for steric reasons only one structure is favoured. The only evidence contrary to such a structure as (e) is the high ($1709cm^{-1}$) azomethine stretching frequency, in addition to that at $1660cm^{-1}$. A rather novel ring system is shown in Figure II.7(f) which contains three different methyleneamino groups, one of them being able to take up a linear Be-N-C conformation suitable to justify the high ($1709cm^{-1}$) absorption frequency.

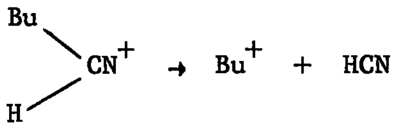
The mass spectra of these methyleneaminoberyllium derivatives are given in Tables II.6-II.12. Very little has been reported on the mass spectra of beryllium compounds and only one systematic study has recently been made.[121,122] For the alkyls $R_2Be$, it was found that the ionisation potentials decrease as the size of the organic group increases: $Me_2Be$ 10.67 (incidentally, this is the highest value measured for any organometallic compound), $Et_2Be$ 9.46, $Pr^n_2Be$ 8.71, $Pr^i_2Be$ 8.80 and $Bu^i{}_2Be$ 8.74 volts. As expected, the bond dissociation energy D(RBe-R), of the order 29-49 kcal. mole$^{-1}$ is less than the bond dissociation energy D[RBe(R-H)-H] which lies in the region 70-87 kcal. mole$^{-1}$. Accordingly, the largest abundances of ions found in the spectra of $R_2C{:}NBeX$ are the large fragments $R^+$, $RCNH^+$ and $R_2CN^+$. A common feature of the spectra of the di-t-butylmethyleneamino derivatives was the presence of two metastable peaks at $^{m}/\underline{e}$ 29.5 and 38.7. These two peaks can be attributed to the following breakdown patterns:

At 29.5



$$\left(\mathrm{Bu})(CH_2{:}CH)CN^+\right) \rightarrow Bu^+ + CH_2{:}CH.CN$$

At 38.7



$$(\mathrm{Bu})(\mathrm{H})CN^+ \rightarrow Bu^+ + HCN$$

The relative ease with which the butyl ion parts from the main fragment and its stability is evident by its large abundance in many of the spectra.

The first spectrum (Table II.6) gives the mass spectroscopic results for $(Ph_2C{:}NBeBu^i)_2$ and for $^{m}/\underline{e}$ > 100 all the identifiable peaks have been listed, to show the complexity of the possible intermediates. Beryllium

## TABLE II.6

## Mass Spectroscopic Results for $(Ph_2C{:}NBeBu^i)_2$

| m/e | Relative Intensity | Assignment (*doubly charged) |
|---|---|---|
| 492 | 0.1 | $(Ph_2CNBeBu)_2$ |
| 491 | 0.2 | $(Ph_2CNBeBu)_2$ minus H |
| 464 | trace | $(Ph_2CNBeBu)_2$ minus $C_2H_4$ |
| 462 | 0.2 | $(Ph_2CNBeBu)_2$ minus 2Me |
| 377 | 0.1 | $(Ph_2CNBeBu)_2$ minus $Bu_2H$ |
| 327 | 0.7 | $Ph_2CNBeBu.BuBeMe$ |
| 313 | 0.3 | $Ph_2CNBeBu.BuBeH$ |
| 256 | 0.5 | $Ph_2CNBeBu.BeH$ |
| 246 | 1 | $Ph_2CNBeBu$ |
| 237 | 1 | $Ph_2CNBu$ |
| 195 | 1 | $Ph_2CNMe$ |
| 194 | 3 | $Ph_2CNMe$ minus H |
| 190 | 0.6 | $Ph_2CNBeH$ |
| 189 | 0.4 | $Ph_2CNBe$ |
| 183 | 5 | $Ph_2CNH_3$ |
| 182 | 16 | $Ph_2CNH_2$ |
| 181 | 57 | $Ph_2CNH$ |
| 180 | <u>100</u> | $Ph_2CN$ |
| 169 | 0.2 | PhCNBeBu |
| 160 | 0.3 | PhCNBe |
| 154 | 2 | PhCNBeBu minus Me <u>or</u> $Ph_2$ |
| 153 | 4 | $Ph_2$-H |
| 143 | 0.2 | PhBeBu |
| 139 | 1 | PhCNBeBu minus 2Me |
| 127 | 2 | PhCNBeMe |
| 119 | 1 | PhCNHMe |
| 118 | 0.2 | PhCNMe |
| 113 | 0.9 | PhCNBeH |

contd./

Table II.6 contd.

| m/e | Relative Intensity | Assignment (*doubly charged) |
|---|---|---|
| 106 | 15 | $PhCNH_3$ |
| 105 | 20 | $PhCNH_2$ |
| 104 | 79 | PhCNH |
| 103 | 7 | PhCN |
| 101 | 1 | PhBeMe |
| 78 | 40 | PhH |
| 77 | 72 | Ph |
| 69.5 | 0.3 | *PhCNBeBu minus 2Me |
| 66 | 0.3 | BuBe |
| 65 | 7 | BuBe minus H |
| 63.5 | 0.2 | *PhCNBeMe |
| 57 | 7 | Bu |
| 52 | 14 | BuBeH minus Me |
| 51 | 43 | BuBe minus Me |
| 36 | 0.5 | BuBe minus 2Me |
| 25.5 | 0.1 | *BuBe minus Me |
| 25 | 0.6 | MeBeH |

is mono-isotopic so that for $^{m}/_{e} < 100$ the task of recognising beryllium containing species is made difficult by the presence of organic residues; a few suggestions have been made, however. The results for $(Ph_2C{:}NBeBu^{i})_2$ show that in the gas phase the dimer is rather unstable with respect to disproportionation whereas for $(Bu^{t}{}_2C{:}NBeBu^{i})_2$ (Table II.7) various $Be_2$ species exist in comparatively high abundances. Both dimers give beryllium hydride fragments, presumably from the breakdown of $BeBu^{i}$ as in $Bu^{i}{}_2Be$.[122] The main difference between the two compounds is the loss of $R_2CN$, RCN and R; for R=Ph, loss of $Ph_2CN$ is relatively important (intensities 100, 7, 72 respectively) but whe $R = Bu^{t}$ the reverse holds (intensities 1,100,100 respectively).

The mass spectroscopic results for the dimers $(Bu^{t}{}_2C{:}NBeCl)_2$ and $[(Bu^{t}{}_2C{:}N)_2Be]_2$ are given in Tables II.8 and II.9. Both these compounds fail to exhibit a parent peak in the mass spectrum and the most abundant fragments do not contain beryllium, particularly in the case of the former. Of interest is the presence of $Bu_2CNBeBu$ species in both spectra. The bismethyleneamino derivative was prepared from di-isobutylberyllium, $Bu^{i}{}_2Be$, so that it may be possible for there to be some $(Bu^{t}{}_2CNBeBu^{i})_2$ in the sample. However, the chloro-derivative also shows the presence of $Bu_2CNBeBu$ which can only arise from "scrambling" of butyl and chloro groups.

The mass spectroscopic results for the two lithium-beryllium compounds are presented in Tables II.10 and II.11. Both spectra provide evidence for the existence of $LiBe(N{:}CBu^{t}{}_2)_3$ and $Li_2Be(N{:}CBu^{t}{}_2)_4$ even in the vapour state, although in the case of the latter compound the abundance of fragments with $^{m}/_{e} > 150$ was extremely low.

## TABLE II.7

### Mass spectroscopic results for $(Bu^t_2C:NBeBu^i)_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 412 | 0.1 | $(Bu_2CNBeBu)_2$ |
| 397 | 0.1 | $(Bu_2CNBeBu)_2$ minus Me |
| 356 | 6 | $(Bu_2CNBeBu)_2$ minus $C_2H_8$ |
| 355 | 19 | $(Bu_2CNBeBu)_2$minus Bu |
| 300 | 5 | $(Bu_2CNBeH)_2$ |
| 297 | 4 | $(Bu_2CNBe)_2$ minus H |
| 288 | 0.2 | $(Bu_2CN)_2Be$ minus H |
| 281 | 0.2 | $(Bu_2CN)_2H$ |
| 272 | 2.5 | $(Bu_2CNBeBu)_2$ minus $Bu_2CN$ |
| 232 | 1 | $(Bu_2CN)_2Be$ minus Bu |
| 207 | 2 | $Bu_2CNBeBuH$ |
| 191 | 0.2 | $Bu_2CNBeBu$ minus Me |
| 176 | 2 | $Bu_2CNBeBu$ minus 2Me |
| 149 | 9 | $Bu_2CNBe$ |
| 141 | 6 | $Bu_2CNH$ |
| 140 | 1 | $Bu_2CN$ |
| 126 | 17 | $Bu_2CNH$ minus Me |
| 123 | 0.2 | $Bu_2Be$ |
| 107 | 16 | BuCNBeMe |
| 83 | 100 | BuCN |
| 57 | 100 | Bu |
| 51 | 11 | BuBe minus Me |
| 25.5 | 0.4 | *BuBe minus Me |

* doubly charged

Metastable peaks at 29.5 and 38.7

## TABLE II.8

## Mass spectroscopic results for $(Bu^t_2C:NBeCl)_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 281 | 1 | $(Bu_2CN)_2H$ |
| 232,230,228 | 0.02, 0.1, 0.18 | $Bu_2CNBe_2Cl_2$ |
| 207 | 3 | $Bu_2CNBeBu$ |
| 187,185 | 0.2,0.6 | $Bu_2CNBeClH$ |
| 171,169 | 0.1,0.3 | $Bu_2CNBeCl$ minus Me |
| 149 | 0.2 | $Bu_2CNBe$ |
| 142 | 1 | $Bu_2CNH_2$ |
| 141 | 2 | $Bu_2CNH$ |
| 140 | 0.3 | $Bu_2CN$ |
| 126 | 10 | $Bu_2CNH$ minus Me |
| 84 | 84 | BuCNH |
| 57 | <u>100</u> | Bu |
| 38,36 | 11,34 | HCl |
| 37,35 | 2,6 | Cl |

Metastable peaks at 29.5 and 38.7

## TABLE II.9

Mass spectroscopic results for $[(Bu^t{}_2C{:}N)_2Be]_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 464 | 0.1 | $[(Bu_2CN)_2Be]_2$ minus 2Bu |
| 355 | 0.1 | $(Bu_2CN)_2Be_2Bu$ |
| 316 | 0.3 | $(Bu_2CN)_2Be,HCN$ |
| 288 | 0.2 | $(Bu_2CN)_2Be$ minus H |
| 282 | 0.4 | $(Bu_2CNH)_2$ |
| 273 | 0.7 | $(Bu_2CN)_2Be$ minus MeH |
| 259 | 0.2 | $(Bu_2CN)_2Be$ minus 2Me |
| 232 | 0.2 | $(Bu_2CN)_2Be$ minus Bu |
| 207 | 0.4 | $Bu_2CNBeBu,H$ |
| 191 | 0.4 | $Bu_2CNBeBu$ minus Me |
| 176 | 0.2 | $Bu_2CNBeBu$ minus 2Me |
| 149 | 0.7 | $Bu_2CNBe$ |
| 142 | 1 | $Bu_2CNH_2$ |
| 141 | 9 | $Bu_2CNH$ |
| 140 | 1 | $Bu_2CN$ |
| 135 | 1 | $Bu_2CNBe$ minus $CH_2$ |
| 127 | 4 | $Bu_2CNH_2$ minus Me |
| 126 | 35 | $Bu_2CNH$ minus Me |
| 125 | 1 | $Bu_2CN$ minus Me |
| 93 | 2 | $Bu_2CNBe$ minus $C_4H_8$ |
| 84 | 100 | BuCNH |
| 66 | 2 | BuBe |
| 57 | 100 | Bu |
| 41 | 66 | MeCN |

Metastable Peaks at 29.5 and 38.7

## TABLE II.10

Mass spectroscopic results for $LiBe(N{:}CBu^t{}_2)_3$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 429 | 1 | $(Bu_2CN)_3Be$ |
| 355 | 3 | $(Bu_2CN)_2Be_2Bu$ |
| 281 | 2 | $(Bu_2CN)_2H$ |
| 232 | 0.5 | $(Bu_2CN)_2Be$ minus Bu |
| 207 | 0.5 | $Bu_2CNBeBu,H$ |
| 149 | 0.8 | $Bu_2CNBe$ |
| 147 | 1 | $Bu_2CNLi$ |
| 142 | 2 | $Bu_2CNH_2$ |
| 141 | 3 | $Bu_2CNH$ |
| 140 | 1 | $Bu_2CN$ |
| 135 | 1 | $Bu_2CNBe$ minus $CH_2$ |
| 134 | 0.3 | $Bu_2CNBe$ minus Me |
| 127 | 1 | $Bu_2CNH_2$ minus Me |
| 126 | 2 | $Bu_2CNH$ minus Me |
| 93 | 1 | $Bu_2CNBu$ minus $C_4H_8$ |
| 84 | 21 | BuCNH |
| 57 | 100 | Bu |
| 41 | 9 | MeCN |

Metastable Peaks at 29.5 and 38.7

## TABLE II.11

### Mass spectroscopic results for $Li_2Be(N:CBu^t_2)_4$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 576 | 0.2 | $LiBe(NCBu_2)_4$ |
| 526 | 0.1 | $Li_2Be(NCBu_2)_4$ minus Bu |
| 500 | 0.1 | $Li_2Be(NCBu_2)_4$ minus BuCN |
| 429 | 0.5 | $(Bu_2CN)_3Be$ |
| 281 | 1.4 | $(Bu_2CN)_2H$ |
| 149 | 1.5 | $Bu_2CNBe$ |
| 147 | 1 | $Bu_2CNLi$ |
| 57 | 1000 | Bu |

Metastable peaks at 29.5 and 38.7

## TABLE II.12

### Mass spectroscopic results for $Bu^t_2C:NBeN(SiMe_3)_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 299 | 0.1 | $Bu_2CN.N(SiMe_3)_2$ minus H |
| 294 | 0.2 | $Bu_2CNBeN(SiMe_3)_2$ minus $CH_2$ |
| 281 | 0.2 | $(Bu_2CN)_2H$ |
| 222 | 0.7 | $Bu_2CNBeSiMe_3$ |
| 221 | 1 | $Bu_2CNBeSiMe_3$ minus H |
| 220 | 1 | $Bu_2CNBeSiMe_3$ minus 2H |
| 161 | 2 | $(Me_3Si)_2NH$ |
| 160 | 0.2 | $(Me_3Si)_2N$ |
| 149 | 2 | $Bu_2CNBe$ |
| 148 | 4 | $Bu_2CNBe$ minus H |
| 146 | 100 | $(Me_3Si)_2NH$ minus Me |
| 141 | 0.5 | $Bu_2CNH$ |
| 130 | 6 | $(Me_3Si)_2N$ minus 2Me |
| 126 | 1 | $Bu_2CNH$ minus Me |
| 84 | 11 | BuCNH |
| 73 | 4 | $BuNH_2$ or $Me_3Si$ |
| 57 | 13 | Bu |

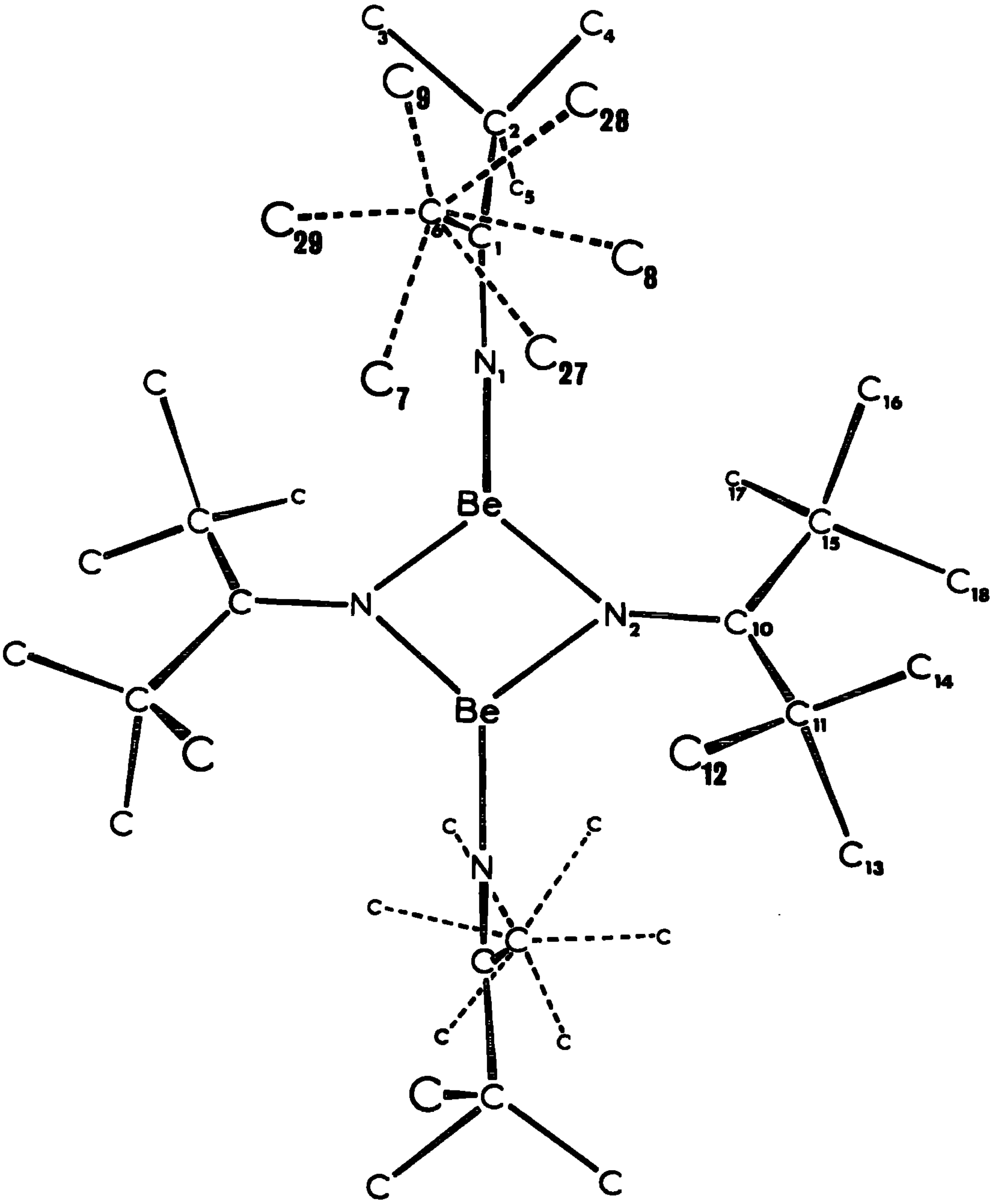
Table II.12 gives the mass spectroscopic details for the monomer $Bu^t_2C{:}NBeN(SiMe_3)_2$. There is no peak higher than its molecular weight and considering its volatility, the results confirm its monomeric nature. Not unexpectedly, there is a greater abundance of $(Me_3Si)_2NH$ than $Bu^t_2C{:}NH$; silicon containing fragments were generally more common. Again some "scrambling" appears to have taken place with the presence of Be-$SiMe_3$ units although Be-Bu units were absent.

## The Crystal Structure of Bis(di-t-butylmethyleneamino)beryllium,[51] $[(Bu^t_2C{:}N)_2Be]_2$.

Crystals of $[(Bu^t_2C{:}N)_2Be]_2$ were prepared in the manner described and analysed by X-ray diffraction by J.D. Sowerby and H.M.M. Shearer. On the basis of its molecular weight and infra-red spectrum it was assigned a molecular structure consisting of a four membered $(BeN)_2$ ring which is confirmed by this crystallographic study (Figure II.8). Table II.13 gives some selected bond angles and bond distances.

A comparison of the parameters shows that N(2), C(10), C(11) and C(15) are coplanar, as are Be, N(1), C(1), C(2), and C(6). The atom C(10) is in the same plane as $(BeN)_2$ but the bridging methyleneamino group consisting of N(2), C(10), C(11) and C(15) is twisted out of this central plane, the dihedral angle being 37°. Further distortion occurs in the terminal methyleneamino group where Be-N(1) and N(1)-C(1) are bent progressively away from the $(BeN)_2$ plane (Figure II.9) in two stages, Be'-Be-N(1) is 160.7° and Be-N(1)-C(1) is 160.5°. It is this distortion that gives rise to the observed n.m.r. spectrum in which there are three

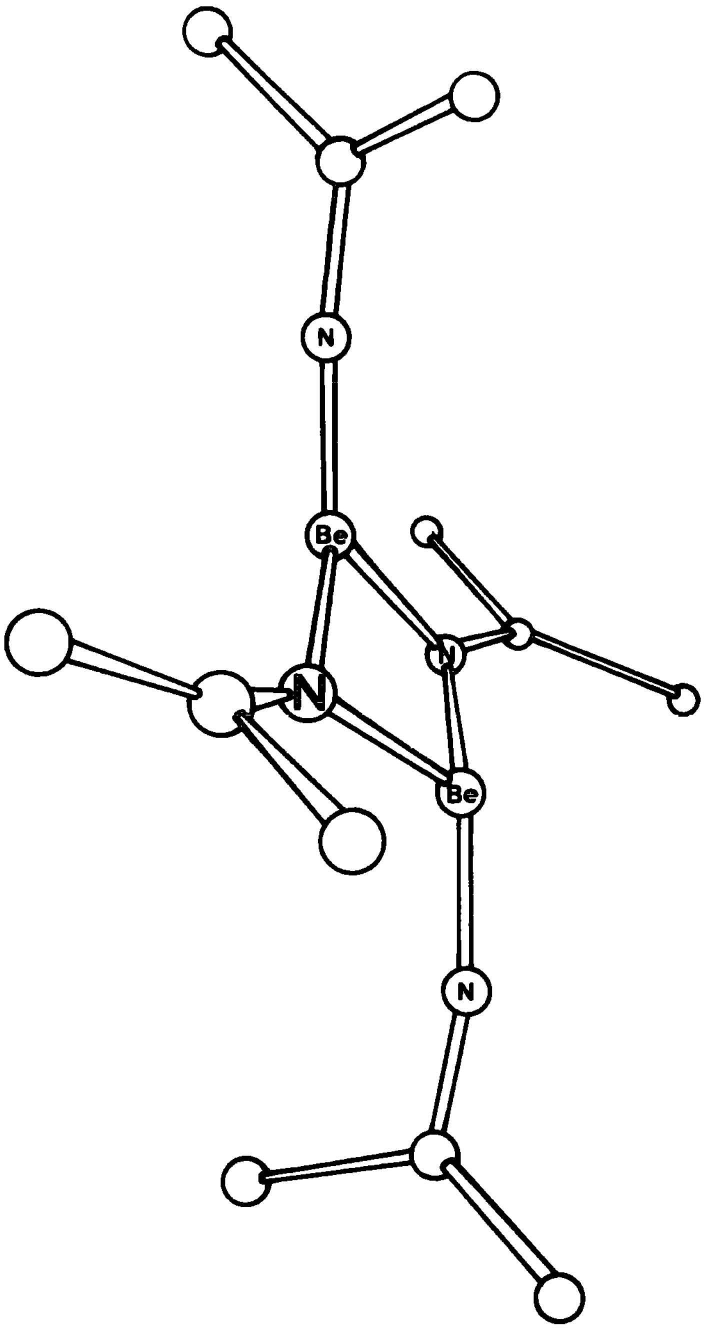
"TABLE II.13 overleaf"



$[(Bu^t_2C{:}N)_2Be]_2$

Numbering of the Atoms

FIGURE II.8



$[(Bu^t_2C{:}N)_2Be]_2$

Central portion of the molecule

FIGURE II.9

peaks of relative intensity 1:1:2. It is seen (Figure II.9) that the two butyl groups on the terminal ligand are non-equivalent and may be expected to give two signals in the $^1H$ n.m.r. The bridging ligands are equivalent through the centre of symmetry. Hence the predicted signal ratio is 1:1:2.

The two C=N bond lengths of 1.27 and 1.28Å fall well in the range of other methyleneamino derivatives (Table I.5) and are nearly identical despite the difference in the co-ordination number of the nitrogens. The ring angle at N(2) of 83.1° is consistent with other Be-N-Be angles (Table II.14) but is markedly different from the corresponding values for $(Me_2AlN{:}CMeBu^t)_2$,[17] $(Ph_2AlN{:}CPh.C_6H_4Br)_2$[18] and $(Me_2BN{:}CMeH)_2$[17] of 94.6°, 97.1° and 93.5° respectively. The relatively large angle (96.9°) at the beryllium atoms in this structure may arise through the fact that beryllium, being of low atomic number, is less tolerant of deformation of valence angles away from the values expected for the particular hybridisation state adopted than atoms of higher atomic numbers (a review of bridging angles in $M_2X_2$ species is found in Ref. 126).

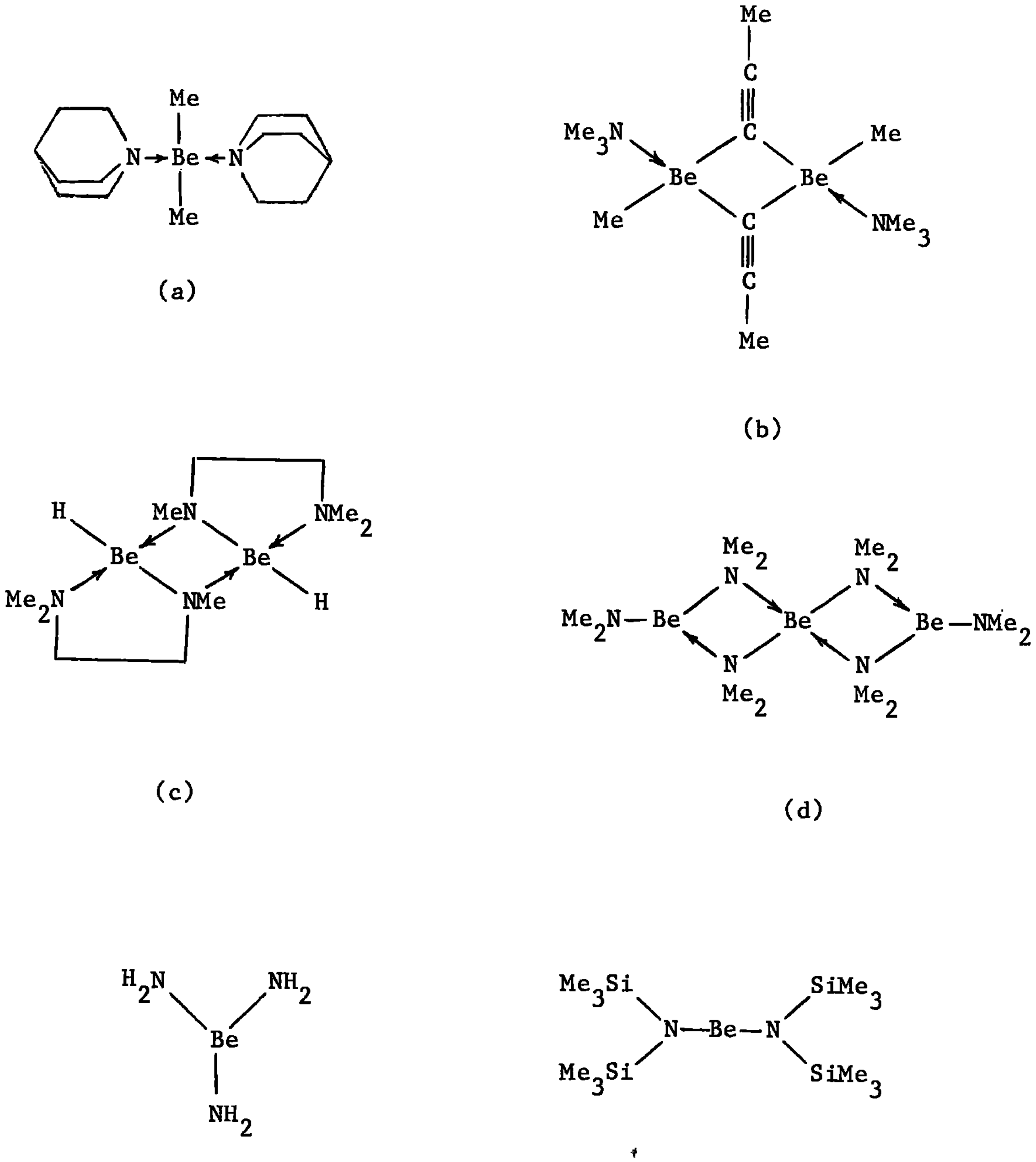
The Be-N (terminal) bond length of 1.50Å is the shortest known and is indicative of substantial $(p \rightarrow p)$ N $\rightleftharpoons$ Be dative π-bonding. From beryllium structures known, a length between 1.50 and 1.60Å is appropriate for such bonding. In $[(Me_2N)_2Be]_3$ this distance is 1.57Å for the terminal nitrogen and the Be,N and C(Me) atoms are coplanar;[95] for $[(Me_3Si)_2N]_2Be$ it is 1.56Å [85] and finally for $Be(NH_2)_3^-$ this distance is 1.59Å.[97] Another comparison can be made between the Be-N (bridging) distances of $[(Bu^t{}_2C{:}N)_2Be]_2$ and $[(Me_2N)_2Be]_3$; the former is 1.68Å and the latter 1.65Å. The Be-N(1)-C(1) angle of 160.5° is less than 180°, the angle appropriate for maximum overlap of beryllium and nitrogen p-orbitals, but such a distortion from linearity is necessary to accommodate all the tertiary butyl groups. Table II.14 shows the effect of the co-ordination numbers of beryllium and nitrogen on the Be-N bond length (molecular structures of these compounds are shown in Figure II.10); it is seen that as the co-ordination numbers of beryllium and nitrogen fall, the Be-N bond distances also decrease. This is consistent with the idea that the beryllium atom, when not co-ordinatively saturated, allows $p_\pi$-$p_\pi$ bonding from the nitrogen. Also, as the degree of 's' character of the hybrid increases (changing from $sp^3$ to $sp^2$ to sp), the strength of the bond through effective overlap increases, thus shortening the Be-N bond distance.

There are only two distances between the methyl carbons of neighbouring methyleneamino groups that are less than 4Å. These are C(13)-C(29) and C(16)-C(8') whose values are 3.93 and 3.76Å. One of the reasons put forward why some beryllium compounds oligomerize rather than polymerise is the steric hindrance between ligands. In $[(Me_2N)_2Be]_3$ the smallest non-bonded methyl-methyl distance is 3.11Å (see Figure II.2).[95] In a higher oligomer, this distance would need to be shorter still, and the crowding would be excessive. However, bis(dimethylamino)magnesium[96] can accommodate the strain and is a polymer. Another effect caused by nearness of ligands is observed in $Me_2Be(quinuclidine)_2$ where the Me-Be-Me angle is 118°.[123] This is somewhat large but can be explained by considering Me-Me interactions - the C-C distance is 3.14Å. (NB however,

### TABLE II.14

### Structural Data for some beryllium-nitrogen compounds

| Compound | (Be-N)Å | Co-ord. numbers Be | Co-ord. numbers N | Angle N-Be-N | Angle Be-N-Be | Reference |
|---|---|---|---|---|---|---|
| $Me_2Be(quinuclidine)_2$ | 1.91 | 4 | 4 | 111° | - | 123 |
| $(MeBeC{:}CMe,NMe_3)_2$ | 1.81 | 4 | 4 | - | - | 124 |
| $[HBeN(Me)C_2H_4NMe_2]_2$ | 1.75 | 4 | 4 | 97° | 83.1° | 125 |
| $[(Me_2N)_2Be]_3$ | 1.78 | 4 | 4 | 91° | 83.9° | 95 |
| " | 1.65 | 3 | 4 | 101° | 83.9° | 95 |
| " | 1.57 | 3 | 3 | 130° | - | 95 |
| $[(Bu^t{}_2C{:}N)_2Be]_2$ | 1.68 | 3 | 3 | 97° | 83.1° | 51 |
| " | 1.50 | 3 | 2 | 129° |  | 51 |
| $KBe(NH_2)_3$ | 1.59 | 3 | 3 | 120° | - | 97 |
| $[(Me_3Si)_2N]_2Be$ | 1.56 | 2 | 3 | 180° | - | 85 |



(a) (b) (c) (d) (e) (f)

Figure II.10

Molecular configurations of beryllium-nitrogen compounds the magnesium analogue[127] has a Me-Mg-Me angle of 129Å!). This kind of steric effect has obviously caused both the bridging and terminal methyleneamino groups to distort in a manner which minimises any strain in the molecule.

## Summary of the methyleneamino derivatives of beryllium.

Eight new di-alkyl- and di-aryl-methyleneamino compounds of beryllium have been prepared. Five of them, $(Bu^t{}_2C{:}NBeCl)_2$, $[(Bu^t{}_2C{:}N)_2Be]_2$, $(Bu^t{}_2C{:}NBeBu^i)_2$, $(Ph_2C{:}NBeBu^i)_2$ and $(Ph_2C{:}NBeBu^t)_2$ are dimers with four membered $(BeN)_2$ rings. A new monomeric two co-ordinate beryllium compound, $Bu^t{}_2C{:}NBeN(SiMe_3)_2$, is believed to have a near linear C:N.Be bond on the basis of its infra-red spectrum. The crystal structure of $[(Bu^t{}_2C{:}N)_2Be]_2$ shows that the terminal CNBe unit is nearly linear and that the Be-N bond is short, appropriate for (p → p) N → Be multiple bonding. The structure determination supports the postulate that a high azomethine stretching frequency, ν(C=N), is indicative of a linear CNBe unit and Be-N multiple bonding. For beryllium, the frequency ranges are 1608-1648cm$^{-1}$ for bridging methyleneamino groups and 1721-1747cm$^{-1}$ for terminal ligands. Two lithium beryllates, $LiBe(N{:}CBu^t{}_2)_3$ and $Li_2Be(N{:}CBu^t{}_2)_4$, were prepared but their structures are in doubt owing to a conflict in the spectroscopic data.

These new compounds and other reported[19] beryllium derivatives are listed in Table II.15.

## TABLE II.15

### Methyleneamino derivatives of Beryllium

| Compound | ν(C=N) bridging ($cm^{-1}$) | ν(C=N=Be) terminal ($cm^{-1}$) | Reference |
|---|---|---|---|
| $(Ph_2C{:}NBeCl)_2$ | 1608 | - | 19 |
| $[(p\text{-}tolyl)_2C{:}NBeCl]_2$ | 1610 | - | 19 |
| $[(p\text{-}tolyl)Bu^tC{:}NBeCl]_2$ | 1614 | - | 19 |
| $(Bu^tC{:}NBeCl)_2$ | 1626 | - | a |
| $[(Ph_2C{:}N)_2Be]_n$ | 1627 | 1732 | 19 |
| $[\{(p\text{-}tolyl)_2C{:}N\}_2Be]_3$ | 1626 | 1731 | 19 |
| $[\{(p\text{-}tolyl)Bu^tC{:}N\}_2Be]_2$ | 1637 | 1739 | 19 |
| $[(Bu^t{}_2C{:}N)_2Be]_2$ | 1631 | 1721 | a |
| $(Bu^t{}_2C{:}NBeBu^i)_2$ | 1635 | - | a |
| $(Ph_2C{:}NBeBu^i)_2$ | 1610 | - | a |
| $(Ph_2C{:}NBeBu^t)_2$ | 1648 | - | a |
| $Bu^t{}_2C{:}NBeN(SiMe_3)_2$ | - | 1734,1747 | a |
| $LiBe(N{:}CBu^t{}_2)_3$ | 1663 | | a |
| $Li_2Be(N{:}CBu^t{}_2)_4$ | 1660,1709 | | a |

i.r. recorded as Nujol mulls.

a. this work.

# CHAPTER III

# METHYLENEAMINO DERIVATIVES OF ZINC

This chapter describes the preparation and properties of dimeric di-t-butylmethyleneaminozinc chloride, $(Bu^t_2C{:}NZnCl)_2$, dimeric bis(di-t-butylmethyleneamino)zinc, $[(Bu^t_2C{:}N)_2Zn]_2$, and dimeric methyl(di-t-butylmethyleneamino)zinc, $(Bu^t_2C{:}NZnMe)_2$. Features of their infra-red and nuclear magnetic resonance spectra are discussed and related to corresponding beryllium derivatives. The attempted preparation of $LiZn(N{:}CBu^t_2)_3$ is also described.

## EXPERIMENTAL SECTION

### Starting Materials

Zinc chloride was obtained commercially and used without further purification. Dimethylzinc was a gift from Dr. D. Ridley. t-Butyl cyanide and t-butyl-lithium (approx. 2M in pentane) were obtained commercially and di-t-butylmethyleneamine was prepared by the methanolysis of di-t-butylmethyleneaminolithium.[21]

All materials throughout were handled under dry nitrogen or in vacuo.

### Preparation of Di-t-butylmethyleneaminozinc chloride, $(Bu^t_2C{:}NZnCl)_2$

A solution of di-t-butylmethyleneaminolithium was prepared by adding t-butyl-lithium (10 ml. of a 1.96M solution in pentane, 19.6 mmole) to a frozen ($-196^o$) solution of t-butyl cyanide (1.63 g., 19.7 mmole) in pentane (40 ml.). After stirring for 30 min. at room temperature, this mixture was added to a frozen solution of zinc chloride (2.69 g., 19.7 mmole) in ether (50 ml.). On warming to room temperature, a white precipitate formed and left a dirty yellow solution. The mixture was stirred overnight, the solvent pumped away and the white precipitate of lithium chloride was separated by filtration in hot toluene. The residual yellow solid after recrystallisation from toluene-hexane was identified as dimeric di-t-butylmethyleneaminozinc chloride, $(Bu^t_2C:NZnCl)_2$, (Found: C,43.9; H,7.4; Cl,14.2; N,5.6; Zn,26.5%; M,491. $C_{18}H_{36}Cl_2N_2Zn_2$ requires C,44.9; H,7.5; Cl,14.8; N,5.8; Zn,27.0%; M,481); $\nu_{max}$ (Nujol mull) 1608s, 1597s, 1266s, 1242w, 1205w, 1096m, 1055m, 1024m, 976w, 937w,br, 873m, 847vw, 803s, 729w, 694vw, 600vw,br and 505vw,br $cm^{-1}$.

Preparation of dimeric Bis(di-t-butylmethyleneamino)zinc, $[(Bu^t_2C:N)_2Zn]_2$

Di-t-butylmethyleneaminolithium (2.94 g., 20 mmole) in hexane (40 ml.) was added to a frozen solution of zinc chloride (1.36 g., 10 mmole) in ether (40 ml.). After stirring at room temperature for six hours, the precipitated lithium chloride was separated by filtration in hot toluene. The pale yellow solution afforded crystals which were identified as dimeric bis(di-t-butylmethyleneamino)zinc, $[(Bu^t_2C:N)_2Zn]_2$, m.p. 158-160° decomp. (Found: H,10.7; N,8.0; Zn,20.0%; M,685. $C_{36}H_{72}N_4Zn_2$ requires H,10.4; N,8.1; Zn,18.8%; M,690); $\nu_{max}$ (Nujol mull) 1683vs, 1608sh, 1594sh, 1585vs, 1330w, 1271w, 1218s, 1089w, 1047m, 1038sh, 970m, 958s, 945s, 879w, 827w, 800w, 722w, 704w, 678vw, 671vw, 662m, 603m, 592sh, 562w,br and 471m,br $cm^{-1}$.

Preparation of Di-t-butylmethyleneamino-methylzinc, $(Bu^t_2C:NZnMe)_2$

Dimethylzinc (1.9 g., 20 mmole) was condensed on di-t-butylmethyleneamine (2.82 g., 20 mmole) at -196° and the mixture allowed to attain room temperature. There was no visible evolution of gas even when the solution was refluxed at 35° in pentane (30 ml.) for 6 hr. The solution was concentrated by removal of solvent under vacuum, whereupon pale yellow crystals were deposited and identified as di-t-butylmethyleneaminomethylzinc, $(Bu^t{}_2C{:}NZnMe)_2$, m.p. 67-69° decomp. (Found: C,54.5; H,9.8; N,6.6; Zn,28.8%; M,430. $C_{20}H_{22}N_2Zn_2$ requires C,54.5; H,9.5; N,6.4; Zn,29.5%; M,440); $\nu_{max}$ (Nujol mull) 1592vs, 1325w, 1264m, 1220sh, 1212s, 1160s, 1095w, 1036vs, 961vs, 935w, 881s, 845w, 833vw, 807m, 792m, 727m, 721sh, 671sh, 667s, 639s, 600m, 568w, 545w, 514vs and 482w,br $cm^{-1}$.

Reaction of Di-t-butylmethyleneamine with Dimethylzinc (2:1 molar equivalents)

Dimethylzinc (0.95 g., 10 mmole) was condensed on di-t-butylmethyleneamine (2.82 g., 20 mmole) at -196° and the procedure used for obtaining a product was the same as in the previous experiment. On the basis of its infra-red spectrum, the crystalline product obtained was identified as bis(di-t-butylmethyleneamino)zinc, $[(Bu^t{}_2C{:}N)_2Zn]_2$.

Reaction of Di-t-butylmethyleneaminolithium with Zinc Chloride (3:1 molar equivalents - attempted synthesis of $LiZn(N{:}CBu^t{}_2)_3$)

Di-t-butylmethyleneaminolithium (3 molar equiv.) was added to zinc chloride (1 molar equivalent) in ether at -196°. A white precipitate formed as the mixture warmed to room temperature and after stirring overnight, the solvent was replaced by toluene-hexane and refluxed at 80°. Filtration yielded a colourless solution which contained products of no fixed composition: carbon content varied between 30 and 40% and there was no sign of lithium.

## DISCUSSION

The organometallic chemistry of zinc is in many ways comparable with that of magnesium and beryllium, although as zinc has a higher electronegativity value (Zn 1.66, Be 1.47, Mg 1.23[108]) its organo derivatives are less reactive than the derivatives of the other metals. The first observable difference is in the state of association of the dialkyls, $Me_2M$ (M = Be,Mg,Zn). Dimethylberyllium is a polymer[129] as is dimethylmagnesium[130] but dimethylzinc is monomeric. It has been suggested[131] that if $Me_2Zn$ were to associate then the expected acute bridge angle, Zn-C-Zn, would lead to a very short Zn-Zn distance and serious inner core repulsions. All the dialkyl- and diaryl-zinc compounds known to date are monomeric, dimethylzinc being one of the most volatile organometallic compounds (B.p. 44.0° [132,133]).

The literature on organozinc compounds is rather scattered; pre-1967 work can be found in Ref.134, reviews for 1969-1970 in Refs.135 and 136; Organometallic Chemistry Reviews cover the intermediate years. Much attention has focussed on the co-ordination chemistry of zinc[137-145] and its synthetic uses in the well established Reformatsky reaction. Zinc forms relatively unstable complexes with sulphides, phosphines and arsines, although if the metal if bonded to relatively electron attracting groups then its acceptor character is enhanced. Thus dibutylzinc does not complex with triphenylphosphine but bispentafluorophenyl zinc gives $(C_6F_5)_2Zn(PPh_3)_2$.[145] With tertiary amines, dimethylzinc affords the complexes $Me_2Zn.NMe_3$, $Me_2Zn(NMe_3)_2$ and $Me_2Zn.(NEt_3)_2$ having boiling points 84°, 84.5° and 95° respectively.[139] The complex $Me_2Zn.(NMe_3)_2$ is believed to dissociate into the 1:1 complex at its boiling point, as it does when dissolved in benzene. The triethylamine and pyridine 1:2 adducts dissociate in benzene solution yielding the amine and the 1:1 complex.[139]

There have been several studies into the formation of chelate complexes, $R_2Zn.Ch$, where R ranges from $CH_3$. to $C_9H_{19}$. and Ch = 2,2'-bipyridyl,[139,142-144,146,147] N,N,N',N'-tetramethylethylenediamine,[145,147] 1,10-phenanthroline[139,142,146] quinoline,[140] isoquinoline[140] and N,N,N',N'-tetraethylethylenediamine.[139,142] Of interest is the colour of the bipyridyl and phenanthroline complexes;[143,146] the colour of these complexes was found to depend on the electronegativity of the alkyl group and it has been suggested that the absorption spectra are due to a charge transfer process involving donation of electrons from the $ZnR_2$ group into the lowest unoccupied orbitals of the ligand. Participation of the zinc "3d" orbitals is believed to play an important role as the intensity of the charge-transfer band increases with increasing electronegativity of the alkyl group, R, unlike the analogous beryllium compounds.

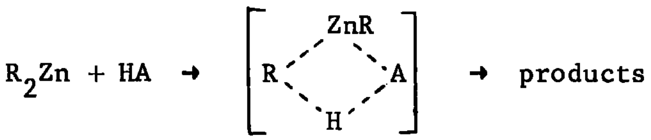
The influence of π-bonding on the stability of the adducts $R_2Zn.bipy$ has been investigated using a dielectric constant titration technique.[147] The stabilities of such compounds, where R = Me, Et, $Pr^i$, $Bu^n$, $Bu^i$ and $Bu^t$, were compared with corresponding $R_2Zn.TMED$ derivatives. It was found that for the TMED complexes, the order of stability was Me > Et > $Pr^i$ > $Bu^t$ which is to be expected either on steric grounds, or if electron releasing alkyl groups weakened the co-ordinate bonds between zinc and the TMED (this ligand has a pure σ-bond function only). On the other hand, the reverse order of stability holds for the bipyridyl complexes, i.e. $Bu^t$ > $Pr^i$ > Et > Me which can be attributed to a (σ-π) synergic effect which will be more pronounced for $Bu^t$ than for lower alkyl groups.

Recent studies on the effect of zinc 3d-orbital participation in chemical reactions have been made on the $R_2Zn$/donor solvent/secondary amine systems.[148,149] In the reaction between $R_2Zn$ and diphenylamine,[148] it was found that the rate of reaction (to give $RZnNPh_2$) was accelerated by the presence of bipyridyl or pyridine, but with dimethoxyethane, tetrahydrofuran, TMED, etc., there was no effect. The reason given for this was the back donation from zinc 3d-orbitals to complexing agents having conjugated structures, thus making the zinc relatively more electropositive and able to react with the acidic donor, $Ph_2NH$, more easily. The more recent investigation[149] looked into the reaction between diethylzinc and $Pr^n{}_2NH$, $Ph_2NH$, pyrrole, indole and carbazole. The conclusion drawn from the results was that the reactivity of diethylzinc towards amines must be dependent upon three factors: (i) the acidity of the N-H bond of the amine, (ii) the nucleophilicity of the Et-Zn bond, and (iii) the co-ordination of the amine to zinc.

The chemistry of mono-organozinc compounds, RZnX, is probably the most active area of research. These are easily prepared by the acidolysis of the dialkyl- or diaryl-zinc:

$$R_2Zn + HA \rightarrow \frac{1}{n}(RZnA)_n + RH$$

The mechanism of this reaction has been investigated[150] and the proposed scheme involves an $S_Ei$ mechanism in which there is both electrophilic attack at the α-carbon atom and nucleophilic attack at the zinc atom:

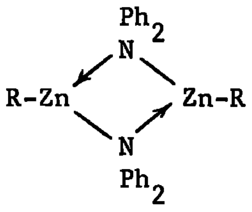


The lower reactivity of dialkylzinc compounds relative to analogous beryllium compounds is apparent in the reaction between diethylzinc and water in ether. Unlike the beryllium system where complete hydrolysis is rapid, only one ethyl group of $Et_2Zn$ is cleaved:[151]

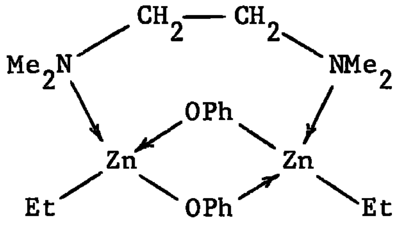
$$Et_2Zn + H_2O \longrightarrow EtZnOH \xrightarrow{slow}$$

Also, ethylzinc isopropoxide, $(EtZnOPr^i)_4$, is stable in the presence of excess alcohol.[151] All the alkylzinc alkoxides are associated as dimers, trimers or tetramers, e.g. $(EtZnOC_6Cl_5)_2$, $(EtZnOC_6F_5)_2$, $(Bu^tZnOBu^t)_3$[152] (although in this latter case it was originally assigned a dimeric structure[153]), $(MeZnOMe)_4$, $(MeZnOPh)_4$[154] etc. The structure of one of these alkoxides, namely $(MeZnOMe)_4$, has been determined by X-ray diffraction and found to have a cubic structure with a $(ZnO)_4$ cage.[155] A similar geometry has been formulated for the tetrameric phosphorane $(MeZn.N{=}PR_3)_4$, (R = Me,Et).[156] Alkylzinc thiols tend to be higher oligomers or polymers as in $(MeZnSBu^t)_5$, $(EtZnSBu^t)_5$, $(MeZnSPr^i)_6$ and $(MeZnSMe)_x$.[154]

The reaction between secondary amines and dialkylzincs has not been thoroughly studied. Dimethylamine and dimethylzinc in molar ratio 1:1 yield an insoluble and involatile bisamine, $[(Me_2N)_2Zn]_x$[154] (<u>cf</u>. the formation of $(MeBeNMe_2)_3$ under similar conditions[80]). The diphenylamino derivatives $RZnNPh_2$ are all dimers[154,157] (R = Me, Et, $Pr^i$, $Bu^n$, Ph) and since amino groups form stronger bridges than do alkyl or aryl groups, they are believed to have the structure:



This geometry has been confirmed for the compound $(MeZnNPh_2)_2$.[158] The relative weakness of $Ph_2N$ as a bridging ligand compared to $Me_2N$ of $[(Me_2N)_2Zn]_x$ or PhO of $(EtZnOPh)_2$ is seen in the different behaviour towards donors such as bipyridyl and TMED:- $[Zn(NPh_2)_2]_2$ dissolves in bipyridyl to give the complex $Zn(NPh_2)_2$.bipy[159] whereas $[(Me_2N)_2Zn]_x$ does not[154] and $(EtZnNPh_2)_2$ gives the complex $EtZnNPh_2$.TMED[159] but $(EtZnOPh)_4$ retains two bridging oxygens to yield $(EtZnOPh)_2$.TMED:[152]



Dimeric $(MeZnNPh_2)_2$ adds pyridine to give bright yellow $MeZnNPh_2.py_2$ and on heating affords the disproportionation product $py_2Zn(NPh_2)_2$.[154]

The product of the reaction between the primary amine $Bu^tNH_2$ and diethylzinc yields monomeric $EtZnN(Bu^t)ZnEt$,

$$Et_2Zn + Bu^tNH_2 \rightarrow EtZnN(Bu^t)H \xrightarrow{Et_2Zn} EtZnN(Bu^t)ZnEt$$

which is used as a polymerisation catalyst for propylene oxide. Much interest is attached to $(EtZnNPh_2)_2$ in its ability to trimerise isocyanates. The zinc-nitrogen bond in zinc amides readily adds across double bonds[157,159]

viz.

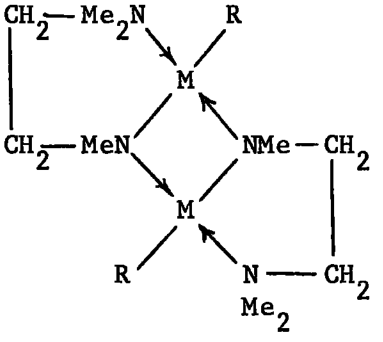
$$EtZnNPh_2 + PhNCO \rightarrow EtZnNPh.CO.NPh_2 \quad (I)$$

$$EtZnNPh_2 + CO_2 \rightarrow EtZnO.CO.N\overset{Ph_2}{Et_2}$$

The products of the type I are trimeric in benzene and when a further isocyanate molecule is added, the isocyanate trimer, $(RNCO)_3$, is displaced.[162]

In catalysing its formation, the trimer $(EtZnNPhCONPh_2)_3$ is believed to function as a template.

The trimethylethylenediamine derivatives of zinc are dimeric, like their magnesium counterparts. The general structure for these Group II metal compounds has been formulated as:



Dimers: M = Be R = Me,[81] Et,[81] Ph[109]

M = Zn R = Me,[154] H[163]

M = Mg R = Me,[164] $Pr^i$,[165] $Bu^t$[165]

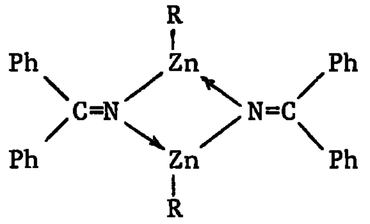
The derivative $Bu^tBeNMe.CH_2CH_2NMe_2$ is monomeric, doubtless due to the steric congestion about the beryllium atom.

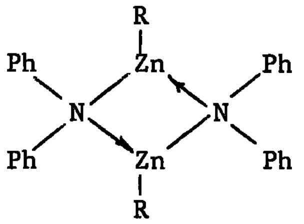
Diphenylmethyleneamine, $Ph_2C:NH$, reacts at 60-65° with dimethyl-, diethyl- and diphenyl-zinc to form methyleneamino derivatives $(Ph_2C:N.ZnR)_2$.[166] The phenyl compound, $(Ph_2C:NZnPh)_2$ decomposes at 80° to form polymeric $[(Ph_2C:N)_2Zn]_n$. The reactions of nitriles PhCN and $Bu^tCN$ were also studied but the reaction products varied. With diphenylzinc, benzonitrile yielded an adduct $PhCN,ZnPh_2$ which decomposed at 100° to give the bisimino derivative $[(Ph_2C:N)_2Zn]_2$:

$$PhCN,ZnPh_2 \xrightarrow{100^\circ} [Ph_2C:NZnPh]_2 \rightarrow (Ph_2C:N)_2Zn + Ph_2Zn$$

Neither dimethyl- nor diethyl-zinc formed adducts with benzonitrile but in both cases 2,4,6-triphenyltriazine $(PhCN)_3$ was recovered, thus confirming earlier observations.[167,168] There was no evidence for adduct formation or oligomeric organic by-products when t-butyl cyanide was used, even at elevated temperatures.

The compounds $(Ph_2C:NZnR)_2$ were assigned a structure analogous to those of $(Ph_2N.ZnR)_2$,[154] the crystal structure of $(Ph_2N.ZnMe)_2$ having confirmed the four membered $(ZnN)_2$ ring:[158]





Another similarity between these imino and amino derivatives of zinc is in adduct formation; $(Ph_2C:NZnMe)_2$ complexes with pyridine in benzene to give a yellow crystalline solid $Ph_2C:NZnMe,py_2$. The amino compound, $(Ph_2N.ZnMe)_2$ gives $Ph_2N.ZnMe,py_2$.[154]

The spectroscopic data for these compounds are given in Table III.1. The infra-red results are the most informative as they can be related to previous beryllium data (See Chapter II). Since the C=N-Zn skeleton is necessarily non-linear in the species $(Ph_2C:N.ZnR)_2$ then the asymmetric stretching frequency $\nu(C=N)$ for such a unit must lie within or near the frequency range 1607-1624 $cm^{-1}$. On arguments previously discussed, an absorption $\nu(C=N)$ appreciably higher than this can be taken as indicating a linear C=N-Zn unit. For the bismethyleneamino derivative $[(Ph_2C:N)_2Zn]_n$ there is only one absorption in the azomethine stretching region, and that one (1600 $cm^{-1}$) is appropriate for bridging imino groups only. This implies that this compound is probably a long polymer:

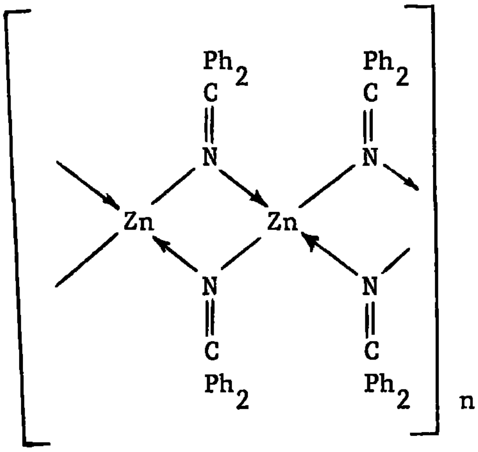
## TABLE III.1

## Spectroscopic Results for diphenylmethyleneamino derivatives of zinc[166]

| Compound | Infrared in Nujol mulls ($cm^{-1}$) |  |  | N.m.r. τ values of peaks (p.p.m.; $C_6D_6$ solvent) |  |
|---|---|---|---|---|---|
|  | ν(C=N) | ρ(Zn-Me) | ν(Zn-Me) | $=CPh_2$ | ZnR |
| $(Ph_2C:NZnMe)_2$ | 1624 | 673 | 538 | 2.77s | 10.63s |
| $(Ph_2C:NZnEt)_2$ | 1611 | 622* | 520* | 2.79s | 8.77q, 9.54t |
| $(Ph_2C:NZnPh)_2$ | 1607 | - | - | 2.80s | 2.91s |
| $[(Ph_2C:N)_2Zn]_n$ | 1600 | - | - | - | - |
| $Ph_2C:NZnMe,py_2$ | 1613 | 622 | 503 | 2.7br | 10.01s |

* $CH_2$ modes.

s = singlet q = quartet t = triplet br = broad



In such a case, the ratio of bridging to terminal ligands will be high and any relatively high terminal azomethine stretching frequency ν(C=N) may go unnoticed.

The fifth compound in the table, $Ph_2C:NZnMepy_2$, has a value of ν(C=N) which is consistent with there being a non-linear C=N-Zn skeleton. In this example the zinc atom has achieved its maximum valence saturation and dative π-bonding from nitrogen to zinc is prevented. Thus, had the azomethine stretch ν(C=N) been notably high, then it might have indicated that the C=N-Zn unit was probably linear, possibly to accommodate the bulk of the zinc ligands.

Zinc has the electronic structure $[Ar]4s^2 3d^{10}$ and as has been noted for zinc systems having donor molecules with conjugated structures (bipyridine, phenanthroline, etc.)[143,146-149] there may be zinc 3d orbital participation with the anti-bonding orbitals of the azomethine unit. Donation of electron density from the nitrogen atom to a metal by σ- or π-bonding generally increases the azomethine stretching frequency, ν(C=N). Any back donation from metal d-orbitals into the antibonding orbitals of $\gt$C=N will weaken the bond and cause a corresponding decrease in ν(C=N). Some work has been done on the methyleneamino derivatives of molybdenum and tungsten and this (σ-π) synergic process has been observed.[169,170] For example, the molybdenum compound $\pi$-$CpMo(CO)(Ph_3P)N{:}CPhBu^t$ has an azomethine stretching frequency, $\nu(C{=}N)$, of 1547 $cm^{-1}$, some 71 $cm^{-1}$ lower than the free methyleneamine ($\nu(C{=}N)$ 1618 $cm^{-1}$).[170]

All the diphenylmethyleneaminozinc compounds prepared so far apparently have non-linear C=N-Zn skeletons and the values of $\nu(C{=}N)$ in the range 1600-1624 $cm^{-1}$ are not appreciably different from the values for bridging methyleneamino ligands of beryllium, 1608-1648 $cm^{-1}$ (Table II.15). It seems unlikely that back donation from the zinc 3d orbitals into the antibonding orbitals of the azomethine link plays a major part in the zinc-nitrogen bonding in these compounds, not only because of the infrared evidence but also because interaction of the zinc d-orbitals and the $\pi^*$ orbital of $>$C=N- would be at a maximum when the C=N-Zn unit is linear and would decrease as the angle C-N-Zn decreases. There are no examples of a terminal methyleneamino group attached to a co-ordinatively unsaturated zinc atom. The bis derivative, $[(Ph_2C{:}N)_2Zn]_n$, must necessarily have two terminal groups but the spectroscopic characteristics of the compound are dominated by the bridging methyleneamino ligands. The di-t-butylmethyleneamino ligand was chosen for the compounds prepared in this latest study of zinc since its bulk was expected to give small oligomers.

Di-t-butylmethyleneaminolithium was treated with an ethereal solution of zinc chloride in three different stoichiometric quantities:

$$ZnCl_2 + Bu^t{}_2C{:}NLi \rightarrow \tfrac{1}{2}(Bu^t{}_2C{:}NZnCl)_2 + LiCl$$

$$ZnCl_2 + 2Bu^t{}_2C{:}NLi \rightarrow \tfrac{1}{2}[(Bu^t{}_2C{:}N)_2Zn]_2 + 2LiCl$$

$$ZnCl_2 + 3Bu^t{}_2C{:}NLi \not\rightarrow LiZn(N{:}CBu^t{}_2)_3 + 2LiCl$$

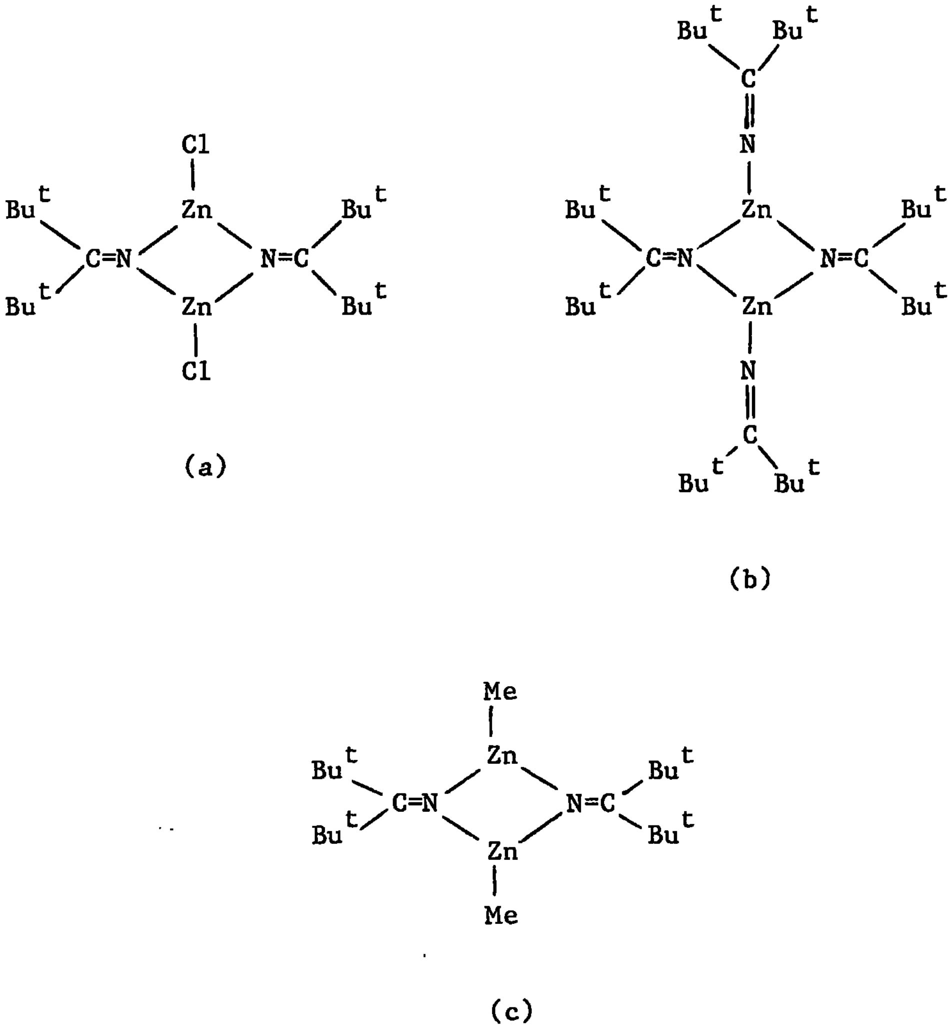
The first reaction yielded a yellow solid identified as dimeric di-t-butylmethyleneaminozinc chloride, $(Bu^t{}_2C{:}NZnCl)_2$. When two equivalents of di-t-butylmethyleneaminolithium were used, the dimeric bis(di-t-butylmethyleneamino)zinc, $[(Bu^t{}_2C{:}N)_2Zn]_2$ was formed, in contrast to the analogous beryllium reaction which afforded $LiBe(N{:}CBu^t{}_2)_3$. An attempt was made to prepare $LiZn(N{:}CBu^t{}_2)_3$ in the third reaction but no products of fixed composition or containing lithium were recovered.

An alkylzinc compound, $(Bu^t{}_2C{:}NZnMe)_2$, was prepared by condensing dimethylzinc on di-t-butylmethyleneamine:

$$Me_2Zn + Bu^t{}_2C{:}NH \rightarrow \tfrac{1}{2}(Bu^t{}_2C{:}NZnMe)_2 + MeH$$

The reaction proceeded very rapidly at room temperature to give a very air- and moisture-sensitive solid. The zinc methyl group proved to be very labile since addition of a further equivalent of methyleneamine yielded the bis-derivative, $[(Bu^t{}_2C{:}N)_2Zn]_2$. However, unlike the diphenylmethyleneamino compounds, $(Ph_2C{:}NZnR)_2$ where R = Me, Et, Ph,[166] decomposition at elevated temperatures did not occur. Such a disproportionation to give $[(Ph_2C{:}N)_2Zn]_x$ but not $[(Bu^t{}_2C{:}N)_2Zn]_2$ may be due to solubility factors resulting from the differing state of association. A similar reaction occurs in the aminozinc chemistry; when dimethylamine is added to dimethylzinc (1:1), unchanged dialkyl and insoluble, polymeric $[(Me_2N)_2Zn]_x$ are recovered.[154]

The three new zinc compounds are all dimeric in benzene and can be assigned four membered $(ZnN)_2$ rings (Fig.III.1). The chloro derivative, $(Bu^t{}_2C{:}NZnCl)_2$, resembles its Group II and Group III counterparts[19,23-25] where the methyleneamino ligand is predicted to have greater ability to bridge than chlorine. Di-t-butylmethyleneaminomethylzinc can be assumed



(a)

(b)

(c)

FIGURE III.1

to have the structure shown in (c) based on previous studies on beryllium (this work), zinc,[166] aluminium[50] and gallium.[115] Furthermore, the X-ray crystallographic study of $(MeZnNPh_2)_2$[158] shows a planar skeleton based on a $(ZnN)_2$ ring. Bis(di-t-butylmethyleneamino)zinc, $[(Bu^t{}_2C{:}N)_2Zn]_2$, being dimeric must necessarily have the structure shown in (b) with two terminal and two bridging ligands.

The n.m.r. spectra and characteristic infra-red stretching frequencies are shown in Tables III.2 and 3. The distinction between the absorptions for bridging and terminal ligands is clearly seen. All three groups of frequencies for the bridging ligands are lower than that of the parent ketimine (at 1610 $cm^{-1}$ [21]); the three peaks at 1585, 1594 and 1608 $cm^{-1}$ for $[(Bu^t_2C:N)_2Zn]_2$ may arise from distortion within the molecule or slight hydrolysis. Likewise, the two peaks for $(Bu^t_2C:NZnCl)_2$, at 1597 and 1608 $cm^{-1}$. The frequency $\nu$(C=N) for the terminal ligand (1683 $cm^{-1}$) is some 40 $cm^{-1}$ less than for beryllium compounds (Table II.15). It is a common feature that within Groups of the Periodic Table, as the co-ordinating element becomes heavier, $\nu$(C=N) becomes less. For example, $(Bu^t_2C:NMCl_2)_2$ when M = Al,[24] $\nu$(C=N) = 1664 $cm^{-1}$ and when M = Ga,[35] $\nu$(C=N) = 1647 $cm^{-1}$. However, there are anomolies; for $(Ph_2C:NMMe_2)_2$ where M = B,[171] Al[172] and Ga[173] the values for $\nu$(C=N) are 1662, 1616 and 1626 $cm^{-1}$ respectively. Indeed, recent investigations[174] into methyleneaminomagnesium chemistry have shown that for $[(Bu^t_2C:N)_2Mg]_2$, the two methyleneamino frequencies are ca.1605 and 1664 $cm^{-1}$. The comparison

TABLE III.2

Selected Infra-red spectroscopic data (Nujol mulls) in $cm^{-1}$)

| Compound | $\nu$(C=N) bridging | $\nu$(C=N) terminal | $\delta(\text{Zn-Me})_{sym}$ | $\rho$(Zn-Me) | $\nu$(Zn-Me) |
|---|---|---|---|---|---|
| $(Bu^t_2C:NZnCl)_2$ | 1597,1608 | - | - | - | - |
| $[(Bu^t_2C:N)_2Zn]_2$ | 1585,1594sh,<br>1608sh | 1683 | - | - | - |
| $(Bu^t_2C:NZnMe)_2$ | 1592 | - | 1160 | 667 | 514 |

with its beryllium and zinc analogues is made clear below:

| For $[(\mathrm{Bu^t{}_2C{:}N})_2\mathrm{M}]_2$ | $\nu$(C=N) cm$^{-1}$ (bridging) | $\nu$(C=N) cm$^{-1}$ (terminal) | $\Delta\nu$cm$^{-1}$ |
|---|---|---|---|
| Be | 1631 | 1721 | 90 |
| Mg | 1605 | 1664 | 59 |
| Zn | 1585 | 1683 | 98 |

The relatively high value for zinc (1683 cm$^{-1}$) implies that there is a considerable amount of $\mathrm{N}\overset{\rightarrow}{-}\mathrm{Zn}$ dative bonding. The covalent radii for the three metals are 1.06(Be), 1.40(Mg) and 1.31(Zn)[52] so it would be expected that $p_\pi$-$p_\pi$ bonding would be in the order Be > Zn > Mg. Anpther contributory factor is the electronegativity of the metals - the more electronegative metal will withdraw the electron density away from the ligand, possibly weakening the azomethine bond and so causing a corresponding reduction in $\nu$(C=N). The electronegativity values for the three metals are 1.47(Be), 1.23(Mg), 1.66(Zn)[108] so that the expected order for $\nu$(C=N) is Mg > Be > Zn.

Three zinc-methyl frequencies are also given in Table III.2. The symmetrical Zn-Me deformation absorption at 1160 cm$^{-1}$ is a strong sharp peak in the infra-red spectrum and is well within the range of 1145-1178 cm$^{-1}$ quoted for zinc-methyl compounds.[154] Both the Zn-Me rock (667 cm$^{-1}$) and $\nu$(Zn-Me) at 514 cm$^{-1}$ are also within the range of quoted values. It has been shown that $\nu$(Zn-Me) tends to fall as the co-ordination number of zinc increases; from 615 cm$^{-1}$ for $\mathrm{Me_2Zn}$ to 506-514 cm$^{-1}$ when the metal is tetraco-ordinate. The observed value of 514 cm$^{-1}$ for $(\mathrm{Bu^t{}_2C{:}NZnMe})_2$ falls within the latter range, though the metal is only three co-ordinate in this compound.

The n.m.r. spectroscopic data are shown in Table III.3.

## TABLE III.3

## N.m.r. spectroscopic results for the new methyleneaminozinc derivatives

| Compound | $\tau(Bu^t)$ | $\tau(Me)$ |
|---|---|---|
| $(Bu^t_2C{:}NZnCl)_2$ | 8.92 | - |
| $[(Bu^t_2C{:}N)_2Zn]_2$ | 8.64(1), 8.68(1), 9.03(2) | - |
| $(Bu^t_2C{:}NZnMe)_2$ | 8.59(6) | 10.21(1) |

Spectra were recorded for saturated solutions in benzene using benzene as internal reference.

$\tau(C_6H_6)$ = 2.73 p.p.m.

Relative intensities in parentheses

Temperature $40^o$.

The spectrum of $[(Bu^t_2C{:}N)_2Zn]_2$ is remarkably similar to that of its beryllium counterpart in that there are three peaks in intensity ratio 1:1:2. This may mean that it is structurally similar to $[(Bu^t_2C{:}N)_2Be]_2$ shown in Figures II.8 and 9, with the same distortion of ligands. The Zn-Me resonance at $\tau$ = 10.21 is appropriate for a zinc methyl and compares favourably with the values given in Table II.1 (10.01 and 10.63 p.p.m.). Variation of the position of the Zn-Me peak is quite marked; $Ph_2C{:}NZnMe,py_2$ absorbs at 10.01 p.p.m. and dimethylzinc adducts with ethylene oxide or 1,2-dimethoxyethane at 10.85 p.p.m.[175]

The mass spectroscopic results for one of these compounds, $[(Bu^t_2C{:}N)_2Zn]_2$, are given in Table III.4. No peaks were found above the monomer molecular weight and only three peaks corresponding to fragments that unambiguously contained zinc.

## TABLE III.4

## Mass Spectroscopic results for $[(Bu^t{}_2C{:}N)_2Zn]_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 345 | 0.2 | $(Bu_2CN)_2Zn$ |
| 288 | 1 | $(Bu_2CN)_2Zn$ minus Bu |
| 205 | 0.3 | $Bu_2CNZn$ |
| 142 | 0.8 | $Bu_2CNH_2$ |
| 141 | 1.2 | $Bu_2CNH$ |
| 140 | 0.6 | $Bu_2CN$ |
| 126 | 10 | $Bu_2CNH$ minus Me |
| 84 | $\underline{100}$ | BuCNH |
| 57 | $\underline{100}$ | Bu |

Metastables at 29.5 and 38.7

## Summary of the methyleneamino derivatives of zinc

Three new dimeric compounds were prepared, namely $(Bu^t{}_2C{:}NZnCl)_2$, $[(Bu^t{}_2C{:}N)_2Zn]_2$ and $(Bu^t{}_2C{:}NZnMe)_2$. Details of the azomethine stretching frequency ν(C=N) of these compounds and of known zinc and magnesium analogues are given in Table III.5. All the dimers have four membered $(ZnN)_2$ rings and the frequency range for the bridging methyleneamino ligands is 1585-1624 $cm^{-1}$. The bis derivative, $[(Bu^t{}_2C{:}N)_2Zn]_2$ provides the first example of a probably near-linear C=N-Zn unit, having ν(C=N) of 1683 $cm^{-1}$. On the basis of its n.m.r. spectrum, its molecular structure is assumed to be similar to that of its beryllium counterpart and there is likely to be substantial (N → Zn) $p_\pi$-$p_\pi$ dative bonding.

Attempts to prepare the species $LiZn(N:CBu^t_2)_3$ were unsuccessful. Secondly, unlike the analogous beryllium reaction, zinc chloride and di-t-butylmethyleneaminolithium (2 molar equivalents) yielded the expected compound $[(Bu^t_2C:N)_2Zn]_2$.

# TABLE III.5

## Methyleneamino derivatives of magnesium and zinc

| Compound | $\nu$(C=N) $cm^{-1}$ | Reference |
|---|---|---|
| $(PhEtC:NMgEt)_x$ | 1626 | 96 |
| $(Bu^tEtC:NMgEt)_y(THF)_n$ | 1631 | 96 |
| $[(Bu^t_2C:N)_2Mg]_2$ | 1605,1664 | 174 |
| | | |
| $[(Bu^t_2C:N)_2Zn]_2$ | 1585,1683 | a |
| $[(Ph_2C:N)_2Zn]_n$ | 1600 | 166 |
| $(Ph_2C:NZnPh)_2$ | 1607 | 166 |
| $(Ph_2C:NZnEt)_2$ | 1611 | 166 |
| $(Ph_2C:NZnMe)_2$ | 1624 | 166 |
| $Ph_2C:NZnMe,py_2$ | 1613 | 166 |
| $(Bu^t_2C:NZnMe)_2$ | 1592 | a |
| $(Bu^t_2C:NZnCl)_2$ | 1597,1608 | a |

x. 21-31

y. ?

a. this work.

# CHAPTER IV

# METHYLENEAMINO DERIVATIVES OF GALLIUM

This chapter describes the preparation of the compounds tris(di-t-butylmethyleneamino)gallium, $(Bu^t{}_2C:N)_3Ga$, tris(diphenylmethyleneamino)gallium,$(Ph_2C:N)_3Ga$, lithium tetrakis(di-t-butylmethyleneamino) gallate, $LiGa(N:CBu^t{}_2)_4$, and dilithium pentakis(di-t-butylmethyleneamino) gallate, $Li_2(N:CBu^t{}_2)_5$. Their chemical and spectroscopic properties are discussed and compared with the aluminium analogues which show the presence of N → Al multiple π-bonding. The attempted synthesis of bis(di-t-butylmethyleneamino)gallium chloride, $(Bu^t{}_2C:N)_2GaCl$, is also described.

## EXPERIMENTAL SECTION

### Starting Materials

Pure gallium trichloride was obtained by subliming commercial samples under reduced pressure. Di-t-butylmethyleneaminolithium was prepared by adding t-butyl-lithium to t-butyl cyanide as described in Chapter II and diphenylmethyleneaminolithium prepared by the reaction between n-butyllithium and diphenylmethyleneamine in ether at low temperatures.

All manipulations were carried out in an atmosphere of dry nitrogen.

### Preparation of tris(di-t-butylmethyleneamino)gallium, $(Bu^t{}_2C:N)_3Ga$

A solution of gallium trichloride (1.41 g., 8 mmole) in ether (20 ml.) was added to di-t-butylmethyleneaminolithium (3.53 g., 24 mmole) in hexane (40 ml.) at $-196^o$. As the mixture attained room temperature, lithium chloride separated as a thick white precipitate. After refluxing for an hour, the solvents were pumped off under reduced pressure and replaced by toluene. Filtration followed by gradual evaporation of solvent yielded pale yellow crystals which were identified as tris(di-t-butylmethyleneamino) gallium, $(Bu^t{}_2C:N)_3Ga$, m.p. $128-130^o$. (Found: C,64.2; H,10.7; N,8.4; Ga,14.1%; M,476. $C_{27}H_{54}N_3Ga$ requires C,66.2; H,11.0; N,8.6; Ga,14.2%;

M,490); $\nu_{max}$ (Nujol mull) 1672s, 1653s, 1613vs, 1594sh, 1364s, 1316w, 1258vw, 1211m, 1089vw,br, 1037m, 952s, 933s, 926sh, 875m, 840vw, 794w, 783w, 726w, 719w, 697m, 671m, 588m,br, 560m,br, 543w,br and 485m,br $cm^{-1}$.

### Preparation of tris(diphenylmethyleneamino)gallium, $(Ph_2C:N)_3Ga$

Gallium trichloride (1.76 g., 10 mmole) in ether (20 ml.) was added by syringe to a solution of diphenylmethyleneaminolithium (5.61 g., 30 mmole) in ether (60 ml.) at -196°. The colour of the mixture changed from the deep red of the ketiminolithium to a pale yellow as room temperature was reached. After 1 hr. the ether was pumped away, toluene (30 ml.) added and the mixture heated at 70° for a further 4 hr. Filtration followed by crystallisation from benzene afforded yellow crystals of tris(diphenylmethyleneamino)gallium, $(Ph_2C:N)_3Ga$, m.p. 186-189°. (Found: C,71.8; H,4.7; N,7.1; Ga,11.1%; M,600. $C_{39}H_{30}N_3Ga$ requires C,76.7; H,4.9; N,6.9; Ga,11.5%; M,610); $\nu_{max}$ (Nujol mull) 1961w, 1905vw, 1813w, 1645s, 1620vs, 1600sh, 1577m, 1307w, 1285w, 1266sh, 1245m, 1190w, 1176w, 1156vw, 1143w, 1074w, 1038sh, 1026m, 1000w, 986vw, 971vw, 955m, 935m, 928sh, 915w, 904m, 887sh, 851vw, 842vw, 788sh, 782sh, 775s, 761sh, 734w, 720sh, 708sh, 696vs, 676vs, 665s, 656sh, 620m, 615sh, 541s, 521m, 508w, 467m, 452w and 428m,br $cm^{-1}$.

### Preparation of lithium tetrakis(di-t-butylmethyleneamino)gallate, $LiGa(N:CBu^t_2)_4$

A solution of gallium trichloride (1.76 g., 10 mmole) in ether (20 ml.) was added to di-t-butylmethyleneaminolithium (5.88 g., 40 mmole) in hexane (60 ml.) at -196°. On stirring overnight at room temperature, lithium chloride was precipitated leaving a pale yellow solution. Solvent was then pumped off and the lithium chloride separated by filtration using hot hexane (40 ml.), from which the expected product, lithium tetrakis(di-t-butylmethyleneamino)gallate, $LiGa(N:CBu^t{}_2)_4$, was crystallised. M.p.188° (Found: C,67.4; H,11.5; N,8.6; Ga,10.3; Li,1.10%. $C_{36}H_{72}N_4GaLi$ requires C,67.8; H,11.3; N,8.8; Ga,11.0; Li,1.10%). The low solubility of the product in benzene did not permit a molecular weight determination. $\nu_{max}$ (Nujol mull) 1673vs, 1649vs, 1629vs, 1616vs, 1264s, 1215m, 1205sh, 1081w,br, 1043m, 1020sh, 958s, 936m, 926sh, 877w, 837vw, 797w, 725m,br, 699m, 683m, 589m,br, 562m,br, 539vw,br, 502w and 485w,br $cm^{-1}$.

## Preparation of di-lithium pentakis(di-t-butylmethyleneamino)gallate, $Li_2Ga(N:CBu^t{}_2)_5$

Using similar conditions to those described above, the product of the reaction between gallium trichloride (1.41 g., 8 mmole) and di-t-butylmethyleneaminolithium (5.88 g., 40 mmole) yielded a white crystalline powder which was identified as di-lithium pentakis(di-t-butylmethyleneamino) gallate, $Li_2Ga(N:CBu^t{}_2)_5$, m.p. 112-117°. (Found: C,67.1; H,11.3; N,9.4; Ga,8.8; Li,1.87%. $C_{45}H_{90}N_5GaLi_2$ requires C,68.9; H,11.5; N,8.9; Ga,8.9; Li,1.78%). $\nu_{max}$ (Nujol mull) 1670s, 1656sh, 1626sh, 1612vs, 1596sh, 1325m, 1266m, 1215s, 1205sh, 1100m, 1081sh, 1042s, 957s, 936s, 929sh, 876s, 840w, 803m,br, 727w, 720w, 697m,br, 671m, 590s,br, 560s,br, 543sh and 484m,br $cm^{-1}$.

## Attempted Synthesis of bis(di-t-butylmethyleneamino)gallium chloride, $(Bu^t{}_2C:N)_2GaCl$

A solution of gallium trichloride (2.46 g., 14 mmole) in ether (25 ml.) was added to di-t-butylmethyleneaminolithium (4.12 g., 28 mmole) in hexane (30 ml.) at -196°. On warming to room temperature, a white precipitate formed, leaving a pale yellow solution. Solvent was pumped off and the residue extracted with hot toluene. Crystallisation afforded a pale yellow solid which was identified by its i.r. spectrum as tris(di-t-butylmethyleneamino)gallium, $(Bu^t{}_2C:N)_3Ga$; there was no sign of the other disproportionation product, $(Bu^t{}_2C:NGaCl_2)_2$, in the i.r. spectrum.[35]

## DISCUSSION

The organic chemistry of gallium, indium and thallium has been very much less extensively studied than for the first two members of Group III, boron and aluminium. Chemical properties vary considerably between the two sets of elements; trimethylaluminium is instantaneously and completely hydrolysed by wet alcohols whereas $Me_3GaOEt_2$ only goes as far as forming $(Me_2GaOH)_4$.[176] The metal-nitrogen chemistry of gallium has been virtually ignored by comparison with boron- and aluminium-nitrogen chemistry. Nearly all the methyleneamino derivatives of Group III elements prepared hitherto were derivatives of boron and aluminium.

Methyleneamino derivatives of boron have been prepared by a variety of routes. Insertion of a nitrile into a reactive B-X bond (e.g. X = H, S or halogen) has proved a useful route for preparing unsymmetrical methyleneamino ligands:

$Me_2BH + MeCN \rightarrow (MeCH{:}NBMe_2)_2$ Ref.49

$B_2H_6 + CCl_3CN \rightarrow (CCl_3CH{:}NBH_2)_2$ Ref.177

$(C_3H_5)_3B + RCN \rightarrow [C_3H_5CR{:}NB(C_3H_5)_2]_2$ Ref.178

$R_2BSR' + MeCN \rightarrow (MeC(SR'){:}NBR_2)_2$ Ref.179

$BCl_3 + CF_3CN \rightarrow (CF_3CCl{:}NBCl_2)_2$ Ref.180

However, this reaction does not always work as noted for the reaction between acetonitrile, MeCN, and dichloroborane, $HBCl_2$, which failed to give the expected insertion product.[23] Moreover, the method is not generally applicable to the synthesis of ketiminoboranes $R_2C{:}NBR_2$, most organoboranes $R_3B$ being unreactive towards insertion of nitriles.

A route similar to that used for the amination of boron compounds has been employed for the preparation of diphenylmethyleneaminoboron derivatives:[171]

$$Ph_2C{:}NH + Me_3B \rightarrow Ph_2C{:}NH,BMe_3 \xrightarrow{200^{o}} (Ph_2C{:}NBMe_2)_2 + MeH$$

Of increasing importance in recent years is the use of lithio- and silyl-methyleneamino compounds as reagents[15,16,23,30,100] since separation of the product is easier than by other routes.

$$Ph_2C{:}NSiMe_3 + Ph_2BCl \rightarrow Ph_2C{:}NBPh_2 + Me_3SiCl \qquad \text{Ref.100}$$

$$Bu^t{}_2C{:}NLi + BCl_3 \rightarrow Bu^t{}_2C{:}NBCl_2 + LiCl \qquad \text{Ref.16}$$

The majority of the products $R_2C{:}NBR'_2$ formed in such reactions are dimers $(R_2C{:}NBR'_2)_2$ but when the size of R or R' in $R_2C{:}NBR'_2$ is large, monomeric species are formed.[11,15,16,30,100] Under these circumstances it would be expected that there would be (N → B) dative π-bonding of the type $R_2C{:}N\overset{\rightharpoonup}{=}BR'_2$ in order that the boron could achieve maximum valence saturation. This is evidenced by a comparison of the infra-red and n.m.r spectra and by X-ray crystallography. The azomethine stretching frequencies ν(C=N), for associated derivatives $(Ph_2C{:}NBR_2)_2$[15,23,100] in which there are necessarily bent C-N-B skeletons fall within the range 1586-1662 $cm^{-1}$, whereas monomers $Ph_2C{:}NBR_2$, have ν(C=N) <u>ca</u>. 1790 $cm^{-1}$ when unassociated.[15,100] Monomeric di-t-butylmethyleneaminoboranes not only have ν(C=N) at 1820-1840 $cm^{-1}$, ($Bu^t{}_2C{:}NH$[21] has ν(C=N) at 1610 $cm^{-1}$) but the low temperature n.m.r. results imply that the C-N-B unit is linear.[16] The predicted pseudo-allene geometry of monomeric $R_2C{=}N\overset{\rightharpoonup}{=}BR'_2$ has been confirmed in the case of $Ph_2C{:}NB(mesityl)_2$[15] whose crystal structure[11] shows a linear C-N-B skeleton with a relatively short B-N bond length (see Figure I.6 and further discussion in Chapter I).

Methyleneamino derivatives of aluminium have been prepared by similar methods to boron. The most common way used for preparing compounds having the formula $(R^1R^2C{:}NAlR^3R^4)_2$ (where $R^1$ = alkyl, aryl; $R^2$ = alkyl, aryl, H, $R_2N$; $R^3,R^4$ = alkyl, aryl, halogen) is by an insertion reaction of a nitrile into an organoaluminium compound:

$$R^1CN + R^2R^3R^4Al \rightarrow R^1CN.AlR^3R^4R^2 \xrightarrow[heat]{} \frac{1}{n}(R^1R^2CNAlR^3R^4)_n$$

The nitrile that has received most attention is benzonitrile, PhCN[181-188] followed by alkyl nitriles,[50,181,189] acrylonitriles[190,191] and dimethylcyanamide.[192]

The products of this reaction are determined by the nature of the reactants, reaction conditions and molecular proportions used. For instance, when $R^2$ = Et,[50,181,184,190,191] then the product is often $(R^1CH{:}NAlR^3R^4)_n$, $EtAlR^3R^4$ acting as a source of $HAlR^3R^4$. Also, if $R^1$ of the nitrile contains hydrogen attached to the α-carbon ($R^1$ = Me, Et[50,181,189,190,191]) polymeric products may be formed through reaction of the nitrile as ketenimine, $R_2C{=}C{=}NH$

i.e.

$$\begin{tikzcd}
R_2CH.CN + AlR^2R^3R^4 \arrow[rr] & & R_2CHCN,AlR^2R^3R^4 \arrow[dl] \arrow[dr] & \\
& \frac{1}{n}[R_2C{:}C{:}NAlR^3R^4)_n + R^2H & & \frac{1}{n}[R_2C(AlR^3R^4)CN]_n + R^2H
\end{tikzcd}$$

An effective route for preparing methyleneaminoaluminium derivatives, particularly those where a symmetrical product $(R_2C{:}NAlR^1_2)_2$ is required, is the reaction between a triaryl- or trialkyl-aluminium and the methyleneamine:

$$R_2C{:}NH + \tfrac{1}{2}(R^1{}_3Al)_2 \rightarrow R_2C{:}NH,AlR^1{}_3 \xrightarrow{heat} \tfrac{1}{n}(R_2C{:}NAlR^1{}_2)_n + R^1H$$

$R = Ph,^{172}$ $Me_2N,^{193}$ $Bu^t,^{194}$

$R^1 = Me,^{172,193,194}$ $Et,^{172,193}$ $Ph,^{172,193}$ $Bu^i,^{194}$

The elimination of alkane takes place smoothly below 100° in contrast to the boron analogues which require temperatures of up to 200°.[171]

Nearly all the compounds prepared by these two methods are dimers with four membered $(AlN)_2$ rings. Crystal structures for two of them, namely $(Bu^tMeC{:}NAlMe_2)_2$[17] and $[p\text{-}BrC_6H_4(Ph)C{:}NAlPh_2]_2.2C_6H_6$,[18] show the planar $(AlN)_2$ ring with an acute angle at the aluminium (85.4° and 87.1° respectively). It is interesting that whereas the apparent angular strain might be relieved by adoption of a six-membered ring structure, as in $(Me_2AlNHMe)_3$[195,196] or $(Et_2AlN_3)_3$,[197] examples of this $(AlN)_3$ ring in methyleneamino chemistry are unknown.

The third type of reaction employed for preparing methyleneamino-aluminium derivatives is the metathetical reaction between $AlX_3$ (X = Cl or Br) and $Ph_2C{:}NLi$ or $R_2C{:}NSiMe_3$ ($R = Bu^t$,Ph) to give $(R_2C{:}NAlX_2)_2$, and also between $AlCl_3$ and $R_2C{:}NLi$ (3 molar equivalents) to form monomeric $(R_2C{:}N)_3Al$. A further molecule of $Bu^t{}_2C{:}NLi$ yields $LiAl(N{:}CBu^t{}_2)_4$.[24]

The last three aluminium derivatives mentioned are of particular interest. The two monomers have azomethine stretching frequencies ν(C=N) at the relatively high values of 1686 and 1690 cm$^{-1}$ respectively, frequencies which can be contrasted with values for bridging groups:

| | | | | |
|---|---|---|---|---|
| e.g. | $(Ph_2CN)_3Al$[24] | 1686 cm$^{-1}$ | $(Ph_2CNAlMe_2)_2$[172] | 1616 cm$^{-1}$ |
| | $(Bu^t{}_2CN)_3Al$[24] | 1690 cm$^{-1}$ | $(Bu^t{}_2CNAlMe_2)_2$[194] | 1637 cm$^{-1}$ |

Clearly, the high frequency absorptions ν(C=N) can be assigned to a linear $C{=}N{\doteq}Al$ system in which there is significant (N → Al) dative π-bonding. It would seem feasible, therefore, to suggest that for di-t-butylmethyleneaminoaluminium derivatives, $Bu^t_2C{=}N{-}Al\langle$, the azomethine stretching frequency ranges for bridging and terminal ligands are 1637-1664 $cm^{-1}$ and ca.1690 $cm^{-1}$ respectively. Likewise for $Ph_2C{=}N{-}Al\langle$, the corresponding ranges are 1587-1616 $cm^{-1}$ and ca. 1690 $cm^{-1}$ respectively (Table IV.6 on page 130). The infra-red spectrum for $LiAl(N{:}CBu^t_2)_4$[35] shows absorptions in the ν(C=N) region of 1700,1642 and 1602 $cm^{-1}$, the first of which can be attributed to a near linear $C{=}N{\doteq}Al$ skeleton and the latter two to non-linear C=N-Al units. The crystal structure of this compound has been determined[48] and accordingly there are two linear methyleneamino and two non-linear methyleneamino ligands.

The azomethine stretching frequency of $Bu^t_2C{:}NAlBu^i_2$ at 1709 $cm^{-1}$ is appropriate for a terminal methyleneamino ligand. Further investigations are being made into this compound, particularly with respect to its molecular weight, but since all three ligands are bulky, a monomeric state of association would not be unexpected.[194]

There have only been two main investigations into the methyleneamino chemistry of gallium prior to this work. The first[115] dealt with the reaction between nitriles and trialkylgalliums. The immediate product formed was the adduct:

$$RCN + R^1_3\overset{Ga}{Al} \rightarrow RCN.\overset{Ga}{Al}R^1_3 \quad (R = Me,Ph \text{ or } Bu^t;\ R^1 = Me \text{ or } Et)$$

Earlier work on trimethylgallium adducts[198] included the preparation of $MeCN.GaMe_3$ but no study was made into its thermal decomposition. Pyrolysis of the adducts in this later investigation gave various products:[115]

| Adduct | Temp. in $^{o}$C | Products |
|---|---|---|
| $MeCN,GaMe_3$ | 145 | $MeH$ + polymeric $(Me_2GaNC_2H_2)_n$ |
| $Bu^tCN,GaMe_3$ | 150 | $Bu^tCN + Me_3Ga$ |
| $PhCN,GaMe_3$ | 118 | $Me_3Ga + Ph_3C_3N_3$ (trimerisation) |
| $Bu^tCN,GaEt_3$ | 158 | $C_2H_4 + (Bu^tHC{:}NGaEt_2)_2$ |
| $PhCN,GaEt_3$ | 158 | $C_2H_4 + (PhHC{:}NGaEt_2)_2$ |

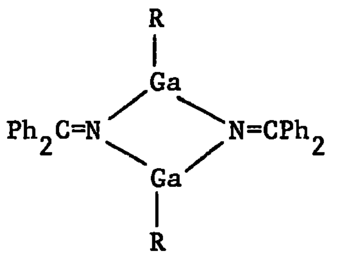
The last two decompositions follow a similar course to that of their aluminium counterparts.[50,181,184,190,191]

The second report was in the same year, 1967, when the reaction between diphenylmethyleneamine and $R_3Ga$ (R = Me,Et or Ph) was studied.[173] When R = Me, a crystalline adduct is formed which eliminates methane at 100$^{o}$ to yield $(Ph_2C{:}NGaMe_2)_2$. For both R = Et and Ph, viscous liquids were formed which lost RH readily at 100-120$^{o}$ to give $(Ph_2C{:}NGaEt_2)_2$ and $(Ph_2C{:}NGaPh_2)_2$ respectively:

$$\begin{tikzcd}
Ph_2C{:}NH + R_3Ga \arrow[r] & Ph_2C{:}NH,GaR_3 \arrow[d, "100\text{-}120^{o}"] & \\
 & \tfrac{1}{2}(Ph_2C{:}NGaR_2)_2 + RH & R = Me,Et \text{ or } Ph.
\end{tikzcd}$$

This course is analogous to that used for preparing corresponding boron[171] and aluminium[172,193,194] derivatives although the ease of elimination of RH decreases in the sequence Al > Ga > B. This is in accord with the reverse order of electronegativity of these elements (B,2.01; Ga,1.82; Al,1.47).[108]

The three products are all white, crystalline dimers and have been assigned structures with planar four membered $(GaN)_2$ rings:[173]



R = Me, Et or Ph

Details of the infra-red absorptions for the azomethine stretching frequencies, $\nu(C{=}N)$, for the methyleneaminogallium compounds prepared by the above routes, including selected boron and aluminium analogues are listed in Table IV.1.

Organogallium compounds are intermediate in their reactions between organoboron and organoaluminium compounds[199] and this is reflected in methyleneaminogallium compounds as noted above; the infra-red data also show the sequence B-Ga-Al. Although only one absorption for boron is shown in Table IV.1, it is generally true that for similar compounds, e.g. $(Ph_2C{:}NMMe_2)_2$ where M = B,Al,Ga, the azomethine stretching frequency, $\nu(C{=}N)$, decreases in the sequence B > Ga > Al. If the electronegativity of the element played an important role, that is in reducing the electron density in the azomethine link to cause a corresponding reduction in $\nu(C{=}N)$, then the expected order of frequencies would be Al > Ga > B (electronegativities 1.47, 1.82 and 2.01 respectively).[108] Furthermore, for $(Ph_2C{:}NMR_2)_2$ (M = Al,Ga; R = Me,Et), the electron withdrawing properties of the alkyl group should lead to a higher frequency, $\nu(C{=}N)$, for R = Et than R = Me. Neither of these electronic factors seem to be important.

TABLE IV.1

| Compound | $\nu(C{=}N)$ $cm^{-1}$ | Compound | $\nu(C{=}N)$ $cm^{-1}$ |
|---|---|---|---|
| $(Ph_2C:NBMe_2)_2$ | 1662[171] | | |
| $(Ph_2C:NAlMe_2)_2$ | 1616[172] | $(Ph_2C:NGaMe_2)_2$ | 1626[173] |
| $(Ph_2C:NAlEt_2)_2$ | 1609[172] | $(Ph_2C:NGaEt_2)_2$ | 1613[173] |
| $(Ph_2C:NAlPh_2)_2$ | 1604[172] | $(Ph_2C:NGaPh_2)_2$ | 1612[173] |
| $(PhCH:NAlEt_2)_2$ | 1633[181] | $(PhCH:NGaEt_2)_2$ | 1688m, 1633vs[115] |
| $(Bu^tCH:NAlEt_2)_2$ | 1656[50] | $(Bu^tCH:NGaEt_2)_2$ | 1658[115] |

Dative π-bonding, $(N \overset{\rightharpoonup}{=} M)$, is another contributary factor. On the grounds that greater interaction between the non-bonding nitrogen p-orbitals with vacant orbitals of an adjacent atom will be at a maximum when that atom is of comparable size, then the expected order of π-bonding ability will be B > Al = Ga (Covalent radii: N,0.7; B,0.88; Ga = Al; 1.26Å).[52]

A third factor is the variation in mass of substituents in each series and the varying mechanical constraint it imposes on the stretching vibration; the effect of mass would lead to the order B > Al > Ga.

In the work to be described, the di-t-butylmethyleneamino ligand is used to try and rationalise the arguments over the factors affecting the spectroscopic data, and to determine if there is significant $N \overset{\rightharpoonup}{=} Ga$ multiple π-bonding as has been found in some aluminium compounds.[37]

The compounds $(Bu^t_2C{:}N)_3Ga$, $(Ph_2C{:}N)_3Ga$, $LiGa(N{:}CBu^t_2)_4$ and $Li_2Ga(N{:}CBu^t_2)_5$ were all prepared by the metathetical reaction between anhydrous gallium trichloride and $R_2C{:}NLi$. This route has been used to prepare two other gallium derivatives, $(Bu^t_2C{:}NaGaCl_2)_2$[35] and $(Ph_2C{:}NGaCl_2)_2$.[25]

The reaction between di-t-butylmethyleneaminolithium and gallium trichloride (3:1 molar proportions) yielded pale yellow crystals of $(Bu^t_2C{:}N)_3Ga$, m.p. 128-130°, which was found to be monomeric in the vapour (mass spectrometry) and in benzene (by cryoscopy). A similar product, $(Ph_2C{:}N)_3Ga$, was also obtained by the same method:

$$GaCl_3 + 3R_2C{:}NLi \rightarrow (R_2C{:}N)_3Ga + 3LiCl$$

$$R = Ph,\ Bu^t$$

Both compounds were very air and moisture sensitive which is indicative of three rather than four co-ordinative gallium. Similar observations were also made for the aluminium counterparts, $(Ph_2C{:}N)_3Al$[24,37] and $(Bu^t_2C{:}N)_3Al$.[24,35,37]

When di-t-butylmethyleneaminolithium and gallium trichloride were mixed in 2:1 molar proportions the product was not the expected $(Bu^t_2C{:}N)_2GaCl$ but $(Bu^t_2C{:}N)_3Ga$:

$$\begin{array}{l} GaCl_3 + 2Bu^t_2C{:}NLi \rightarrow [(Bu^t_2C{:}N)_2GaCl] + 2LiCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow \text{(probably)} \\ \qquad\qquad \tfrac{1}{2}(Bu^t_2C{:}N)_3Ga + \tfrac{1}{4}(Bu^t_2C{:}NGaCl_2)_2 \end{array}$$

The second product in this equation, $(Bu^t_2C{:}NGaCl_2)_2$ was not detected but no doubt was present in the supernatant liquid on crystallisation of

$(Bu^t_2C:N)_3Ga$. This disproportionation has also been observed in the systems $AlCl_3 + 2R_2C:NLi$ (R = Ph[24] or Bu[t35]) and $BCl_3 + 2Ph_2C:NLi$.[15,100] In contrast $(Bu^t_2C:N)_2BCl$ is stable with respect to disproportionation[35] which may be a consequence of steric crowding in the product, $(Bu^t_2C:N)_3B$, or in the disproportionation intermediate which is likely to involve four co-ordinate boron. Also, $Bu^t_2C:NBCl_2$ is a liquid so it provides no lattice energy incentive to disporportionation, whereas $(R_2C:NMCl_2)_2$ and $(R_2C:N)_3M$ (R = Bu$^t$,Ph; M = Al,Ga)[24,25,35] are crystalline solids.

Two further reactions were carried out: an ethereal solution of gallium trichloride was treated with four and five molar equivalents of di-t-butylmethyleneaminolithium to afford $LiGa(N:CBu^t_2)_4$ and $Li_2Ga(N:CBu^t_2)_5$ respectively. Both compounds were air- and moisture-sensitive but did not decompose as rapidly as $(R_2C:N)_3Ga$ (R = Ph, Bu$^t$). Their low solubility in benzene prevented a molecular weight determination.

$$GaCl_3 + 4Bu^t_2C:NLi \rightarrow LiGa(N:CBu^t_2)_4 + 3LiCl$$

$$GaCl_3 + 5Bu^t_2C:NLi \rightarrow Li_2Ga(N:CBu^t_2)_5 + 3LiCl$$

Similar iminometallates have been characterised:- $LiAl(N:CBu^t_2)_4$[35] (and its structure determined by X-ray crystallography[48]), $LiBe(N:CBu^t_2)_3$ and $Li_2Be(N:CBu^t_2)_4$ (Chapter II of this thesis).

A conductometric titration was run on the same lines as for the lithio beryllate compounds (Chapter II). Di-t-butylmethyleneaminolithium (0.2 mmole ml$^{-1}$ in hexane) was titrated against tris(di-t-butylmethyleneamino)gallium (0.206 mmole in 5 ml. hexane) in a conductivity cell with platinum electrodes. The conductance was measured on a Wayne Kerr B224

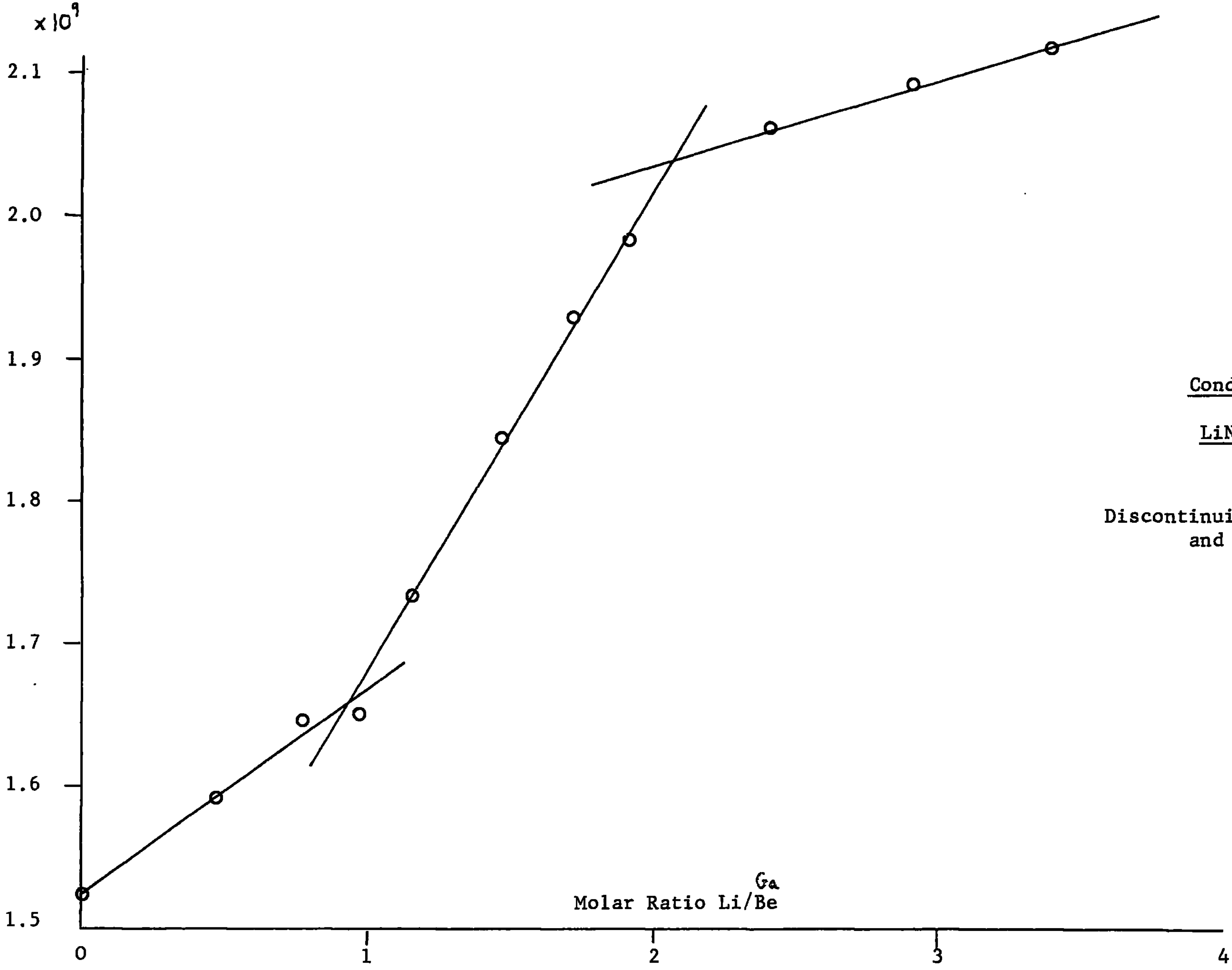


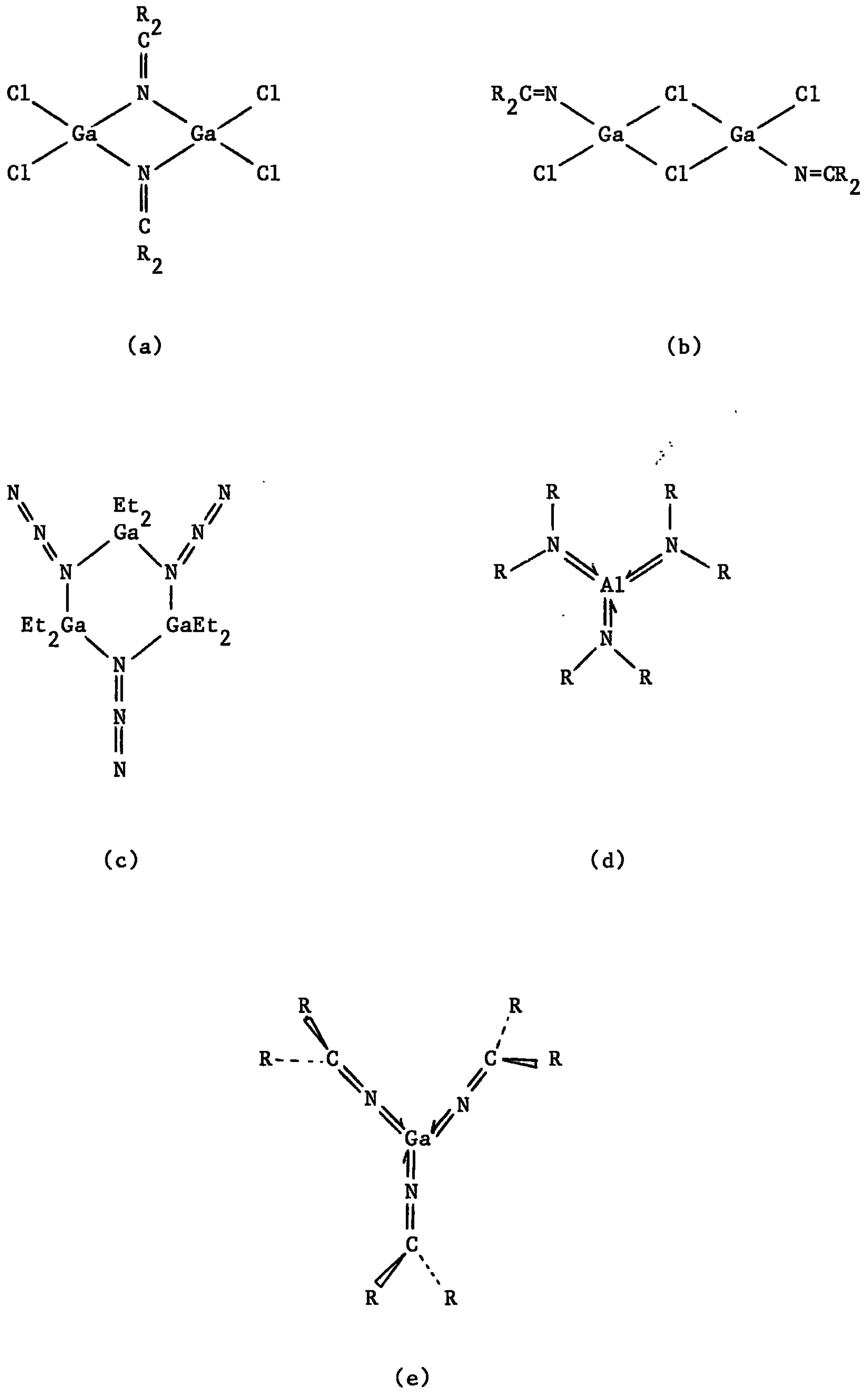
FIGURE IV.1

Conductometric titration of $LiN{:}CBu^t{}_2$ against $(Bu^t{}_2C{:}N)_3Ga$

Discontinuities at Li/Be = 0.92
and 2.07

Universal Bridge (further details of the titration are given in Appendix II). Despite the low values of specific conductance (through having to resort to a solvent of low dielectric constant), the plot of specific conductance against the ratio Li:Ga shows two discontinuities in the curve corresponding to the approximate constitutions $LiGa(N:CBu^t_2)_4$ and $Li_2Ga(N:CBu^t_2)_5$ (Figure IV.1). Thus it appears as though these two compounds do exist in hydrocarbon solvents.

The two chloro derivatives, $(R_2C:NGaCl_2)_2$, can be assigned a four membered $(GaN)_2$ ring with bridging methyleneamino ligands by analogy with their aluminium counterparts[24] (Figure IV.2(a)) rather than chlorine bridging as in (b). The structures of $[C_6H_4Br(Ph)C:NAlMe_2]_2$[18] and $(Bu^tCMe:NAlMe_2)$[17] have been determined crystallographically, and show the $(MN)_2$ four membered ring. There are many examples in gallium-nitrogen chemistry of four membered rings, mainly of the type $(R^1R^2Ga.NR^3R^4)_2$.[200-205] Other oligomers of such aminogallium compounds are known[203,204,206,207] and it appears as though the bulk of the substituents on gallium and nitrogen play the most important role in determining the degree of association. The strain in a fourmembered ring can be relieved if a trimer is formed, allowing the ring angles to expand from ca. 90° to 120°. However, steric hindrance between substituents on gallium and nitrogen is greater in the trimer than the dimer. Thus $(H_2NGaH_2)_n$ is polymeric, [203] $(MeNHGaH_2)_3$ is trimeric[203] and $(Me_2NGaH_2)_2$ is dimeric in benzene and monomeric in the gas phase.[202] The X-ray crystallographic determination of the structure of $[(CH_2)_2NGaH_2]_3$[206,207] shows it to have a chair conformation, as found for $(MeNHGaH_2)_3$,[203] presumably so that steric



<u>FIGURE IV.2</u>

hindrance between neighbouring substituents is minimised. In contrast, the structure of the azide $(Et_2GaN_3)_3$[208,209] as determined by its infra-red and Raman spectra[210] apparently involves a planar $(GaN)_3$ ring system (Figure IV.2(c)). In view of the π-bonding system in $R_2C{=}N-$ and the possibility of $(N \rightleftharpoons M)$ dative π-bonding, then trimeric methyleneamino derivatives may be expected to have a structure similar to $(Et_2GaN_3)_3$ rather than the chair conformation structure. However, it appears as though the steric requirements are the dominant factors in the state of association of methyleneamino derivatives since no trimers with an $(M\text{-}N)_3$ ring have yet been prepared.

Details of the azomethine stretching frequencies, ν(C=N), for the methyleneamino derivatives of gallium are listed in Table IV.2. Corresponding frequencies for the aluminium analogues are shown in Table IV.3.

TABLE IV.2

Characteristic azomethine stretching frequencies, ν(C=N), $cm^{-1}$

(Nujol mulls)

| Compound | $\nu(C{=}N{\rightleftharpoons}Ga)$ terminal | ν(C=N) bridging |
|---|---|---|
| $(Bu^t_2C{:}NGaCl_2)_2$ | | 1647[35] |
| $(Ph_2C{:}NGaCl_2)_2$ | | 1591[25] |
| $(Bu^t_2C{:}N)_3Ga$ | 1672s | (1653s), 1613vs |
| $(Ph_2C{:}N)_3Ga$ | 1645s | (1620vs) |
| $LiGa(N{:}CBu^t_2)_4$ | 1673vs | 1649vs, 1629vs, 1616vs |
| $Li_2Ga(N{:}CBu^t_2)_5$ | 1670s | 1656sh, 1626sh, 1612vs |

## TABLE IV.3

Characteristic azomethine stretching frequencies, ν(C=N) cm$^{-1}$

(Nujol mulls)

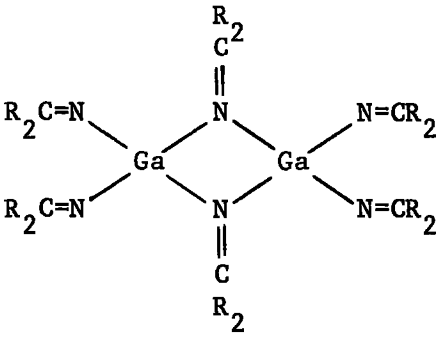
| Compound | ν(C=N=Al) terminal | ν(C=N) bridging | Ref |
|---|---|---|---|
| $(Bu^t_2C{:}NAlCl_2)_2$ | | 1664 | 24 |
| $(Ph_2C{:}NAlCl_2)_2$ | | 1593 | 24 |
| $(Bu^t_2C{:}N)_3Al$ | 1690 | | 24,37 |
| $(Ph_2C{:}N)_3Al$ | 1686 | | 24,37 |
| $LiAl(N{:}CBu^t_2)_4$ | 1700 | 1642,1602 | 35 |

The four chloro derivatives can immediately be listed under the frequencies for ν(C=N) bridging ligands. The difference between the di-t-butylmethyleneamino and diphenylmethyleneamino values for both metals is surprisingly large (Ga, $\Delta\nu$ = 56 cm$^{-1}$; Al, $\Delta\nu$ = 71 cm$^{-1}$) when compared with the difference between $(Bu^t_2C{:}NBeCl)_2$ and $(Ph_2C{:}NBeCl)_2$[19] ($\Delta\nu$ = 14 cm$^{-1}$).

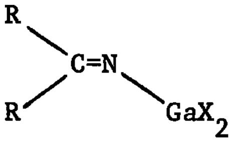
Aluminium and gallium have approximately the same covalent radius (1.26Å)[52] so that in analogous compounds, the steric hindrance between substituents should be approximately the same for both elements. Thus it is found that the compounds $(R_2C{:}N)_3Ga$ (R = Ph or $Bu^t$) are monomeric like their aluminium counterparts.[24,37] Hitherto there were no known monomeric $GaN_3$ compounds but some aluminium derivatives are known. For instance, both $(Pr^i_2N)_3Al$[211] and $[(Me_3Si)_2N]_3Al$[212] are monomeric but in order for there to be (N$\doteq$Al) dative π-bonding to satisfy the co-ordination deficiency of the aluminium atom, the R, N and Al atoms of $(R_2N)_3Al$ would all have to lie in the same plane (Figure IV.2(d)). Under such circumstances, the steric hindrance between R groups is at a maximum, and consequently the crystal structure of $[(Me_3Si)_2N]_3Al$[212] shows that the dihedral angle between the $AlN_3$ and $Si_2NAl$ planes is $50^o$. However, in the methyleneamino derivatives $(R_2C{:}N)_3M$ overlap of the nitrogen 2p and metal 3p orbitals appropriate for maximum $(N \overset{\bullet}{=} M)$ π-bonding will occur when the dihedral angle between the $MN_3$ and $MNC_2$ planes is $90^o$ (Figure IV.2(e)), i.e. when there is minimal interaction between methyleneamino ligands.

With the prediction that monomeric $(R_2C{:}N)_3Al$ compounds should possess a linear $C{=}\dot{N}\overset{\bullet}{=}Al$ system it was not surprising that this was reflected in the high azomethine stretching frequencies ν(C=N): 1690 $cm^{-1}$ for R = $Bu^t$ and 1686 $cm^{-1}$ for R = Ph[24,37] (Table IV.3).

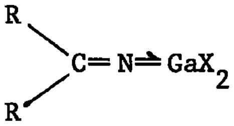
For the gallium analogues, a similar effect in the infrared spectra was observed, although with minor complications. The high (1672 $cm^{-1}$) stretching frequency for $(Bu^t{}_2C{:}N)_3Ga$ is appropriate for a linear $C{=}N\overset{\bullet}{=}Ga$ system but there were additional peaks at 1653 $cm^{-1}$ and 1613 $cm^{-1}$. The first of these was effectively a shoulder to that at 1672 $cm^{-1}$. The latter peak at 1613 $cm^{-1}$ is appropriate for a bridging ligand but alternatively may be present due to hydrolysis of the compound, particularly as ν(C=N) for $(Bu^t{}_2C{:}NGaCl_2)_2$ is at 1647 $cm^{-1}$. That $(Bu^t{}_2C{:}N)_3Ga$ is a monomer with linear or near-linear C-N-Ga units is further indicated by its n.m.r. spectrum which shows a single resonance at 8.73 p.p.m. both at $+33^o$ and $-50^o$. Had it been a dimer then there would have been two absorptions due to the differing methyleneamino ligand environments (Figure IV.3(a)). In addition, the R groups of Figure IV. 3(b) would be magnetically inequivalent and hence distinguishable at some



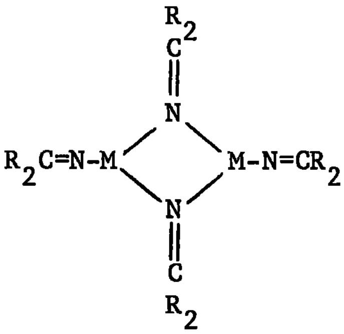
(a)



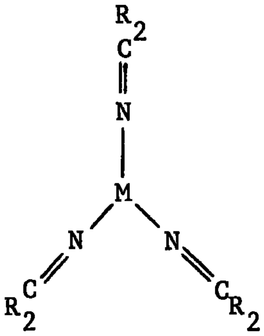
(b)



(c)



(d)



(e)

FIGURE IV.3

temperature in the n.m.r. spectrum, in contrast to the magnetically equivalent R groups in 3(c).

The tris(diphenylmethyleneamino)gallium infra-red spectrum also showed two azomethine stretching absorptions (1645 and 1620 $\mathrm{cm}^{-1}$). The first of these may be due to a linear $\mathrm{C{=}N\hat{=}Ga}$ system and the second may be due to contamination by $\mathrm{Ph_2C{:}NLi}$ ($\nu$(C=N) at 1620 $\mathrm{cm}^{-1}$ [213]) although no lithium could be detected by flame spectroscopy.

An interesting comparison can be made between beryllium, zinc, aluminium and gallium. Figure IV.3(d) and (e) show the molecular structures of $[(\mathrm{R_2C{:}N})_2\mathrm{M}]_2$ (M = Be or Zn) and $(\mathrm{R_2C{:}N})_3\mathrm{M'}$ (M' = Al or Ga) in which all four metals are surrounded by three methyleneamino ligands. For R = $\mathrm{Bu^t}$ it has been shown that the four compounds contain at least one linear $\mathrm{C{=}N\hat{=}M}$ system each and so a comparison of $\nu(\mathrm{C{=}N\hat{=}M})$ may prove of interest. The appropriate values in decreasing order are:

| | |
|---|---|
| Be | 1721 $\mathrm{cm}^{-1}$ |
| Al | 1690 $\mathrm{cm}^{-1}$ [24,37] |
| Zn | 1683 $\mathrm{cm}^{-1}$ |
| Ga | 1672 $\mathrm{cm}^{-1}$ |

Withdrawal of electron charge from the azomethine link (C=N) will weaken that bond and cause a reduction in $\nu(\mathrm{C{=}N\hat{=}M})$. For compounds having the empirical formula $\mathrm{R_2C{=}NMX_nY_y}$, the electronegativity of R,X,Y and the metal will affect the azomethine stretching frequency. Considering the metal M alone, for constant R,X and Y, the absorptions for $\nu(\mathrm{C{=}N\hat{=}M})$ should decrease in the order (Electronegativities: Ga, 1.82; Zn, 1.66; Al, 1.47; Be, 1.47)[108]

$$\mathrm{Be = Al > Zn > Ga}$$

The size of the metal atom is also important if there is to be significant (N → M) dative π-bonding. Greater overlap between nitrogen 2p and metal p orbitals available for such bonding will occur when the nitrogen and metal atoms are of similar size. The covalent radii for these elements are N,0.7; Be,1.06; Al,1.26; Ga,1.26; Zn,1.31Å [52] which would suggest the sequence

$$\text{Be} > \text{Al} = \text{Ga} > \text{Zn}$$

for the corresponding values of $\nu(\text{C}=\text{N}\overset{\rightharpoonup}{=}\text{M})$.

The infra-red spectrum of $\text{LiGa(N:CBu}^t{}_2)_4$ shows four strong absorptions at 1673, 1649, 1629, 1616 $\text{cm}^{-1}$ (Table IV.2). The first of these is appropriate for the skeletal stretching frequency $\nu(\text{C}=\text{N}\overset{\rightharpoonup}{=}\text{Ga})$ of terminally attached di-t-butylmethyleneamino ligands. The other absorptions are within the $\nu(\text{C}=\text{N})$ region (1600-1650 $\text{cm}^{-1}$) for bridging or terminally bent di-t-butylmethyleneamino ligands. The crystal structure of the aluminium derivative $\text{LiAl(N:CBu}^t{}_2)_4$ has been determined[48] (Figure IV. 4) and shows the presence of both bridging and near-linear di-t-butylmethyleneamino ligands. The terminal ligands have short (1.78Å) Al-N bonds (cf. 1.94Å for Al-N single bonds[214a]) and a C-N-Al angle of 167°. 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, it leans towards it; the Li-C(4) distance (2.37Å) is barely longer than the Li-C distance of 2.31Å in $(\text{MeLi})_4$ and 2.36Å between tetramers of the same.[214b]

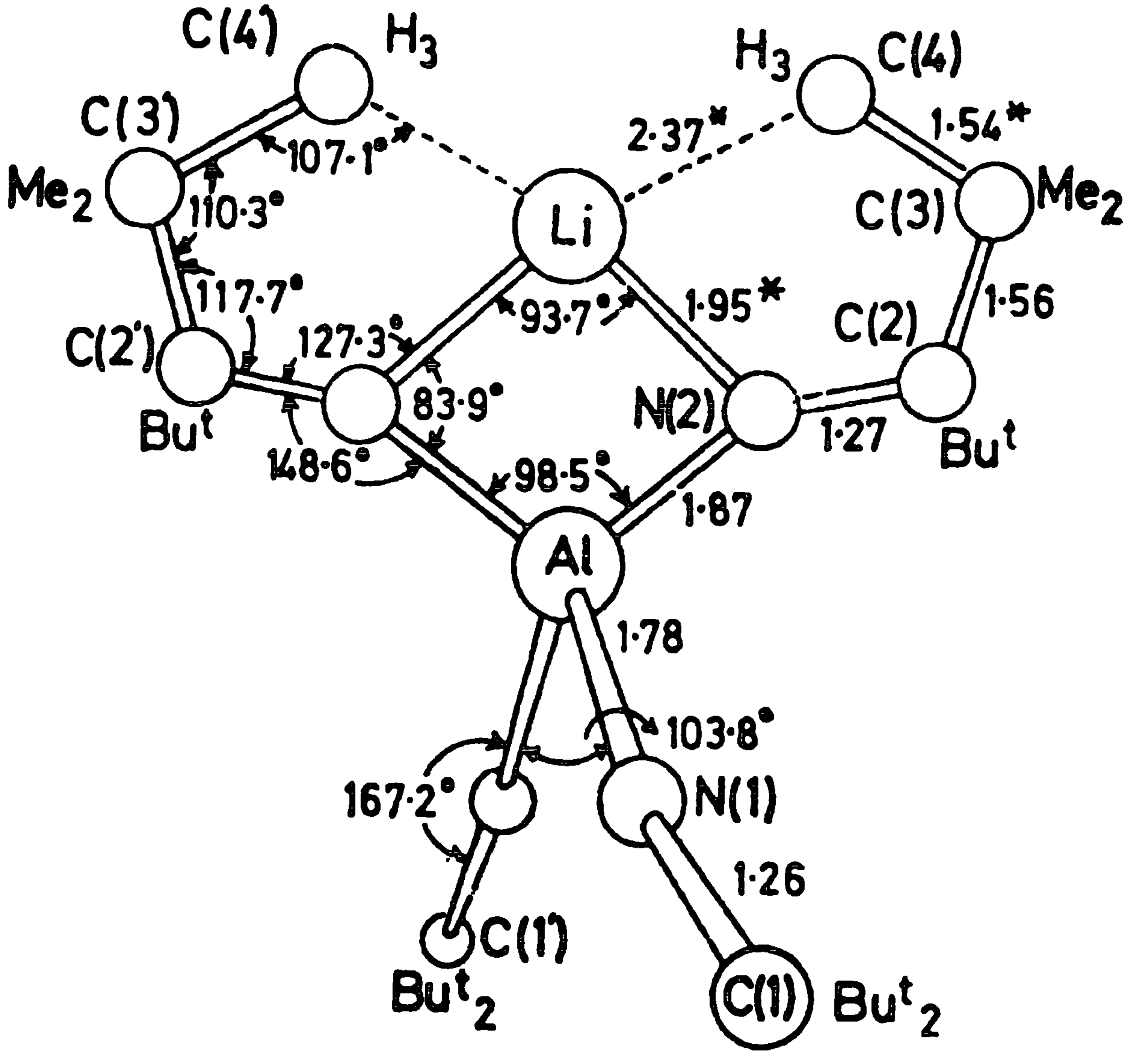


FIGURE IV.4

Crystal Structure of $LiAl(N{:}CBu^t_2)_4$

TABLE IV.4

$^1H$ n.m.r. for di-t-butylmethyleneamino derivatives of gallium

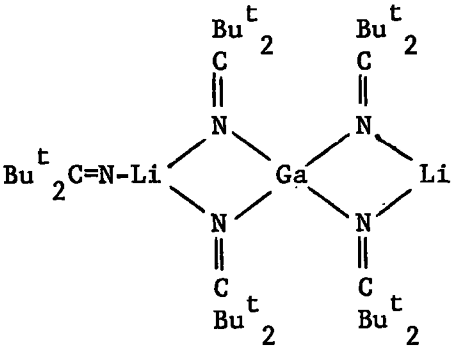
| Compound | Temperature | $\tau(Bu^t)$ |
|---|---|---|
| $(Bu^t_2C{:}NGaCl_2)_2$ | | $8.44^{35}$ |
| $(Bu^t_2C{:}N)_3Ga$ | +33° | 8.73 |
| | -50° | 8.73 |
| $LiGa(N{:}CBu^t_2)_4$ | +33° | 8.66(3),8.68(3),8.99(3),9.12(2) |
| | -50° | 8.72(3),8.79(3),9.18(3),9.36(2) |
| $Li_2Ga(N{:}CBu^t_2)_5$ | +33° | 8.69(1), 9.02(1) |

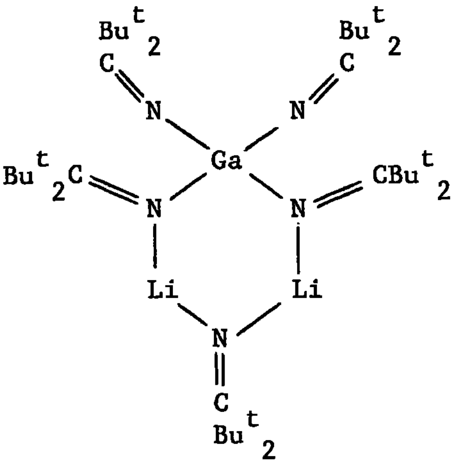
Spectra were recorded for 10 wt.% solutions in toluene, except for $(Bu^t_2C{:}NGaCl_2)_2$ in $CHCl_3$, using T.M.S. as internal reference. $\tau(Me_4Si)$ = 10.00 p.p.m.

Relative intensities in parentheses.

The n.m.r. spectrum of $LiGa(N{:}CBu^t_2)_4$ and other gallium derivatives is given in Table IV.4. Four resonances were observed for the lithio gallate with intensities 3:3:3:2. Comparison of the chemical shifts indicates that the resonances at 8.66 and 8.68τ belong to the terminal ligands since the two butyl groups of $Bu^t_2C{=}N{\doteq}Ga$ will differ only slightly, that at 8.99τ probably to the "free" butyl group attached to C(2) (Figure IV.4), and 9.12τ to the two methyl groups attached to C(3). It is possible that the third methyl resonance went undetected in the "noise" level of the n.m.r. spectrum. On cooling to -50° no further resonances appeared but the 9.12τ resonance shifted to 9.36τ, the highest value yet recorded for $Bu^t_2C{:}NM$, the previous record being 9.21τ for $LiAl(N{:}Bu^t_2)_4$.[35] On the basis of its infra-red and n.m.r. spectra, this compound is probably isostructural with $LiAl(N{:}CBu^t_2)_4$ (Figure IV.4).

The spectroscopic evidence for the formation of $Li_2Ga(N{:}CBu^t_2)_5$ is not very convincing. The infra-red frequencies for the azomethine stretch, ν(C=N), are given in Table IV.2, and by comparison with the absorptions for $(Bu^t_2C{:}N)_3Ga$, it becomes apparent that there is a marked similarity:- 1670s, 1656sh, 1626sh, 1612vs and 1672s, 1653sh, 1613vs respectively. Furthermore, the n.m.r. spectrum shows just two resonances of equal intensity at 8.69 and 9.02τ which is somewhat surprising for an expectedly complex molecule. Assigning a structure to this compound also poses a difficult problem. To accommodate five bulky di-t-butylmethyleneamino groups around gallium appears sterically improbable. Possible structures are:





the second of these being regarded as the less likely.

## TABLE IV.5

## Mass spectroscopic results for $(Bu^t_2C{:}N)_3Ga$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 491,489 | 1.2,1.8 | $(Bu_2CN)_3Ga$ |
| 490,488 | 3.6,4.9 | $(Bu_2CN)_3Ga$ minus H |
| 434,432 | 0.3,0.5 | $(Bu_2CN)_3Ga$ minus Bu |
| 433,431 | 1.3,1.8 | $(Bu_2CN)_3Ga$ minus BuH |
| 351,349 | 1.7,2.4 | $(Bu_2CN)_2Ga$ |
| 350,348 | 7,11 | $(Bu_2CN)_2Ga$ minus H |
| 238,236 | 0.2,0.3 | $Bu_2CNGa.HCN$ |
| 237,235 | 1.2,1.8 | $Bu_2(CN)_2Ga$ |
| 212,210 | 0.4,0.6 | $Bu_2CNGaH$ |
| 196,194 | 0.4,0.6 | $Bu_2CNGa$ minus Me |
| 155,153 | 1,1.4 | BuHCNGa |
| 154,152 | 15,24 | BuCNGa |
| 142 | 2 | $Bu_2CNH_2$ |
| 141 | 5 | $Bu_2CNH$ |
| 140 | 1 | $Bu_2CN$ |
| 126 | 31 | $Bu_2CNH$ minus Me |
| 84 | 99 | BuCNH |
| 71,69 | 4,6 | Ga |
| 57 | 100 | Bu |
| 42 | 67 | MeCNH |
| 41 | 99 | MeCN |

Peaks with m/e less than 41 not shown

Isotopes of gallium: $^{69}Ga = 60\%$

$^{71}Ga = 40\%$

Metastable peaks at m/e = 29.5 and 94.3

The mass spectroscopic results for $(Bu^t_2C:N)_3Ga$ are given in Table IV.5. Gallium-containing fragments were readily identified, there being two isotopes for the metal ($^{69}Ga$, 60% and $^{71}Ga$, 40%). In contrast to $(Bu^t_2C:N)_3Al$,[24] the parent peak was detected followed by three fragments still containing the $GaN_3$ skeleton. Although $(Bu_2CN)_2Ga^+$ was present, the nearest fragment to $Bu^t_2CNGa$ was $Bu^t_2CNGaH^+$. The relatively high abundance of $BuCNGa^+$ indicates that the preferred breakdown is

$$Bu_2CNGa(H) \rightarrow BuCNGa + Bu(H)$$

Loss of Bu is prevalent in most di-t-butylmethyleneamino derivatives of metals and understandably it is the most prominent peak in many spectra. Mass spectroscopic data for $LiGa(N:CBu^t_2)_4$ and $Li_2Ga(N:CBu^t_2)_5$ show peaks corresponding to $(Bu^t_2C:N)_3Ga$ and $Bu^t_2C:NLi$ but no higher peaks containing $GaN_4$ or $LiGaN_x$. The spectrum of $(Ph_2CN)_3Ga$ showed only peaks relating to the breakdown of $Ph_2CNH$, an indication of the hydrolytic instability of the monomer.

## Summary of work on Methyleneaminogallium derivatives

Four new gallium derivatives have been prepared and characterised. $(Bu^t_2C:N)_3Ga$ and $(Ph_2C:N)_3Ga$ are monomeric and on the basis of their $^1H$ n.m.r. and infra-red spectra are believed to have linear or near-linear $C{=}N{\doteq}Ga$ systems with substantial $(N{\doteq}Ga)$ dative π-bonding. Lithium tetrakis(di-t-butylmethyleneamino)gallate, $LiGa(N:CBu^t_2)_4$ is believed to be isostructural with its aluminium counterpart, with two terminal ligands and two ligands bridging the gallium and lithium atoms. The high (1673 $cm^{-1}$) azomethine stretching frequency of the terminally attached ligands is appropriate for $N{\doteq}Ga$ ($p \rightarrow d$) dative π-bonding. A second lithium-containing product, $Li_2Ga(N:CBu^t_2)_5$, was obtained but its spectroscopic properties could not be rationalised. An attempt to prepare $(Bu^t_2C:N)_2GaCl$ failed owing to disproportionation to $(Bu^t_2C:N)_3Ga$ and $(Bu^t_2C:NGaCl_2)_2$.

Methyleneamino-aluminium and -gallium derivatives are listed in Tables IV.6 and 7.

## TABLE IV.6

## Aluminium Derivatives $(R^1R^2C:NAlR^3R^4)_2$

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $\nu(C=N)$ $cm^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Me | H | Me | Me | 1675 | 50 |
| $Bu^t$ | H | Me | Me | 1661 | 50 |
| Ph | H | Me | Me | 1630 | 50,181 |
| $Bu^t$ | H | Et | Et | 1656 | 50 |
| Ph | H | Et | Et | 1633 | 50,181 |
| Pr | H | $Bu^i$ | $Bu^i$ | ? | 7 |
| Me | Me | Me | Me | 1658 | 50 |
| Et | Me | Me | Me | 1653 | 50 |
| $Bu^t$ | Me | Me | Me | 1630 | 50 |
| Ph | Me | Me | Me | 1634 | 50,181 |
| Me | Et | Et | Et | 1650 | 50 |
| Me | Ph | Ph | Ph | 1621 | 50 |
| $Bu^t$ | Ph | Ph | Ph | 1616 | 50 |
| Ph | Ph | Ph | Ph | 1604 | 24,172 |
| Ph | Ph | Me | Me | 1616 | 24,172 |
| Ph | Ph | Et | Et | 1609 | 172 |
| $Bu^t$ | $Bu^t$ | Me | Me | 1637 | 194 |
| $Bu^t$ | $Bu^t$ | $Bu^i$ | $Bu^i$ | 1709 | 194 |
| Me | Me | Cl | Me | 1650 | 50 |
| $Bu^t$ | Me | Cl | Me | 1625 | 50 |
| Ph | Me | Cl | Me | 1619 | 50,181 |
| $Me_2N$ | H | Et | Et | 1626 | 192 |
| $Me_2N$ | Ph | Et | Et | 1573 | 182 |
| $Me_2N$ | p-tolyl | Et | Et | 1557 | 182 |
| $Me_2N$ | p-$NO_2C_6H_4$ | Et | Et | 1587 | 182 |
| $Me_2N$ | p-$MeOC_6H_4$ | Et | Et | 1568 | 182 |
| $Me_2N$ | p-$Me_2NC_6H_4$ | Et | Et | 1565 | 182 |
| $Me_2N$ | Me | Et | Et | 1578 | 182 |

contd./

Table IV.6 contd.

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $\nu$(C=N) $cm^{-1}$ | Ref |
|---|---|---|---|---|---|
| $Me_2N$ | $C_6H_5CH_2$ | Et | Et | 1571 | 182 |
| $Me_2N$ | $Me_2N$ | Me | Me | 1618 | 193 |
| $Me_2N$ | $Me_2N$ | Et | Et | 1610 | 193 |
| $Me_2N$ | $Me_2N$ | Cl | Cl | 1647,1658 | 193 |
| Ph | Ph | Cl | Cl | 1593 | 24 |
| Ph | Ph | Br | Br | 1587 | 24 |
| $Bu^t$ | $Bu^t$ | Cl | Cl | 1664 | 24 |
| $(Ph_2C:N)_3Al$ | | | | 1686 | 24,37 |
| $(Bu^tC:N)_3Al$ | | | | 1690 | 24,37 |
| $LiAl(N:CBu^t{}_2)_4$ | | | | 1700,1642,1602 | 35 |

## TABLE IV.7

### Methyleneamino derivatives of gallium

| Compound | $\nu$(C=N) | Ref |
|---|---|---|
| $(PhCH{:}NGaEt_2)_2$ | 1688,1633 | 115 |
| $(Bu^tCH{:}NGaEt_2)_2$ | 1658 | 115 |
| $(Ph_2C{:}NGaMe_2)_2$ | 1626 | 173 |
| $(Ph_2C{:}NGaEt_2)_2$ | 1613 | 173 |
| $(Ph_2C{:}NGaPh_2)_2$ | 1612 | 173 |
| $(Ph_2C{:}NGaCl_2)_2$ | 1591 | 25 |
| $(Ph_2C{:}N)_3Ga$ | 1645,1620 | a |
| $(Bu^t{}_2C{:}NGaCl_2)_2$ | 1647 | 35 |
| $(Bu^t{}_2C{:}N)_3Ga$ | 1672,1653*,1613 | a |
| $LiGa(N{:}CBu^t{}_2)_4$ | 1673,1649,1629,1616 | a |
| $Li_2Ga(N{:}CBu^t{}_2)_5$ | 1670,1656*,1626*,1612 | a |

a. this work

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# CHAPTER V

# DIPHENYLMETHYLENEAMINO DERIVATIVES OF SILICON

This chapter describes the reactions between methylchlorosilanes, $Me_nSiCl_{4-n}$ (n = 0-2) and diphenylmethyleneaminolithium, $Ph_2C:NLi$. The extent to which the shapes of their C=N-Si units can be inferred from their infra-red spectra is discussed and related to corresponding di-t-butylmethyleneaminosilanes.

## EXPERIMENTAL SECTION

### Starting materials

Chlorosilanes (gifts from Midland Silicones Ltd.) were all distilled before use. Diphenylmethyleneamine was prepared by methanolysis of the product of reaction between benzonitrile and phenylmagnesium bromide.[61] Its N-lithio derivative was prepared in solution from equimolar proportions of diphenylmethyleneamine in ether and n-butyl-lithium in hexane. Manipulations were carried out using a dry nitrogen-filled glove box or nitrogen-filled apparatus as appropriate.

### Preparation of Diphenylmethyleneaminochloro(dimethyl)silane, $Ph_2C:NSiMe_2Cl$

When $Me_2SiCl_2$ (2.58 g., 20 mmole) and $Ph_2C:NLi$ (20 mmole) in ether (60 ml.) were mixed at -196° and then stirred at 20° for 3h, lithium chloride was precipitated. The ether was removed under vacuum, toluene was added, and the solution filtered, all at room temperature. Removal of the toluene under reduced pressure left a pale yellow viscous oil which was identified as diphenylmethyleneaminochloro(dimethyl)silane, $Ph_2C:NSiMe_2Cl$. Vacuum distillation of this product was not attempted in view of the reported[9] disproportionation reaction. (Found: C,65.5; H,6.0; Cl,12.3; N,5.0%; M,260. $C_{15}H_{16}ClNSi$ requires C,65.8; H,5.9; Cl,13.0;

N,5.1%; M,273); $\nu_{max}$ (Liquid film) 1660vs, 1653vs, 1600m, 1582m, 1488vw, 1447m, 1400w, 1377w, 1362w, 1312m, 1271sh, 1255s, 1193w, 1176w, 1149w, 1075m, 1028m, 1000w, 971vw,br, 935m, 907s, 864vs, 825s, 790vs, 757m, 696vs, 660m, 627m, 621m, 568w, 535m,br and 470m,br $cm^{-1}$. After samples of this compound had been kept at about 15° for a week or held a few minutes at 50°, they deposited solid bis(diphenylmethyleneamino)dimethylsilane, $(Ph_2C:N)_2SiMe_2$, m.p. 126-128°, identified by comparison of its infra-red spectrum with that of an authentic sample prepared from $Me_2SiCl_2$ + $2Ph_2C:NLi$ (see next experiment) and data reported[9] for the same disproportionation reaction.

Preparation of bis(diphenylmethyleneamino)dimethylsilane, $(Ph_2C:N)_2SiMe_2$

$Me_2SiCl_2$ (1.29 g., 10 mmole) was added to a solution of $Ph_2C:NLi$ (20 mmole) in ether (60 ml.) at -196°. As the mixture warmed up to room temperature, the red colour of the reactants changed to yellow and lithium chloride was precipitated. After stirring overnight, the solvent was pumped off and the lithium chloride separated by filtration using toluene (40 ml.) as solvent. The product was obtained as yellow-brown crystals from hexane solution and identified as bis(diphenylmethyleneamino)dimethylsilane, $(Ph_2C:N)_2SiMe_2$, m.p.126-128°. (Found: C,81.7; H,6.4; N,6.6%; M,401. $C_{28}H_{26}N_2Si$ requires C,80.4; H,6.2; N,6.7%; M,418); $\nu_{max}$ (Nujol mull) 1645sh, 1634s, 1597m, 1581m, 1311m, 1290w, 1266m, 1248m, 1179w, 1160vw, 1149w, 1093w,br, 1074w, 1026w, 1000w, 973w, 936m, 910sh, 905s, 853vs, 803w, 793sh, 785s, 756w, 720w, 708s, 700sh, 696vs, 649w, 628m, 619w, 545m, 535w and 429m $cm^{-1}$.

Preparation of Bis(diphenylmethyleneamino)chloro(methyl)silane, $(Ph_2C:N)_2SiMeCl$.

$MeSiCl_3$ (2.99 g., 20 mmole) was added to a solution of $Ph_2C:NLi$ (20 mmole) in ether (60 ml.) at -196°. The red colour of $Ph_2C:NLi$ persisted until room temperature was reached and then a thick precipitate of lithium chloride formed. After stirring overnight, the ether was removed and replaced by toluene. The LiCl was filtered off and solvent pumped away under vacuum. A translucent oil remained which when dissolved in pentane and allowed to stand for an hour, deposited a very pale yellow solid identified as bis(diphenylmethyleneamino)chloro(methyl)silane, $(Ph_2C:N)_2SiMeCl$. (Found: C,73.9; H,5.1; Cl,8.1; N,6.4%; M,436. $C_{27}H_{23}ClN_2Si$ requires C,73.9; H,5.2; Cl,8.1; N,6.4%; M,438.5); $\nu_{max}$ (Nujol mull) 1661sh, 1655sh, 1645s, 1630vs, 1596s, 1578s, 1314m, 1272s, 1261sh, 1193vw, 1179w, 1156w, 1096vw, 1074m, 1026m, 1000w, 973vw, 937s, 907s, 859vs, 838s, 787s, 766m, 758m, 727s, 700sh, 695vs, 676sh, 627s, 618sh, 568w, 545s, 500s, 490sh, 451w,br and 431m,br $cm^{-1}$.

Preparation of Bis(diphenylmethyleneamino)dichlorosilane, $(Ph_2C:N)_2SiCl_2$

An excess of silicon tetrachloride (5.1 g., 30 mmole) was added to a solution of diphenylmethyleneaminolithium (20 mmole) in ether (60 ml.) at -196°. The red colour of the diphenylmethyleneaminolithium solution gradually changed to orange and finally yellow as the mixture attained room temperature. After several hours stirring at room temperature, the lithium chloride was separated by filtration and solvent removed from the filtrate under reduced pressure. Crystallisation of the residue from pentane afforded the pale yellow product bis(diphenylmethyleneamino)dichlorosilane, $(Ph_2C:N)_2SiCl_2$, m.p. 103-105° (Found: C,67.8; H,4.3; Cl,15.4; N,5.9%; M,445. $C_{26}H_{20}Cl_2N_2Si$ requires C,68.0; H,4.4; Cl,15.4; N,6.1%; M,459); $\nu_{max}$ (Nujol mull) 1663sh, 1656vs, 1602s, 1582m, 1316m, 1279s, 1247sh, 1178w, 1160w, 1105vw,br, 1074w, 1028w, 1000w, 973w, 939m, 932m, 913s, 885s, 855m, 844m, 789m, 760m, 724w, 702vs, 692vs, 633s, 618vw, 613vw, 567s, 556s 536s, 474m and 449w,br $cm^{-1}$.

This same product was obtained when an attempt to synthesise $(Ph_2C:N)_3SiCl$ was made by reacting $SiCl_4$ and $Ph_2C:NLi$ in 1:3 molar proportions.

## Attempted synthesis of Diphenylmethyleneaminodichloro(vinyl)silane, $Ph_2C:NSi(CH:CH_2)Cl_2$.

Reaction of equimolar proportions of $Ph_2C:NLi$ and $CH_2:CHSiCl_3$ using the procedure described above yielded an oil with a chlorine content of 12.7% ($Ph_2C:NSi(CH:CH_2)Cl_2$ requires Cl,23.2% and $(Ph_2C:N)_2Si(CH:CH_2)Cl$ requires Cl,7.9%). Attempted distillation of the oil resulted in a brown residue with a composition that was inappropriate for either of the possible products mentioned (Cl,19.8%).

## DISCUSSION

Considerable interest has been focussed on the nature of the Si-N bonding in silicon-nitrogen chemistry. Silicon, in its most common state, is four co-ordinate and surrounded by an octet of electrons, thus preventing any possibility of N → Si (p → p) π-bonding. However being an element of the second row of the Periodic Table, it is theoretically possible for there to be N → Si (p → d) π-bonding through use of the vacant silicon d-orbitals. The extent of (p → d) π-bonding should be maximal when the nitrogen "lone pair" occupies a pure p-orbital and the σ-bonds about the nitrogen are planar. Furthermore, any such multiple bonding between nitrogen and silicon should lead to an Si-N bond length shorter than that for a σ-bonded Si-N system. Several structures of silicon-nitrogen compounds have been determined that do show these effects: $(H_3Si)_3N$[215,216] with a planar $NSi_3$ unit, $(H_3Si)_2NMe$,[217] $H_3SiNMe_2$,[218] $ClSi(NMe_2)_3$[219] which is planar about the nitrogen atoms, $(H_3Si)_2NH$,[220] $(Me_3Si)_2NH$,[220] $(H_3Si)_2NBF_2$[220,221] with both planar $Si_2NB$ and $NBF_2$ groups, and $(H_3Si)_2NN(SiH_3)_2$[222] which has a planar $Si_2NN$ conformation. The Si-N bond lengths in these compounds lie in the range 1.71 to 1.74Å, shorter than the sum of the covalent radii of silicon and nitrogen (1.17 + 0.7 respectively = 1.87Å [52]). For the Group IV elements in general, N → M (p → d) π-interactions have been studied by several techniques. Investigations into the N-methyl $^{13}C$-H coupling constants for $Me_3MNMe_2$ and $M(NMe_2)_4$ (M = C,Si,Ge and Sn) established the order for decreasing (p-d) π-overlap of Si > Ge > Sn.[223] Similarly, the $^{15}N$ n.m.r. and infra-red spectroscopic results for trimethylsilyl-, trimethylgermyl- and trimethylstannyl-anilines[224] led to the same conclusion. Force constants have been calculated from the spectroscopic data[225,226] and they indicate that the N-M bond orders for silicon, germanium and tin are all greater than unity. Even tin exhibits multiple π-bonding with nitrogen, as reflected in the near-linear M-N-C groups (M = Si or Sn) which would be appropriate for maximum N → M (p → d) π-bonding:

| Compound | Angle M-N-C |
|---|---|
| $Si(NCS)_4$[227] | 180° |
| $Si(NCO)_4$[228] | 180° |
| $H_3SiNCS$[229] | 180° |
| $Me_3SnNCS$[230] | 173° |
| $Me_2Sn(NCS)_2$[231,232] | 164° |
| $[(Me_2SnNCS)_2O]_2$[233] | 169° |

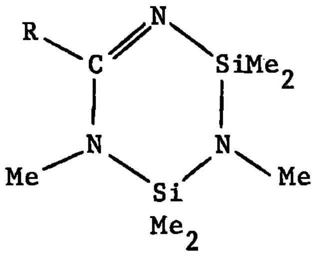
Both $Me_3SiNCS$ and $Me_3SiNCO$ have non-linear Si-N-C groups (Si-N-C angles, 154° and 150° respectively)[234] but it has been noted by Ebsworth[10] that dative π-bonding can still be appreciable even when the Si-N-C skeleton is non-linear. Photoelectron spectroscopy has been employed to determine the electronic structure of several systems within Group IV and it was concluded that d-orbital participation in the bonding with other elements was significant with silicon and germanium.[235,236] Electronic absorption spectroscopy has been used to detect N → Si (p → d) dative π-bonding and three comprehensive studies have been made, two on methyleneaminosilanes[9,237] (see Introductory chapter) and the third on aminosilanes.[238] Theoretical molecular-orbital calculations on silylamine also predict the presence of silicon d-orbital participation with the lone pair of electrons on the nitrogen.[239,240]

An area of silicon-nitrogen chemistry that has not been exhaustively explored is that in which methyleneamino groups are among the silicon ligands. Knowing the shape of the Si-N=C skeleton can potentially provide much insight into N → Si (p → d) dative π-bonding. Only four studies have been reported on such compounds:- $R^1R^2C{:}NSiR^3R^4R^5$;[9] $Ph_2C{:}NSiR_3$ (R = Me,Et,Ph) and $(Ph_2C{:}N)_4Si$;[100] $Bu^t{}_2C{:}NSiMe_nCl_{3-n}$ and $(Ph_2C{:}N)_2SiMeCl_{2-n}$;[39] and $[(CF_3)_2C{:}N]_nSiMe_{4-n}$.[237] Described below is a further study of the $Ph_2C{:}NSi$ system. The properties, in particular the infra-red spectra, are discussed and compared with the properties of the $Bu^t{}_2C{:}NSi$ systems which are believed to have linear C-N-Si units.[39]

The first methyleneamino derivative of silicon to be reported was $PhCH{:}NSiEt_3$ which was prepared by the reaction between benzonitrile and triethylsilane:[241]

$$PhCN + Et_3SiH \rightarrow PhCH{:}NSiEt_3$$

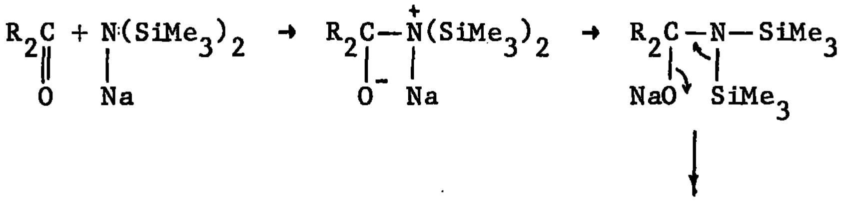
Since then numerous silicon compounds, $R^1R^2C{:}NSiR^3R^4R^5$, have been prepared by a variety of methods: for $R^1 = OSiR_3$,[242-245] $R^1 = NR_2$,[246] $R^1 = OR$ and $R^2 = NR_2$,[247] and also cyclic imines[248] of the type shown:



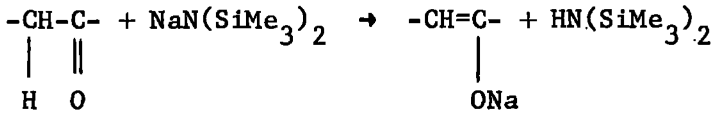
A route to these compounds that has been most extensively studied is the reaction between sodium bis(trimethylsilyl)amide, $NaN(SiMe_3)_2$, and non-enolisable aldehydes and ketones:[249]

$$NaN(SiMe_3)_2 + R^1R^2C{=}O \rightarrow R^1R^2C{=}NSiMe_3 + NaOSiMe_3$$

The reaction is thought to proceed thus:



This method is not applicable to all syntheses since carbonyl compounds having hydrogen atoms attached to the α-carbon atom react in the enol form giving hexamethyldisilazane and the sodium enolate only:[250]



$$\underset{H}{-CH}-\underset{O}{\overset{}{C}}- + NaN(SiMe_3)_2 \rightarrow -CH{=}\underset{ONa}{C}- + HN(SiMe_3)_2$$

The use of methyleneaminolithium derivatives to prepare methyleneaminosilicon compounds is the other main route:[9,39,100,237]

$$\begin{tikzcd}
R^1CN + R^2Li \arrow[dr] & & \\
& R^1R^2C{:}NLi \arrow[r, "R_3SiCl"] & R^1R^2C{:}NSiR_3 + LiCl \\
R^1R^2C{:}NH + R^3Li \arrow[ur] & &
\end{tikzcd}$$

Again, the lithio derivative should not have hydrogen atoms attached to the $\alpha$-carbon atom or imine-enamine tautomerism will result. In the present work, this complication was avoided by using diphenylmethyleneaminolithium, $Ph_2C{:}NLi$.

A few compounds having the formula $(Ph_2C{:}N)_nSiMe_{4-n}$ have been reported: $Ph_2C{:}NSiMe_3$,[9,100] $(Ph_2C{:}N)_2SiMe_2$,[9] $(Ph_2C{:}N)_3SiMe$[9] and $(Ph_2C{:}N)_4Si$ but attempts[9] to prepare methyleneamino(chloro)silanes failed owing to disproportionation reactions.

In this present investigation, equimolar proportions of the methylchlorosilanes $Me_nSiCl_{4-n}$ (n = 0-2) and diphenylmethyleneaminolithium $Ph_2C{:}NLi$ were mixed at or below room temperature in a hydrocarbon solvent, the solvent was removed by low pressure distillation, and the residue purified either by crystallisation or by vacuum distillation, the product in each case was the bis(diphenylmethyleneamino)silane $(Ph_2C{:}N)_2SiMe_nCl_{2-n}$, showing that the required mono-substituted compound $Ph_2C{:}NSiMe_nCl_{3-n}$ had disproportionated:

$$Me_nSiCl_{4-n} + Ph_2C{:}NLi \rightarrow Ph_2C{:}NSiMe_nCl_{3-n} + LiCl$$

$$2Ph_2C{:}NSiMe_nCl_{3-n} \rightarrow (Ph_2C{:}N)_2SiMe_nCl_{2-n} + Me_nSiCl_{4-n}$$

Such a disproportionation had already been noted for the system with n = 2 by Chan and Rochow[9] who obtained the compound $(Ph_2C{:}N)_2SiMe_2$ as the product of reaction between equimolar proportions of $Me_2SiCl_2$ and

$Ph_2C{:}NLi$. This particular disproportionation proved to be slow enough at room temperature to allow the mono-substituted compound $Ph_2C{:}NSiMe_2Cl$ to be isolated and characterized. It was obtained as an oil from the reaction between $Ph_2C{:}NLi$ and $Me_2SiCl_2$ at room temperature. It disproportionated during several days at 15-20°, and much more rapidly above about 50°, depositing $(Ph_2C{:}N)_2SiMe_2$ as a yellow solid.

The stability of the compounds $Ph_2C{:}NSiMe_nCl_{3-n}$ to disproportionation apparently decreases as n decreases; it was not found possible to isolate samples of either $Ph_2C{:}NSiMeCl_2$ or $Ph_2C{:}NSiCl_3$ even from the reaction mixtures which had not been allowed to warm above 15°; the products obtained were the new bis(diphenylmethyleneamino)silanes $(Ph_2C{:}N)_2SiMeCl$ and $(Ph_2C{:}N)_2SiCl_2$.

Disproportionation reactions are not an uncommon feature of silicon chemistry. Chan and Rochow also found that diphenylmethyleneamino-(diethylamino)dimethylsilicon gave the bis derivative:[9]

$$2Ph_2C{:}NSiMe_2(NEt_2) \rightarrow (Ph_2C{:}N)_2SiMe_2 + (Et_2N)_2SiMe_2$$

Kinetic data for such reactions have been reviewed.[251] Of interest is the reaction between bis(dimethylamino)dimethylsilane and dimethyldichlorosilane:[251,252]

$$Me_2Si(NMe_2)_2 + Me_2SiCl_2 \xrightarrow{25^{o}} 2Me_2Si(NMe_2)Cl$$

The equilibrium is established within three minutes and $K_{eq} = 6000$, thus favouring the mixed species. This is in marked contrast to the disproportionation of $Ph_2C{:}NSiMe_2Cl$ as described above.

Bis(diphenylmethyleneamino)dimethylsilane, $(Ph_2C{:}N)_2SiMe_2$, was also prepared by reacting $Ph_2C{:}NLi$ (2 moles) with $Me_2SiCl_2$ (1 mole). The product was obtained as yellow-brown crystals m.p. 126-128°. The physical properties of this compound compare favourably with the properties of the same product Chan and Rochow prepared from the disproportionation of $Ph_2C:NSiMe_2Cl$.[9]

Two other reactions were attempted. The first was the reaction between 3 moles of diphenylmethyleneaminolithium and one mole of silicon tetrachloride, in an attempt to prepare $(Ph_2C:N)_3SiCl$. However, the only product obtained was the bis-substituted product:

$$3Ph_2C:NLi + SiCl_4 \rightarrow (Ph_2C:N)_2SiCl_2 \text{ not } (Ph_2C:N)_3SiCl$$

The formation of bis-,[9,39] tris-[9] and tetrakis-[100] diphenylmethyleneaminosilanes can be contrasted with the inability of di-t-butylmethyleneaminosilanes, $Bu^t_2C:NSiMe_nCl_{3-n}$ (n = 0-2), to undergo further substitution of chlorine.[39]

A second difference between diphenyl- and di-t-butylmethyleneaminosilanes was the failure of the reaction between $Ph_2C:NLi$ and $CH_2:CHSiCl_3$:

$$Bu^t_2C:NLi + CH_2:CHSiCl_3 \rightarrow Bu^t_2C:NSi(CH:CH_2)Cl_2 + LiCl \quad \text{Ref.39.}$$

$$Ph_2C:NLi + CH_2:CHSiCl_3 \not\rightarrow Ph_2C:NSi(CH:CH_2)Cl_2$$

The chlorine content of the residue from the second reaction was intermediate between that appropriate for $Ph_2C:NSi(CH:CH_2)Cl_2$ and $(Ph_2C:N)_2Si(CH:CH_2)Cl$. Possibly the residue consisted of an equilibrium mixture of the last two mentioned compounds.

Selected infra-red absorptions of the new compounds are given in Table V.1. The assignment of a band at 905 $cm^{-1}$ to the silicon-nitrogen stretching vibration for the compound $(Ph_2C:N)_2SiMe_2$ differs from that of Chan and Rochow,[9] whose figure (970 $cm^{-1}$) may arise from a transposition

## TABLE V.1

## Characteristic infra-red absorptions for the new diphenylmethyleneaminosilanes

| Compound | ν(C=N) | ν(Si-N) | ρ(Si-Me) | ν(Si-Cl) |
|---|---|---|---|---|
| $Ph_2C:NSiMe_2Cl$ | 1660,1653 | 907 | 864,825 | 535,470 |
| $(Ph_2C:N)_2SiMe_2$ | 1634 | 905 | 853 | - |
| $(Ph_2C:N)_2SiMeCl$ | 1645,1630 | 907 | 859,838 | 545,500 |
| $(Ph_2C:N)_2SiCl_2$ | 1656 | 913 | - | 567,556,536 |

| | |
|---|---|
| ν(C=N) | is C=N stretching |
| ν(Si-N) | is Si-N stretching |
| ρ(Si-Me) | is methyl rocking and Si-C stretching |
| ν(Si-Cl) | is Si-Cl stretching |

of the last two digits. The assignment of the bands in this region (~ 907 $cm^{-1}$) is in accord with the assignments made for azidotrimethylsilane (800 $cm^{-1}$),[253] N-trimethylsilylaniline (899 $cm^{-1}$)[224] and chlorosilylamines (ca.940 $cm^{-1}$).[254] The bands in the regions 800-865 $cm^{-1}$ and 470-570 $cm^{-1}$ are tentatively assigned to methyl rocking/Si-C stretching and Si-Cl stretching respectively; Smith[255] quotes ranges 760-840 $cm^{-1}$ and 417-625 $cm^{-1}$ for these assignments. In the spectra of the new compounds, peaks at ca.787, 758, 694 $cm^{-1}$ appear which can be attributed to the presence of the hydrolysis product, $Ph_2C:NH$, which absorbs at these frequencies. The figures for ρ(Si-Me) quoted for compounds prepared by Chan and Rochow appear to be suspiciously near to the frequencies of the free ketimine.[9]

Of interest in the spectra are the values for ν(C=N). These are listed again in Table V.2 along with analogous di-t-butylmethyleneaminosilanes. The absorptions attributable to both the C=N and the Si-N skeletal stretching vibrations occur at significantly lower frequency than the corresponding di-t-butylmethyleneaminosilanes. The parent imines $Bu^t_2C:NH$ and $Ph_2C:NH$, have very similar azomethine stretching frequencies (1610 and 1607 $cm^{-1}$ respectively[21]) so it appears possible that the two sets of imino-derivatives differ in geometry.

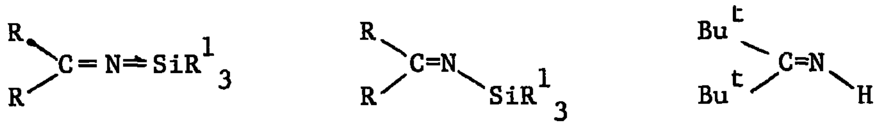
TABLE V.2

Skeletal stretching frequencies ($cm^{-1}$) of some methyleneaminosilanes

| Compound | ν(C=N) | ν(Si-N) | Compound† | ν(C=N) | ν(Si-N) |
|---|---|---|---|---|---|
| $(Ph_2C:N)_4Si$[100] | 1646 | 913 | | | |
| $(Ph_2C:N)_3SiMe$[9] | 1643 | 910 | | | |
| $(Ph_2C:N)_2SiMe_2$ | 1634 | 905 | | | |
| $Ph_2C:NSiMe_3$[9] | 1642 | 907 | $Bu^t_2C:NSiMe_3$ | 1735 | 959 |
| $Ph_2C:NSiMe_2Cl$ | 1660,1653 | 907 | $Bu^t_2C:NSiMe_2Cl$ | 1736 | 965 |
| $(Ph_2C:N)_2SiMeCl$ | 1645,1630 | 907 | $Bu^t_2C:NSiMeCl_2$ | 1736 | 966 |
| $(Ph_2C:N)_2SiCl_2$ | 1656 | 913 | $Bu^t_2C:NSiCl_3$ | 1729 | 967 |

† the data for di-t-butylmethyleneaminosilanes are taken from Ref.39.

The di-t-butylmethyleneaminosilanes have an azomethine stretching frequency, ν(C=N), of about 1730 $cm^{-1}$ which is some 120 $cm^{-1}$ higher in frequency than the parent imine. Such an increase in frequency is appropriate for a linear C-N-Si group (Figure V.1 where R = $Bu^t$) as has been observed in other systems: $(mesityl)_2BN{:}CPh_2$,[11,15] $LiAl(N{:}CBu^t_2)_4$[35,48] and $[(Bu^t_2C{:}N)_2Be]_2$[51] for which X-ray crystallography has shown the presence of near linear C=N-M units with correspondingly high azomethine stretching frequencies. Additional evidence to support the proposed linear C=N-Si groups is provided by the $^1H$ n.m.r. spectra which show that the signal (a singlet) for the tertiary butyl groups of $Bu^t_2C{:}NSiMe_nSl_{3-n}$ does not change significantly in shape or chemical shift when the solutions are cooled to $-60^o$. This is consistent with structure (a) rather than (b) (Figure V.1 where R = $Bu^t$). The less likely alternative is that a bent



(a) (b) (c)

FIGURE V.1

structure (b), containing two types of t-butyl group is inverting at nitrogen so rapidly at $-60^o$ as to render all the t-butyl protons apparently equivalent. In view of the fact that the $^1H$ n.m.r. spectrum of $Bu^t_2C{:}NH$ in toluene at $-60^o$ shows two resonances of equal intensity attributable to the magnetically distinct t-butyl groups in its bent structure (c), such an inversion at nitrogen is improbable.

The azomethine stretching frequencies, ν(C=N), for the diphenylmethyleneaminosilanes do not show the same consistency as the di-t-butylmethyleneaminosilanes (ca. 1730 $cm^{-1}$) but fall within the range 1630-1660 $cm^{-1}$. Also, the silicon-nitrogen stretching frequencies are lower than the frequencies for $Bu^t_2C{:}NSiMe_nCl_{3-n}$. Both sets of frequencies for $\nu$(C=N) and $\nu$(N-Si) appear appropriate for a non-linear C=N-M group (Figure V.1(b) where R = Ph).

For analogous methyleneamino derivatives within Group IV the variation of $\nu$(C=N) decreases in the sequence Si > Ge[9] > Sn[9] (compare, for example, $Ph_2C{:}NSiMe_3$, 1642 $cm^{-1}$; $Ph_2C{:}NGeMe_3$, 1630 $cm^{-1}$; $Ph_2C{:}NSnMe_3$, 1613 $cm^{-1}$). The electronegativity of the metal (Si,1.74; Ge,2.02; Sn,1.72)[108] may be expected to affect $\nu$(C=N) but the values cited would not lead to the observed sequence. Of greater importance are the covalent radii of the metals (Si,1.17; Ge,1.22; Sn,1.40Å)[52] since any N → M (p → d) π-bonding will be maximal when the p-orbitals of nitrogen and the d-orbitals of the metal are of the same size. Thus any multiple bonding would be expected to decrease in the order Si > Ge > Sn and lead to a decrease in $\nu$(C=N) in the same order. The mass of the metal, M, in $Ph_2C{:}NMR_3$ would also lead to the sequence of $\nu$(C=N) of Si > Ge > Sn. A significant factor is the mechanical constraint imposed on the C=N vibration by the M-N bond. The force constants of the M-N bond follow the sequence Si > Ge > Sn[225] which is consistent with the decrease of $\nu$(C=N) from silicon to tin compounds.

Unfortunately, it was not possible to use the $^1H$ n.m.r. spectra of the diphenylmethyleneaminosilanes to obtain further structural information. The broadness of the resonance due to their aryl protons was too great to allow this to be used as a guide to whether they contained only one type or two magnetically distinct types of phenyl group.

The electronic spectra of a number of diarylmethyleneaminosilanes[9] have been investigated to study the $d_\pi$-$p_\pi$ interaction between the empty d-orbitals of silicon and the π-system of the C=N bond. On the basis of the results, it was postulated that $R_2C{:}NSiR^1{}_3$ (R = aryl) had a bent N=C-Si skeleton and consequently little multiple bonding in the Si-N bond.

The mass spectra of the new diphenylmethyleneaminosilanes were recorded and are presented in Tables V.3,4 and 5. The three spectra clearly show the monomeric nature of $Ph_2C{:}NSiMe_2Cl$, $(Ph_2C{:}N)_2SiMeCl$ and $(Ph_2C{:}N)_2SiCl_2$. Common to both the latter compounds are appearance of fragments derived from the presumably more volatile mono-derivatives, $Ph_2C{:}NSiMeCl_2$ and $Ph_2C{:}NSiCl_3$ respectively. Phenyl groups attached to the imino ligand seem fairly labile as evidenced by the peaks attributable to $PhSi^+$, $PhSiCl_2{}^+$, $PhSiMeCl^+$ and $Ph_2SiCl^+$. The bond energy terms for Si-N, Si-C and Si-Cl are 77,[256] 65[257] and 102[257] kcal.mole$^{-1}$ and the intensities of certain peaks reflect these bond strengths; chlorine-containing fragments appear to be the most abundant, followed by nitrogen-silicon fragments.

## Summary of the Diphenylmethyleneaminosilanes

Equimolar proportions of $Me_nSiCl_{4-n}$ (n = 0-2) and $Ph_2C{:}NLi$ afford the diphenylmethyleneaminosilanes $(Ph_2C{:}N)_2SiMe_nCl_{2-n}$, apparently through disporportionation of the mono-substituted compounds $Ph_2C{:}NSiMe_nCl_{3-n}$ which could be isolated only when n = 2. The infra-red spectra of these compounds have an azomethine stretching frequency, $\nu(C{=}N)$ within the range 1630-1660 cm$^{-1}$ which has been interpreted in terms of a bent C:NSi skeleton in contrast to the di-t-butylmethyleneaminosilanes.[39] No evidence was found to support any N → Si (p → d) multiple $\pi$-bonding.

Attempts to prepare $Ph_2C{:}NSi(CH{:}CH_2)Cl_2$ and $(Ph_2C{:}N)_3SiCl$ were unsuccessful, probably due to partial disproportionation.

A review of methyleneamino derivatives of silicon has been written[258] that contains some seventy compounds. Since then, work on bis(trifluoromethyl) methyleneamino derivatives of Group IV elements has been prominent. A recent report on $[(CF_3)_2C{:}N]_nMMe_{4-n}$ compounds has been published[237] and the infra-red results are shown in Table V.6. The azomethine stretching frequencies, $\nu(C{=}N)$, of the listed compounds follow the trends noted above for $(Ph_2C{:}N)_nMMe_{4-n}$ (M = Si, Ge or Sn).

## TABLE V.3

## Mass spectroscopic results for $Ph_2C:NSiMe_2Cl$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 275,273 | 5.5, 14 | $Ph_2CNSiMe_2Cl$ |
| 260,258 | 0.75,1.4 | $Ph_2CNSiMeCl$ |
| 245,243 | 0.4, 1.2 | $Ph_2CNSiCl$ |
| 238 | 2 | $Ph_2CNSiMe_2$ |
| 207 | 4 | $Ph_2CNSi$ minus H |
| 199,197 | 3,9 | $PhHCNSiMe_2Cl$ |
| 198,196 | 19,55 | $Ph_2CNSiMe_2Cl$ minus Ph |
| 182 | 6 | $Ph_2CNH_2$ or $Ph_2Si$ |
| 181 | 42 | $Ph_2CNH$ |
| 180 | <u>100</u> | $Ph_2CN$ |
| 155 | 16 | $Ph_2H$ |
| 154 | 22 | $Ph_2$ |
| 131 | 19 | PhCNSi |
| 105 | 9 | PhSi |
| 104 | 70 | PhCNH |
| 103 | 9 | PhCN |
| 95,93 | 33,90 | $Me_2SiCl$ |
| 78 | 25 | PhH |
| 77 | 75 | H |
| 65,63 | 2,6 | SiCl |
| 43 | 9 | SiMe |

For this table and Tables V.4 and 5, the m/e values for silicon isotopes relate to $^{28}Si$ ($^{28}Si$,92.3%; $^{29}Si$, 4.7%; $^{30}Si$, 3.0%)

## TABLE V.4

## Mass spectroscopic results for $(Ph_2C:N)_2SiMeCl$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 440,438 | 0.7, 2 | $(Ph_2C:N)_2SiMeCl$ |
| 425,423 | v.weak | $(Ph_2C:N)_2SiCl$ |
| 403 | 0.3 | $(Ph_2C:N)_2SiMe$ |
| 388 | 0.2 | $(Ph_2C:N)_2Si$ |
| 363,361 | 0.8, 0.24 | $(Ph_2C:N)_2SiMeCl$ minus Ph |
| 311 | 0.2 | $(Ph_2C:N)_2Si$ minus Ph |
| 310 | 1 | $(Ph_2C:N)_2Si$ minus PhH |
| 297,295,293 | 5,28,48 | $Ph_2C:NSiMeCl_2$ |
| 282,280,278 | 0.5,3,4 | $Ph_2C:NSiCl_2$ |
| 260,258 | 4,12 | $Ph_2C:NSiMeCl$ |
| 223 | v.weak | $Ph_2C:NSiMe$ |
| 220,218,216 | 13,63,$\underline{100}$ | $Ph_2C:NSiMeCl_2$ minus Ph |
| 208 | 0.3 | $Ph_2C:NSi$ |
| 181 | 23 | $Ph_2C:NH$ |
| 180 | 50 | $Ph_2C:N$ |
| 179,177,175 | 1,4,7 | $PhSiCl_2$ |
| 168,166 | 0.6, 1.8 | PhC:NSiCl |
| 157,155 | 8,22 | PhSiMeCl |
| 117,115,113 | 11,60,$\underline{100}$ | $SiMeCl_2$ |
| 104 | 28 | PhC:NH |
| 103 | 11 | PhC:N |
| 77 | 50 | Ph |
| 65,63 | 10,28 | SiCl |

## TABLE V.5

## Mass spectroscopic results for $(Ph_2C:N)_2SiCl_2$

| m/e | Relative Intensity | Assignment |
|---|---|---|
| 462,460,458 | 0.75,3.8,6.4 | $(Ph_2C:N)_2SiCl_2$ |
| 461,459,457 | 2.2,12,16 | $(Ph_2C:N)_2SiCl_2$ minus H |
| 425,423 | 6,16 | $(Ph_2C:N)_2SiCl$ |
| 424,422 | 14,36 | $(Ph_2C:N)_2SiCl$ minus H |
| 385,383,381 | 3,16,23 | $(Ph_2C:N)_2SiCl_2$ minus Ph |
| 322,320 | 3,9 | $Ph_2C:N(Ph)SiCl$ |
| 319,317,315,313 | 2,9,26,25 | $Ph_2C:NSiCl_3$ |
| 283,281,279; | 2.5,14,21 | $Ph_2C:NSiCl_2H$ |
| 282,280,278 | 8,31,44 | $Ph_2C:NSiCl_2$ |
| 245,243 | 1.3,4 | $Ph_2C:NSiCl$ |
| 242,240,238,236 | 3,31,88,88 | $PhC:NSiCl_3$ |
| 219,217 | 17,47 | $Ph_2SiCl$ |
| 181 | 39 | $Ph_2C:NH$ |
| 180 | <u>100</u> | $Ph_2C:N$ |
| 179,177,175 | 10,53,79 | $PhSiCl_2$ |
| 139,137,135,133 | 3,18,51,51 | $SiCl_3$ |
| 104 | 46 | PhCNH |
| 103 | 18 | PhC:N |
| 77 | 61 | Ph |
| 65,63 | 1.4,4 | SiCl |

## TABLE V.6

## Bis(trifluoromethyl)methyleneamino derivatives of Group IV metals[237]

| Compound | Azomethine stretching frequencies $\nu(C{=}N)$ cm$^{-1}$ for metal M | | |
|---|---|---|---|
| | Si | Ge | Sn |
| $(CF_3)_2C{:}NMMe_3$ | 1765 | 1730 | 1720 |
| $[(CF_3)_2C{:}N]_2MMe_2$ | 1770 | 1730 | 1719 |
| $[(CF_3)_2C{:}N]_3MMe$ | 1774 | 1733 | 1717 |
| $[(CF_3)_2C{:}N]_4M$ | 1786 | 1730 | 1717 |

# APPENDIX 1

# EXPERIMENTAL DETAILS

## General Techniques

All of the reactions described involved the handling of air- and moisture-sensitive compounds. Reactions were normally carried out in an atmosphere of dry nitrogen in a limb of a double schlenk tube and purification of the product was effected by crystallisation in the second limb of the schlenk tube. Occasionally, reactions were effected by using apparatus consisting of two flasks separated by a filter stick.

Distillations or removal of solvents under reduced pressure were done in a conventional vacuum line system fitted with a rotary oil pump backed by a mercury diffusion pump.

## Nitrogen Supply

"White-spot" quality nitrogen was purified by passage through a furnace containing reduced wire-form copper at *ca*.400° and then through two traps at -196°. Periodically, the copper was regenerated with hydrogen. A constant pressure of nitrogen was maintained in the system by means of an oil bubbler connected to one of the outlets.

## Glove Box

Samples of compounds for analysis, infra-red spectra, nuclear magnetic resonance spectra and mass spectra were made up under nitrogen in a glove box of conventional design. The nitrogen was purified as described above and, when not in use, the nitrogen inside the glove box was continuously recycled through hot (400°) copper towers and cooling traps (at -196°) by a small pump fitted inside the box. Where possible, external tubing was of copper or glass to reduce diffusion of oxygen or moisture into the system. A further precaution to avoid the presence of moisture was taken by placing a drying agent, phosphorus pentoxide, in the glove box.

Owing to the toxicity of beryllium alkyls and oxides, a concentrated sulphuric acid bubbler was inserted into the recycle system.

## Infra-red Spectra

Infra-red spectra (range 2.5 to 25 microns) were recorded on a Grubb-Parsons Spectromaster. For the wavelength range corresponding to the azomethine stretching absorption, $\nu(C=N)$, between 5 to 6.5 microns, the wavelength scale was expanded. Samples were in the form of Nujol mulls or thin films in potassium bromide cells.

## Nuclear Magnetic Resonance Spectra

Proton magnetic resonance spectra were recorded at 60 MHz on either a Perkin-Elmer R10 spectrometer or a Varian A56/60D spectrometer. Samples were prepared as solutions in toluene, benzene or deutero-benzene. Tetramethylsilane was commonly used as the reference standard but for some zinc and beryllium compounds, the solvent (toluene or benzene) was the internal standard. Sample tubes were filled by syringe against a counter-current of nitrogen and were sealed under nitrogen.

## Mass Spectra

Mass spectra were recorded on an A.E.I. M.S.9 instrument at 70 eV and an accelerating potential of 8 kV, with a source temperature of 150-200° and electromagnetic scanning. Samples were introduced by direct insertion into the ion source, and protected from atmospheric moisture during transfer from glove box to instrument by a nitrogen filled tube attached to the probe.

## Molecular Weights

Molecular weights were determined cryoscopically in benzene or by osmometry. The benzene, of analytical reagent purity, was dried over extruded sodium and calibrated with biphenyl. A Beckman apparatus of conventional type was used and all measurements were taken while a slow stream of nitrogen was passed through the apparatus.

## Solvents

Pentane, hexane, petroleum ether, benzene, toluene and diethyl ether were dried and stored over extruded sodium.

## Analytical Methods

### Carbon, Hydrogen and Nitrogen Analyses

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Occasionally, nitrogen was determined by the normal Kjeldahl method by Mr. R. Coult of the departmental analytical group.

### Chlorine Analysis

The chlorine content was determined by fusion of the compound with potassium metal followed by a volumetric titration technique to measure the concentration of halide ion.

### Lithium Analysis

Lithium was determined by flame photometry. A weighed sample of the lithium compound was hydrolysed with water and the organic matter destroyed by repeatedly boiling to dryness with concentrated nitric acid. The resulting solid was dissolved in distilled water and made up to a known volume. This solution was introduced into an EEL flame photometer, previously calibrated with standard lithium solutions, and the lithium concentration read directly from the calibration curve.

## Beryllium Analysis

Beryllium was determined by titrating the alkaline solution formed by addition of excess potassium fluoride to beryllium hydroxide. Aliquots of a standard beryllium solution (0.01M $BeSO_4$) were prepared to cover the range 0-6 mg.$Be^{2+}$. To each was added 5 ml. of a 0.5M solution of potassium sodium tartrate followed by five drops of a 1% alcoholic solution of bromothymol blue, and the solution was titrated to a blue (alkaline) end-point with 0.1M sodium hydroxide solution. The neutral point (green-blue) was then gained by adding 0.1M sulphuric acid. 5 ml. of M potassium fluoride solution was added and the resulting blue solution allowed to stand for 5 min. in a stoppered flask before titrating with 0.1M sulphuric acid (to a green end-point). A linear calibration plot of beryllium concentration against volume of acid titrant was plotted.

The solutions resulting from the hydrolysis of the compounds to be analysed were treated in the same way, after boiling to dryness with nitric acid to destroy organic matter, and the beryllium concentration read directly from the calibration curve.

## Zinc and Iron Analyses

Weighed samples of the compound to be analysed were destroyed by concentrated nitric or perchloric acid and made up to a known volume. Determination of the metal content was effected by using a previously calibrated Perkin-Elmer 403 Atomic Absorption Spectrometer.

## Gallium Analysis

A weighed sample (ca.0.1 g.) of the compound was destroyed by repeatedly boiling to dryness with concentrated nitric acid. The residue was dissolved in about 100 ml. of distilled water containing 1 ml. of 0.1M hydrochloric acid and warmed to 60-70°. To this was added 25 ml. of a 2% solution of 8-hydroxyquinoline in 2M acetic acid followed by the slow addition of a 2M solution of ammonium acetate until a precipitate formed. A further 25 ml. of 2M ammonium acetate was then added and the liquid allowed to stand for an hour, with continued stirring, before being filtered through a previously dried and weighed sintered glass crucible. The green-yellow precipitate was washed several times with distilled water, dried at 150° and weighed in the crucible. The gallium content of the compound was calculated from the weight of gallium 8-hydroxyquinolate, $Ga(C_9H_6NO)_3$.

# APPENDIX II

## CONDUCTOMETRIC TITRATION DETAILS

Conductometric titrations were carried out between $Bu^t_2C{:}NLi$ and $[(Bu^t_2C{:}N)_2Be]_2$, and $Bu^t_2C{:}NLi$ and $(Bu^t_2C{:}N)_3Ga$ to determine if lithiometallates of the type $Li_nBe(N{:}CBu^t_2)_{2+n}$ and $Li_nGa(N{:}CBu^t_2)_{3+n}$ (n = 1 or 2) are present in solution.

Through the chemical nature and method of preparation of the titrants, the solvent was hexane, which gave very low conductance values (ca. $10^{-9}$ $ohms^{-1}$). The conductivity cell consisted of two platinum electrodes of 1 $cm^2$ area each, held parallel to each other 0.5 cm. apart. These electrodes were previously scrupulously cleaned with nitric acid and distilled water, followed by acetone and ether. The titrations were carried out under nitrogen and the cell immersed in a water bath to maintain a constant temperature of 22°C throughout the experiment. The conductivities of the solutions were measured on a Wayne Kerr B224 Universal Bridge.

## Standardisation of Cell

The cell constant, $K_c$, for different volumes of liquid was measured using 0.01M potassium chloride solutions for which the specific conductance at 25° is $1.41 \times 10^{-3}$ $ohms^{-1} cm^{-1}$.[259] The equation used for the cell constant for volume V of liquid in the cell was

$$K_c(V) = \frac{1.41 \times 10^{-3}}{\text{conductance of KCl (V)}} \ cm^{-1}$$

The results are shown in Table A, and plotted graphically in Graph A to illustrate the increase in $K_c$ with volume V.

## TABLE A

| Volume of KCl solution in ml. | 5.0 | 7.5 | 10.0 | 12.5 | 15.0 |
|---|---|---|---|---|---|
| Conductance in $\text{ohms}^{-1}$ | 0.0123 | 0.01184 | 0.01152 | 0.0110 | 0.0109 |
| Cell constant, $K_c$, in $\text{cm}^{-1}$ | 0.115 | 0.1191 | 0.1225 | 0.1272 | 0.1288 |

## Specific Conductance of Hexane

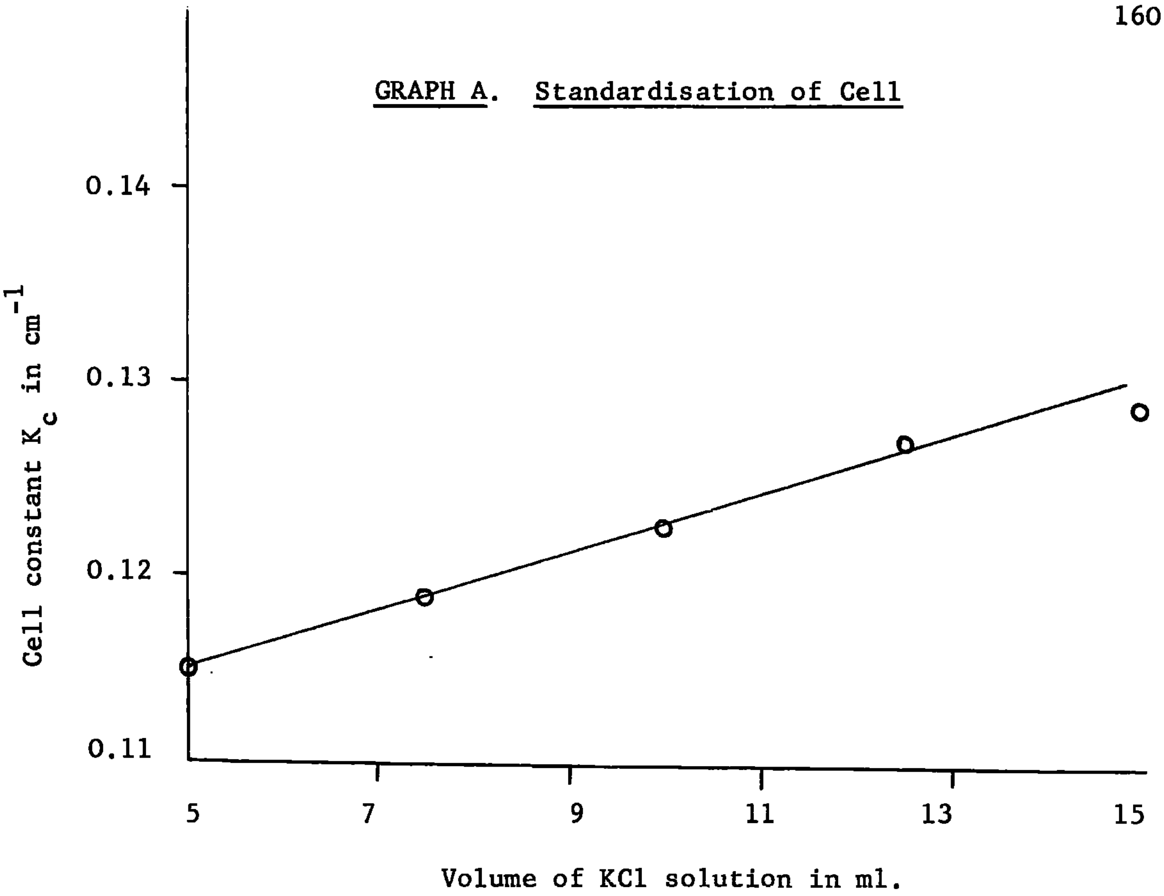
The specific conductance of hexane, $K_h$, for different volumes of hexane in the cell was determined by measuring the conductance for a particular volume V and using the equation

$$K_h(V) = K_c(V) \text{ x Conductance of hexane } (V)$$

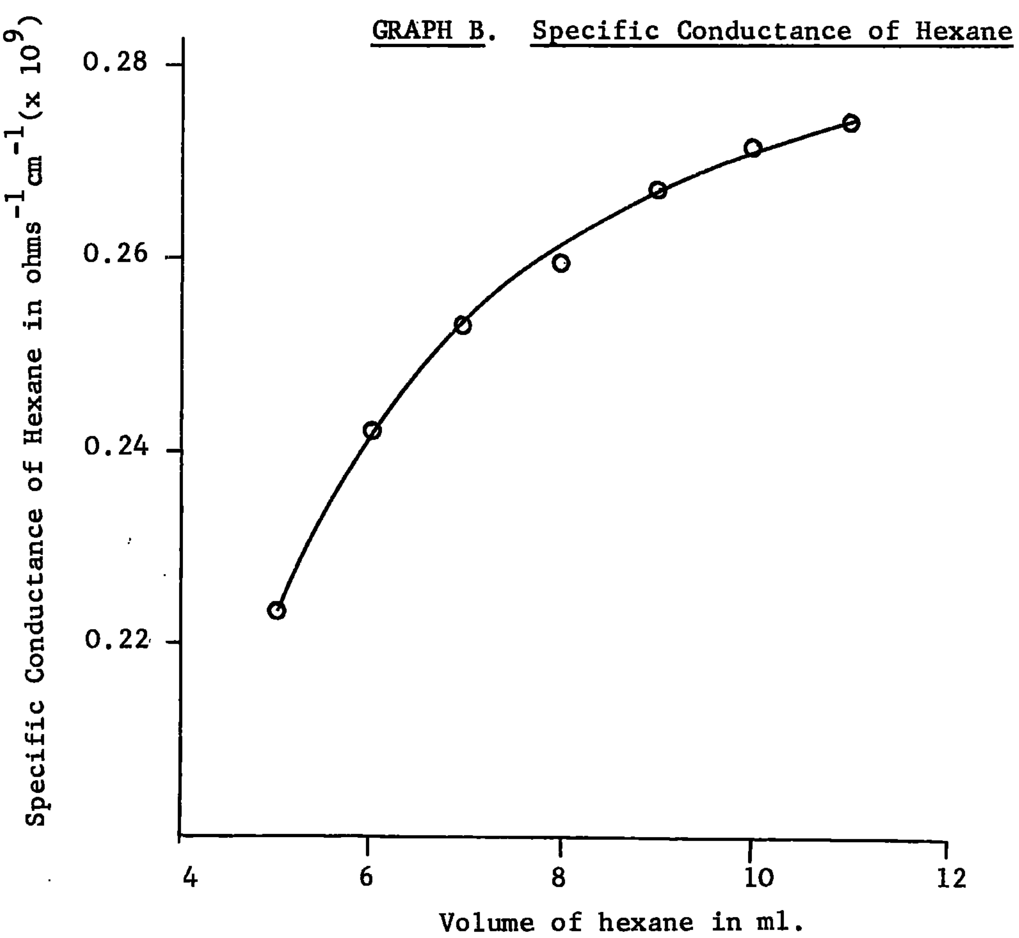
The values of $K_c$ (V) were taken from Graph A. Table B shows the data for these measurements and Graph B shows the plot of the specific conductance of hexane, $K_h$, against the volume of hexane in the cell.

## TABLE B

| Volume hexane in ml. | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|
| Conductance in $\text{ohms}^{-1}$ (x $10^9$) | 1.94 | 2.09 | 2.15 | 2.18 | 2.22 | 2.224 | 2.225 | 2.21 |
| Cell constant, $K_c$, in $\text{cm}^{-1}$ | 0.115 | 0.1165 | 0.118 | 0.1195 | 0.121 | 0.1225 | 0.124 | 0.1255 |
| Specific Conductance of hexane, $K_h$, in $\text{ohms}^{-1}\text{cm}^{-1}$ ($\times 10^9$) | 0.223 | 0.243 | 0.254 | 0.260 | 0.268 | 0.272 | 0.276 | 0.277 |



GRAPH A. Standardisation of Cell



GRAPH B. Specific Conductance of Hexane

## Conductometric Titrations

A weighed sample of $[(Bu^t{}_2C{:}N)_2Be]_2$ or $(Bu^t{}_2C{:}N)_3Ga$ was dissolved in 5 ml. of hexane and the solution syringed into the conductivity cell. Aliquots of $Bu^t{}_2C{:}NLi$ in hexane were added and the conductance of the mixture after each addition was measured, having allowed the temperature rise caused by the heat of reaction to drop to water bath temperature.

The specific conductance of the solution, $K_{soln.}$, was calculated from

$$K_{soln} = \text{measured conductance} \times K_c \quad \text{ohms}^{-1}\text{cm}^{-1}$$

and for the solute,

$$K = K_{soln.} - K_h \quad \text{ohms}^{-1}\text{cm}^{-1}.$$

The values of $K_c$ and $K_h$ for a particular volume of solution in the cell were taken from Graphs A and B respectively.

### Beryllium titration

Concentration of $Bu^t{}_2C{:}NLi$ = 0.2 mmole $ml^{-1}$

Weight of $[(Bu^t{}_2C{:}N)_2Be]_2$ in 5 ml. of hexane = 0.306 mmole (of monomer)

The calculations sre shown in Table C and plotted graphically on page 41 (Figure II.4).

The discontinuities are at Li/Be = 0.92 and 1.98 representing $LiBe(N{:}CBu^t{}_2)_3$ and $Li_2Be(N{:}CBu^t{}_2)_4$ respectively.

## Gallium titration

Concentration of $Bu^t{}_2C{:}NLi$ = 0.2 mmole ml.$^{-1}$

Weight of $(Bu^t{}_2C{:}N)_3Ga$ in 5 ml. of hexane = 0.206 mmole.

The calculations are shown in Table D and plotted graphically on page 115 (Figure IV.1).

The two discontinuities in the plot occur at Li/Be = 0.92 and 2.07 representing $LiGa(N{:}CBu^t{}_2)_4$ and $Li_2Ga(N{:}CBu^t{}_2)_5$.

TABLE C. Beryllium Titration

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Volume of $Bu^t{}_2C:NLi$ solution in ml. | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 |
| Quantity of $Bu^t{}_2C:NLi$ in mmole | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
| Ratio $Bu^t{}_2C:NLi/(Bu^t{}_2C:N)_2Be$ | 0 | 0.327 | 0.652 | 0.980 | 1.306 | 1.634 | 1.960 | 2.287 | 2.612 | 2.940 | 3.270 |
| Conductance of solution in ohms$^{-1}$ (x $10^9$) | 6.27 | 7.66 | 9.04 | 10.40 | 10.91 | 11.47 | 12.11 | 12.15 | 12.25 | 12.35 | 12.36 |
| Cell Constant $K_c$ in cm$^{-1}$ | 0.115 | 0.116 | 0.1165 | 0.1175 | 0.118 | 0.119 | 0.1195 | 0.1204 | 0.1211 | 0.1219 | 0.1226 |
| Specific Conductance of solution $K_{soln}$ in ohms$^{-1}$cm$^{-1}$ (x $10^9$) | 0.721 | 0.889 | 1.053 | 1.221 | 1.289 | 1.364 | 1.446 | 1.461 | 1.483 | 1.502 | 1.512 |
| Specific Conductance of hexane, $K_h$, in ohms$^{-1}$cm$^{-1}$ (x $10^9$) | 0.223 | 0.235 | 0.243 | 0.249 | 0.254 | 0.258 | 0.261 | 0.264 | 0.268 | 0.270 | 0.272 |
| Specific Conductance of solute, K, in ohms$^{-1}$cm$^{-1}$ (x $10^9$ | 0.498 | 0.654 | 0.810 | 0.972 | 1.035 | 1.106 | 1.185 | 1.197 | 1.215 | 1.232 | 1.240 |

## TABLE D. Gallium Titration

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Volume of $Bu^t_2C:NLi$ solution in ml. | 0 | 0.5 | 0.8 | 1.0 | 1.2 | 1.5 | 1.8 | 2.0 | 2.5 | 3.0 | 3.5 |
| Quantity of $Bu^t_2C:NLi$ in mmole | 0 | 0.1 | 0.16 | 0.2 | 0.24 | 0.3 | 0.36 | 0.4 | 0.5 | 0.6 | 0.7 |
| Ratio $Bu^t_2C:NLi/(Bu^t_2C:N)_3Ga$ | 0 | 0.485 | 0.776 | 0.980 | 1.165 | 1.456 | 1.747 | 1.941 | 2.425 | 2.915 | 3.400 |
| Conductance of solution in $ohms^{-1}$ (x $10^9$) | 15.16 | 15.74 | 16.16 | 16.22 | 16.91 | 17.78 | 18.54 | 18.90 | 19.46 | 19.68 | 19.80 |
| Cell constant, $K_c$, in $cm^{-1}$ | 0.115 | 0.116 | 0.1164 | 0.1165 | 0.117 | 0.1174 | 0.1179 | 0.1181 | 0.119 | 0.1195 | 0.1204 |
| Specific conductance of solution, $K_{soln}$, in $ohms^{-1}cm^{-1}$ (x $10^9$) | 1.744 | 1.825 | 1.880 | 1.890 | 1.977 | 2.089 | 2.182 | 2.235 | 2.318 | 2.351 | 2.383 |
| Specific conductance of hexane, $K_h$, in $ohms^{-1}cm^{-1}$ (x $10^9$) | 0.223 | 0.235 | 0.240 | 0.243 | 0.246 | 0.249 | 0.252 | 0.254 | 0.258 | 0.261 | 0.264 |
| Specific conductance of solute, K, in $ohms^{-1}cm^{-1}$ (x $10^9$) | 1.521 | 1.590 | 1.640 | 1.647 | 1.731 | 1.840 | 1.930 | 1.981 | 2.060 | 2.090 | 2.119 |

# APPENDIX III

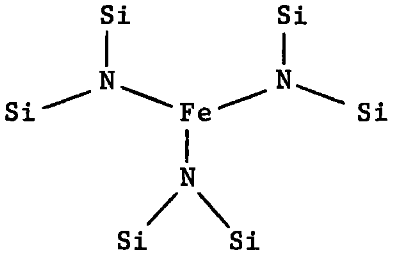
# PRELIMINARY INVESTIGATIONS INTO METHYLENEAMINO DERIVATIVES OF IRON AND CHROMIUM

## DISCUSSION

The field of the amino chemistry of transition metals has been widely investigated by Bradley and co-workers. Of interest is the degree of N → M (p → d) π-bonding and in this respect most of the studies have concentrated on the structural nature of such compounds.

The crystal structure of tris[bis(trimethylsilyl)amino]iron, $[(Me_3Si)_2N]_3Fe$, has been determined[260,261] and shows planar $FeN_3$ and $FeNSi_2$ units. For maximum π-bonding between nitrogen and iron, the $FeN_3Si_6$ atoms should all be coplanar,

viz.



in order for there to be effective overlap between the vacant d-orbitals on the iron atom and the 'lone-pair' of electrons on the nitrogen. Sterically, this situation predictably does not arise, and it is found that the dihedral angle between the $FeN_3$ and $FeNSi_2$ planes is 49.2° which can be compared with an angle of 50° for the aluminium analogue, $[(Me_3Si)_2N]_3Al$.[212] Dative π-bonding between nitrogen and iron should lead to a shortening of the Fe-N bond length. In this compound this value is 1.917Å but data with which it can be convincingly contrasted is lacking.[261] The Si-N bond length of 1.731Å is appropriate for dative π-bonding between silicon and nitrogen.[212]

Several other compounds of the type $[(Me_3Si)_2N]_3M$ have been prepared: From vibrational spectroscopy and magnetic susceptibility measurements, the compound with M=Cr is isoelectronic with the iron analogue,[262] as is M=Eu (from preliminary X-ray crystallographic results)[263] and M = Ti, V (from electron paramagnetic resonance spectra).[264] Monomeric compounds within the lanthanide group that have been prepared and characterised include M = La, Pr, Sm, Gd and Lu.[263]

Dialkylamino derivatives of transition metals also exhibit N → M (p → d) dative π-bonding characteristics. The crystal structure and electron spin resonance spectra of $Cr(NPr^i_2)_3$[262,265] show it to have planar $CrN_3$ and $CrNC_2$ groups, the dihedral angles between the planes being $68^o$, $72^o$ and $73^o$. The Cr-N distance (1.87Å) is 0.1Å shorter than expected and was interpreted as being indicative of dative π-bonding between nitrogen and chromium.[265] Experiments on chromium nitrosyl amides and alkoxides,[266] $Cr(NO)(NR_2)_3$ and $Cr(NO)(OR')_3$, showed that the π-donor ability of the ligands used decreased in the order $NPr^i_2$ > 2,6-dimethylpiperidide > $N(SiMe_3)_2$ > $OBu^t$ > $OPr^i$. The position of $N(SiMe_3)_2$ in this sequence was attributed to the delocalisation of the nitrogen's lone-pair of electrons into the silicon d-orbitals.

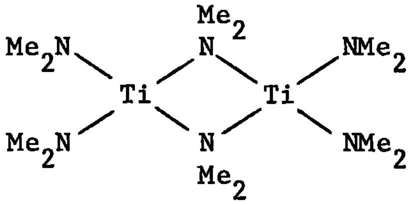
Disproportionation reactions are a common occurrence in the preparation of amino derivatives. Illustrative examples are given below:

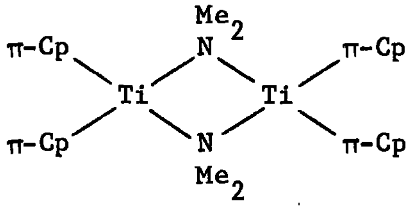
$$\begin{tikzcd} CrCl_3 + 3LiNEt_2 \arrow[r, "THF"] & Cr(NEt_2)_3 + 3LiCl \arrow[d, "heat"] \\ & Cr(NEt_2)_4 + Cr(NEt_2)_2 \end{tikzcd}$$ Ref.267.

$$MoCl_5 + 5LiNEt_2 \rightarrow Mo(NEt_2)_4 + \text{unidentified product}$$ Ref.268.

$$2TiX(NR_2)_2 \rightarrow TiX_2 + Ti(NR_2)_4$$ Ref.269.

The structures of some of these compounds have been predicted from spectroscopic data: $Mo(NR_2)_4$ (R = Me,Et) is believed to have a distorted tetrahedral arrangement of amino groups[268] and $Ti(NR'_2)_3$ (R' = $Pr^i$,Ph) a trigonal arrangement of groups about the titanium.[270] Dialkylamino derivatives of titanium have bridging amino groups.[269,271] For example:





The structures of $W(NMe_2)_6$ and $Nb(NMe_2)_5$ have recently been established by X-ray crystallography. Amino derivatives of niobium(IV) are well known[272] but for niobium(V) only a handful have been characterised. The compound $Nb(NMe_2)_5$ has a distorted tetragonal pyramidal array of amino groups about the niobium atom and it appears as though only the apical nitrogen atom participates in any π-bonding with the niobium atom.[273] The tungsten derivative, $W(NMe_2)_6$, has an octahedral $WN_6$ configuration. Each $WNC_2$ unit is planar as are the three $C_2NWNC_2$ groups which implies that there is delocalised N → W (p → d) π-bonding.[274]

Methyleneamino derivatives of transition metals have been studied but only for metal carbonyl complexes. The first structural report was in 1967 with the results of the X-ray crystal structure determination of $[Fe(CO)_3(N{:}Ctolyl_2)]_2$[275] which was prepared from the reaction between iron pentacarbonyl and ($tolyl_2C{:}NN{:}Ctolyl_2$). The Fe-N distance in this compound was extremely short, indicating appreciable Fe-N π-bonding.[275]

There are two main methods of preparation of such compounds and the products depend on the reagents (M = Mo or W):

$Fe(CO)_4I_2 + R^1R^2C{:}NLi \rightarrow Fe_2(CO)_6I(N{:}CR^1R^2) + LiCl$ Ref.276.

$\pi\text{-}CpM(CO)_3Cl + R_2C{:}NSiMe_3 \rightarrow \pi\text{-}CpM(CO)_2N{:}CR_2$ Ref.277.

or

$[\pi\text{-}CpM(CO)N{:}CR_2]_2$

$\pi\text{-}CpM(CO)_3Cl + R_2C{:}NLi \rightarrow \pi\text{-}CpM(CO)_2(R_2CNCR_2)$ Refs.277-280

but

$\pi\text{-}CpM(CO)_3Cl + RBu^tC{:}NLi \rightarrow \pi\text{-}CpM(CO)_2(N{:}CBu^tR)$ Refs.169, 170,281.

The spectroscopic properties of these compounds with respect to the azomethine link, C=N, have been recorded but the interpretation of the data, particularly the infra-red spectra, have not provided much insight into the linearity of the M-N=C linkage. The reason for this is the (σ - π) synergic process which is a common feature in transition metal chemistry. The electronic effects involved are withdrawal of electron charge from the azomethine link via σ-donation and dative π-bonding from nitrogen to the metal, and in contrast, back donation of charge from the metal d-orbitals into the antibonding orbital of the azomethine unit.

For one compound, $\pi\text{-}CpMo(CO)_2N{:}CBu^t{}_2$, the X-ray crystal analysis shows a near-linear Mo-N=C unit[169] which is in accord with its $^1H$ n.m.r. spectrum at $-60^o$ (a single signal for the butyl protons).

Other work in this field has been on $(CF_3)_2C{:}N\text{-}M$ systems such as $(\pi\text{-}Cp)_2TiCl[N{:}C(CF_3)_2]$ and $(Ph_3P)_2PtH[N{:}C(CF_3)_2]$ but no conclusions were drawn concerning N → M (p → d) π-bonding.[282]

In the investigations to be described, the attempted preparations of $(Bu^t{}_2C{:}N)_3Fe$, $(Ph_2C{:}N)_3Fe$ and $(Bu^t{}_2C{:}N)_3Cr$ are recorded and compared with related amino derivatives discussed above.

## STARTING MATERIALS

Ferric chloride was purified by sublimation under reduced pressure. Chromium trichloride was purified by refluxing with thionyl chloride to remove any moisture. The solvents tetrahydrofuran and monoglyme were dried over extruded sodium.

### Attempted Synthesis of tris(di-t-butylmethyleneamino)iron(III), $(Bu^t{}_2C{:}N)_3Fe$.

A solution of di-t-butylmethyleneaminolithium, $Bu^t{}_2C{:}NLi$, was added to an ethereal solution of ferric chloride, $FeCl_3$, in 3:1 molar proportions at -196°. On warming to room temperature, a brown-black solution formed. After stirring for 24 hr. the solvent was removed under reduced pressure and the suspected product extracted with hot toluene. Crystallisation from hexane was attempted but the only product was a brown residue.

Analysis: C,54.9; H,10.9; Fe,15.9; N,7.55%.

$C_{27}H_{54}FeN_3$ requires C,68.1; H,11.3; Fe,11.8; N,8.8%.

No lithium was detected (by flame photometry).

Infra-red spectrum (Nujol mull): $\nu_{max}$ at 1653m, 1609m, 1326w, 1267m, 1202s, 1103m, 1034m, 952m, 935w, 877m, 844w, 803m and 722w $cm^{-1}$.

### Attempted Synthesis of tris(diphenylmethyleneamino)iron(III), $(Ph_2C{:}N)_3Fe$.

Diphenylmethyleneaminolithium, $Ph_2C{:}NLi$, was added to an ethereal solution of ferric chloride, $FeCl_3$, at -196° in 3:1 molar proportions and the same procedure as above was employed to obtain a product. A brown residue was obtained in this way.

Analysis: C,75.0; H,5.72; Fe,9.12; N,7.59%.

$C_{39}H_{30}FeN_3$ requires C,78.5; H,5.0; Fe,9.40; N,7.05%.

No lithium was detected (by flame photometry).

Infra-red spectrum (Nujol mull): $\nu_{max}$ at 1620m,br, 1575m, 1312w, 1266s, 1250sh, 1198w, 1183w, 1099s, 1075sh, 1031s, 931w, 901m, 847vw, 800s, 787sh, 735vw, 721vw, 696vs, 683w, 650w, 643vw, 622m and 483w,br $cm^{-1}$.

Attempted Synthesis of tris(di-t-butylmethyleneamino)chromium(III), $(Bu^t{}_2C:N)_3Cr$.

A solution of di-t-butylmethyleneaminolithium, $Bu^t{}_2C:NLi$, (30 mmole) was added to chromium trichloride, $CrCl_3$, (10 mmole) in ether (30 ml.) at -196°. Initially, the purple solution of $CrCl_3$ turned grey-green in colour and on reaching room temperature changed to dark green, almost black. On stirring for 18 hr. the solution regained its grey-green colour, and then to light green after refluxing for 5 hr. Solvent was removed and toluene added. Filtration gave a green solid and a colourless filtrate.

Solvent was removed from the colourless solution to yield an oily drop which had $\nu_{max}$ at 1663vw, 1607vw, 1449w, 1418m, 1266vs, 1099vs,br, 1020vs,br, 866s, 816sh, 797vs, 699s and 662w $cm^{-1}$.

Monoglyme was added to the residue in the schlenk tube and the solution filtered. Removal of solvent from the filtrate under reduced pressure left a very small white residue which showed no absorptions in the infra-red spectrum. Tetrahydrofuran (THF) was then used as the filtration solvent and this time a green filtrate was obtained. Evaporation of solvent afforded a very small quantity of a green oil. The infra-red spectrum (contact film) of this oil only showed absorptions belonging to the solvent, THF.

In all three reactions, a product was obtained with an azomethine stretching frequency higher than the parent imine. However, analytical data show that the products were not those expected, unless contaminated with impurities. It is quite likely that redox reactions have taken place:

$$2Fe^{III} \rightarrow Fe^{II} + Fe^{IV}$$

$$e + Fe^{III} \rightarrow Fe^{II}$$

$$2Cr^{III} \rightarrow Cr^{II} + Cr^{IV}$$

Particularly in the case of chromium, the colour changes observed at various stages during the reaction are indicative of a change in the electronic state of the chromium atom. Furthermore, separation of the $Cr^{II}$ and $Cr^{IV}$ possible products appears feasible by careful choice of solvents: Toluene or perhaps hexane dissolves one component and THF the other. The infra-red spectrum of the toluene compound (colourless oil) showed weak absorptions at 1663 and 1607 $cm^{-1}$. The latter may be due to hydrolysed product but the relatively high value of the former indicates that the Cr-N=C group may be near-linear.

An alternative argument to consider for the chromium example is that no disproportionation reaction occurred and that the THF green filtrate consisted of unreacted reagents, hydrolysed chromium species (probably green) etc. The azomethine stretching frequency of 1663 $cm^{-1}$ of the toluene extract would then be appropriate for three co-ordinate chromium, a planar

$CrN_3$ group and near-linear C=N-M groups. Such an arrangement would be appropriate for optimum π-bonding and minimal steric hindrance between ligands, as has been found for $(Bu^t{}_2C{:}N)_3M$ (M = Al,Ga) (See Chapter IV for discussion), and $Cr(NPr^i{}_2)_3$.[265]

The iron compound, $(Bu^t{}_2C{:}N)_3Fe$, also has a relatively high azomethine stretching frequency of 1653 $cm^{-1}$ which again could be due to the presence of a planar $FeN_3$ group. The other iron derivative, $(Ph_2C{:}N)_3Fe$, shows too many peaks in the infra-red spectrum characteristic of $Ph_2C{:}NLi$ and $Ph_2C{:}NH$.

In conclusion, it appears as though some fruitful research can be done in the field of methyleneamino derivatives of low-valent transition metals. These preliminary studies indicate that there may be species having a planar $MN_3$ group and that the azomethine stretching frequency, ν(C=N), may provide yet another useful tool in the prediction of N → M (p → d) π-bonding in transition metal systems.

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