Studies on imino, amidino and related derivatives of some main group elements

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STUDIES ON IMINO, AMIDINO AND RELATED DERIVATIVES OF SOME MAIN GROUP ELEMENTS

By

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My thanks are also due to Brian Hall for his occasional but valuable technical assistance and to my many friends, fellow workers in Laboratory 104, for the pleasure of their company.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September, 1974 and August 1979. It has not been submitted for any other degree and is the original work of the author except (i) where acknowledged by reference and (ii) Chapter 7 which was carried out in collaboration with Mr. P. G. Huggett of this University.

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

"The diphenylmethyleneaminomagnesium bromide tetrahydrofuran adduct $Mg_2Br_2(THF)_2(\mu\text{-}N{:}CPh_2)_2(\mu\text{-}THF)$; X-ray crystal structure."

By Kenneth Manning, Elizabeth A. Petch,
Harrison M. M. Shearer, Kenneth Wade,
and Graham R. Whitehead.

J. Chem. Soc. Chem. Commun., 1976, 107.

"The relative Lewis acidities of silicon tetrachloride, germanium tetrachloride and tin tetrachloride towards acetonitrile, acrylonitrile, ethylacetate, diethyl ether and tetrahydrofuran: vapour pressure - composition studies."

By Paul G. Huggett, Kenneth Manning and
Kenneth Wade.

J. Inorg. Nucl. Chem., in the press.

ABSTRACT

This thesis describes studies on the co-ordination chemistry of Group II elements, magnesium and zinc, and Group IV elements silicon, germanium and tin. Attention is focussed principally on systems with ligands containing multiple-bonded nitrogen attached to these Groups II and IV elements viz., Ketimino and amidino derivatives containing $R_2C{=}N$ and $R^1NC(R){=}NR^1$ ligands respectively.

After an introductory survey of the relevant chemistry, Chapter 2 describes studies on fifteen ketiminomagnesium derivatives of formula types $(R_2C{=}NMgBr)_2(L)_x$, $\left[(R_2C{=}N)_2Mg\right]_n(THF)_x$, $(R_2C{=}NMgX)_nL_m$ and includes an X-ray crystal structure of $(Ph_2C{=}NMgBr)_2(THF)_3$. All compounds described are associated species, often dimeric, and are believed to co-ordinate via bridging methyleneamino ligands with additional bridging ligands (OEt_2, THF and TMED) in some cases. Where compounds also contain terminally attached methyleneamino ligands, their infrared spectra are consistent with linear C=N-Mg units.

Chapter 3 describes related studies on ten methyleneaminozinc compounds of formula types $(R_2C{=}NH)_xZnX_2$, R = Ph, p-tolyl, X = Cl, x = 2; R = Bu^t, X = Cl, x = 1; R = p-tolyl, X = Ph, x = 1; $RCN.ZnPh_2$ (R = p-tolyl); $(R_1R_2C{=}NZnX)_n$, $R_1 = R_2$ = p-tolyl, X = Cl, n = 2; $R_1 = R_2$ = p-tolyl, X = Ph, n = 2; R_1 = Ph, R_2 = p-tolyl, X = Ph, n = 2; $R_1 = R_2$ = p-tolyl, X = $(p\text{-tolyl})_2C{=}N$. The associated species are thought to have bridging methyleneamino units with three-co-ordinate zinc.

Chapter 4 describes methyleneamino and N,N^1-diphenyl- and N,N^1-di-p-tolylacetamidino (Am, Am^1) derivatives of tin(II) including formula types $R_2C{=}NH.Sn^{II}Cl_2$, $(R_2C{=}NSn^{II}Cl)_2$, $\left[(R_2C{=}N)_2Sn^{II}\right]_n$, $Am^1H.Sn^{II}Cl_2$, $(Am^1Sn^{II}Cl)_2$, $(Am_2Sn^{II})_n$, $(Am^1{}_2Sn^{II})_n$. Amidino derivatives $Am_nSn^{IV}Cl_{4-n}$ (n = 2, 3, 4), $Am^1{}_nSn^{IV}Cl_{4-n}$ (n = 1-4), $Am^1{}_2MCl_2$ (M = Si, Ge) are described in Chapter 5. Attempts to prepare $Am(\text{or}Am^1)_nMCl_{4-n}$ (n = 1, 3, 4; M = Si, Ge) were unsuccessful. $Am^1Sn^{IV}Cl_3$ is monomeric with five co-ordinate tin. The associated species are believed to contain bridging methyleneamino/amidino ligands.

The final two chapters describe work which stemmed from studies of nitrile - Group IV metal systems. In Chapter 6, the use of vapour pressure/composition studies to monitor the weak interactions of Lewis acids MCl_4 (M = Si, Ge) with various Lewis bases is demonstrated.

Finally, the hydrostannation of nitriles by tin(II) chloride and hydrogen chloride is described. The product is considered to be dimeric with an amidinium structure $Cl_3Sn^{IV}C(R){=}NC(R){=}NH_2{}^+Sn^{II}Cl_3{}^-$.

CHAPTER 1

INTRODUCTION

1.1 Nomenclature

Various names have been used in the past for compounds containing the C=N - group. To avoid ambiguity the Chemical Society and I.U.P.A.C. recommend that ketimines, $R_2C{=}NH$, should be named as derivatives of the (unknown) parent compound methyleneamine $CH_2{=}NH$. Hence diphenylketimine, $Ph_2C{=}NH$, is diphenylmethyleneamine and metallo-derivatives containing the unit $Ph_2C{=}NM$ are consequently spoken of as diphenylmethyleneamino derivatives of M. Similarly RCH=NH, formerly aldimines, are correctly termed alkyl (aryl) methyleneamines. In this introduction both nomenclatures are used, but subsequently systematic nomenclature is solely employed.

1.2 Historical Background

Methyleneamino- derivatives of metals have been known since about 1901 when Blaise (1) described, but did not isolate, methyleneaminomagnesium- and methyleneaminozinc halides $R^1R^2C{=}NMX$ (M = Mg, Zn), as products of the insertion of a nitrile into the metal-carbon bond of an organomagesium- or organozinc-halide (equation 1.1)

$$R^1C{\equiv}N + R^2MX \longrightarrow R^1R^2C{=}NMX \qquad 1.1$$

Indeed the most widely used route to the synthesis of ketimines employs a nitrile and a Grignard reagent (R^2MX, M = Mg) followed by partial hydrolysis (equation 1.2). This addition of a nitrile to an organomagnesium or -zinc halide has been extended to the preparation of other related zinc (2), lithium (3) and aluminium (2) compounds.

$$R^1R^2C{=}NMX_n + H_2O \longrightarrow R^1R^2C{=}NH + MX(OH) \qquad 1.2$$

In general, however, interest has centred on the products obtained by the complete hydrolysis of such initial insertion intermediaries, i.e. Ketones (equation 1.3)

$$R^1R^2C{=}NMX_n + 2H_2O \longrightarrow R^1R^1C{=}O + NH_3 + HOMX_n \qquad 1.3$$

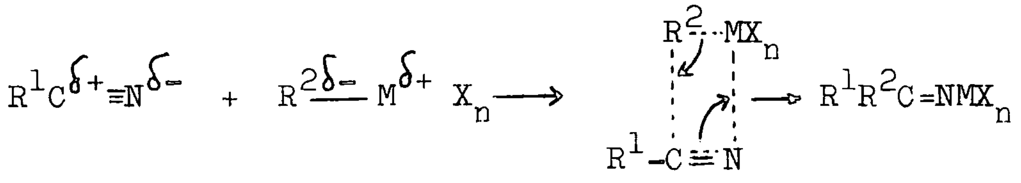
The first aldimino derivative of a metal, propylmethyleneamino di-i-butylaluminium $(PrCH{=}NAlBu^i{}_2)_n$, to be isolated in a pure form was reported some twenty years ago (4). Interest in this field has subsequently developed quite extensively. Additional methods by which such methyleneamino- derivatives may be synthesised, their co-ordination chemistry, and the reactions of their metal-nitrogen bonds have been studied, but only in comparatively recent time have their structures and spectra been investigated. The work described in this thesis had as its broad objective the study of nitrile adducts or methyleneamino derivatives of metal or metalloids. Chapter 2 and 3 describe studies which involve $R_2C{=}NM$ species (M = Mg and Zn respectively) themselves being intermediates in the reaction of organometallic reagents with nitriles. Particular attention is paid to the structure of these diaryl (or dialkyl)-methyleneaminomagnesium or -zinc derivatives and to the use of the $R_2C{=}N{-}M$ unit as a probe for the study of metal-nitrogen π-bonding. To this end, this chapter will describe later the spectroscopic features of $-C{=}N{-}M$ units that allow their structures to be determined. Chapters 4 and 5 are concerned with features of the co-ordination chemistry of selected N, N^1-diarylacetamidino- derivatives of tin in both its II and IV oxidation states. A detailed discussion of this work is offered in Chapter 4. Chapters 6 and 7 examine respectively (i) interactions between nitriles (and other Lewis bases) and MCl_4(M = Si, Ge) as monitored by vapour pressure measurements, and (ii) the behaviour of selected systems incorporating alkyl or aryl nitrile, tin(II)chloride and hydrogen chloride. The present chapter includes a survey of nitrile insertion reactions by which methyleneamino- derivatives can be prepared. Other routes to methyleneamino- derivatives are also reviewed together with the characteristic spectroscopic features of the C=N-M units.

1.3 Insertion Reactions of Nitriles

Insertion reactions of nitrile involve the insertion of a nitrile triple bond into a bond $A^{\delta+} - B^{\delta-}$ such that B and A add to the nitrile carbon atom and nitrile nitrogen atom respectively (equation 1.4).

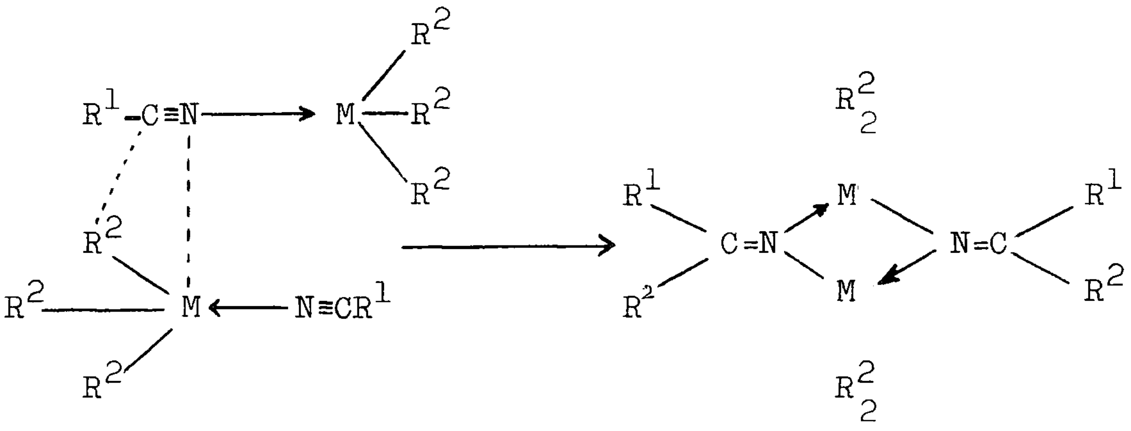
$$RC\equiv N \quad + \quad \overset{\delta+}{A}-\overset{\delta-}{B} \longrightarrow RBC{=}NA \qquad 1.4$$

The ease with which the reaction occurs reflects the strength and polarity of the bond between A and B. In particular, nitriles can insert into M-C bonds where M = Li, Mg, Zn and Al, for example, to give N-metallated methyleneamines (equation 1.5). The majority of reactions like this are frequently regarded as 1,2-dipolar additions and proceed probably by way of some cyclic transition state such as that in (equation 1.5).



$$R^1C^{\delta+}{\equiv}N^{\delta-} \quad + \quad R^{2\delta-}\!-\!M^{\delta+}X_n \longrightarrow \begin{array}{ccc} R^2 & \cdots & MX_n \\ \vdots & & \vdots \\ R^1-C & \equiv & N \end{array} \longrightarrow R^1R^2C{=}NMX_n \qquad 1.5$$

Such would also rationalise those situations where evidence exists of the initial formation of a nitrile adduct as a precursor to the insertion reaction. Some of these adducts are isolable eg. $R^1C{\equiv}N.MR^3_3$, R^1 = Me, R^2 = Me, Et, Ph; R^1 = Et, R^2 = Me; R^1 = Bu^t, R^2 = Me, Ph; M = Al (5), and their infrared spectra reveal the characteristic increase in $\nu(C{\equiv}N)$ of nitrile on formation of adducts $RC{\equiv}N.MX_n$ (6). They do, however, often rearrange, and feasibly by a mechanism which involves nucleophilic attack, by the migrating group, on the carbon of the nitrile (equation 1.6) A study of nitrile-organoaluminium adducts has indicated that such rearrangement occurs less readily if electronic charge is withdrawn from the migrating group and this seems consistent with the proposed mechanism of migration (equation 1.6) (5).



1.6

Specific examples of insertion reactions of nitriles are now given, which will not only illustrate the general principles so far established by proving a favoured route to various methyleneamino- metal or metalloid derivatives but also serve to illustrate the formation of rather different products.

Methyleneaminolithium derivatives, $R^1R^2C{=}NLi$ have been widely studied in their own right and have been extensively used in the preparation of methyleneamino - derivatives of other electropositive metals. Insertion reactions of nitriles $R^1C{\equiv}N$ with R^2Li ($R_1 = R_2$ = Ph (7); $R^1 = R^2 = Bu^t$ (8); R^1 = Ph, $R^2 = NR_2$ (9) have been used to produce $R^1R^2C{=}NLi$ in good yield, but PhCN gives a very low yield of PhMeC=NLi when treated with MeLi because of the competing reaction involving the polymerisation of the benzonitrile in the presence of organolithium (3). Furthermore, reactions between alkylcyanides, $R^1C{\equiv}N$ (eg R^1=Me, Et), and lithium alkyls (eg R^2=Me, Et) do not normally yield dialkylmethyleneaminolithium deriviatives as might be expected (eg $Me_2C{=}NLi$) because of the acid character of hydrogen atoms attached to the α-carbon atom of the nitrile. Instead the products are an alkane and polymeric materials (equation 1.7) - $R^1{=}R^2$=Me, Et). Dimethylcyanamide, $Me_2N{-}C{\equiv}N$,

$$R^1CH_2C{\equiv}N \quad + \quad R^2Li \longrightarrow R^2H \quad + \quad (R^1CH{=}C{=}NLi)_n \qquad 1.7$$

whilst not possessing a hydrogen atom on the α-carbon atom does, none the less behave as a protic acid toward methyl lithium eliminating methane (7) according to equation 1.8:

$$Me_2N{-}C{\equiv}N \quad + \quad MeLi \longrightarrow MeH + LiCH_2N(Me)C{=}N \qquad 1.8$$

Acetonitrile and excess t-butyl lithium on the other hand, react at -78° by polylithiation to give Li_2C_2HN and two equivalents of 2-methypropane. Tertiary- butyl cyanide (pivalonitrile) with no α-hydrogen atoms has been reported not to react with alkyl lithium, RLi,(R=Me, Et, (7) but nevertheless reacts smoothly with t-butyl lithium inserting at about -20°

(equation 1.9) in quantitative yield. This represents the most convenient route to the synthesis of di-t-butylmethyleneaminolithium.

$$Bu^t\,C\equiv N \;+\; Bu^t\,Li \longrightarrow Bu^t{}_2C{=}NLi \qquad 1.9$$

The insertion of a nitrile into the metal-carbon bond of a Grignard reagent, R^2MgX, has been used to prepare a series of methyleneaminomagnesium derivatives, $R^1R^2C{=}NMgX$, (R^1 = Ph, R^2 = Me, Et, $PhCH_2$; R^1 = cyclopropyl, R^2 = Me, Ph (10) $R^1 = R^2$ = Ph (11) (equation 1.10.) In a

$$R^1C\equiv N \;+\; R^2MgX \longrightarrow R^1R^2C{=}NMgX \qquad 1.10$$

similar way benzonitrile reacts with diethylmagnesium to give ethylphenylmethyleneaminoethylmagnesium (equation 1.11) which is extensively associated in benzene.

$$PhC\equiv N \;+\; Et_2Mg \longrightarrow (EtPhC{=}NMgEt)_n \qquad 1.11$$

A similar reaction employing t-butylcyanide, also in ether gave a syrup which yielded a crystalline derivative with tetrahydrofuran $(EtBu^tC{=}NMgEt)_x y$ THF, whilst, by contrast, the reaction between di-isopropylmagnesium and t-butylcyanide gave a crystalline adduct $Bu^tCN.MgPr^i{}_2$. The adduct, again showing the characteristically high $\nu(C\equiv N)$, decomposes in benzene precipitating di-isopropylmagnesium (12).

Benzonitrile reacts with diphenylzinc to form the adduct $PhCN.ZnPh_2$ which rearranges at about 100° to bis(diphenylmethyleneamino)zinc, presumably by way of the disproportionation of the insertion product, dimeric diphenylmethyleneaminophenylzinc (13) (equation 1.12). By comparison, p-tolunitrile also forms

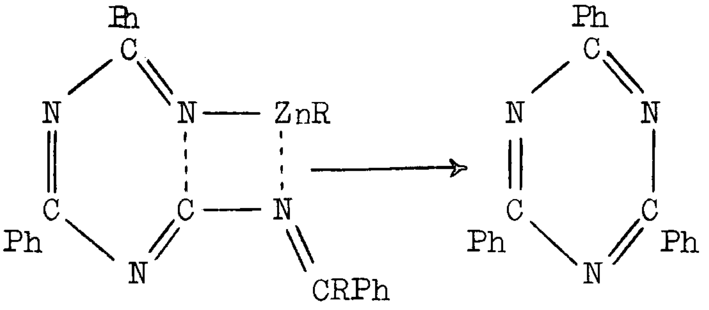
$$PhC\equiv N + Ph_2Zn \rightarrow PhC\equiv N.ZnPh_2 \rightarrow (Ph_2C{=}NZnPh)_2 \rightarrow \Big[(Ph_2C{=}N)_2Zn\Big]_n + ZnPh_2 \qquad 1.12$$

an adduct $\left(p\text{-tolyl}\right)C{\equiv}N.ZnPh_2$, and its pyrolysis at about $100^{\circ}C$ yields the expected insertion product p-tolylphenylmethyleneaminophenylzinc dimer $\left[(p\text{-tolyl})PhC{=}NZnPh\right]_2$ (equation 1.13). This product however, whilst supporting

$$2\left(p\text{-tolyl}\right)C{\equiv}N.ZnPh_2 \longrightarrow \left[(p\text{-tolyl})PhC{=}NZnPh\right]_2 \qquad 1.13$$

the likely reaction route postulated for the benzonitrile-diphenylzinc system (equation 1.12) is much more resistant to disproportionation and indeed it was not possible to prepare the bis(methyleneamino)zinc derivative $\left[\left\{(p\text{-tolyl})PhC{=}N\right\}_2Zn\right]_n$ in this way (see chapter 3). No evidence of interaction was found in studies of the systems $Bu^tC{\equiv}N$- R_2Zn (R = Me, Et, Bu^t) (13) but benzonitrile is trimerised by zinc alkyls, apparently by successive insertion of benzonitrile into zinc-carbon and ultimately zinc-nitrogen bonds, when equimolar mixtures of benzonitrile and dimethyl- (14) or diethyl-zinc (13 , 15) are heated in sealed tubes to 100° - 150° (equations 1.14 - 1.15). Such a mechanism (1.14 and 1.15) is similar to the

$$R\text{-}ZnR + PhC{\equiv}N \rightarrow R(Ph)C{=}NZnR \xrightarrow{PhC{\equiv}N} R(Ph)C{=}NC(Ph){=}NZnR \qquad 1.14$$



+ RZnN=CRPh 1.15

polymerisation of benzonitrile in the presence of organolithium reagents mentioned earlier (3). Other substances which catalyse this trimerisation reaction include sodium (16 , 17), organomagnesium compounds (18) and Me_3M(M = Al (19), Ga (20).

Aldiminoboron hydrides $(R^1CH{=}NBH_2)_n$, (21) alkyl hydrides $(R^1CH{=}NBHBu^t)_2$ (22), and alkyls $(MeCH{=}NBR_2)_2$ (23) result from the insertion of nitriles into the B-H bonds of BH_3, BH_2Bu^t and HBR_2 respectively. However, the aldiminoboron dihalide, $MeCH{=}BCl_2$, *expected* from the reaction of acetonitrile with dichloroborane, or monochloroborane, (*equation 1.16*) was not produced. Instead, small traces of acetonitrile.borontrichloride adduct were obtained and evidence of substituted borazines. (24) Whilst aldimine

$$MeC{\equiv}N \quad + \quad HBCl_2 \;\not\longrightarrow\; MeCH{=}NBCl_2 \qquad 1.16$$

derivatives of *gallium* are also accessible by an insertion of a nitrile into a gallium-carbon bond of GaR_3 (25) (*equation 1.17*), in general the lower reactivity of organoboron and organogallium compounds towards the insertion of an unsaturated functional group such as nitrile causes ketimine deriviatives $(R^1R^2C{=}NMR^3_2)_2$ to be inaccessible by this

$$2PhCN + 2GaEt_3 \longrightarrow (PhCH{=}GaEt_2)_2 \quad + 2C_2H_4 \qquad 1.17$$

route. On the other hand *both* aldimino, $R^1CH{=}NAlX_2$, and ketimino $(R^1R^2C{=}NAlX_2)_n$ derivatives of aluminium are preparable from the nitrile and the appropriate organoaluminium compound.

Such insertion reactions of the nitrile group into aluminium-carbon (or aluminium-hydrogen) bonds yield methyleneaminoalanes only when the organo-group R^2 is an aryl or alkyl group, other than ethyl, and the nitrile substituent R^1 has no α-hydrogen atoms (equation 1.18 and 1.19, R^1 = Ph, Bu^t; R^2 = X = Me, Ph. (5 , 26) R^1 = Ph, R^2 = H, X = Et (4 , 5 , 26)

$$R^1C{\equiv}N \quad + \tfrac{1}{2}(R^2AlX_2)_2 \longrightarrow R\ C{\equiv}N.AlR^2X_2 \qquad 1.18$$

$$n\ R^1C{\equiv}NAlR^2X_2 \xrightarrow{\Delta} (R\ R^2C{=}NAlX_2)_n \qquad 1.19$$

Pyrolysis of the benzonitrile.triethylalane adduct, PhCN.AlEt$_3$, yielded both ketiminoalane PhC(Et):NAlEt$_2$, and aldiminoalane PhCH=NAlEt$_2$ because of concurrent loss of ethene and hydrogen (16, 26). A different behaviour is observed however, when the nitrile has an α-hydrogen atom as in, for example, aceto- and propio- nitriles. Such nitriles act as weak protic acids cleaving organic groups from aluminium forming alkanes and polymeric products (equations 1.20, 1.21), showing that, in addition to cleavage

$$RCH_2C{\equiv}N \quad + \quad R^2AlX_2 \longrightarrow RCH_2CN.AlR^2X_2 \qquad 1.20$$

$$\begin{tikzcd} & (RCH{=}NAlX_2)_n \quad + \quad R^2H \\ n\ RCH_2CN.AlR^2X_2 \arrow[ur] \arrow[dr] & & 1.21 \\ & (RCH(AlX_2)CN)_n \quad + \quad R^2H \end{tikzcd}$$

of groups R^2 from aluminium, some rearrangement has also occurred. Aldimino derivatives, (R^{1}CH=NAlX$_2$)$_n$, are formed when R^2 = H or Et, the EtAlX$_2$ in the latter instance acting as a source of HAlX$_2$ (5, 17, 18, 26-28) by loss of ethene. Methyleneaminoalanes can also arise by the insertion of nitriles into aluminium-nitrogen bonds in compounds of general formula R^{2}R^{3}AlNR^{4}R^5 (equation 1.22) (19, 29 - 31).

$$R^1C{\equiv}N \quad + \quad R^2R^3AlNR^4R^5 \longrightarrow R^1C(NR^4R^5){:}NAlR^2R^3 \qquad 1.22$$

Methyleneamino-derivatives of Group IV elements (Si, Sn, Pb) result from the insertion of nitriles into M-N bonds (Si, Sn, Pb), M-H bonds (M = Si) and M-O bonds (Sn, Pb) as indicated in equation 1.23.

$$R^1C{\equiv}N \quad + \quad XMR^2_3 \longrightarrow R^1XC{=}NMR^2_3 \qquad 1.23$$

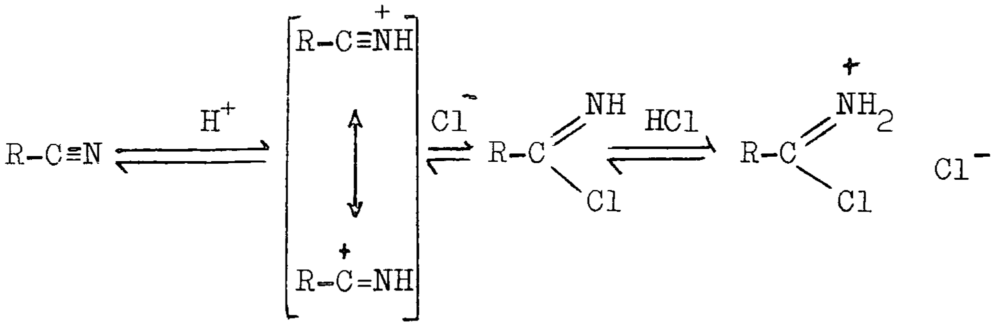
M = Si R^1 = Ph, X = H, R^2 = Me (32); R^1 = OR, X = NR_2, NHR, R^2 = Me (33)

M = Sn R^1 = Ph, X = NMe_2, R^2 = Me (34 35); R^1 = CCl_3, X = OMe, R^2 = Bu (36)

M = Pb R^1 = Ph, X = NEt_2, R^2 = Bu (37); R^1 = CCl_3, X = OMe, R^2 = Ph (38)

The above examples of nitrile insertion into M-C and M-X bonds show the reactivity of the nitrile functional group is due to two factors, viz its polarity ($\overset{\delta+}{C}{\equiv}N^{\delta-}$) and the lone pair of electrons on nitrogen. Moreover when this lone pair is used to co-ordinate with a Lewis acid the electrophilic character of the nitrile carbon is enhanced. A brief description of the reactions of nitriles with selected substrates, some of which have particular relevance to the work reported in Chapter 7, is now offered.

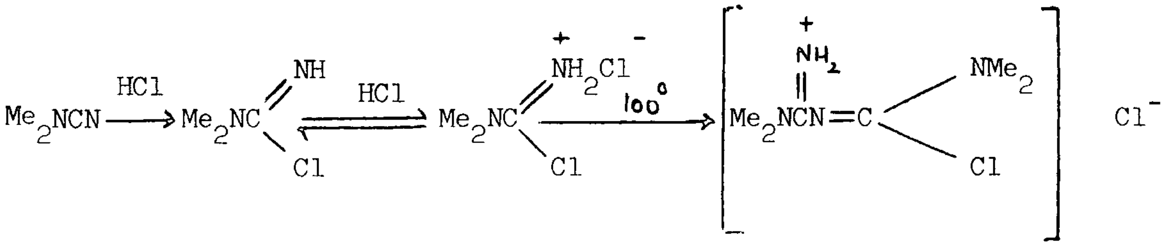
The interaction of hydrogen halides, HX, with nitriles has been well documented (39 , 40) the addition of a proton being followed or accompanied by co-ordination of halide ion at the electrophilic carbon atom to give imidoyl halides (I - equation 1.24) which themselves are normally sufficiently basic to accept a second proton to form nitrilium salts (II equation 1.24). The weak basicity of the simple nitriles



1.24

I II

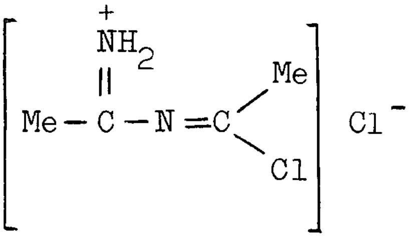
may be attributable to either the lone pair of electrons on nitrogen or (much more rarely) to the π-electrons of the triple bond. Complexes of nitriles with various Lewis acids are normally bound through the lone pair (6) but the enhancement of π-electron availability in, for example,, 4-methoxybenzonitrile markedly accelerates the formation of the imidoyl chloride salt (II). In addition to the imidoyl halides or halide salts (I and II) already referred to, some nitriles are known to form isolable dimeric hydrochlorides. Some of these products are of somewhat uncertain composition but the reaction between hydrogen chloride and dimethylcyanamide at room temperature is rather more clear (equation 1.25). The cystalline derivative (IV) is produced which, when heated,



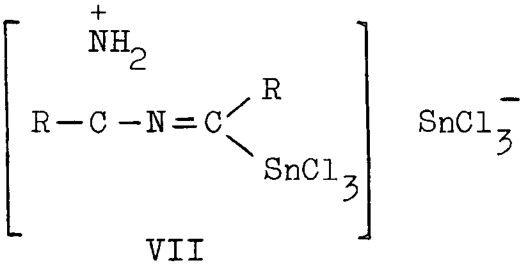
1.25

III IV V

elimates HCl and forms (V) in high yield (41) probably by displacement of Cl^- from (IV) by the nucleophilic chloroformamidine base (III). The analogous aliphatic imidyl hydrochlorides behave similarly (42) but the α-halogenated monomeric compounds are stable only at low temperature, the reactions at room temperature yielding dimeric N-(α-haloalkylidene) amidines directly (43). Acetimidyl chloride, for example (II; R = Me) changes on standing to form N-(Chloroethylidene)- acetamidine hydrochloride (VI) having the composition 2 MeCN.2HCl. (42). The N-(α-haloalkylidene)amidines (VI) are in

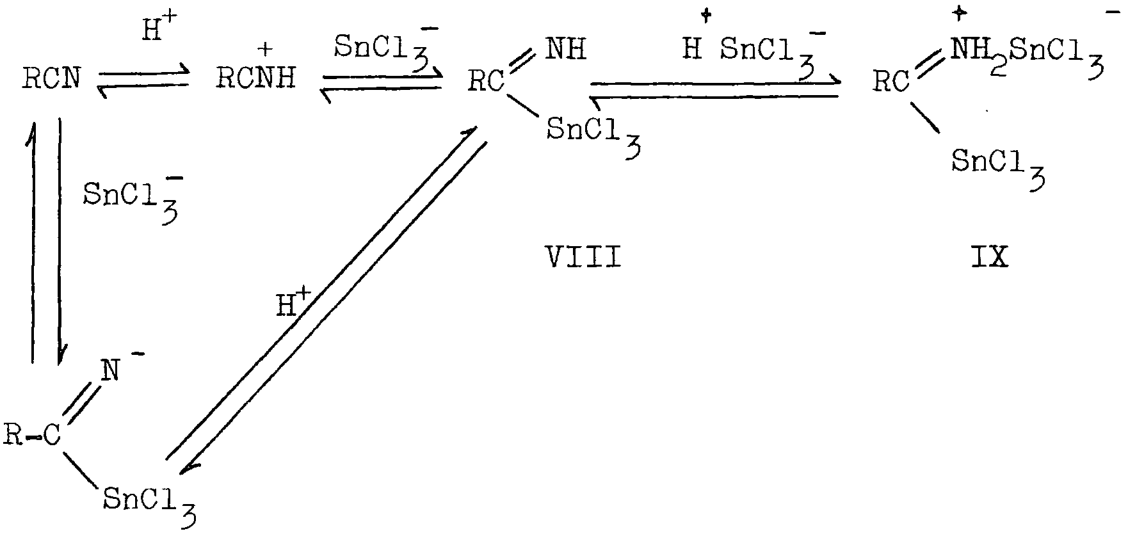


VI



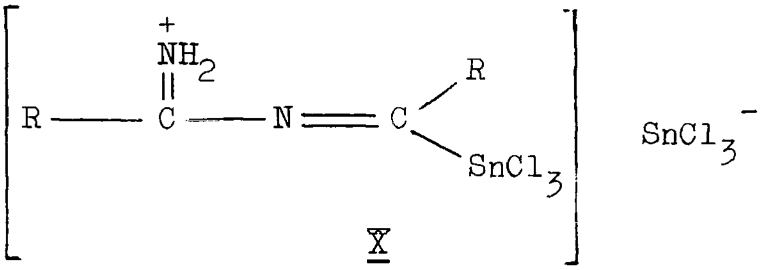
VII

general weakly basic and their salts readily release hydrogen halide. This may be one explanation for the lack of agreement regarding their composition. Chapter 7 gives an account of a study of various nitrile - hydrogen chloride - tin (II) chloride systems, in the presence of diethyl ether as solvent. The solid waxy products isolated in the four systems studied using different nitriles RCN (R = Me, Et, Bu^t and Ph) were also dimeric with an amidinium salt structure (VII). Whilst the precise nature of the reacting species in an ethereal solution of hydrogen chloride/tin(II) chloride is debatable - see later, Chapter 7 - it seems likely that the reaction with nitriles proceeds in a manner similar to that described for nitrile-hydrogen chloride systems. The first step probably involves the protonation of the nitrile followed or accompanied by co-ordination of the nucleophilic trichlorostannate (II) ion, $SnCl_3^-$, to give products (equation 1.26) analogous to I and II



1.26

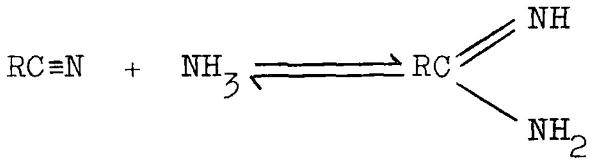
(equation 1.24) - produced by 1,2-addition of H^+ and Cl^- to a nitrile - viz an alkyl trichlorostannyl imine (VIII) or iminium salt (IX). The first step this reaction i.e. the forming of $RC(=NH)SnCl_3$-analogous to the formation of an imidoyl chloride (I) - may only be termed a hydrostannation in the broadest sense since the reacting species probably has no Sn-H bonds (contrast Et_3SnH) into which the unsaturated nitrile group might insert. The dimerisation of IX affording X with an amidinium salt structure may



X

well proceed by a mechanism similar to that described for the dimerisation of II but this is dealt with in much greater detail in Chapter 7.

Nitriles may also be used in the synthesis of amidines by reacting with (inserting into) ammonia or amines establishing an equilibrium (equation 1.27).

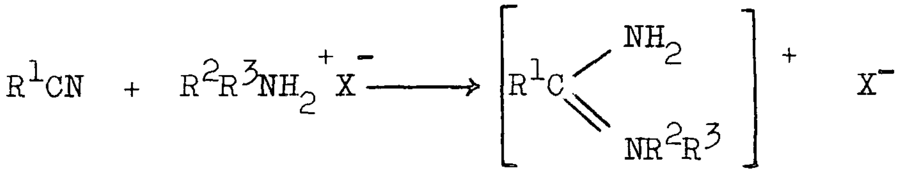


$$RC{\equiv}N + NH_3 \rightleftharpoons RC(=NH)NH_2 \qquad 1.27$$

Conversion to amidine is favoured by electron attracting substituents in the nitrile, and indeed very strongly activated nitriles, RCN (R = CCl_3, (44) CF_3,(45)) react rapidly with ammonia or amines at low temperatures,but such amidine products react rapidly with additional nitrile (equation 1.28) to give unstable imidylamidines. In general,

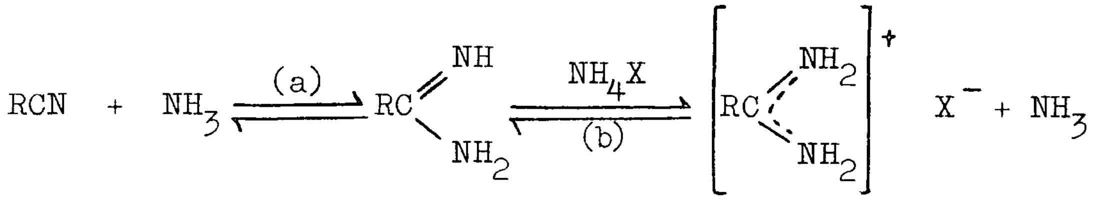
$$2CCl_3C{\equiv}N + NH_3 \longrightarrow Cl_3CC(=NH){-}N{=}C(NH_2)CCl_3 \qquad 1.28$$

however, most nitriles in their reaction with ammonia/ amines give very low yields of amidine, (46) but if the amidine can be stabilised as an amidinium salt, higher temperatures can be used to accelerate the reaction. Basically the reaction involves the fusion of an ammonium salt with the nitrile (equation 1.29) and this scheme



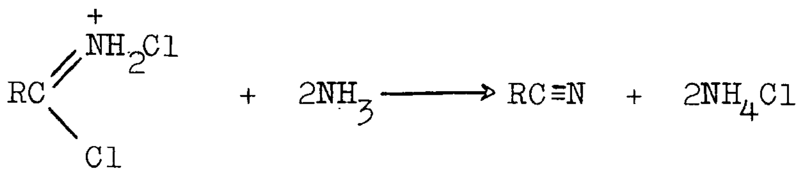
$$R^1CN + R^2R^3NH_2{}^+X^- \longrightarrow \left[R^1C(NH_2)(=NR^2R^3)\right]^+ X^- \qquad 1.29$$

has been found to be particulaly useful for the synthesis of N-substituted amidines from aryl nitriles (46). Best results are obtained at temperatures ranging from 180° - 250°, and employing benzenesulphonates or thiocyanates (in a large excess). Unsubstituted amidine salts can be prepared however in high yield from a wide variety of nitriles by reaction with ammonium chloride or bromide in the presence of ammonia under pressure at 125°-150° (47). An adequate reaction rate in the slow step (<u>equation 1.30 (a)</u>) needs to be achieved at a temperature where



1.30

the equilibrium concentration of amidine salt is high. A high concentration of ammonia promotes the forward reaction but too much necessitates an increase in the salt content to ensure the protonation of the amidine product (<u>equation 1.30 (b)</u>) It is of interest to note that the monomeric imidyl halide salts (II), previously discussed, do not react with either ammonia or amines to give amidines, but rather regenerate the original nitrile (<u>equation 1.31</u>).



1.31

Following this brief survey of some selected reactions of nitriles, further information on which may be found in the references quoted and in later chapters of this thesis, other methods by which methyleneamino derivatives may be prepared are now discussed.

<u>1.4 The Preparation of N-Metallated Methyleneamines</u>

Insertion reactions of nitriles with M-H, M-C, M-N, and M-O bonds and their utility in affording methyleneamino derivatives of various metals or metalloids have already been discussed in the previous section. It is now proposed to consider other methods by which N-metallated amines have been prepared and then to tabulate the known methyleneamino derivatives - and the method(s) by which they have been made - of selected metals/metalloids.

(a) Metathetical reactions of a methyleneaminolithium (on a methyleneamino-silicon compound) with a metal halide. (equation 1.32)

$$R_2C{=}NLi \quad + \quad M^1X \longrightarrow LiX \quad + \quad R_2C{=}NM^1 \qquad 1.32$$

This is the most widely - applicable method for the preparation of imino derivatives of metals and metalloids. Iminolithium compounds in general are most conveniently prepared by the reaction between a methyleneamine - which itself is a product of the partial hydrolysis of the product obtained from the nitrile insertion reaction into a lithium -carbon bond of an alkyl lithium - and an alkyl lithium (equation 1.33). In the same way that amino-derivatives of

$$R^1R^2C{=}NH \quad + \quad R^3Li \longrightarrow R^1R^2C{=}NLi \quad + \quad R^3H \qquad 1.33$$

lithium react with halides of less electropositive elements to transfer the amino group to the other element so methyleneaminolithium compounds may be employed to transfer the methyleneamino ligand to other less electropositive elements (equation 1.34 - $R^1{=}R^2{=}$p-tolyl). (48) Iminolithium compounds

$$R^1R^2C{=}NLi \quad + \quad BeCl_2 \longrightarrow \tfrac{1}{2}(R^1R^2C{=}NBeCl)_2 \quad + \ LiCl \qquad 1.34$$

are suitable starting materials when the organometallic product is soluble in an appropriate solvent from which the lithium halide may be separated by filtration. Methyleneamino- derivatives of several metals and metalloids eg. beryllium, zinc, boron, aluminium, gallium, silicon, germanium, tin (II) and tin (IV), and lead (also of a non-metals phosphorus and sulphur) have been made by this method. By varying the groups R^1 and R^2, and the relative molar proportions of each reagent, a series of derivatives of considerable diversity may be prepared (equations 1.35 - 1.38).

$$4Ph_2C{=}NLi + SnCl_4 \longrightarrow (Ph_2C{=}N)_4Sn + 4LiCl \quad (49) \qquad 1.35$$

$$3Ph_2C{=}NLi + BBr_3 \longrightarrow (Ph_2C{=}N)_3B + 3LiBr \quad (7) \qquad 1.36$$

$$2Bu^t{}_2C{=}NLi + ZnCl_2 \longrightarrow \tfrac{1}{2}\left[(Bu^t{}_2C{=}N)_2Zn\right]_2 + 2LiCl \quad (50) \qquad 1.37$$

$$(p\text{-tolyl})_2C{=}NLi + PPh_2Cl \longrightarrow (p\text{-tolyl})_2C{=}NPPh_2 + LiCl \quad (51) \qquad 1.38$$

Methyleneamino- derivatives which are only sparingly soluble in an appropriate solvent (eg. toluene) make for tedious and imperfect separation from the associated product lithium halide. Such is the case for example in the preparation, from diphenylmethyleneaminolithium and boron (III) halides, of diphenylmethyleneaminoboron dihalides, for whilst the iodide, bromide and chloride ($Ph_2C{=}NBX_2$ X=I, Br, Cl) can be separated - but with increasing difficulty - from lithium halide, the analogous fluoride derivatives, $Ph_2C{=}NBF_2$, cannot be isolated by this route (24). However, analogy with an established route to aminoboranes (equation 1.39) employing aminosilanes (52), suggested that the

$$nMe_3SiNR^1{}_2 + R^2_{3-n}BX_n \longrightarrow nMe_3SiX + (R^1{}_nN)_nBR^2_{3-n} \qquad 1.39$$

comparable reaction between the methyleneaminosilane, $R_2C{=}NSiMe_3$, made by the reaction between methyleneaminolithium and trimethylchlorosilane Me_3SiCl (equation 1.40),

$$R_2C{=}NLi + Me_3SiCl \longrightarrow LiCl + R_2C{=}NSiMe_3 \qquad 1.40$$

and boron (III) halide might provide a useful alternative route to methyleneaminoboron-dihalides as exemplified by (equation 1.41). Diphenylmethyleneaminoboron difluoride

$$Ph_2C{=}NSiMe_3 + BX_3 \longrightarrow Me_3SiX + \frac{1}{n}(Ph_2C{=}NBX_2)_n \qquad 1.41$$

was indeed preparable in this way (53). The byproduct in this reaction (Me_3SiX) is volatile and can be separated from the desired product by distillation. A further example of this method, described in a general way by (equation 1.42) A = Li, $SiMe_3$; X = Y = F, Cl, Br; X = halogen, Y = Ph-

$$R^1R^2C{=}NA + XMY_n \longrightarrow R^1R^2C{=}NMY_n + AX \qquad 1.42$$

is provided by the reaction between a methyleneaminolithium moiety (eg. $R^1 = R^2 = Bu^t$, A = Li) and a Grignard reagent ethylmagnesium bromide, RMgX (X = Br, R = Et) described in Chapter 2. The separation of the desired product,

$$Bu^t{}_2C{=}NLi + EtMgBr \longrightarrow \frac{1}{n}(Bu^t{}_2C{=}NMgEt)_n + LiBr \qquad 1.43$$

di-t-butylmethyleneaminoethylmagnesium, $(Bu^t{}_2C{=}NMgEt)_n$ - probably dimeric - from lithium bromide (equation 1.43) proved difficult and accordingly it was prepared much more conveniently by method (b) the principles of which are now presented.

(b) Metathetical reaction of a methyleneamine with a metal - alkyl or -hydride (equation 1.44)

$$R^1R^2C{=}NH \quad + \quad R^3MX_n \longrightarrow R^3H \quad + \quad R^1R^2C{=}NMX_n \qquad 1.44$$

This type of reaction involves the elimination of an alkane, or hydrogen, and formation of the N-metallated methyleneamine. As with the insertion reactions of a nitrile group between a metal and a more electronegative element, already referred to in section 1.3, this type of reaction is suitable only for compounds RMX_n possessing a sufficiently reactive R-M bond i.e. for M = Li, Be, Mg, Zn, B, Al and Ga. The most common type of organometallic compound, formulated as R^3MX_n in equation 1.44, employed to react with the free methyleneamine to give n-metallated methyleneamines is the metal alkyl R_nMR_{n-1}, eg RLi (R usually Me, Bu^n), R_2Be(R = Bu^i, Bu^t), R_2Mg (R = Et see chapter 2), R_2Zn (R = Me, Et, Ph), R_3B (R = Me), R_3Al (R = Me, Et, Ph) and R_3Ga (R = Me, Et, Ph). The use of such metal alkyls for the purpose described (eg equation 1.45) parallels in several instances the established route to N-metallated amines (equation 1.46)

$$2Bu^t{}_2C{=}NH \quad + \quad Bu^i{}_2Be \longrightarrow \left[(Bu^t{}_2C{=}N)_2Be\right]_2 \quad + \quad 2Bu^iH \ (54) \qquad 1.45$$

$$Me_2NH \quad + \quad Pr^i{}_2Be \longrightarrow \tfrac{1}{3}(Me_2NBePr^i)_3 \quad + \quad Pr^iH \ (55) \qquad 1.46$$

Methyleneaminolithium derivatives are prepared with considerable ease in this way, employing usually methyl- or n-butyl lithium (equation 1.47)

$$R^1R^2C{=}NH \quad + \quad RLi \longrightarrow R^1R^2C{=}NLi \quad + \quad RH \qquad 1.47$$

$R^1 = R^2 = Ph$ (7), p-tolyl (23 , 56), Bu^t (57),

Me_2N (9 , 58) and CF_3 (23 , 56)

Several methyleneaminoberyllium compounds have also been prepared (equations 1.48 - 1.49)

$$R^1R^2C{=}NH \quad + \quad R_2Be \longrightarrow (R^1R^2C{=}NBeR)_2 \quad + \quad RH \qquad 1.48$$

$R^1 = R^2 = Ph$, $R = Bu^t$, Bu^i; $R^1 = R^2 = Bu^t$, $R = Bu^i$ (54)

$$2R^1R^2C{=}NH \quad + \quad R_2Be \longrightarrow \tfrac{1}{2}\left[(R^1R^2C{=}N)_2Be\right]_2 \quad + \quad 2RH \qquad 1.49$$

$R^1 = R^2 = Bu^t$, $R = Bu^i$

In Chapter 2, the preparation of several N-magnesium methyleneamines is described employing diethylmagnesium or another Grignard species, RMgBr (R = Et, Pr^i, Ph). Such reactions are exemplified by equations 1.50 and 1.51

$$2Bu^t{}_2C{=}NH \quad + \quad Et_2Mg \longrightarrow \tfrac{1}{2}\left[(Bu^t{}_2C{=}N)_2Mg\right]_2 \quad + \quad EtH \qquad 1.50$$

$$R^1R^2C{=}NH \quad + \quad Pr^iMgBr \longrightarrow \tfrac{1}{n}(R^1R^2C{=}NMgBr)_n \quad + \quad Pr^iH \qquad 1.51$$

$R^1 = R^2 = Ph$, p-tolyl, Bu^t.

Several N-metallated methyleneamino derviatives of zinc have been products of the interaction of methyleneamines and dialkyl - (R = Me, Et) and diarylzinc (R = Ph) - see references (13 , 50) and Chapter 3 (equations 1.52 and 1.53).

$$R^1R^2C{=}NH \quad + \quad R_2Zn \longrightarrow \tfrac{1}{2}(R^1R^2C{=}NZnR)_2 \quad + \quad RH \qquad 1.52$$

$R^1 = R^2 = Ph$, R = Me, Et, Ph (13); $R^1 = R^2 = Bu^t$,

R = Me (50) $R^1 = R^2 =$ p-tolyl, R = Ph

$$2R^1R^2C{=}NH \quad + \quad R_2Zn \longrightarrow \tfrac{1}{2}\left[(R^1R^2C{=}N)_2Zn\right]_2 \quad + \quad 2RH \qquad 1.53$$

$R^1 = R^2 = Bu^t$, $R = Me$ (50)

Boron-carbon bonds are less readily cleaved by protic acids, so this method is of limited use for the synthesis of methyleneaminoboranes few of which have been made by this course (equation 1.54).

$$R^1R^2C{=}NH \quad + \quad R_3B \longrightarrow R^1R^2C{=}NBR_2 \quad + \quad RH \qquad 1.54$$

$R^1 = R^2 = Ph$, $R = Me$ (59); $R^1 = R^2 = Bu^t$, $R = Et$ (57)

The $Ph_2C{=}NH/BMe_3$ system, which behaves similarly to the Me_2NH/BMe_3 reaction mixture (60) affords initially an unstable but isolable solid adduct which however eliminates methane on being heated to give the monomeric diphenylmethyleneamino-dimethylborane. No evidence of adduct formation was detectable in studies of the diphenylmethyleneamine-BR_3 systems (R = Et, Ph) both the alkylboranes being weaker Lewis acids than trimethylborane. After $Ph_2C{=}NH{-}BEt_3$ mixtures had been held at 160° for about a week the only involatile product isolated was the N.-substituted ketimine $Ph_2C{=}NCHPh_2$. This somewhat unexpected product in addition to ethene, may be rationalised as follows. Amines, R^1NH_2, displace ammonia from imines $R_2C{=}NH$ to yield N-substituted imines $R_2C{=}NR^1$ (60). In the $Ph_2C{=}NH.BEt_3$ reaction some $Ph_2C{=}NH$ may be reduced to the amine Ph_2CHNH_2 by interaction with Et-B groups (which in the process lose ethene). Subsequent condensation between such an amine and a molecule of $Ph_2C{=}NH$ could afford

$Ph_2C{=}NCHPh_2$ together with some associated material such as $(EtBNH)_n$. A study of other $Ph_2C{=}NH/BX_3$ systems (X = H, NMe_2, OMe, F or Cl) with the projected purpose of isolating diphenylmethyleneamino boranes, $Ph_2C{=}NBX_2$, by the elimination of HX from the initially formed adduct $Ph_2C{=}NH.BX_3$ proved to be unsuccessful. (61)

Methyleneamino-alanes and gallanes, $(R_2C{=}NMX_2)_n$ M = Al, Ga, are obtainable by the reaction between methyleneamines and organo-aluminium or - gallium compounds via adduct formation (equation 1.55).

$$R_2C{=}NH \;+\; R^1{}_3M \longrightarrow R_2C{=}NH.MR^1{}_3 \xrightarrow{\Delta} \tfrac{1}{2}(R_2C{=}NMR^1{}_2)_2 \;+\; R^1H \qquad 1.55$$

<u>M = Al</u> R = Ph, R^1 = Me, Et, Ph; (62) R = Bu^t, R^1 = Me

Bu^i (57); R = Me_2N, R^1 = Me, Et (58)

<u>M = Ga</u> R = Ph, R^1 = Me, Et, Ph (63)

Cleavage of R^1H from the adduct $Ph_2C{=}NH.MR_3$ occurs less readily as M becomes less electropositive (electronegativities: B = 2.01; Ga = 1.82; Al = 1.47) (64), paralleling the decrease in M - C bond polarity. It is of interest to note that increasingly forcing conditions are also needed for the comparable thermal decompostion of the dimethylamine adducts $Me_2NH.AlMe_3$ (90^o) (64), $Me_2NH.GaMe_3$ (120^o) (66) and $Me_2NH.BMe_3$ (300^o) (67) into analogous dimethylamino-metal derivatives $(Me_2NMMe_2)_n$. Tris (di-t-butylmethyleneamino) alane, $(Bu^t{}_2C{=}N)_3Al$, has been prepared by reacting aluminium hydride (from lithium aluminium hydride and aluminium trichloride) with three equivalents of di-t-butylmethyleneamine (equation 1.56) (11). This is analogous to the elimination reactions used to prepare tris(amino)alanes from aluminium hydride and secondary amines (68).

$$3Bu^t{}_2C{=}NH \quad + \quad AlH_3 \longrightarrow (Bu^t{}_2C{=}N)_3Al \quad + \quad 3H_2 \qquad 1.56$$

The methods so far described represent the most generally used routes to methyleneamino derivatives of metal or metalloids. Other approaches have also been employed in specific cases (equations 1.57 - 1.58).

$$R_2C{=}NH_2Cl \quad + \quad NaBPh_4 \longrightarrow R_2C{=}NBPh_2 \quad + \quad NaCl \quad + \quad 2C_6H_6 \qquad 1.57$$

R = Ph (69), p-tolyl (70)

$$R_2C{=}NH_2Cl \xrightarrow{Br_2} R_2C{=}NBr \xrightarrow{Mg} R_2C{=}NMgBr \qquad 1.58$$

R = Ph (Chapter 2)

An extensive survey of many methyleneamino derivatives of metals and metalloids which have been reported and characterised has been provided by the Ph.D. Thesis of E. A. Petch of this laboratory. Material supplementary to this is provided in Tables 1.1 - 1.4 which relate in particular to methyleneamino derivatives of magnesium, zinc, tin (II) and (IV), and germanium, their mode of preparation and azomethine stretching frequencies ν(C=N). Material from Chapters 2 and 3 of this Thesis is included.

Table 1.1

Methyleneamino-Derivatives of Magnesium

Compound	R	Method of Preparation	ν(C=N)* cm^{-1}	Reference
(R$_2$C=NMgBrTHF)$_2$THF	Ph	1,2,3,	1630	11 and a
	p-tolyl	1	1624	11 and a
(R$_2$C=NMgBr)$_2$	Ph	1,3	1605	a
	p-tolyl	1	1602	a
(R$_2$C=NMgBr)$_2$OEt$_2$	Bu^t	1	1622	a
[(R$_2$C=N)$_2$Mg]$_3$ 2THF	Ph	4	1655, 1613	11 and a
	p-tolyl	4	1661, 1620	a
(R$_2$C=N)$_2$Mg $_2$	Bu^t	4,6	1665, 1613	11 and a
(R$_2$C=NMg(Et)OEt$_2$)$_n$	Ph	4,5	1619	a
	p-tolyl	4,5	1619	a
(R$_2$C=NMgEt)$_n$	Bu^t	4,5	1605	11 and a
(R$_2$C=NMgPh)$_n$	Ph	5	1618	11 and a
	Bu^t	5	1607	11 and a
(R$_2$C=NMgEt)$_2$TMED	Ph	7	1620	a
	p-tolyl	7	1618	a
LiMg(NCR$_2$)$_3$OEt$_2$	Ph	8	1623	11
Li$_2$Mg(NCR$_2$)$_4$	Ph	8	1658, 1598	11

a: this work

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1. Methyleneamine and Grignard RMgX.
2. Nitrile and Grignard RMgX.
3. N-bromomethyleneamine and magnesium.
4. Methyleneamine and dialkylmagnesium.
5. Methyleneaminolithium and Grignard RMgX.
6. Disproportionation of (Bu$^t{}_2$C=NMgBr)$_n$ with THF
7. Methyleneamine and dialkylmagnesium/TMED
8. Methyleneamino lithium and bis(diphenylmethyleneamino) magnesium.

Table 1.2

Methyleneamino-Derivatives of Zinc

Compound	R	Method of Preparation	ν(C=N)* cm^{-1}	Reference
$(R_2C{=}NH)_2ZnCl_2$	Ph	1	1604	a
	p-tolyl	1	1608	a
$R_2C{=}NH.ZnCl_2$	Bu^t	1	1613	a
$(R_2C{=}NZnCl)_2$	Ph	2	1604	a
	p-tolyl	2	1600	a
	Bu^t	2	1608	50
$(R_2C{=}NZnMe)_2$	Ph	3	1624	13
	Bu^t	3	1592	50
$(R_2C{=}NZnEt)_2$	Ph	3	1611	13
$(R_2C{=}NZnPh)_2$	Ph	3,4	1607	50
	p-tolyl	3	1615	a
$(RC(Ph){=}NZnPh)_2$	p-tolyl	4	1605	a
$R_2C{=}NH.ZnPh_2$	p-tolyl	3	1607	a
$RCN.ZnPh_2$	Ph	4	-	13
	p-tolyl	4	-	a
$\left[(R_2C{=}N)Zn\right]_n$	Ph	2	1600	13
	p-tolyl	2	(1664), 1607	a
	Bu^t	2	1683, 1585	50

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1. Methyleneamine and zinc chloride
2. Methyleneaminolithium and zinc chloride
3. Methyleneamines and zinc alkyl.
4. Nitrile and zinc alkyl.

Table 1.3

Methyleneamino-Derivatives of Tin(II)

Compound	R	Method of Preparation	ν(C=N)* cm^{-1}	Reference
$R_2C=NH.SnCl_2$	Ph	1	1594	80
	p-tolyl	1	1606	a
	Bu^t	1	1598	a
$(R_2C=NSnCl)_2$	Ph	2	1564	80
	p-tolyl	2	1578	a
	Bu^t	2	1551	a
$(R_2C=N)_2Sn$	Ph	2	1603, 1570	80
	p-tolyl	2	1608, 1589	a
	Bu^t	2	1628, 1560	80
$R_2C=NH(R_2C=NSnCl)_2C_7H_8$	Ph	2	1564	80
$(R_2CN)_2NSn_2Cl_3$	Bu^t	3	1552	80
$(R_2CN)_3H_2Sn_3Cl_5$	Bu^t	3	1534	80
$Li(R_2CN)_3Sn$	Bu^t	2	1619	80

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1. Methyleneamine and tin(II) chloride
2. Methyleneaminolithium and tin(II) chloride
3. Thermal decomposition of $(Bu^t{}_2C=N)_2Sn^{IV}Cl_2$

Table 1.4

Some Selected Methyleneamino Derivatives of Germanium and Tin(IV)

Compound	R	Method of Preparation	ν(C=N) cm^{-1} *	Reference
$R_2C{=}NGeBr_3$	Bu^t	1	1624	49
$R_2C{=}NGeCl_3$	Ph	1	1609	80
$(R_2C{=}N)_2GeBr_2$	Bu^t	1	1646	49
$(R_2C{=}N)_2GeCl_2$	Bu^t	1	1645	49
	Ph	1	1610	80
$(R_2C{=}N)_3GeCl$	Bu^t	1	1652	49
$(R_2C{=}N)_4Ge$	Ph	1	1601	49
	p-tolyl	1	1598	49
$(R_2C{=}N)_2SnCl_2$	Bu^t	1	1627	80
	Ph	1	1607,1553	80
$(R_2C{=}N)_3SnCl$	Ph	1	1612,1535	80
	Bu^t	1	1627	80
$(R_2C{=}N)_4Sn$	Ph	1	1590	49
	Bu^t	1	1627	80
$(R_2C{=}N)_6Sn_2$	Bu^t	2	1635	80
$R_2C{=}NHSnCl_4$	Bu^t	3	1641	80
$(R_2C{=}NH)_2SnCl_4$	Bu^t	3	1662,1583	80

1. Methyleneaminolithium and $GeX_4/SnCl_4$
2. Lithium tris(di-t-butylmethyleneamino)tin(II) and tris(di-t-butylmethyleneamino)tin(IV)chloride
3. Methyleneamine and tin(IV)chloride

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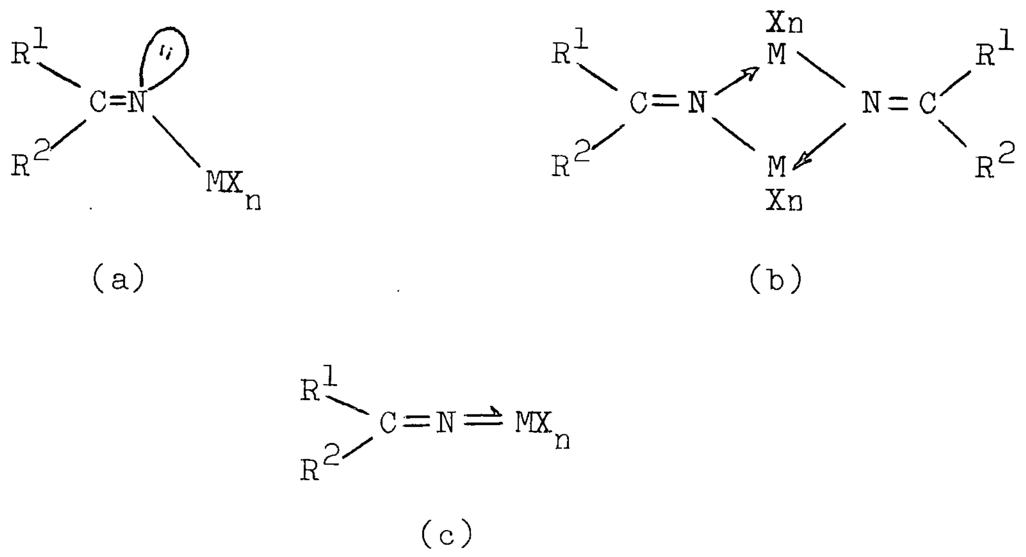
1.5 Structures and Bonding of Methyleneamino Derivatives of Metals and Metalloids

Considerable interest has been focused on the shape and bonding of the -C=N-M linkage. Several structures are possible for the N=metallated methyleneamino unit (Figure 1.1) with the ligand acting as a one or three electron donor. A non-linear structure (Figure 1.1(a)- with the ligand acting as a one electron donor, with sp^2 hybridisation at N, the lone pair of electrons formally occupying an sp^2 hybrid orbital, and the angle CNM being about 120° - has been demonstrated by ^{1}H-NMR spectroscopy at room temperature for a number of N-organomethyleneamines, $R^1R^2C{=}NR^3$ (71-75), and at - 30° for di-t-butylmethyleneamine (75). Such a structure may be expected for any derivative in which there is no bonding-interaction between the lone pair of electrons on nitrogen and the N-attached substituent eg in $R^1R^2C{=}NMX_n$ where M is co-ordinatively saturated. If the metal however is co-ordinatively unsaturated then saturation may be

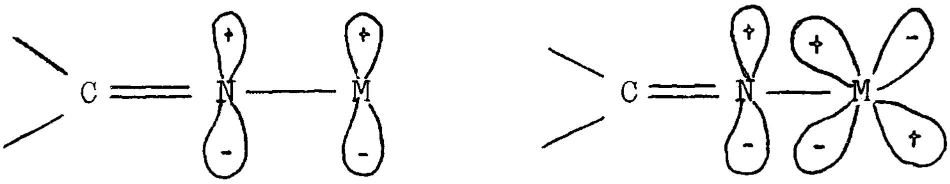


(a) (b)

(c)

Figure 1.1

achieved by donation of the lone pair on nitrogen - i.e. the establishing of N→M dative σ-bonds the ligands thereby becoming three electron donors - to a second metal atom of an adjacent monomer (Figure 1.1 (b). Formation of associated molecules, often dimers or oligomers is a consequence. Alternatively, particularly when association may be prevented because of steric hindrance between R^1 and R^2, co-ordinative saturation may be achieved by means of $N\overset{\rightarrow}{-}M$ dative π-bonding (Figure 1.1 (c). An increase in bond order between M and N results, with appropriate shortening of the bond length from that of a single M-N bond. In this instance maximum overlap between the N p-orbital, which contains the lone pair, and the vacant p or d orbitals on M is achieved when the C=N-M unit is linear at N with modification of hybridisation to sp (Figure 1.2 a and b shows cases of (p→p) and (p→ d)πbonding respectively). Whilst it has been shown for a nitrogen-silicon π-bond that considerable



(a) (b)

Figure 1.2

(p→d) π-interaction is possible even in a bent or non-linear skeleton (76), none the less such interaction is maximised by a linear arrangement, and therefore the angle at nitrogen may be a significant criterion in the establishment of dative π-bonding. The influence of steric hindrance on structure is demonstrated in series of methyleneamino derivatives of various metals or metalloids. These include several bis(methyleneamino)beryllium derivatives $[(R^1R^2C=N)_2Be]_n$ for which the degree of association - polymeric ($R^1 = R^2 = Ph$) trimeric ($R^1 = R^2 =$ p-tolyl), and dimeric ($R^1 =$ p-tolyl, $R^2 = Bu^t$; $R^1 = R^2 = Bu^t$)- is reduced significantly as the steric demands of the groups R^1 and R^2 increase (48). Crystallographic data for dimeric bis(di-t-butylmethyleneamino)beryllium, $[(Bu^t{}_2C=N)_2Be]_2$ (Figure 1.3) M = Be), shows the molecule to contain two types of imino-group, bridging and terminal. The latter units have almost linear C-N-Be units, with C-N-Be angles 161°, and the bond lengths consistent with substantial $N \rightarrow Be(p \rightarrow p)\pi$-bonding (77). A series of methyleneaminoboranes, $R^1R^2C=NBPh_2$, also evidence the effect of steric hindrance for when $R^1 = R^2 =$ Ph, p-tolyl, p-XC_6H_4(X = Cl, Br) the structures are monomeric but the derivative with $R^1 = Ph, R^2 = H$ is dimeric viz. $(PhCH=NBPh_2)_2$ (70). Similarly in the bis(methyleneamino) magnesium series described in Chapter 2, $[(R_2C=N)_2Mg]_x$ yTHF, trimeric structures are obtained with co-ordinated THF for R = Ph, p-tolyl (x = 3; y = 2) but bis(di-t-butymethylene-amino)magnesium appears to be dimeric without co-ordinated solvent. Its structure is assumed to be similar to its beryllium analogue (Figure 1.3 M = Mg) with both bridging and terminally attached methyleneamino ligands. The bonding capacity of the three-co-ordinate magnesium is presumably saturated by $N \rightarrow Mg$ dative $(p \rightarrow p)\pi$ bonding and the C=N-Mg units are likely to be near linear.

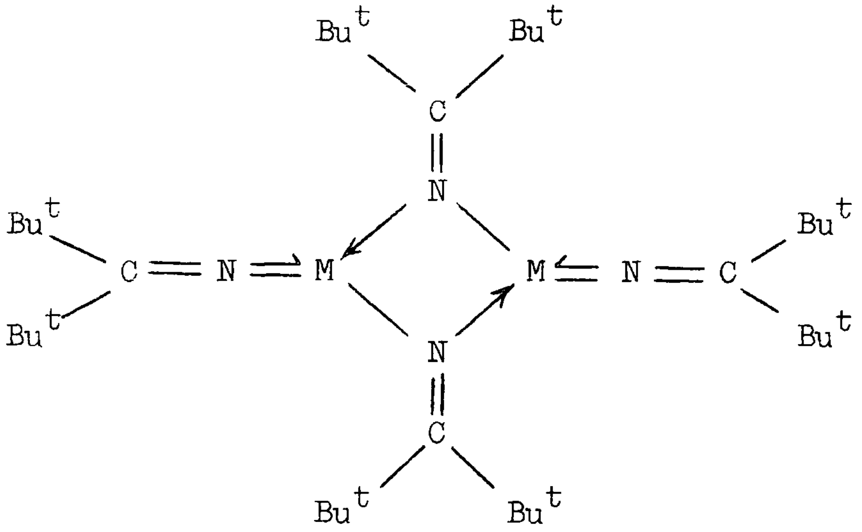
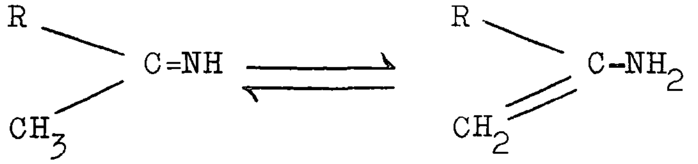


Figure 1.3

When the groups R^1 and R^2, in the methyleneamino derivative $R^1R^2C{=}NMX_n$, are small then the groups attached to the metal, viz X_n, may influence the degree of association. An interesting example of the subtlety of this influence may be seen in the monomeric nature of fluorenylmethyleneaminodiphenylborane, $C_{12}H_8C{=}NBPh_2$, and its more associated isomer diphenylmethyleneaminofluorenylborane, $(Ph_2C{=}NBC_{12}H_8)_n$. The increased steric demand of the fluorenyl group when placed nearer to the C=N-B unit is thereby demonstrated. (70) The methyleneamines employed in the course of the studies outlined in this work were diarylmethyleneamines, $R_2C{=}NH$(R = Ph, p-tolyl), and di-t-butylmethyleneamine, the latter being particularly useful. It avoids the problems of ketimine-enamine tautomerism (equation 1.60) inherent to dialkylmethyleneamines possessing α-hydrogen atoms - the presence of the enamine form of the N-organosilyl-methyleneamine, $PhMeC{=}NSiMe_3$ (viz $PhCH_2{:}CNHSiMe_3$) was detected by the presence



1.60

of olefinic protons in the ^{1}H-NMR spectrum (78) - provides bulky substituents which discourage association via methyleneamino bridges, and furthermore furnishes a simple ^{1}H-NMR spectroscopic probe. Several methods for the determination of the linearity of the C=N-M unit have been explored. The most conclusive technique is that of X-ray crystallographic analysis but as this is not always possible, various spectroscopic means have been employed - in particular, infrared, nuclear magnetic resonance and ultra-violet.

1.6 Spectroscopic Studies of Methyleneamino Derivatives

1.6.1. Infrared spectroscopy

The methyleneamine stretching frequences ν(C=N) of some symmetrical di-substituted methyleneamines R_2C=NH are provided in Table 1.5

Table 1.5

ν(C=N) For Selected Methyleneamines, R_2C=NH

R	ν (C=N cm^{-1}	Reference
Ph	1603	79
$pMeC_6H_4$	1610	a
Pr^n	1645	79
Bu^t	1604	80

a:this work

The change in this value when the N-attached hydrogen is replaced by other groups has been used to provide structural data concerning the organometallic derivatives i.e. the non-linearity/linearity of the C=N-M unit and consequently the extent of N→M dative π-bonding. For a methyleneamino derivative, $R_2C{=}NMX_n$, an increase in ν(C=N)- relative to the parent imine- generally occurs when the C=N-M unit approaches linearity. Such an increase has been explained in terms of a coupling between the C=N and $N \rightleftharpoons M$ vibrations (maximised by the linearity of the cumulative π-bonded system) and the observed high energy absorption has been assigned to the asymmetric stretching vibration of the $C{=}N \rightleftharpoons M$ unit (81). Valid comparison can be made with a similar increase in ν(C=N) which is observed on co-ordination of methyleneamines to strong Lewis acids eg BF_3 (8), paralleling a shift to higher energy which occurs on co-ordination with nitriles (6). The latter is believed to arise partly from the mechanical constraint which is applied to nitrogen on co-ordination (82-84), although crystallographic data demonstrates that co-ordination results in a slight increase in bond order and bond strength i.e. a shortening of the C≡N bond (85,86). The increase in ν(C=N) for co-ordinating methyleneamines and linear $C{=}N \rightleftharpoons M$ units may also result in part from bond order changes, though no firm evidence of this has been obtained.

Table 1.6 provides azomethine stretching frequencies ν(C=N) for selected methyleneamino metal derivatives whose structures have been determined by X-ray crystallography.

Table 1.6

ν(C=N) For Some Methyleneaminometal Derivatives

Compound	$\nu(C{=}N)_{cm^{-1}}$	Reference
$[(Bu^t{}_2C{=}N)_2Be]_2$	1739, 1637	77
$Ph_2C{=}NB(C_6H_2Me_3)_2$	1792	70
$(Bu^t{}_2C{=}N)_3B$	1730	11
$(Ph_2C{=}NMgBrTHF)_2THF$	1630	87

Compounds having more than one absorption may be assumed to possess more than one methyleneamino unit and if the two absorptions are widely separated these might arise from terminal and bridging imino groups. In such instances the higher value is assigned to the terminally attached ligand, the lower value being assigned to the bridging ligand. Hence for dimeric bis(di-t-butylmethyleneamino)beryllium the absorptions due to the terminal and bridging ligands are 1739cm^{-1} and 1637cm^{-1} respectively. The argument used for such assignments is that linear units allow the maximum overlap of nitrogen p and metal p/d orbitals with the consequent maximisation of N→M dative π-bonding. In the methyleneaminomagnesium derivative, $(Ph_2C{=}NMgBrTHF)_2THF$, discussed in greater detail in Chaper 2, the single absorption at 1630cm^{-1}

is attributed to bridging ligands. Although no X-ray crystallographic studies have been done on methyleneamino magnesium compounds possessing both terminal and bridging ligands it is of interest that in a series of bis(methyleneamino) magnesium derivatives - discussed in detail in the next chapter - all of which possess both terminal and bridging units, two absorptions in the azomethine stretching region are observed. The lower frequency absorption (1605-1620 cm^{-1} and the higher frequency absorption (1655-1668 cm^{-1}) are assigned to bridging and terminal ligands respectively. In the latter case there is good reason to expect a virtually linear $C{=}N \rightleftharpoons Mg$ unit with substantial $N \rightarrow Mg$ (p-p)π-bonding

The azomethine stretching frequency thus reflects the skeletal geometry of the molecule but other factors also influence thechanges in absorption frequencies. Such factors involve a consideration of the nature of M and X_n in the derivatives $R^1R^2C{=}NMX_n$.

(a) The nature of the central metal M

The manner in which ν(C=N) depends upon the nature of M is illustrated in Table 1.7 where the structures of the methyleneamino derivatives in each of the two groups of selected compounds are believed to be similar if not identical. The change in ν(C=N) is influenced by the electronegativity of M, its mass and its capacity to sigma-and pi-bond, all of which factors may be involved in frequency changes. Indeed, that it is not possible to isolate a single parameter to rationalise the changes shown, can be exemplified by considering a single factor such as the size of the metal. The

Table 1.7

ν(C=N) Frequencies of Related Methyleneamino Derivatives

of some Groups II and IV Elements

Compound	M	ν(C=N)terminal cm^{-1}	ν(C=N)bridging cm^{-1}	Reference
$[(Bu^t{}_2C=N)_2M]_2$	Be	1732	1627	54
	Mg	1668	1605	a
	Zn	1683	1585	50
$Ph_2C=NMPh_3$	Si	1662	-	78
	Ge	1633	-	78
	Sn	1613	-	78

a: this work

extent and efficacy of orbital overlap, between the nitrogen lone pair in the p-orbital and a vacant metal p/d, orbital, will be greater when M is of similar size to N and hence the smaller the atom M the more effective will be the dative π-bonding with nitrogen and this should be reflected in the stretching frequency ν(C=N). Whilst the consequential effect is well shown for the three Group IV methyleneamino derivatives, $Ph_2C=NMPh_3$, M = Si, Ge, Sn, the trend observed in Group II compounds $[(Bu^t{}_2C=N)_2M]_2$ M = Be, Mg, Zn, is by comparison inconsistent.

(b) The nature of the substituents on M

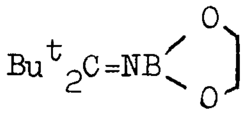
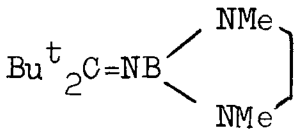
For methyleneamino derivatives $R_2C=NMX_n$ the nature of X may influence the metal-nitrogen bond, and therefore ν(C=N), by both π and σ effects. The π-bonding capacity of X may be of importance since as well as competing with the N-lone pair for the orbitals of M, any $X \rightarrow M$ π-back donation would reduce the ability of M to accept futher electron density from nitrogen, so weakening the N-M bond and tending to reduce ν(C=N). Electron releasing/withdrawing groups also effect the strength of M-N bond and therefore ν(C=N). Electron withdrawing groups increase the polarity of metal-nitrogen σ bond, strengthen the bond and may well 'induce' $N \rightarrow M$ dative π-bonding i.e. increasing ν(C=N). Electron releasing groups, on the other hand, will weaken the M-N σ-bond by reducing its polarity and hence reduce ν(C=N). Table 1.8 shows the azomethine stretching frequencies of some substituted methyleneaminoboranes which demonstrate these points.

(c) The nature of the alkyl or aryl group R

The azomethine stretching frequencies, ν(C=N) for $R^1R^2C{=}NH$ does vary with the nature of R^1 and R^2 - see reference (8) for example, and the degree of variation is at least comparable with that caused by the substituent on nitrogen already considered. This therefore is another factor which could swamp other influences when specific comparisons are being made.

Table 1.8

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

Compound	ν(C=N)	Reference
$Bu^t_2C{=}NBCl_2$	1839	92
$Bu^t_2C{=}NBPh_2$	1820 *	92
$Bu^t_2C{=}NBBu^n_2$	1821	92
$Bu^t_2C{=}NBEt_2$	1818	57
$Bu^t_2C{=}NBF_2$	1796 **	11
	1736	11
	1739 *	11

* pentane solution; ** Nujol mull; all others liquid films

1.6.2. Nuclear Magnetic Resonance Spectroscopy

The ^1H-NMR spectra of methyleneamine derivatives may in principle, be used to deduce whether the C=N-M unit is linear or bent. For this purpose, in this study, the substituent groups R in the methyleneamine unit $R_2C{=}N$ were chosen in order to give a singlet signal. In this context, suitable groups chosen were R = Bu^t, pMe - C_6H_4 but the use of the phenyl group is spectroscopically disadvantageous because of the complexity of the phenyl ^{1}H-NMR signals. The general basis of the use of the methyleneamino unit $R_2C{=}N$ as a probe for the purpose already described may be illustrated by reference to Figure 1.4. The linear skeleton (Figure 1.4 (a)) has both R groups in magnetically equivalent environs, but a bent structure (Figure 1.4 (b)) shows the R groups to be magnetically inequivalent. In the former case therefore one signal is expected but in the latter case, in principle, two absorptions would be anticipated.

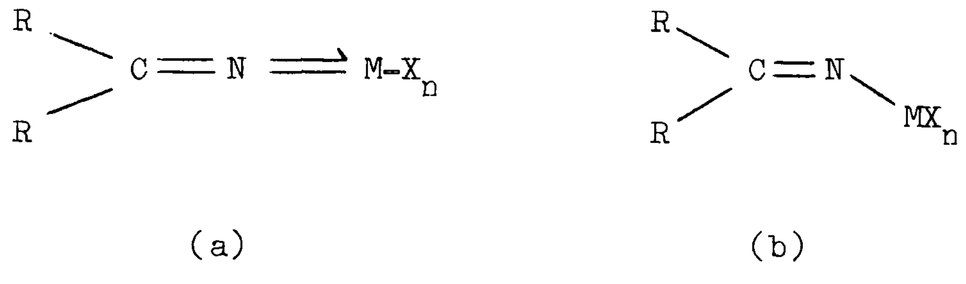


Figure 1.4

In practice however the scope of NMR spectroscopy as a means of determining the linearity of the C=N-M skeleton in the methyleneamino derivative $R_2C{=}NMX_n$ is restricted by the relative ease with which inversion can occur in the bent system and the two signals expected of the skeleton are rarely observed at room temperature. Indeed as a result of the rapid inversion between the syn-and anti-isomers, only one signal is observed for both R groups despite their formal magnetic inequivalence (Figure 1.5). The rate of inversion, however, may be reduced on cooling and sufficiently relative to the NMR time scale, to allow resolution .

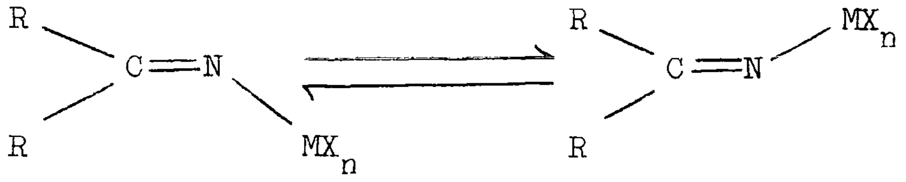


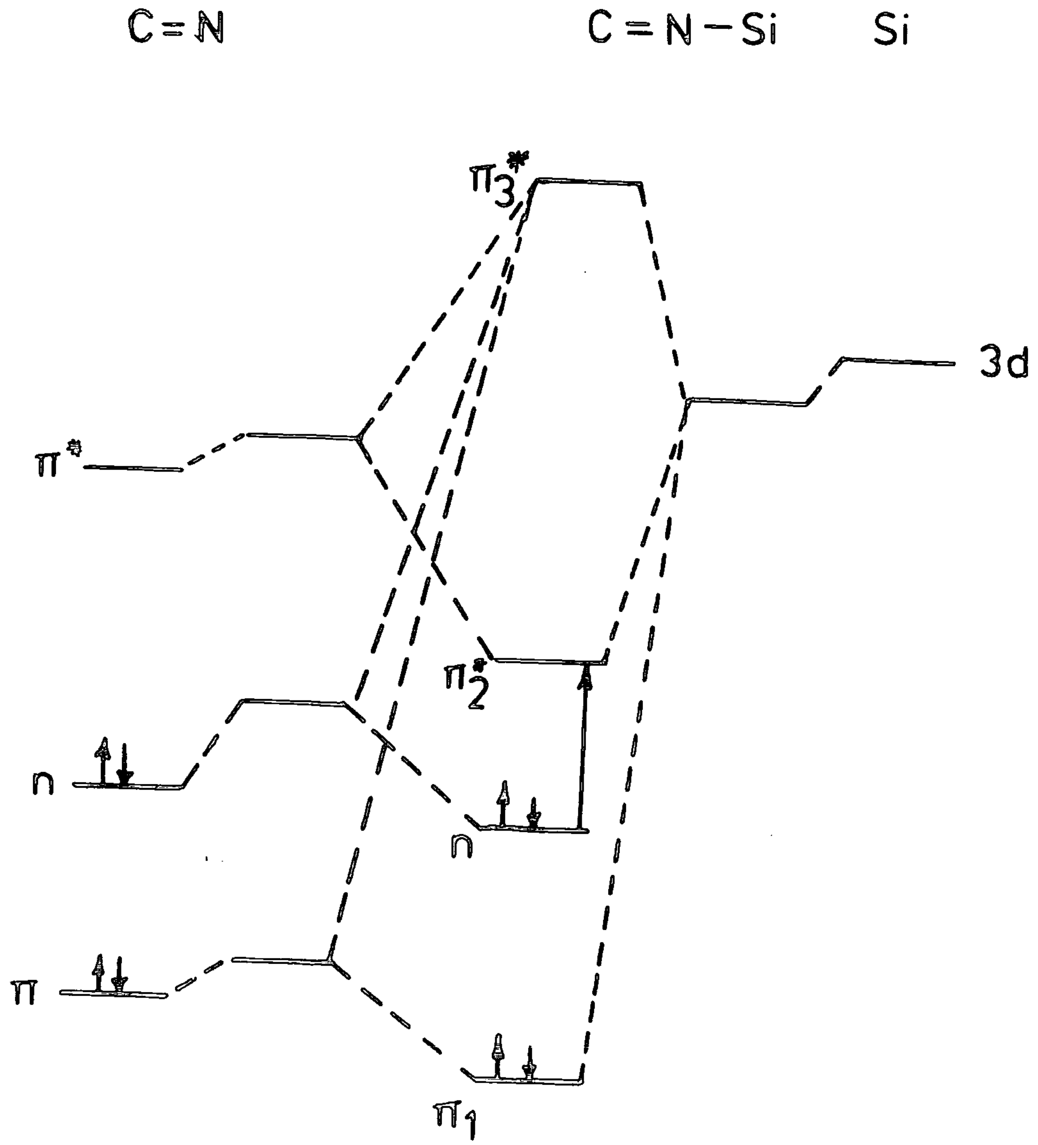
Figure 1.5

As a cautionary note therefore, if a singlet is observed at the lowest temperature obtainable for the sample then such may imply either that the C=N–M unit is linear or that inversion at the nitrogen of a non-linear unit is still occurring at a high rate, relative to the NMR time scale, despite the low temperature. The topic of syn-anti isomerisation in methyleneamines has been reviewed by McCarty (89) and it appears that steric effects play a significant role in the isomerisation process. In the series MeC(R): NCH(Me)Ph - i.e. N-alkylated or N-arylated methyleneamines - where R = Et, Pr^i, Bu^t the syn-anti isomer ratios were 17:83, 7:93 and 0:100 respectively (73, 75). For the less sterically hindered $Me_2C{=}NCH_2Ph$, on the other hand, the methyl resonances were observed as separate signals even at 170°C. The activation energy for the inversion at nitrogen (90) and phosphorus (92) of Group IV compounds has been determined and a study of the system $PhP(R)\text{-}MMe_3$ (91) (R = Me, Pr^i and M = C, Si, Ge and Sn) revealed that the barrier to pyramidal inversion at P is correlatable to the electronegativity of M - the higher the electronegativity the higher the energy barrier. Additionally the ^{1}H-NMR spectrum of $(pCF_3C_6H_4)PhC{=}NGeMe_3$ (90) below -110° consisted of two overlapping singlets corresponding to the syn and anti forms which coalesced at -108°, becoming a sharp singlet at temperatures above -70°C.

In conclusion therefore NMR spectroscopy has proved helpful in detecting bent structures of a few methyleneamino derivatives such as the trimethylgermyl system above. It has also afforded the simple structures expected of linearly attached systems in several instances where near linearity of the C=N-M skeleton has been subsequently established by X-ray crystallography. However since simple spectra could have arisen by rapid inversion of bent structures NMR evidence of linearity is never unambiguous.

1.6.3 Ultra-violet Spectroscopy

The only reported study of the ultra-violet spectra of N-metallated methyleneamines has involved an investigation of a series of diarylmethyleneamino derivatives of metals and metalloids of Group IV (Si, Ge and Sn) (78). The findings showed that for each spectrum, two absorptions were observed, a long wavelength band of low intensity at about 350-380 $m\mu$ and a more intense short wavelength band in the range 240-260 $m\mu$. The former lower energy absorption was attributed to the $n \longrightarrow \pi^*$ transition involving the excitation of an electron in the non-bonding orbital of nitrogen to the antibonding π^*-orbital of the C=N bond, whilst the latter higher energy absorptions corresponds to the $\pi \longrightarrow \pi^*$ transition of the $C{=}N \rightleftharpoons M$ π-system. The qualitative energy level diagram of C=N-Si (Figure 1.6)



Energy levels for the C=N−Si group

Fig.1. 6.

shows that silicon substituents, SiX_3, on the nitrogen atom of the methyleneamino group decrease the energy required for $n \rightarrow \pi^*$ transitions as a consequence of $p \rightarrow d$ π-interaction between nitrogen and silicon and the electropositive character of the metalloid. This interaction would be greatest if the $C{=}N \rightleftharpoons Si$ skeleton were linear and therefore the influence of the SiX_3 group on the $n \longrightarrow \pi^*$ transitions would be greatest if linearity occurred. In practice however, the $n \longrightarrow \pi^*$ transition frequency for a series of methyleneaminosilanes, $R_2C{=}NSiX_n$ (X various π-donating sunstituents on silicon eg phenyl, vinyl, alkoxy and amino groups) showed no significant change with X, and this was interpreted in terms of a non-linear C=N-Si unit, with little $N \rightleftharpoons Si$ π-bonding. But significant $(p \rightarrow d)\pi$-bonding has been shown to be possible even in a bent or non-linear C=N-Si skeleton (76) and therefore, if the energy of the n and π^* levels are reduced by about the same increment as a result of substitution at nitrogen, the observed $n \rightarrow \pi^*$ transition frequency for each compound will be about the same. Since $(p \rightarrow d)$ π interaction is possible in both linear and non-linear C=N-Si skeletons, then the results may well accommodate both structural types. This has been verified, by implication at least, by X-ray crystallographic studies on similar compounds to those mentioned above viz $(Ph_2C{=}N)_4M$ (M = Si, Ge, Sn) results of which show the molecules to have bent structures with substantial $(p \rightarrow d)\pi$ bonding in $(Ph_2C{=}N)_4Si$ (93).

CHAPTER 2

SOME METHYLENEAMINO DERIVATIVES OF MAGNESIUM

2.1 Introduction

The work in this section was prompted by the discovery that a methyleneaminomagnesium halide - ether adduct, prepared in an earlier study (11), contained one ether molecule, the presence of which had not been detected by analytical methods, co-ordinated in a most unusual way. The compound in question was thought to be bis(diphenylmethyleneaminomagnesium bromide)bis-THF, $(Ph_2C{=}NMgBr)_2(THF)_2$, but a crystallographic study (87, 90) showed the molecule to contain an additional molecule of tetrahydrofuran with unexpected features. The structure of this adduct, $(Ph_2C{=}NMgBr)_2(THF)_3$ is now described.

The X-ray Crystal Structure of the Diphenylmethyleneaminomagnesium Bromide Tetrahydrofuran Adduct

$Mg_2Br_2(THF)_2(\mu\text{-}N{:}CPh_2)_2(\mu\text{-}THF)$

Crystals of the adduct were prepared as described in section 2.4 (i) - page 86 and, on the basis of spectroscopic data, it was thought to possess a terminally - co-ordinatd methyleneamino group. The crystallographic study however, established the compound as being dimeric with bridging methyleneamino ligands and a bridging tetrahydrofuran molecule (I;Figures 2.1 and 2.2).

Each magnesium atom of the dimeric molecule, $(Ph_2C{=}NMgBr)_2(THF)_3$, is five - co-ordinate, being co-ordinated to both a terminal bromine atom and tetrahydrofuran molecule and also bridged by two diphenylmethyleneamino units and a tetrahydrofuran molecule. The Mg_2N_2 ring is non-planar, the two diphenylmethyleneamino units being folded slightly away

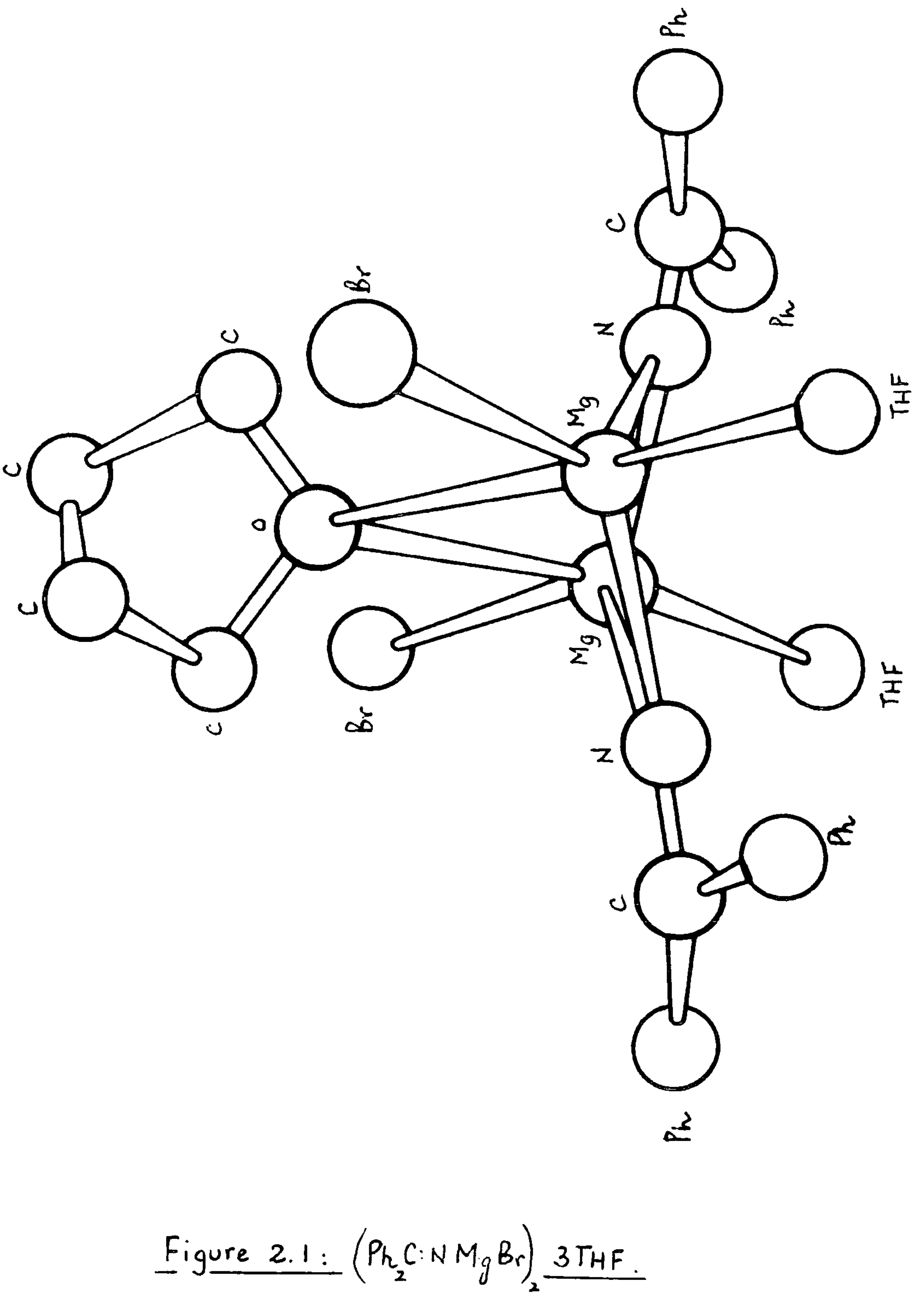


Figure 2.1: $(Ph_2C{:}NMgBr)_2\,3THF$.

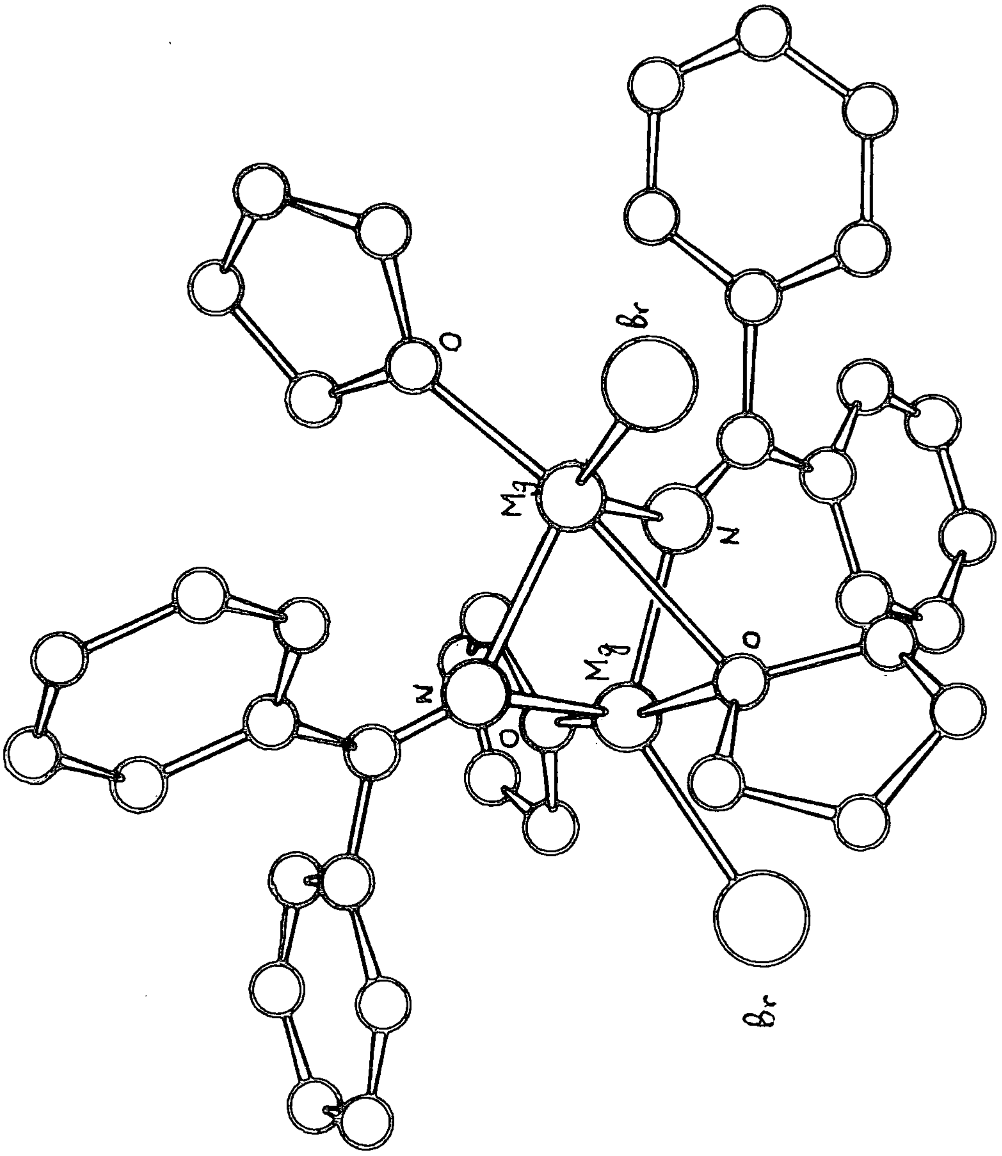


Figure 2.2: $(\mathrm{Ph_2C{:}NMgBr})_2$ 3THF.

from the bridging THF molecule (the dihedral angle between the MgNMg planes is 154°). A common feature of molecules which involve small bridging atoms eg carbon, nitrogen, and oxygen is the relatively small cross-ring metal-metal distances. In this compound the cross-ring Mg-----Mg distance (2.89 Å) compares favourably with such parameters in other molecules viz, 2.85 Å in $(Bu^tOMgBrOEt_2)_2$ (95), and 2.94 Å in $(Me_2NCH_2CH_2N(Me)MgMe)_2$ (96). Correspondingly, bridging through larger atoms such as chlorine and bromine allows greater metal-metal separations - 3.73 Å in $[(EtMg_2Cl_3(THF)_3]_2$ (97), 3.53 Å in $(EtMgBrNEt_3)_2$ (98) and 3.20 Å in $Mg_4Br_6O(OEt_2)_4$ (99). Where bridging units involve electron-deficient alkyl units, with small bridging angles and consequently smaller metal-metal separations, representative Mg-----Mg distances are 2.67 Å and 2.72 Å in polymeric diethyl (100) - and dimethyl (101) - magnesium respectively, significantly less than the cross distance observed in this structure.

The bridging magnesium - oxygen distance ($Mg - O_b$) of 2.45 Å is unusually long when compared with the $Mg - O_t$ distance of 2.07 Å, but significantly shorter than the minimum separation expected for non-bonded magnesium and oxygen atoms (3.25 Å) (102). These bridging Mg - O bonds are effectively opposite to the terminal Mg - O bonds, the OMgO angle being 173°, and may well justify the classification of this interaction as being 'secondary' (103). The remaining bonds to magnesium, $Mg - O_t$, $Mg - N_b$ and Mg - Br are of normal length and are similar to those reported for related organomagnesium compounds, for example $(Me_2NCH_2CH_2NMeMgMe)_2$

(96), $(EtMgBrNEt_3)_2$ (98), $EtMg_2Cl_3(THF)_3$ (97), $PhMgBr(OEt_2)_2$ (99), and $MeMgBr(THF)_3$ (104). Likewise the C=N bond distance lies within the range of values normally found in co-ordinated methyleneamino groups, where the N-atom is sp^2 hybridised, such as in dimeric bis(di-t-butylmethyleneamino)beryllium (77).

This chapter as a whole, supplementing, amending and extending some earlier work of E. A. Petch (11), describes the preparation and properties of some methyleneamino-derivatives of magnesium. Their spectroscopic and structural characteristics are discussed and compared with related compounds. In general the reactions studied involved the use of Grignard species, such as RMgBr (R = Pr^i, Et, Ph) and diethylmagnesium, and methyleneamines $R_2C{=}NH$ (R = Ph, p-tolyl, Bu^t) and their lithium derivatives.

The most widely used route to the synthesis of methyleneamines has involved the insertion of a nitrile into the Mg - C bond of a Grignard reagent and subsequent controlled hydrolysis of the methyleneaminomagnesium product (equation 2.1). Although methyleneaminomagnesium halides

$$RC{\equiv}N + R^1MgX \longrightarrow RR^1C{=}NMgX \longrightarrow RR^1C{=}NH \qquad 2.1$$

feature as intermediates in the reaction, little attention has been given to the methyleneaminomagnesium species involved, and until this work, the reactions between nitriles and Grignard reagents was the only established route to such compounds. In the work about to be described, the two principal routes to methyleneaminomagnesium derivatives involved pathways already established in the synthesis of related methyleneamino derivatives of both beryllium and zinc.

These reactions involved (i) methyleneaminolithium and metal halides and (ii) methyleneamine and metal alkyls. The reaction between methyleneaminolithium and Grignard reagent - the latter being the metal halide in the context of this chapter - proceeded at a convenient rate, although separation of lithium bromide and the desired

$$R_2C{=}NLi \quad + \quad R^1MgBr \longrightarrow R_2C{=}NMgR^1 \quad + \quad LiBr \qquad 2.2$$

R = Ph, p-tolyl, Bu^t; R^1 = Ph, Et

organomagnesium derivative (equation 2.2) was not easy, and not always successfully achieved. The use of methyleneamines and magnesium alkyl derivatives involved no such complication (equation 2.3) although occasionally

$$nR_2C{=}NH \quad + \quad Et_2Mg \longrightarrow (R_2C{=}N)_nMgEt_{2-n} \quad + \quad nEtH \qquad 2.3$$

$n = 1, 2$; R = Ph, p-tolyl, Bu^t

the product of the equimolar reaction, formally the methyleneaminoethylmagnesium derivatives, evidenced traces of the bis(methyleneamino) magnesium complex. Nevertheless reactions between alkylmagnesium compounds and methyleneamines were the most frequently employed, and indeed most successful route, to methyleneaminomagnesium compounds. Methyleneaminomagnesium bromide derivatives, for example, were prepared by the use of i-propylmagnesium bromide (equation 2.4) whilst in preparing methyleneaminoethylmagnesium

$$R_2C{=}NH \quad + \quad Pr^iMgBr \longrightarrow R_2C{=}NMgBr \quad + \quad PrH \qquad 2.4$$

R = Ph, p-tolyl, Bu^t

and bis(methyleneamino) magnesium compounds, diethylmagnesium was employed (equation 2.3). The preparation of diphenylmethyleneaminomagnesium bromide was also accomplished, although in small yield, by the reaction between N-bromodiphenylmethyleneamine, made by reacting bromine with diphenylmethyleneamine hydrochloride (105), and magnesium (equation 2.5).

$$Ph_2C{=}NH \longrightarrow Ph_2C{=}NH.HCl \longrightarrow Ph_2C{=}NBr \xrightarrow{Mg} Ph_2C{=}NMgBr \qquad 2.5$$

Generally, under the conditions employed, there seemed to be little difference in the reactivities of the three methyleneamines studied, $R_2C{=}NH$ (R = Ph, p-tolyl, Bu^t), nor in the yields of products.

2.2 Discussion

The new methyleneaminomagnesium compounds are listed in Table 2.1. Their azomethine stretching frequencies, ν(C=N) are summarised in Table 2.12 (page 85) and the experimental section follows this (Section 2.4 page 84).

Characterisation and Spectroscopic Properties of the New Methyleneaminomagnesium Compounds

To facilitate a comparison of these compounds with analogous beryllium and zinc systems, the new compounds are arranged in three groups.

Table 2.1

The New Methyleneaminomagnesium Compounds

Group A: General formula type $(R_2C{=}NMgBr)_2L_x$ (I)

$(Ph_2C{=}NMgBr)_2(THF)_3$ (I; R = Ph, L = THF, x = 3)

Group A contd.

$\left\{(\text{p-tolyl})_2\text{C=NMgBr}\right\}_2(\text{THF})_3$ (I; R = p-tolyl, L = THF, x = 3)

$(\text{Ph}_2\text{C=NMgBr})_2(\text{THF})_2$ (I; R = Ph, L = THF, x = 2)

$\left\{(\text{p-tolyl})_2\text{C=NMgBr}\right\}_2(\text{THF})_2$ (I; R = p-tolyl, L = THF, x = 2)

$(\text{Bu}^t{}_2\text{C=NMgBr})_2\ \text{OEt}_2$ (I; R = Bu^t, L = OEt_2; x = 1)

Group B General formula type $\left[(\text{R}_2\text{C=N})_2\text{Mg}\right]_n(\text{THF})_x$ (II)

$\left\{(\text{Ph}_2\text{C=N})_2\text{Mg}\right\}_3(\text{THF})_2$ (II; R = Ph, n = 3, x = 2)

$\left[\left\{(\text{p-tolyl})_2\text{C=N}\right\}_2\text{Mg}\right]_3(\text{THF})_2$ (II; R = p-tolyl, n = 3, x = 2)

$\left[(\text{Bu}^t{}_2\text{C=N})_2\text{Mg}\right]_2$ (II; R = Bu^t, n = 2, x = o)

Group C General formula type $(\text{R}_2\text{C=NMgX})_n\text{L}_m$ (III)

$(\text{Ph}_2\text{C=NMgEt})_n(\text{OEt}_2)_n$ (III; R = Ph, n = m, X = Et, L = OEt_2)

$\left\{(\text{p-tolyl})_2\text{C=NMgEt}\right\}_n(\text{OEt}_2)_n$ (III; R = p-tolyl, n = m, X = Et, L = OEt_2)

$(\text{Bu}^t{}_2\text{C=MgEt})_n$ (III; R = Bu^t, X = Et, m = o)

$(\text{Ph}_2\text{C=NMgPh})_n$ (III; R = Ph, x = Ph, m = o)

$(\text{Bu}^t{}_2\text{C=NMgPh})_n$ (III; R = Bu^t; x = Ph, m = o)

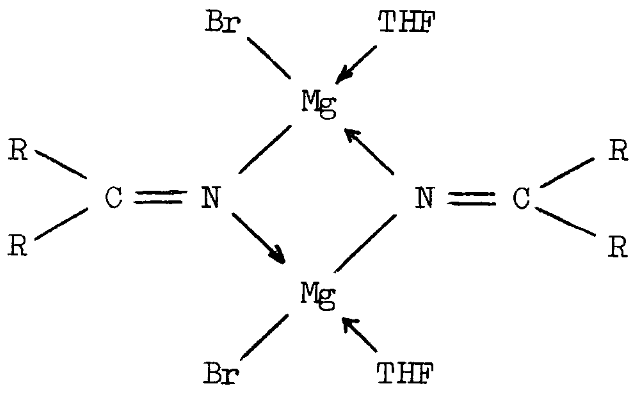
$(\text{Ph}_2\text{C=NMgEt})_2\text{TMED}$ (III; R = Ph, X = Et, n = 2, m = 1, L = TMED)

$\left\{(\text{p-tolyl})_2\text{C=NMgEt}\right\}_2\text{TMED}$ (III; R = p-tolyl, X = Et, n = 2, m = 1, L = TMED)

2.2.1 Group A

The compounds listed in this section are the adducts of diphenyl- and di-p-tolyl-methyleneaminomagnesium bromide with tetrahydrofuran(THF), viz $(R_2C=N)_2Mg_2Br_2(THF)_x$ (R = Ph, p-tolyl, x = 2,3), and the adduct of di-t-butylmethyleneaminomagnesium bromide with diethyl ether, $(Bu^t{}_2C=N)_2Mg_2Br_2(OEt_2)$.

Diphenyl- and di-p-tolyl-methyleneaminomagnesium bromides, $R_2C=NMgBr$ (R = Ph, p-tolyl), prepared in ether solution either from the appropriate nitrile and PhMgBr, or from the parent methyleneamine and Pr^iMgBr, are off-white amorphous solids which readily disolve in THF from which pale-yellow crystalline adducts of composition $(R_2C=N)_2Mg_2Br_2(THF)_3$, R = Ph, p-tolyl, are recoverable. The structure of the diphenylmethyleneaminomagnesium bromide THF adduct (I; Figures 1.1 and 1.2) has already been discussed in Section 2.1 and presumably the analogous di-p-tolylmethyleneaminomagnesium bromide THF adduct is similar. In both of these tris-(THF) adducts, one of the THF molecules, presumably the bridging one, can be removed under reduced pressure, and evidently separates when the adduct dissolves in benzene in which M, by cryoscopy is 379 and 410 (I requires M, 795 and 841 for R = Ph, p-tolyl respectively). The residual compounds, $(R_2C=N)_2Mg_2Br_2(THF)_2$ (R = Ph, p-tolyl), which can also be prepared directly from equimolar proportions of $R_2C=NMgBr$ (R = Ph, p-tolyl) and THF, are also soluble in benzene, their molecular weights, by cryoscopy, being 496 and 520 respectively. Although these values are by themselves inconclusive - the dimeric formulations requiring molecular weights of 713 (R = Ph) and 769 (R = p-tolyl) infrared evidence, based on the established structure of I (R = Ph) and discussed in greater detail later, shows the methyleneamino unit to be a bridging ligand. Accordingly the structure proposed for these bis(THF)adducts $(R_2C{=}N)_2Mg_2Br_2(THF)_2$, R = Ph, p-tolyl (II) is shown in Figure 2.3 with bridging methyleneamino ligands and four-co-ordinate magnesium.



(II) Figure 2.3

The bis(THF) adduct (II; R = Ph) gives a different X-ray powder diffraction pattern to I (R = Ph) and recrystallisation of (II) from THF regenerates I.

The influence of the bulk of the substituents upon the association number of methyleneamino- derivatives of Group II elements beryllium and zinc is well established, and will be detailed in the next section. Related diphenyl-, di-p-tolyl- and di-t-butylmethyleneamino derivatives frequently illustrate the reduction in the degree of association of related compounds as the bulk of R in the methyleneamino-ligand, $(R_2C{=}N)$, increases. The steric demands of such ligands would appear to follow the sequence $(Ph_2C{=}N) \sim (p\text{-tolyl})_2C{=}N \ll (Bu^t{}_2C{=}N)$ and whilst little difference is demonstrated between related diphenyl- and di-p-tolyl-methyleneamino derivatives, significant changes occur when the di-t-butylmethyleneamino ligand is employed. Generally this study of methyleneaminomagnesium compounds would endorse this trend and, in particular, the similarity in the methyleneaminomagnesium bromide THF adducts, $(R_2C{=}NMgBrTHF)_2(THF)_x$ (R = Ph, p-tolyl; x = 0,1), has already been established. It was hoped therefore, from the reaction between di-t-butylmethyleneamine and i-propylmagnesium bromide, an organomagnesium derivative might be prepared where the bulkier di-t-butylmethyleneamino ligand might stabilise magnesium in a low co-ordinative state. The reaction proceeds smoothly and the product di-t-butylmethyleneaminomagnesium bromide, $(Bu^t{}_2C{=}NMgBr)_n$, is ether soluble. This contrasts with the insolubility of $(R_2C{=}NMgBr)_n$ R = Ph, p-tolyl) in ether and suggest di-t-butylmethyleneaminomagnesium bromide is less associated that the corresponding phenyl- and p-tolyl derivatives. Furthermore $(Bu^t{}_2C{=}NMgBr)_n$ does not form an adduct with THF but instead disproportionates to yield solvated magnesium bromide, $MgBr_2(THF)_4$ and bis(di-t-butylmethyleneamino)magnesium (equation 2.6).

$$\left[Bu^t{}_2C{=}NMgBr\right]_n \rightleftharpoons \left[(Bu^t{}_2C{=}N)_2Mg\right]_2 + MgBr_2 \qquad 2.6$$

From the solution of $(Bu^t{}_2C{=}NMgBr)_n$ in ether, yellow etherated crystals were obtained which, on the basis of analytical and infrared evidence, estimation of co-ordinated ether liberated by pyrolysis and molecular weight determination by cryoscopy in benzene, were formulated as $(Bu^t{}_2C{=}NMgBr)_2OEt_2$. Such a formulation suggests bridging $(Bu^t{}_2C{=}N)$ units and a bridging ether molecule, the latter feature causing the magnesium atoms to be four-co-ordinate (Figure 2.4).

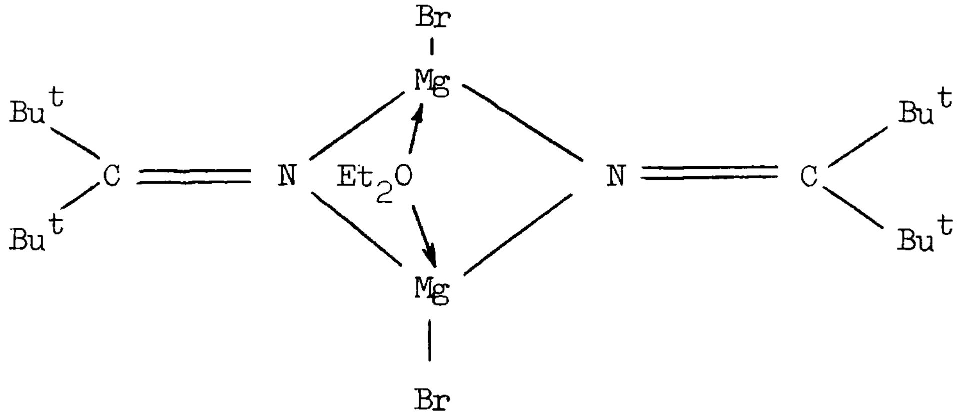


Figure 2.4

In benzene, the bridging ether may also separate (M by cryoscopy 297, formulation requires 563). An X-ray crystallographic study proved abortive, the sample deteriorating markedly in the X-ray beam during data collection and its instability therefore prevented the accummulation of adequate information (106). Hence whilst the t-butylmethyleneamino ligand has not established a three co-ordinate state for magnesium, its increased steric demands and the effects of such, relative to the phenyl and p-tolyl ligands, are evident in the structures of the series of methyleneaminomagnesium compounds discussed thus far.

Spectroscopic Properties

The established role of the methyleneamino unit as a bridging ligand in these compounds necessarily requires the

C=N-M skeleton to be non-linear. Consequently the frequencies of the methyleneamino stretching absorptions, ν(C=N), in the infrared spectra of the new compounds can be assigned with confidence to bridging methyleneamino ligands. These absorptions lie in a well defined region from 1602 - 1630 cm^{-1} (Table 2.2).

Table 2.2

The Methyleneamino Stretching Frequencies, ν(C=N) of the Adducts of $(R_2C{=}NMgBr)_2$ with (i) THF, R = Ph, p-tolyl and (ii) Et_2O, R = Bu^t

Compound	ν(C=N) cm^{-1} (Nujol Mulls)
$(Ph_2C{=}NMgBr)_2\ (THF)_3$	1630
$(Ph_2C{=}NMgBr)_2\ (THF)_2$	1605
$\{(p\text{-tolyl})_2C{=}NMgBr\}_2(THF)_3$	1624
$\{(p\text{-tolyl})_2C{=}NMgBr\}_2(THF)_2$	1602
$(Bu^t{}_2C{=}NMgBr)_2\ OEt_2$	1622

It is of interest to note at this stage that all the new methyleneaminomagnesium compounds discussed in this Chapter have methyleneamino (azomethine) stretching frequencies in this range and consequently their proposed structures also contain bridging methyleneamino ligands (Table 2.12; page 85).

The details of the <u>^{1}H-NMR</u> spectra of these compounds are provided in <u>Table 2.3</u>

<u>Table 2.3</u>

<u>The ^{1}H-NMR of Some New Methyleneaminomagnesium Compounds</u>*

Compound	τ values in ppm [a]
$(Ph_2C{=}NMgBrTHF)_2THF$	3.0,3.12,3.45(c)(10); 6.70(c), 8.98c (11)
$(Ph_2C{=}NMgBrTHF)_2$	2.77,3.08,3.16c (5); 6.62c, 8.92c (4)
$\left[(p\text{-tolyl})_2C{=}NMgBrTHF\right]_2THF$	2.58,2.71,3.15,3.28c(18) 8.16s (12); 6.56c, 8.88c (24)
$\left[(p\text{-tolyl})_2C{=}NMgBrTHF\right]_2$	2.67,2.78,3.04,3.23,3.34c (16); 8.19s (13); 6.53c, 8.82c (17)
$(Bu^t{}_2C{=}NMgBr)_2OEt_2$	8.95(s); 6.64 - 6.98c; 8.92, 9.06, 9.20t [b]

* Spectra taken in C_6D_6 at ~40°C; s = singlet; c = complex; t = triplet.

[a] Reference standard employed <u>external TMS</u> $\tau = 10$.

[b] Poorly resolved spectrum, proton intergration impossible.

For the adducts $(R_2C{=}NMgBrTHF)_2(THF)_x$ R = Ph, p-tolyl; x = 0,1, the complex absorptions between $\tau(2.58 - 3.34)$ are attributable to protons on the aromatic ring whether phenyl or p-tolyl; the singlet peaks due to the methyl protons on the (p-tolyl) units are about $\tau = 8.16 - 8.19$, whilst the peaks assigned to co-ordinated tetrahydrofuran are in the regions $\tau = (6.53 - 6.70)$ and $\tau = (8.82 - 8.98)$, the relative intensities of these peaks supporting the structures already assigned. Interestingly the spectra of $(Ph_2C{=}NMgBrTHF)_2\,(THF)_x$ (x = 0,1) are very similar whatever the value of x, and the same is true for the related pair of (di-p-tolylmethyleneaminomagnesium bromide) THF adducts. Furthermore the two absorptions due to co-ordinated THF in the four adducts occur at lower field than the corresponding peaks in unco-ordinated THF, and this shift is in the same direction (i.e. downfield) to that observed in the spectra of BF_3 and BH_3 solutions in THF (107). In such solutions, peaks due to co-ordinated solvent were observed at lower field than those due to free solvent. The shift of the peak due to the hydrogen atoms on the α-carbons of THF ($\Delta\alpha$), being significantly greater than the shift due to the hydrogen atoms on the β-carbons ($\Delta\beta$) parallels the observed behaviour in the BX_3/THF systems (Table 2.4).

The spectrum of the di-t-butylmethyleneaminomagnesium bromide, already formulated as a dimer with bridging methyleneamino units and an additional bridging ether molecule, $(Bu^t{}_2C{=}NMgBr)_2OEt_2$ (Figure 2.4), is very poorly resolved. A singlet absorption due to the t-butyl groups is consistent with its proposed structure in which the t-butyl groups are magnetically equivalent. There seems little doubt that the molecule is solvated - cryoscopic

Table 2.4

^{1}H-NMR Spectroscopic Data Due To THF For The Adducts

$(R_2C{=}NMgBrTHF)_2(THF)_x$; R = Ph, p-tolyl; x = 0, 1

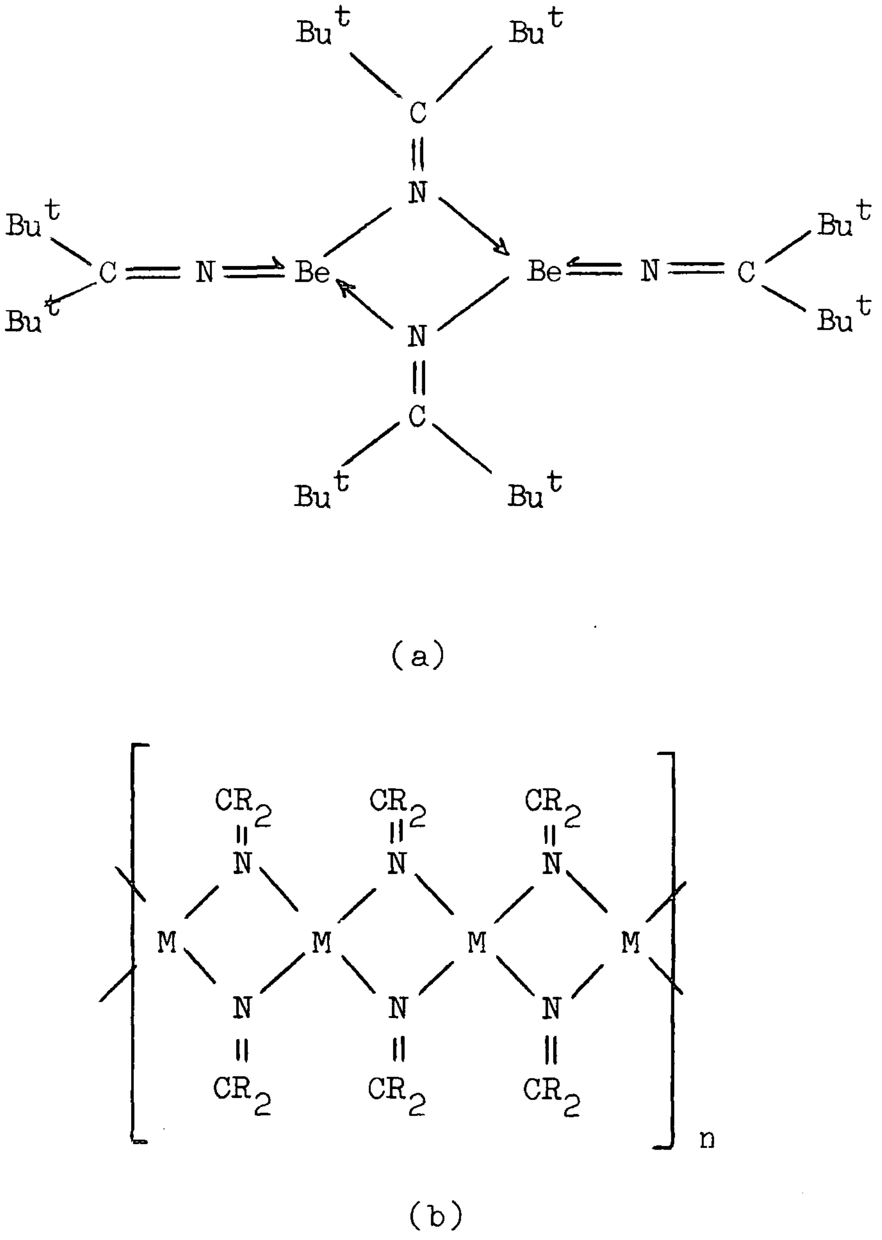
Compound	τ values ppm (external TMS; τ = 10			
	α	$\Delta\alpha$	β	$\Delta\beta$
THF	7.09		9.16	
$(Ph_2C{=}NMgBrTHF)_2THF$	6.70	0.39	8.98	0.18
$(Ph_2C{=}NMgBrTHF)_2$	6.62	0.47	8.92	0.24
$\{(p\text{-tolyl})_2C{=}NMgBrTHF\}_2THF$	6.56	0.53	8.88	0.28
$\{(p\text{-tolyl})_2C{=}NMgBrTHF\}_2$	6.53	0.56	8.82	0.34

All solutions in C_6D_6 at ~40°; α, β = hydrogen atoms on α, β - carbon atoms.

studies suggest that the ether molecule may well separate in solution - and the complex absorption at τ(6.64 - 6.98) and a more clearly resolved triplet at τ(9.12 - 9.32) - hardly shifted from the corresponding peaks in unco-ordinated ether (τ= 6.62, 6.74, 6.86, 6.96 quadruplet; τ= 8.90, 9.02, 9.14 triplet) - may bereasonably assigned to the ethyl groups. It was not possible to measure the relative intensities of these absorptions,integration being prevented by high noise to signal ratios.

2.2.2. Group B

The compounds discussed in this section are the bis(methyleneamino)magnesium derivatives, $\left[(R_2C{=}N)_2Mg\right]_x(THF)_y$, (R = Ph, p-tolyl; x = 3, y = 2; R = Bu^t, x = 2, y = 0. The effect of the bulk of substituents on the state of association of related methyleneamino derivatives, already referred to, is particularly marked in the series of bis(methyleneamino) derivatives, $\left[(R_2C{=}N)_2M\right]_n$ M = Be; R = Ph, Bu^t; M = Zn; R = Ph, p-tolyl, Bu^t, of beryllium and zinc whose molecular state is variably polymeric, trimeric and dimeric. An X-ray crystallographic study of bis(di-t-butylmethyleneamino)beryllium dimer, $\left[(Bu^t{}_2C{=}N)_2Be\right]_2$, presumably stabilised in its dimeric state by the steric demand of the t-butyl groups, has established the presence of a four-membered (Be_2N_2) ring with both terminal and bridging methyleneamino ligands (Figure 2.5a) (77). The zinc analogue bis(di-t-butylmethyleneamino)zinc, dimeric in benzene, monomeric (by mass spectroscopy) in the gas phase, with similar infrared and ^{1}H-NMR spectroscopic data is, likely to have a similar structure, (50) as do related dimeric compounds of boron, aluminium and gallium (24, 75, 108). Furthermore, the probable structures of the bis(diarylmethyleneamino) derivatives of beryllium and zinc, $\left[(R_2C{=}N)_2M\right]_n$ R = Ph, M = Be; R = Ph, (108) p-tolyl, M = Zn, all polymeric by comparison, also involve four membered M_2N_2 rings as shown in Figure 2.5 (b).

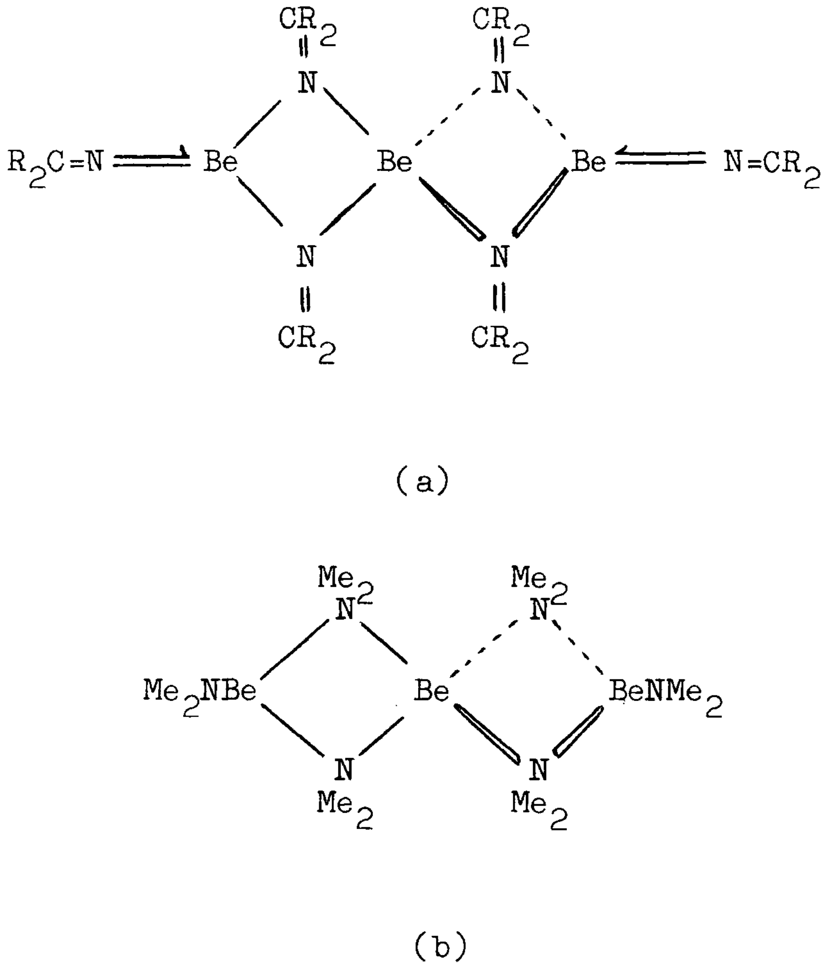


(a)

(b)

Figure 2.5

Whilst $\left[(R_2C{=}N)_2M\right]_n$ (R = Ph, M = Be, Zn; R = p-tolyl, M = Zn) are polymeric, the trimeric nature of bis(di-p-tolylmethyleneamino)beryllium $\left[\left\{(p\text{-tolyl})_2C{=}N\right\}_2Be\right]_3$ reflects the much smaller size of beryllium relative to zinc. The likely structure of the trimer is shown in Figure 2.6 (a) which is presented for comparison purposes alongside the structure of a related compound, trimeric bis(dimethylamido)beryllium, $[(Me_2N)_2Be]_3$, (109 - 111) (Figure 2.6 (b) the structure of which has been established by X-ray crystallography.

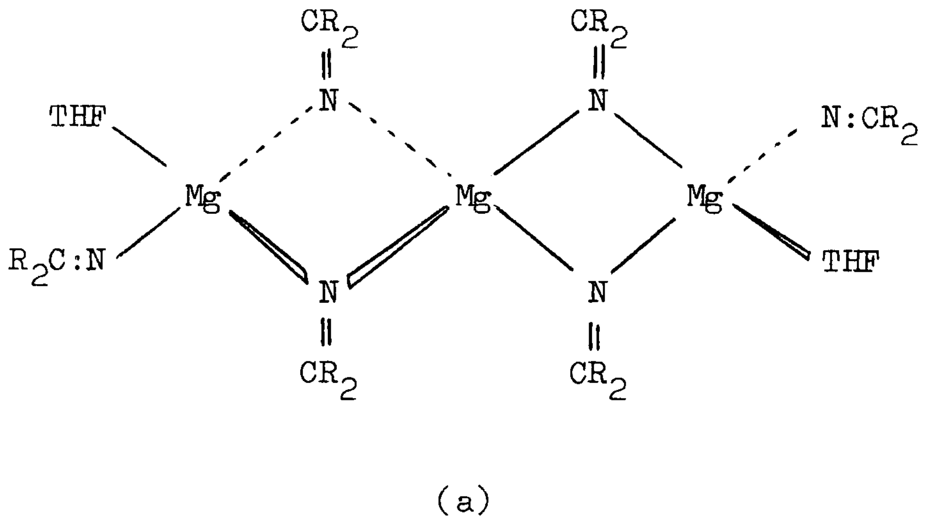


(a)

(b)

Figure 2.6

Both bis(diphenylmethyleneamino)magnesium and bis-(di-p-tolylmethyleneamino)magnesium are thought to be trimeric crystallising with two molecules of THF, $[(R_2C{=}N)_2Mg]_3 2THF$ (R = Ph, p-tolyl, M by cryoscopy 970 and 1052 respectively). Whilst the determined molecular weights are rather low (the trimeric formulations requiring 1296 and 1464 respectively) this is believed to be caused by sample decomposition, and the ^{1}H-NMR spectroscopic data - discussed in greater detail later - supports the proposed formulations. By analogy with compounds already discussed these bis(methyleneamino) magnesium compounds are assigned a structure represented in Figure 2.7 (a) again with mutually perpendicular Mg_2N_2 rings.



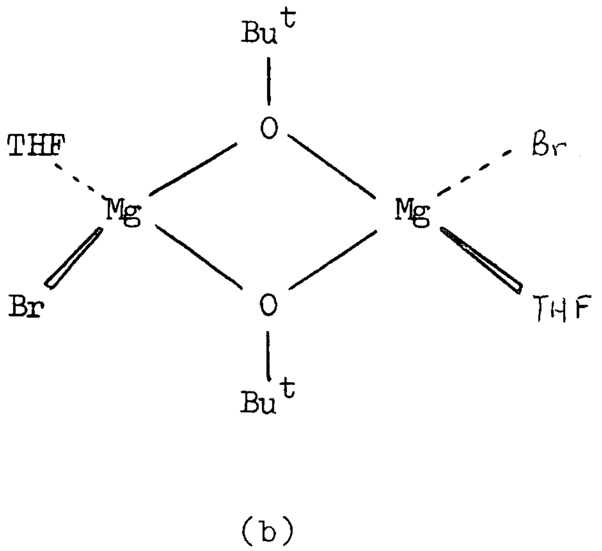


Figure 2.7

The two different terminal ligands probably occupy trans-positions, and overall, the suggested structure is similar to an already established structure (X-ray diffraction), that of $(Bu^tOMgBr)_2 2THF$ (95) with four-membered planar

Mg_2O_2 rings and the two other species linked to magnesium adopting trans positions in a plane perpendicular to the Mg_2O_2 ring (Figure 2.7 (b). These proposed structures are similar to those of other related magnesium derivatives eg $(Bu^tMgSPr^i)_2 2Et_2O$ with four membered Mg_2S_2 rings (112), $(Pr^iOMgBr)_2 2Et_2O$ (113) and $(EtMgOCEt_3)_2 2THF$ (114) with Mg_2O_2 rings.

Attempts to crystallise bis(di-t-butylmethyleneamino) magnesium were unsuccessful and the yellow-green flocculent solid was obtained by complete removal of solvent from the reaction mixture. The product's molecular weight, by cryoscopy in benzene (M,573) compares favourably with that required by the dimer (M, 609), and its suggested structure possessing no solvent molecules of crystallisation is shown in Figure 2.8, being similar to that already descibed for $\left[(Bu^t{}_2C{=}N)_2Be\right]_2$. Whilst each of the bis(methyleneamino) magnesium compounds discussed has both bridging and terminal methyleneamino ligands and, for the bis- phenyl and p-tolyl

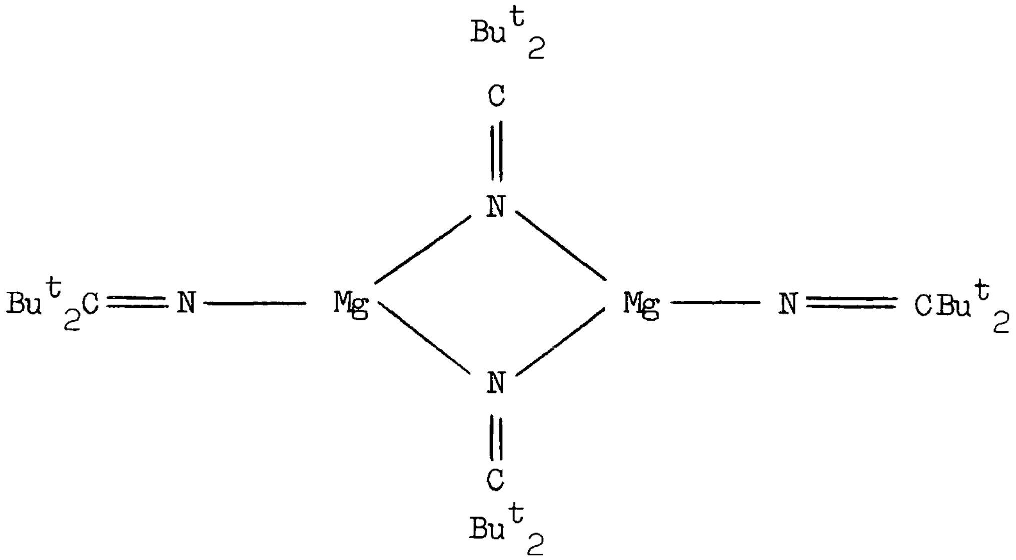


Figure 2.8

derivatives, magnesium in a four-co-ordinate condition, the bulky t-butyl groups have stabilised three-co-ordinate magnesium in the bis-t-butyl compound, $[(Bu^t_2C{=}N)_2Mg]_2$. A three-co-ordinate state for magnesium, whilst not unusual for zinc and beryllium, is not a preferred co-ordinate state, the most common co-ordination number which magnesium exhibits in its covalent compounds being four. Three-co-ordinate magnesium was first found in dimeric di-i-propylamido-i-propylmagnesium (12), $(Pr^i_2NMgPr^i)_2$, whose proposed structure with corresponding bridging amido units is shown in Figure 2.9. The structural differences highlighted in

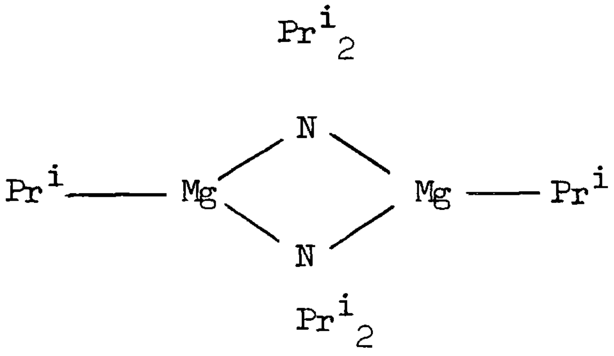


Figure 2.9

this discussion of the bis(methyleneamino)magnesium may well be principally related to the covalent radii of the three metals Be, Mg and Zn and their relative electronegativities. The covalent radius sequence is Mg > Zn > Be (115) whilst with electronegativity values the sequence is Zn > Be > Mg (64), implying that magnesium may adopt a greater co-ordination number than zinc and beryllium. These features will be referred to later in discussing the infrared data of these methyleneaminomagnesium compounds.

The infrared spectral details assigned to the stretching vibrations of the methyleneamino units of the bis(methyleneamino) derivatives of beryllium, zinc and magnesium, and already categorised into bridging and terminal methyleneamino stretching frequencies. are given in <u>Table 2.5</u>. Until fairly recently, although beryllium-nitrogen compounds had been widely studied, there was little indication that $\mathrm{Be} \Leftarrow \mathrm{N}$ π-bonding played any significant role in their chemistry. The first indication that such bonding might influence the geometry of a molecule was revealed in the X-ray diffraction study of $\left[(\mathrm{Me_2N})_2\mathrm{Be}\right]_3$, a compound already alluded to earlier (111). A trigonal planar arrangement of atoms about the non-bridging nitrogen atoms was discovered together with a variation in the Be—N distances consistent with some multiple $(\mathrm{N} \Rightarrow \mathrm{Be})$. Such an orientation would allow maximum overlap between the filled N - 2p orbitals and the vacant orbitals of the terminal Be atom. Studies were also made of some oligomeric bis(methyleneamino)beryllium derivatives (48), $\left[(\mathrm{RR^1C{=}N})_2\mathrm{Be}\right]_n$ in which similar $\mathrm{Be} \Leftarrow \mathrm{N}$ π-bonding was believed to occur, the beryllium atoms participating in a linear configuration maximising overlap of the filled nitrogen and vacant beryllium 2p-orbitals available for such dative $\mathrm{N} \Rightarrow \mathrm{Be}$ π-bonding and allowing most room for the bulky substituents. Arising from the attachment of the <u>terminal</u> methyleneamino units to the three co-ordinate beryllium atoms are characteristic infrared absorptions, a range of frequency values being therefore characteristic of the stretching vibration of linear $(\mathrm{C} = \mathrm{N} \Rightarrow \mathrm{Be})$units. It is equally possible to assign a range of frequencies to a bent (bridging C=N-Be) unit, and <u>Table 2.5</u> extends this process by summarising such findings for a limited number of related compounds of the Group II metals. In all cases the distinction between the absorptions for bridging and terminal ligands is clearly

Table 2.5

Terminal and Bridging Azomethine Stretching Frequencies, ν(C=N)cm^{-1} * of the Bis(methyleneamino) Derivatives of some Group II Elements

M	ν(C=N) Terminal			ν(C=N) Bridging		
	Ph	p-tolyl	Bu^t	Ph	p-tolyl	Bu^t
Be	1732	1731	1721	1627	1626	1631
Mg	1655	1661	1668	1613	1620	1605
Zn	-	1664	1683	1600	1607	1585

* All Nujol Mulls. ν(C=N) $R_2C=NH$ (R = Ph, p-tolyl, Bu^t)= 1603, 1610, 1604cm^{-1} respectively.

seen and the frequencies ν(C=N) of terminally attached units are significantly greater than those of bridging units. Earlier, in Section 2.2.1, a range of frequencies characteristic of bridging (C=N-Mg) units was justified, and generally a comparison of the data obtained for the magnesium systems with the related systems of beryllium and zinc supports the proposed structures of the methyleneamino-magnesium compounds already discussed. They all possess bridging methyleneamino ligands alone, or in combination with terminally - attached methyleneamino ligands. By reference to Table 2.5 it can be seen that the variations in stretching frequencies of terminally attached and bridging methyleneamino units do not show a simple relationship with respect to the nature of the methyleneamino ligand or the metal, a feature expressed earlier in the discussion of infrared spectra (Chapter 1, page 32). Bis(di-t-butylmethyleneamino)beryllium dimer, with both bridging and terminally attached methyleneamino ligands, is known to have for the latter a C-N-Be angle of 160.5° (77), the distortion from linearity being necessary to accommodate the bulky t-butyl groups. The near linearity of the terminal C=N-Be unit strongly suggests that in the bis(di-t-butylmethyleneamino)magnesium dimer, $[(Bu^t{}_2C{=}N)_2Mg]_2$ (M, by cryoscopy, 573; dimer requires M, 609), known to be unsolvated with a proposed structure containing three-co-ordinate magnesium (Figure 2.8), the terminal (C=N-Mg) skeleton could be effectively linear, since the larger magnesium atom could well accommodate without distortion the t-butyl groups.

If this is so, and the ^{1}H-NMR evidence to be presented later would not contradict such reasoning, then the ν(C=N) assigned to the terminally attached methyleneamino ligand might be that of a linear (C=N-Mg) skeleton. The same might also be true of the bis(methyleneamino) derivatives, $[(R_2C{=}N)_2Mg]_3$ 2THF (R = Ph, p-tolyl), with four-co-ordinate magnesium, where the aryl groups are less bulky and the co-ordinated THF molecule may not add significantly to the steric hindrance. Of the new methyleneaminomagnesium compounds studied, only the three bis(methyleneamino) magnesium derivatives have terminally attached methyleneamino ligands - all the others have solely bridging methyleneamino ligands- their asymmetric stretching frequencies lying in the range (1655 - 1668)cm^{-1}.

The ^{1}H-NMR spectra of the bis(methyleneamino)magnesium derivatives show some interesting features, particularly the spectrum of $[(Bu^t_2C{=}N)_2Mg]_2$ when compared with those of $[(Bu^t_2C{=}N)_2M]_2$ M = Be, Zn (50). The spectrum of dimeric bis(di-t-butylmethyleneamino)beryllium in toluene gives three signals, two of which present a poorly-resolved doublet (τ = 8.69, 8.71) and the other at τ = 8.77, of relative intensities 1:1:2 respectively. The implications of this are that the methyleneamino units, terminally attached, are either permanently non-linear in a symmetrical molecule or near linear, the latter being more consistent with the infrared data. Yet there must be some distortion in the molecule for three peaks to be obtained, and its crystal structure (77) confirms the non-equivalence of the t-butyl groups on the terminal ligands. The two peaks of equal relative intensity (τ, 8.69, 8.71) are therefore assignable to t-butyl groups in the different environments of the terminal ligands and the singlet (τ = 8.77) to the magnetically equivalent t-butyl groups of the bridging units. The spectrum of $[(Bu^t_2C{=}N)_2Zn]_2$ is remarkably similar, the logical inference being that its structure is similar to its beryllium counterpart with similar distortion of the terminal ligands and substantial N→Zn ($p\pi$ - $p\pi$) bonding (50). In contrast to the above spectra of dimeric bis(di-t-butylmethyleneamino)- beryllium and zinc, the spectrum of bis(di-t-butylmethyleneamino)magnesium gives only <u>one</u> signal, a relatively sharp singlet at $\tau = 8.86$, with no evidence of further resolution on cooling to about $-50^{o}C$. A <u>doublet</u> of equal intensity would not have been surprising since the equivalence of the t-butyl groups on the terminal ligands - arising from the probable linearity of the (C=N-Mg) skeleton is more likely in the magnesium compound, than in the comparable beryllium and zinc derivatives. The symmetrical nature of the singlet suggests that the t-butyl groups in the bridging and terminal methyleneamino units are making contributions of equal intensity - as they would do were the terminal (C=N-Mg) skeleton linear and without distortion - but the respective signals are so close together that they have not been resolved. The details of the bis(di-t-butylmethyleneamino) derivatives of beryllium, zinc and magnesium are summarised in <u>Table 2.6</u>.

<u>Table 2.6</u>

<u>^{1}H-NMR Spectroscopic Details for $\left[(Bu^{t}{}_{2}C{=}N)_{2}M\right]_{2}$, M = Be, Zn, Mg</u>

Compound	τ Values p.p.m.*
$\left[(Bu^{t}{}_{2}C{=}N)_{2}Be\right]_{2}$	8.69 (1), 8.71 (1), 8.77 (2)
$\left[(Bu^{t}{}_{2}C{=}N)_{2}Zn\right]_{2}$	8.64 (1), 8.68 (1), 9.03 (2)
$\left[(Bu^{t}{}_{2}C{=}N)_{2}Mg\right]_{2}^{**}$	8.86

* $\tau(Me_4Si) = 10.00$ ppm; **using TMS as external standard; others as internal reference.

The ^{1}H-NMR spectra of the bis(diarylmethyleneamino) magnesium derivatives, $\left[(R_2C{=}N)_2Mg\right]_3$ 2THF (R = Ph, p-tolyl), are recorded in Table 2.7. Both spectra show peaks due to co-ordinated THF at τ values 6.98 - 7.19 (R = Ph), 6.88 (R = p-tolyl) assigned to the hydrogen atoms of the α-carbon of THF, and τ (8.92 - 9.27), assigned to the hydrogen atoms of the β-carbon of THF, in relative intensities appropriate to the above formulation. These absorptions, due to co-ordinated THF accur at lower field than the corresponding peaks in unco-ordinated THF, a matter discussed

Table 2.7

^{1}H-NMR Spectra of Bis(diarylmethyleneamino)magnesium Compounds, $\left[(R_2C{=}N)_2Mg\right]_3$ 2THF, R = Ph, p-tolyl

Compound	τ Values p.p.m. *
$\left[(Ph_2C{=}N)_2Mg\right]_3$ 2THF	2.69, 2.97, 3.26c (4); 6.98 - 7.19 c, 8.93 - 9.27c(1)
$\left[\left\{(p\text{-tolyl})_2C{=}N\right\}_2Mg\right]_3$ 2THF	2.57, 2.82, 3.04, 3.45 c (3); 6.88, 8.92 c (1); 8.05 (2)

*τ(Me$_4$Si) = 10.00 p.p.m.; using TMS as external standard; solvent C_6D_6.

earlier in considerable detail in relation to the adducts of diarylmethyleneaminomagnesium bromide and THF, $(R_2C{=}NMgBrTHF)_2xTHF$, R = Ph, p-tolyl; x = 0,1. The complex absorptions, observed in both compounds, in the region

τ(2.57 - 3.34) are attributed to protons on the aromatic rings of phenyl and p-tolyl groups, whilst a peak due to the methyl protons of the p-tolyl groups is observed at τ= 8.05.

2.2.3. Group C

The seven methyleneaminoethyl(or phenyl)magnesium compounds to be discussed comprise (i) $(R_2C{=}NMgEtOEt_2)_n$ R = Ph, p-tolyl, (ii) $(R_2C{=}NMgX)_n$, R = Ph, X = Ph, R = Bu^t X = Et, Ph, and (iii) $(R_2C{=}NMgEt)_2$TMED, R = Ph, p-tolyl. In general, their precise compositions are less certain than the derivatives already discussed, because analytical data obtained are rather ambiguous. Additionally, most of the compounds are of too low solubility to obtain reliable molecular weights by cryoscopy in benzene. The proposed formulations, together with their analytical data are given in Table 2.8.

The azomethine stretching frequencies, ν(C=N), for all of these compounds fall in the range (1605 - 1620)cm^{-1} - see Table 2.9 - a range appropriate to bridging methyleneamino units. These derivatives therefore are regarded as possessing exclusively bridging methyleneamino ligands and, by comparison with analogous Group II derivatives, are probably dimers or small oligomers. Related derivatives of Group II metals, all unsolvated, of general formula $(R_1R_2C{=}NMX)_2$ are M = Be: R_1 = R_2 = Ph, p-tolyl, Bu^t, X = Cl; R_1 = Bu^t, R_2 = p-tolyl, X = Cl. M = Zn: R_1 = R_2 = Ph, X = Me, Et, Ph; R_1 = R_2 = Bu^t, Ph, p-tolyl, X = Cl. The structures proposed for these compounds, with both beryllium

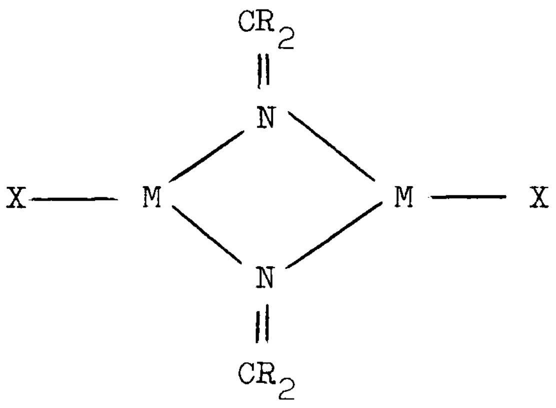
Table 2.8

Analytical Data and Proposed Formulations of Methyleneamino-ethyl (or phenyl) Magnesium Compounds

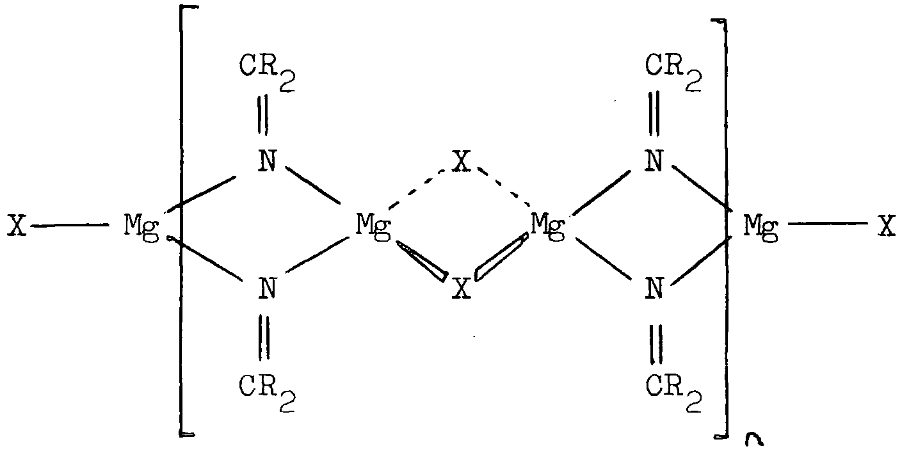
Compound	Analytical Data C:H:N:Mg; Hydrolysable Ethyl (Et)
$(Ph_2C{=}NMgEt.OEt_2)_n$	C = 73.8 (74.2); H = 8.1 (8.1); N = 4.3 (4.6) Mg = 8.1 (7.9); Et = 8.5 (9.7)%.
$\left[(p\text{-tolyl})_2C{=}NMgEtOEt_2\right]_n$	C = 71.3 (75.2); H = 8.2 (8.6); N = 4.1 (4.2); Mg = 8.2 (7.3); Et = 8.0 (8.9)%.
$(Bu^t{}_2C{=}NMgEt)_n$	C = 66.6 (68.3); H = 11.5 (11.9); N = 7.5 (7.2); Mg = 12.2 (12.6); Et = 14.6 (15.5)%.
$(Ph_2C{=}NMgPh)_n$	C = 78.1 (81.1); H = 7.3 (5.3); N = 4.9 (5.3); Mg = 7.7 (8.6)%.
$(Bu^t{}_2C{=}NMgPh)_n$	C = 71.2 (74.6); H = 8.8 (9.5); N = 5.8 (5.8); Mg = 10.1 (10.1)%.
$(Ph_2C{=}NMgEt)_2TMED$	C = 70.0 (74.2); H = 7.4 (7.9); N = 8.8 (9.6); Mg = 8.6 (8.3); Et = 9.7 (10.3)% M, 561 (583)*
$\left[(p\text{-tolyl})_2C{=}NMgEt\right]_2TMED$	C = 75.1 (75.2); H = 10.2 (8.5); N = 8.0 (8.8); Mg = 7.6 (7.6); Et = 9.2 (9.9)% M, 491 (631)*

* by cryoscopy in benzene

and zinc in a three-co-ordinate state, are shown in Figure 2.10 (a). If the methyleneaminomagnesiun derivatives $(R_2C{=}NMgX)_n$, R = Bu^t, X = Et; R = Ph, Bu^t, X = Ph are dimeric, their structure, also containing three-co-ordinate magnesium atoms is likely to be similar (Figure 2.10 (a); M = Mg). If however these compounds are oligomeric, their



(a)



(b)

proposed structures (Figure 2.10 (b) will have both methyleneamino and X units, in adjacent Mg_2N_2 and Mg_2X_2 four-membered rings, acting as bridging ligands with both three-co-ordinate and four-co-ordinate magnesium atoms.

The diarylmethyleneaminoethylmagnesium derivatives were shown to be etherated by ^{1}H-NMR studies, and these together with the estimations of hydrolysable ethyl (Section 2.4 (xvii)) suggest that they are best formulated as $(R_2C{=}NMg(Et)OEt_2)_m$ R = Ph, p-tolyl, m probably 2. Their proposed structure (Figure 2.11) has four co-ordinate magnesium atoms and is similar in principle to the bis(THF)

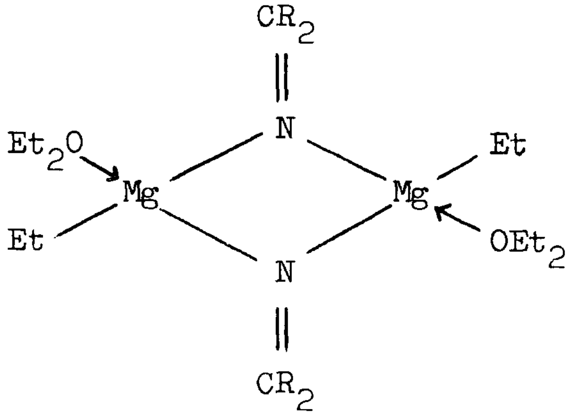
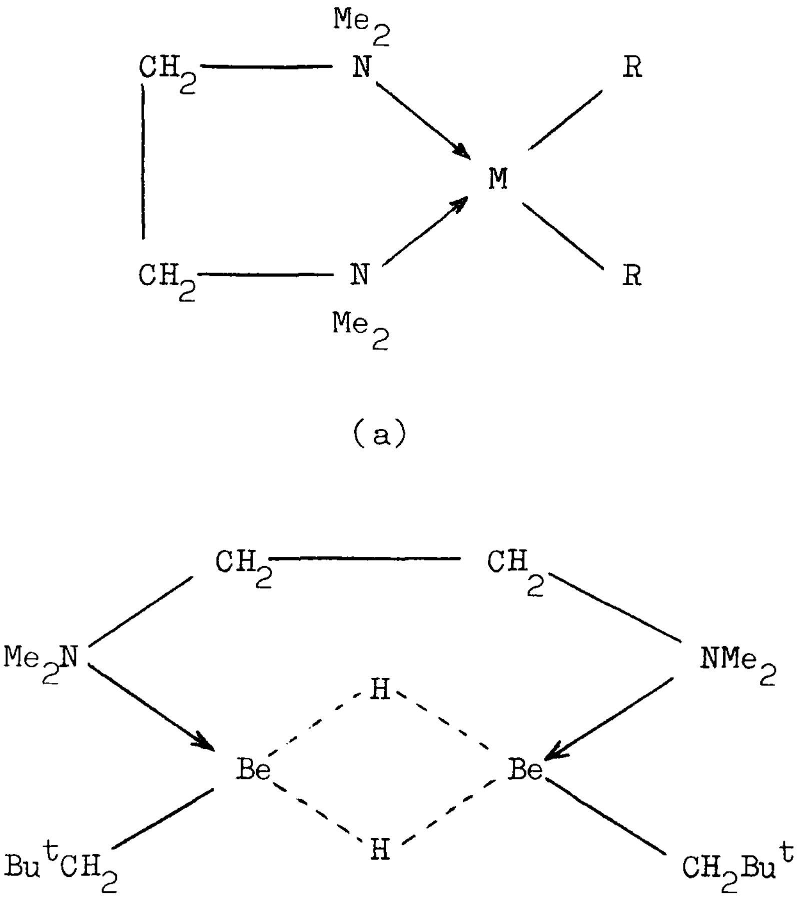


Figure 2.11

adducts of diarylmethyleneaminomagnesium bromide $(R_2C{=}NMgBrTHF)_2$ R = Ph, p-tolyl, discussed earlier (II; Figure 2.3).

By employing a donor molecule, TMED, attempts were made to prepare methyleneaminomagnesium complexes, in which magnesium was co-ordinatively saturated, containing exclusively terminal methyleneamino units. The most common way by which TMED may be bonded to an organometallic compound is as a bidentate chelating amine eg $Me_2Be(TMED)$, Figure 2.12 (a) M = Be. As the organic ligand becomes larger, this bidentate-chelating role becomes impossible and in $Bu^t{}_2Be$ (TMED) the donor base is monodentate in its co-ordination to beryllium. Only one nitrogen atom is attached at any one instant and the ^{1}H-NMR spectrum shows rapid exchange between free and co-ordinated nitrogen (117). Clearly the size of the metal atom is also influential since the magnesium analogue, $Bu^t{}_2Mg$ (TMED) (118), is considered to have the same structure as $Me_2Be(TMED)$, the donor molecule again acting as a bidentate chelating ligand - Figure 2.12 (a) M = Mg. A third type of bonding



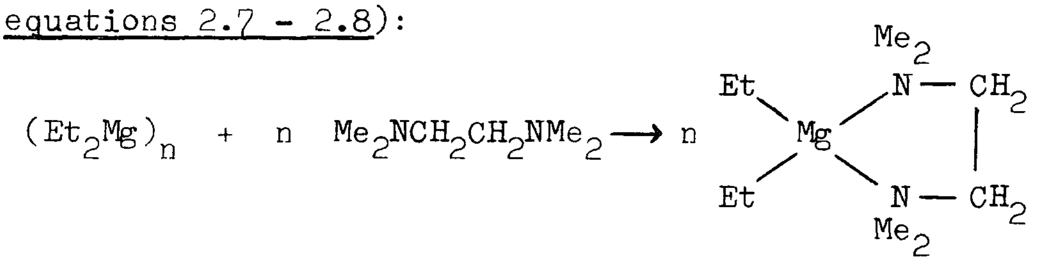
(a)

(b)

Figure 2.12

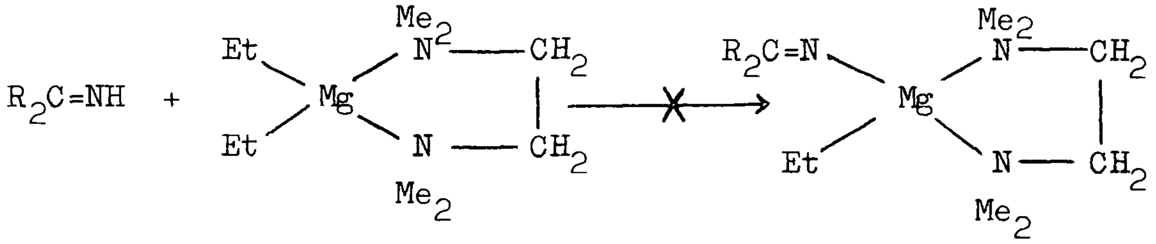
emerges where the diamine co-ordinates to a dimeric species as an additional bridging group. Such a structure has been proposed for alkylberylliumhydride. TMED complexes, $(RBeH)_2TMED$, in benzene where R = Bu^i (119), Bu^tCH_2 (120), Et, Bu^s, Bu^t, nC_5H_{11} (121) - Figure 2.12 (b).

In order to prepare methyleneaminomagnesium-TMED complexes containing co-ordinatively-saturated magnesium atoms, but with exclusively terminal methyleneamino ligands, the theoretical reaction scheme was as follows (equations 2.7 - 2.8):



2.7

The reacting species produced, Et_2Mg.TMED, containing four- co-ordinate magnesium was then reacted in equimolar proportions with $R_2C{=}NH$ (R = Ph, p-tolyl, Bu^t), the expected reaction being as illustrated in (equation 2.8).



2.8

In practice terminally-attached methyleneaminomagnesium complexes were not isolated. Diphenyl- and di-p-tolylmethyleneamines reacted smoothly with Et_2Mg.TMED to yield very air-sensitive products, which - on the basis of their azomethine stretching frequencies ν(C=N) Figure 2.9 -contain exclusively bridging methyleneamino units. By elemental analysis, molecular weight determinations by cryoscopy and estimations of ethane by controlled hydrolysis, the complexes were formulated as $(R_2C{=}NMgEt)_2$TMED, R = Ph, p-tolyl. Their proposed structure (Figure 2.13) contains four-co-ordinate magnesium and both methyleneamino and TMED bridges. There was apparently no reaction between di-t-butylmethyleneamine and $Et_2Mg.TMED$, the only solid product being isolated from the reaction mixture being the diethylmagnesium.TMED adduct.

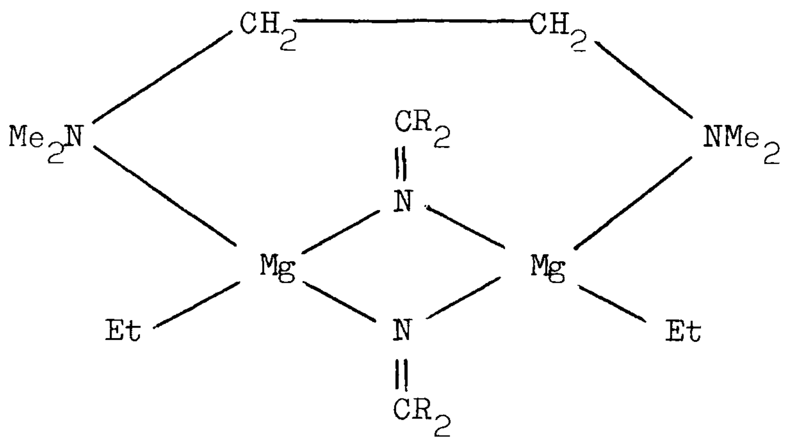


Figure 2.13

Absorptions in the methyleneamino stretching region, $\nu(C{=}N)$, in the infrared spectra of these compounds are shown in Table 2.9 and for reasons which have been presented earlier in considerable detail, they are rationalised as being related to bridging methyleneamino units. Such units are present in all the methyleneaminomagnesium- compounds discussed in this chapter, the majority of which have exclusively bridging methyleneamino ligands whose azomethine stretching frequencies, $\nu(C{=}N)$, are in the range (1602 - 1630)cm^{-1}.

The methyleneamino stretching frequencies of selected beryllium, magnesium and zinc compounds, all of which have non-linear bridging methyleneamino groups, are shown in Table 2.10. Whilst in several cases the formulation of this limited number of compounds is not absolutely equivalent, nor are the series complete, the azomethine stretching

Table 2.9

Azomethine Stretching Frequencies, ν(C=N), of Related Methyleneaminomagnesium Compounds (as Nujol Mulls, in cm^{-1})

Compound	ν(C=N)
$[Ph_2C{=}NMg(Et)OEt_2]_n$	1619
$[(p\text{-tolyl})_2C{=}NMg(Et)OEt_2]_n$	1619
$(Bu^t{}_2C{=}NMgEt)_n$	1605
$(Ph_2C{=}NMgPh)_n$	1618
$(Bu^t{}_2C{=}NMgPh)_n$	1607
$(Ph_2C{=}NMgEt)_2TMED$	1620
$\{(p\text{-tolyl})_2C{=}NMgEt\}_2TMED$	1618

frequencies, ν(C=N), for bridging methyleneamino ligands of beryllium, magnesium and zinc fall in the ranges (1608-1648), 1602-1630) and (1585-1624)cm^{-1} respectively. This trend parallels the variation in the mass of the central metal, for the heavier the metal the lower the stretching frequency.

The ^{1}H-NMR spectra of many of these methyleneaminomagnesium compounds were recorded using deuterated benzene solutions - Table 2.11. The spectra of the di-t-butylmethyleneamino compounds, $(Bu^t{}_2C{=}NMgX)_n$ X = Ph, Et, n probably 2, both show broad singlet signals at τ = 9.05 and 8.73 respectively, due to the t-butyl groups, consistent with

Table 2.10

Stretching Frequencies of Bridging Methyleneamino Ligands, ν(C=N)cm^{-1}, in Selected Methyleneamino Derivatives of Group II Elements *

Compound	M	Ph	(p-tolyl)	Bu^t
$(R_2C{=}NMCl)_2$	Be	1608	1610	1626
	Zn	1604	1600	1597
$[R_2C{=}NMEt(OEt_2)]_x$	Mg	1619 (x=1)	1619 (x=1)	1605 (x=0)
$(R_2C{=}NMEt)_2$	Zn	1611	-	-
$(R_2C{=}NMPh)_2$	Mg	1618	-	1607
	Zn	1607	-	-
$(R_2C{=}NMBu^t)_2$	Be	1648	-	-
$(R_2C{=}NMMe)_2$	Zn	1624	-	1592
$[(R_2C{=}N)_2M]_n$	Be	1627	1626	1631
$[(R_2C{=}N)_2M]_n(THF)_x$	Mg	1613	1620	1605 x=0;n=2
$[(R_2C{=}N)_2M]_n$	Zn	1600	1607	1585 (n=2)

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* As Nujol Mulls

Table 2.11

^{1}H-NMR Spectroscopic Data of Related Methyleneaminoethyl (or phenyl)Magnesium Compounds

Compound	τ ppm (τ(TMS external ref. = 10.00ppm))
$(Ph_2C{=}NMgEtOEt_2)_n$	2.55-2.88c; 6.62-6.97q; 8.93-9.18t
$\{(p\text{-tolyl})_2C{=}NMgEtOEt_2\}_n$	2.50-3.20c; 6.93-7.28q; 8.10s; 9.26-9.54t
$(Bu^t{}_2C{=}NMgEt)_n$	8.73sbr
$(Bu^t{}_2C{=}NMgPh)_n$	2.96-3.12c(1); 9.05s(4)

n probably 2; s = singlet; c = complex; br = broad;
t = triplet; q = quartet.

their proposed structure having bridging methyleneamino ligands in which the t-butyl groups are in magnetically equivalent situations. But whilst a broad complex signal, τ(2.96-3.12), due to the protons of the phenyl group in the spectrum of $(Bu^t{}_2C{=}NMgPh)_n$ - both signals being in the appropriate relative intensities no signals due to ethyl groups were observable in the spectrum of $(Bu^t{}_2C{=}NMgEt)_n$, despite using as concentrated as possible a solution.

Since the signal due to the t-butyl groups was far from strong then perhaps it is unsurprising that the much less intense signals expected for ethyl protons were not seen. Generally the spectra of $(\mathrm{R_2C{=}NMgEtOEt_2})_n$, R = Ph, p-tolyl, were weak and of poor resolution. The rather broad poorly resolved multiplets in the ranges $\tau(2.55\text{-}2.88)$, R = Ph, and $\tau(2.50\text{-}3.20)$, R = p-tolyl, evidenced aromatic protons whilst the singlet absorption ($\tau = 8.10$) is due to the methyl protons of the tolyl group. Two other groups of complex signals, one possibly a quartet in the range τ 6.62-7.28 (τ = 6.62-6.97, R = Ph; τ = 6.93-7.28, R = p-tolyl) and the other a possible triplet in the range τ = 8.93-9.54 (τ = 8.93-9.18, R = Ph; τ = 9.26-9.54, R = p-tolyl of overall intensity approximately equal to that of the aromatic protons in each compound. These signals, of quartet and triplet nature, are assigned to the methylene and methyl components respectively of the ethyl groups of co-ordinated diethyl ether, being found downfield as might be expected, from the corresponding signals of the unco-ordinated molecule (τ = 7.26-7.51q, τ = 9.48-9.71t). High background noise hampered the search for signals due to the protons of the ethyl groups attached directly to magnesium and no unequivocal sighting was made for $(\mathrm{Ph_2C{=}NMgEtOEt_2})_n$.

For the compound $\left\{(\text{p-tolyl})_2\mathrm{C{=}NMgEtOEt_2}\right\}_n$, two weak complex signals at τ(9.90-10.10), possibly a triplet, and τ(10.27-10.44) possibly a quartet, are assigned tentatively to the methyl and methylene units respectively of the ethyl group directly linked to magnesium. High field placements would be expected for ethyl protons when linked to a very electropositive element such as magnesium and the results would seem to be consistent with values reported for dimeric molecules such as diphenylmethyleneamino-diethylaluminium $(Ph_2C{=}NAlEt_2)_2$ (62) τ = 8.7t, 9.8q, diphenylmethyleneamino-diethylgallium $(Ph_2C{=}NGaEt_2)_2$ (63) τ = 8.8t, 9.5q, and diphenylmethyleneaminoethylzinc $(Ph_2C{=}NZnEt)_2$ (13) τ = 8.7t, 9.5q. Confirmation of (Mg-Et) units in these methyleneaminoethylmagnesium compounds was obtained from hydrolysis experiments employing 2-methoxyethanol. The sole volatile product obtained was ethane and hydrolysable ethyl values were reasonably consistent with their proposed formulations. The remaining methyleneaminomagnesium compounds viz $(R_2C{=}NMgEt)_2TMED$, R = Ph, p-tolyl and $(Ph_2C{=}NMgPh)_n$ were too insoluble for satisfactory ^{1}H-NMR spectra to be obtained.

2.3 Summary

Fifteen new methyleneaminomagnesium compounds have been prepared and structures proposed on the basis of their ^{1}H-NMR spectra, infrared spectra, and their azomethine stretching frequencies $\nu(C{=}N)$, and a comparison with established structures of related compounds. It has not been possible to prepare compounds with exclusively terminally-attached methyleneamino ligands. On the contrary all the compounds possess bridging methyleneamino ligands and where terminally-attached methyleneamino ligands do exist, they are in addition to such bridging units. Compounds have also been described which possess bridging ligands additional to methyleneamino bridges. These bridging ligands are <u>tetrahydrofuran</u> in $(R_2C{=}NMgBrTHF)_2THF$, R = Ph, p-tolyl, for which a crystal structure has been obtained and described (R = Ph), diethyl ether in $(Bu^t{}_2C{=}NMgBr)_2OEt_2$, and tetramethyleneethylenediamine in $(R_2C{=}NMgEt)_2$TMED. The bis(methyleneamino)magnesium derivatives $[(R_2C{=}N)_2Mg]_3(THF)_2$, R = Ph, p-tolyl and $[(Bu^t{}_2C{=}N)_2Mg]_2$ have both bridging and terminally co-ordinated methyleneamino ligands, and it seems likely that the terminal units may well have near linear C=N-Mg skeletons with some (N→Mg) $p\pi - p\pi$ bonding. Furthermore as the size of the aryl/alkyl group increases, in this series of compounds, a complementary decrease in the association number of the derivative occurs. The nature of the methyleneaminoethyl(or phenyl-)magnesium compounds $(R_2C{=}NMg(Et)OEt_2)_n$ R = Ph, p-tolyl; $(R_2C{=}NMgX)_n$ R = Bu^t, X = Et, Ph; R = X = Ph, the state of association being dimeric or oligomeric; and $(R_2C{=}NMgEt)_2$TMED R = Ph, p-tolyl, is less certain but all the proposed structures have bridging methyleneamino ligands.

The two remaining derivatives, adducts of THF and diarylmethyleneaminomagnesium bromide $(R_2C{=}NMgBrTHF)_2$, R = Ph, p-tolyl are dimeric with bridging methyleneamino units and four-co-ordinate magnesium atoms. They are related to compounds already referred to, viz $(R_2C{=}NMgBrTHF)_2$THF R = Ph, p-tolyl.

2.4 Experimental

All materials throughout were handled under dry nitrogen. Grignard reagents were made and standardised in the usual way. Diethylmagnesium was made by the disproportionation of an ethereal solution of ethylmagnesium bromide by anhydrous

Table 2.12

The New Methyleneaminomagnesium Compounds With Their Terminal and/or Bridging Azomethine Stretching Frequencies ν(C=N)

Compound	ν(C=N) cm^{-1} *	
	ν C=N Terminal	ν C=N Bridging
$(Ph_2C{=}NMgBr)_2(THF)_3$	-	1630
$\{(p\text{-tolyl})_2C{=}NMgBr\}_2(THF)_3$	-	1624
$(Ph_2C{=}NMgBr)_2(THF)_2$	-	1605
$\{(p\text{-tolyl})_2C{=}NMgBr\}_2(THF)_2$	-	1602
$(Bu^t{}_2C{=}NMgBr)_2OEt_2$	-	1622
$[(Ph_2C{=}N)_2Mg]_3(THF)_2$	1655	1613
$[\{(p\text{-tolyl})_2C{=}N\}_2Mg]_3(THF)_2$	1661	1620
$[(Bu^t{}_2C{=}N)_2Mg]_2$	1665	1613

* Nujol Mulls;

Table 2.12 Continued

Compound	ν(C=N) cm^{-1} *	
	ν(C=N) terminal	ν(C=N) bridging
$(Ph_2C=NMgEtOEt_2)_n$	-	1619
$\{(p\text{-tolyl})_2C=NMgEtOEt_2\}_n$	-	1619
$(Bu^t{}_2C=NMgEt)_n$	-	1605
$(Ph_2C=NMgPh)_n$	-	1618
$(Bu^t{}_2C=NMgPh)_n$	-	1607
$(Ph_2C=NMgEt)_2TMED$	-	1620
$\{(p\text{-tolyl})_2C=NMgEt\}_2TMED$	-	1618

* Nujol Mulls, n probably 2.

dioxan (1:2 molar ratio) and syringing off the ethereal diethylmagnesium from the precipitated magnesium bromide. The ethereal solution obtained was standardised using standard secondary butanol in xylene, with 1,10- phenanthroline as indicator. (122)

(i) The Preparation of bis(diphenylmethyleneaminomagnesium bromide)tris THF.

To a frozen (-196°) solution of diphenylmethyleneamine

(3.0g, 16.6 m.mol.) in about 100 cm^3 anhydrous diethyl ether was added 17.3cm^3 of a 0.96M (ethereal) solution of isopropylmagnesium bromide. On warming with stirring to room temperature a pale yellow solid formed, and after stirring overnight and pumping away solvent, the residual cream coloured solid was recrystallised from THF, affording pale-yellow crystals identified as bis(diphenylmethyleneaminomagnesium bromide)tris THF, $(Ph_2CNMgBr)_2(THF)_3$, m.p. 170 - 180°d

Found: C = 56.7; H = 5.6; Br = 20.8; Mg = 6.2; N = 3.6%
M, (by cryoscopy) 400.

$C_{38}H_{44}Br_2Mg_2N_2O_3$ requires C = 58.1; H = 5.6; Br = 20.4;
Mg = 6.2; N = 3.6%M, 785.

ν Max (Nujol Mulls) 1630s, 1596m, 1575m, 1550sh, 1486w, 1443s, 1400w, 1366w, 1350sh, 1334w, 1296w, 1285w, 1251m, 1239sh, 1182w, 1157w, 1147w, 1074m, 1027s, 1002w, 967w, 934m, 922m, 915sh, 898m, 873s, 841sh, 790s, 779s, 704s, 728w, 704sh, 699s, 673sh, 650s, 641sh, 619w, 609w, 501sh, 466s, 402m cm^{-1}.

A solution of isopropylmagnesium bromide (17.6cm^3, 0.85M, 15 m.mol.) in THF was added to a frozen solution (-196°) of diphenylmethyleneamine (2.72g, 15 m.mol.) in about 60cm^3 of THF. The mixture was stirred at room temperature and the pale yellow solution concentrated under vacuum whereupon pale-yellow crystals were deposited and identified as bis(diphenylmethyleneaminomagnesium bromide)tris THF on the basis of its infrared spectrum.

(ii) Preparation of bis(di-p-tolylmethyleneaminomagnesium bromide)tris THF

A solution of isopropylmagnesium bromide (19.2cm^3, 0.98M, 19.6 m.mol.) in diethyl ether was added to a frozen (-196°) solution of di-p-tolylmethyleneamine (4.10g, 19.6 m.mol) in 80cm^3 ether. A cream coloured solid was formed on warming to room temperature with stirring, and stirring was continued overnight. Solvent was then pumped away and the residual pale yellow solid recrystallised from THF affording pale yellow crystals identified as bis(di-p-tolylmethyleneaminomagnesium bromide)tris THF, $\{(\text{p-tolyl})_2\text{CNMgBr}\}_2\ (\text{THF})_3$, m.p. 190°d.

Found: C = 59.0; H = 5.9; N = 3.3; Br = 18.0; Mg = 6.3% M (by cryoscopy) 410

$C_{42}H_{52}Br_2Mg_2N_2O_3$ requires C = 59.9; H = 6.2; N = 3.3; Br - 19.0; Mg = 5.8%M, 841.

ν Max (Nujol Mull) 1910v.w, 1804v.w, 1624s, 1603s, 1568m, 1562sh, 1520sh, 1504m, 1423sh, 1403v.w, 1367sh, 1346v.w, 1317sh, 1309m, 1296sh, 1288m, 1273w, 1254s, 1240s, 1217sh, 1209m, 1192sh, 1183sh, 1179m, 1158v.w, 1141w, 1117sh, 1109m, 1070w.br, 1032s, 1019s, 957sh, 947w, 919s, 877s, 842sh, 831sh, 826s, 782s, 739s, 735s, 724sh, 683s, 675sh, 640v.w, 631m, 617sh, 601s, 576w, 481sh, 472s, 455sh, 412sh, 388sh, 365w, 340sh, 330w cm^{-1}.

(iii) Preparation of bis(diphenylmethyleneaminomagnesium bromide)bis THF.

A solution of isopropylmagnesium bromide (20cm^3, 0.85M, 17 m.mol.) in THF was added to a frozen (-196°)

solution of diphenylmethyleneamine (3.08g, 17m.mol.) in 80cm^3 THF. After warming to room temperature, stirring overnight and pumping away all solvent from the pale yellow solution the yellow powder so obtained was indentified as bis(diphenylmethyleneaminomagnesium bromide)bis THF m.p. 200^o(d).

Found: C = 55.8; H = 5.1; Br = 22.0; Mg = 7.0; N = 3.9%M by cryoscopy, 496.

$C_{34}H_{36}Br_2Mg_2N_2O_2$ requires C = 57.3; H = 5.1; Br = 22.4; Mg = 6.8; N = 3.9%M, 713.

ν Max (Nujol Mull) 1605s, 1576m, 1565sh, 1545v.w, 1503sh, 1496w, 1428sh, 1417sh, 1408w, 1371sh, 1330v.w, 1295v.w, 1265v.w, 1247s, 1233sh, 1188v.w, 1162m, 1132v.w, 1108v.w, 1079w, 1063w, 1033m, 1006w, 994v.w, 973v.w, 962v.w, 912m, 891m, 880m, 865sh, 852sh, 796s, 773s, 731m, 711s, 701s, 680s, 641s, 590s, 590 v.w.br, 572 v.w.br, 550v.w.br, 500v.w, 474w, 460v.w, 452v.w, 410w.br, cm^{-1}.

This derivative was also prepared by the following two-step reaction, the product being identified by its infrared spectrum:

(a) Preparation of N-bromodiphenylmethyleneamine

13.0g of diphenylmethyleneamine-hydrochloride (59.8 m.mol) was added to a solution of 25.5 sodium carbonate/6g potassium carbonate mixture in 375cm^3 of water to which had been added 39g bromine (~240 m.mol, a liberal excess) at about -3^{o}C. The mixture was stirred at room temperature overnight and chloroform added (100cm^{-3}, two of 25 cm^3) with subsequent extraction and the combined red extracts were dried over anhydrous sodium sulphate prior to concentration using a rotary evaporator. A pale-yellow viscous liquid was ultimately obtained, to which a little 40-60 petrol ether was added. Cooling overnight at ca −20° yielded an off white solid which was washed with cold petrol and pumped solvent free. The solid was identified as N-bromodiphenylmethyleneamine, Ph_2CNBr.

Found: C = 60.0; H = 4.1; N = 5.3; Br = 30.6

$C_{13}H_{10}NBr$ requires C = 60.0; H = 3.9; N = 5.4; Br = 30.7

(b) 2.56g (10 m.mol.) of Ph_2CNBr in anhydrous ether was added to an excess of magnesium (~ 1g, 41 m.mol) covered with ether; there was little sign of reaction during this addition, over a period of about 30 minutes, except the solution becoming somewhat cloudy. Even on warming little evidence of reaction was seen, although an off white powder was slowly formed. THF was added, the solution refluxed for ~ 6 hours and then filtered to remove excess magnesium, the filtrate being golden yellow in appearance. Concentration of a small smount of the filtrate produced a yellow solid whose infrared spectrum was similar to that of $(Ph_2CNMgBr)_2(THF)_3$ (i)

Removal of all solvent from a sample of the filtrate gave $(Ph_2CNMgBr)_2(THF)_2$ (iii) again identified by its infrared spectrum. Addition of dioxane caused a white precipitate to form.

(iv) Preparation of bis(di-p-tolylmethyleneaminomagnesium bromide)bis THF.

A solution of isopropylmagnesium bromide ($15.3cm^3$, 0.98M, 15m.mol) in THF was added to a frozen (−196°)

solution of di-p-tolylmethyleneamine (3.13g; 15 m.mol) in 60cm^3 THF. After stirring at room temperature overnight, the golden yellow solution was pumped solvent free and the yellow solid obtained was identified as bis(di-p-tolylmethyleneaminomagnesium bromide)bis THF, $\left\{(p\text{-tolyl})_2CNMgBr\right\}_2(THF)_2$, m.p. 180 - 190 (d).

Found: C = 58.6; H = 5.6; Br = 20.6; Mg = 6.6, N = 3.7%M, (by cryoscopy) 520.

$C_{38}H_{44}Br_2Mg_2N_2O_2$ requires C = 59.3; H = 5.8; Br = 20.8; Mg = 6.3; N = 3.6%M, 769.

ν Max (Nujol Mull) 1910v.w, 1805v.w, 1602s, 1585sh, 1565m, 1550sh, 1540sh, 1517sh, 1510w, 1443sh, 1424w, 1370w, 1345sh, 1318w, 1311w, 1305w, 1295w, 1255sh, 1246m, 1218m, 1195w, 1190m, 1185m, 1163w, 1155w, 1120m, 1102v.w, 1070w.br, 1042m.br, 1028m, 1000sh, 975v.w, 959m, 938sh, 919s, 897s, 890sh, 880sh, 837s, 822s, 810sh, 788m, 746s, 740s, 729m, 680m.br, 665sh, 639m, 607w, 596m, 577m, 557w.br, 480s, 414w, 374sh cm^{-1}.

(v) Preparation of bis(di-t-butylmethyleneaminomagnesium bromide)monoetherate.

A solution of isopropylmagnesium bromide (10.5cm^3, 1.16M, 12.2 m.mol) in diethyl ether was added to a solution of di-t-butylmethyleneamine (1.72g, 12.2 m.mol) in 80cm^3 diethyl ether at -196°. The mixture was allowed to reach room temperature with stirring which was then continued overnight. The green-yellow solution was concentrated to about half bulk, a little hexane added, then set aside. The yellow crystals which formed were identified as bis(di-t-butylmethyleneaminomagnesium bromide)monoetherate, $(Bu^t{}_2CNMgBr)_2OEt_2$, m.p. 150 -157° (d).

Found: C = 45.6; H = 9.0; N = 4.9; Br = 26.9; Mg = 9.3%M, (by cryoscopy) 297.

$C_{22}H_{46}Br_2Mg_2N_2O$ requires C = 46.9; H = 8.2; N = 5.0; Br = 28.4; Mg = 8.6%M, 563.

ν Max (Nujol Mull). 1660sh, 1622s.br, 1595sh, 1412sh, 1406sh, 1387s, 1368s, 1352m, 1307w.br, 1294w.br, 1264w, 1241w, 1226m, 1213m, 1208sh, 1196w, 1170sh, 1156m, 1123m, 1094m, 1047sh, 1041s, 1030sh, 1005m, 963s, 948s, 930m, 900m, 873m, 850w, 838w, 789m, 751w, 740sh, 726m, 680s, 673sh, 604s, 572sh, 553m, 515s.br, 495sh, 487s.br, 421m, 407sh cm^{-1}.

The above reaction was repeated on a 22.3m.mol. scale and after stirring at room temperature overnight, all solvent was removed and then the yellow green residue was dissolved in THF. After concentration of the solution white crystals were obtained identified as being magnesium bromide$(THF)_4$.

Found: C = 39.5; H = 7.9; N = 0; Mg = 5.1; Br = 33.9%

$C_{16}H_{32}MgBr_2O_4$ requires C = 40.6; H = 6.8; N = 0; Mg = 5.1; Br = 33.8%.

After filtering off the crystals, all solvent was pumped from the yellow-green filtrate, and the yellowish solid obtained was identified by its infrared spectrum as being bis(di-t-butylmethyleneamino) magnesium - prepared later by the use of diethylmagnesium (viii).

(vi) Preparation of bis(diphenylmethyleneamino)magnesium trimer - bis THF.

A solution of diphenylmethyleneamine (9.05g, 50m.mol) in 80cm^3 ether was added to a frozen (-196^o) solution of diethylmagnesium (69.5cm^3, 0.36M, 25 m.mol) in ether. After stirring at room temperature for ~ 24 hours, during which time a red suspension formed, and pumping off all solvent the residue was a red-powdery solid. Recrystallation from THF afforded deep red crystals identified as bis(diphenylmethyleneamino)magnesium trimer-bis-THF, $[(Ph_2CN)_2Mg]_3(THF)_2$, m.p. 90 (d)

Found: C = 78.8; H = 4.4; N = 6.8; Mg = 5.6%M (by cryoscopy), 970.

$C_{86}H_{76}Mg_3N_6O_2$ requires C = 79.6; H = 5.9; N = 6.5; Mg = 5.6%M, 1296.

ν Max (Nujol Mull) 1655m, 1613, 1575m, 1565sh, 1480sh, 1440sh, 1410v.w, 1370w, 1345sh, 1310w, 1302sh, 1282w, 1246m, 1226w, 1196w, 1175w.br, 1157w.br, 1075m, 1068sh, 1030m.br, 1005w, 970w.br, 942w, 931w, 909w, 893m, 853w.br, 790w, 778m, 727w, 710sh, 701s, 685sh, 672sh, 650m, 640sh, 628w, 605v.w.br, 512w.br, 490v.w, 470m, 455v.w, cm^{-1}.

(vii) Preparation of bis(di-p-tolylmethyleneamine)magnesium trimer-bis THF

A solution of di-p-tolylmethyleneamine (4.62g, 22.1 m.mol) in 50cm^3 diethyl ether was added to a frozen (-196^o) solution of diethylmagnesium (30.6 cm^3, 0.36M 11m.mol) in ether. By a procedure outlined in the previous preparation

(vi) a deep orange solid was obtained and was identified as being bis(di-p-tolylmethyleneamino)magnesium trimer-bis-THF, $\left[\left\{(\text{p-tolyl})_2\text{CN}\right\}_2\text{Mg}\right]_3(\text{THF})_2$ m.p. 150 -154° (d).

Found: C = 79.3; H = 7.1; Mg = 5.3; N = 6.3%M (by cryoscopy), 1052.

$C_{98}H_{100}Mg_3N_6O_2$ requires C = 80.3; H = 6.8; Mg = 5.0; N = 5.7%M, 1464.

ν Max (Nujol Mull) 1661m, 1620m, 1603s.br, 1570m, 1565sh, 1507m, 1490v.w, 1442sh, 1407w, 1360sh, 1340sh, 1313w, 1307w, 1289w, 1255sh, 1244m, 1229w, 1212w, 1182m, 1177sh, 1153v.w, 1140v.w, 1118w, 1110sh, 1074m, 1039m, 1027w, 960v.w, 953v.w, 926m, 909m, 888w, 862v.w, 828s, 808sh, 788m, 750sh, 744s, 730w, 690v.w, 685v.w, 676m, 638w, 620sh, 606w, 579m, 504v.w, 483s,br, 402w, 380m, cm^{-1}.

(viii) Preparation of bis(di-t-butylmethyleneamino)magnesium

A solution of di-t-butylmethyleneamine (3.93g, 27.9 m.mol) in 20cm^3 ether was added to a frozen (-196°) solution of diethylmagnesium (38.6 cm^3, 0.36M, 13.9 m.mol). After stirring overnight at room temperature and pumping off solvent an unsuccessful attempt was made to recrystallise the yellow fluffy solid from ether/hexane. The yellow solid was identified as bis(di-t-butylmethyleneamino)magnesium dimer, $\left[(\text{Bu}^t{}_2\text{CN})_2\text{Mg}\right]_2$, m.p. 120°(d).

Found: C = 67.0; H = 11.9; N = 9.3; Mg = 8.3%M (by cryoscopy), 573.

$C_{36}H_{72}Mg_2N_4$ requires C = 71.0; H = 11.8; N = 9.2; Mg = 8.1%M,609

ν Max (Nujol Mull) 1720sh, 1668s, 1605s, 1394sh, 1380s, 1370s, 1360m, 1324m, 1300sh, 1265m, 1230sh, 1209m, 1080m.br, 1038s, 1020sh, 953m, 933m, 920sh, 900sh, 880s, 805m, 736sh, 727s, 680w, 660m, 610sh, 580m.br, 558sh, 545w, 484m, 435sh, 405m, cm^{-1}.

(ix) Preparation of diphenylmethyleneaminoethylmagnesium monoetherate

24.3 cm^3 of ethylmagnesium bromide (1.23M, 29.9m.mol) solution was added to a frozen (-196°) solution of diphenylmethyleneaminolithium in about 60cm^3 pentane/ether. On warming to room temperature a pale-green precipitate formed. After overnight stirring, solvent was pumped off and the yellow-green residue was extracted with hexane-ether and lithium bromide separated by filtration. The filtrate after concentration deposited yellow-green crystals of diphenylmethyleneaminoethylmagnesium monoetherate, $[Ph_2C{=}NMgEtOEt_2]_n$ m.p. 85° (d).

Found: C = 73.8; H = 8.1; N = 4.3; Mg = 8.1; hydrolysable Et = 8.5%

$C_{19}H_{25}MgNO$ requires C = 74.2; H = 8.1; N = 4.6; Mg = 7.9; hydrolysable Et = 9.7%

ν Max (Nujol Mull) 1619s, 1594w, 1576m, 1548v.w.br, 1490sh, 1454sh, 1367sh, 1327v.w, 1308w, 128)v.w.br, 1260m.br, 1240sh, 1226sh, 1193w, 1182w, 1153w, 1142v.w, 1125sh, 1091w, 1074w, 1048m, 1034sh, 1025sh, 999w, 967w, 931m, 917w, 901m, 835w.br, 798sh, 788w, 777m, 736w, 722w, 700s, 677sh, 621v.w, 599w, 511m.br, 468w, 430sh cm^{-1}.

A derivative spectroscopically indentical to this was also prepared by reacting diphenylmethyleneamine with diethylmagnesium in (1:1) molar proportions in diethyl ether solution.

(x) Preparation of di-p-tolylmethyleneaminoethylmagnesium-monoetherate

A solution of di-p-tolylmethyleneamine (1.34g, 6.41m.mol) in 30cm^3 ether was added to a frozen (-196^o) solution of diethylmagnesium (18.3cm^3, 0.35M, 6.41 m.mol) in ether. The mixture was allowed to warm up to room temperature and stirred overnight. Solvent was pumped off and the pale-yellow solid recrystallised from ether-hexane, and orange-yellow crystals were obtained, extremely moisture sensitive, identified as di-p-tolylmethyleneaminoethylmagnesium mono-etherate, $\left[(p\text{-tolyl})_2CNMgEtOEt_2\right]_n$ m.p. 108^o (d)

Found: C = 71.3; H = 8.2; N = 4.1; Mg = 8.2, hydrolysable Et = 8.0%

$C_{21}H_{29}MgNO$ requires C = 75.2; H = 8.6; N = 4.2; Mg = 7.3; hydrolysable Et = 8.9%

ν Max (Nujol Mull) 1619s, 1604s, 1570w, 1563sh, 1512sh, 1507s, 1407w, 1380s.br, 1312s, 1289s, 1260sh, 1243s, 1212s, 1195sh, 1190sh, 1183s, 1157w, 1118w, 1093w, 1053w, 1025w, 1010sh, 955w.br, 925s, 907sh, 825s.br, 788s, 745s, 726sh, 679m, 639s, 607s, 579w, 480s.br, 439s, 376v.w.br, cm^{-1}.

This compound was also prepared by the reaction between ethylmagnesium bromide and di-p-tolylmethyleneaminolithium in 1:1 molar proportions in diethyl ether. Its infrared spectrum was similar to that reported above.

(xi) Preparation of di-t-butylmethyleneaminoethylmagnesium

A solution of di-t-butylmethyleneamine (2.43g, 17.24 m.mol) in 60cm^3 ether was added to a frozen (-196°) solution of diethylmagnesium in ether (49.2cm^3, 0.35M, 17.24 m.mol). The mixture was allowed to reach room temperature, stirred overnight and solvent was removed under vacuum, the amorphous yellow solid so produced being recrystallised from ether-hexane. It was identified as di-t-butylmethyleneaminoethylmagnesium, $[Bu^t{}_2CNMgEt]_n$, n probably = 2, m.p. 104° (d).

Found: C = 66.6; H = 11.5; N = 7.5; Mg = 12.2; hydrolysable Et = 14.6%

$C_{11}H_{23}MgN$ requires C = 68.3; H = 11.9; N = 7.2; Mg = 12.6; hydrolysable Et = 15.5%.

ν Max (Nujol Mull) 1605s, 1585sh, 1387s, 1363s, 1300w.br, 1264m, 1245v.w, 1223sh, 1208m, 1153w, 1223m, 1100s, 1060sh, 1045s, 1023w, 954s, 924m, 900sh, 894m, 800s, 739w, 666s, 615sh, 585sh, 580m.br, 510m.b, 408m, cm^{-1}.

This compound was also prepared by the reaction between di-t-butylmethyleneaminolithium and ethylmagnesium bromide in 1:1 molar proportions.

(xii) Preparation of diphenylmethyleneaminophenylmagnesium

16.5 cm^3 of phenylmagnesium bromide (1.62M, 26.73 m.mol) in ether was added to a pentane-ether solution of diphenylmethyleneaminolithium (26.73 m.mol) at -196°. As the mixture warmed to room temperature with stirring its colour changed from red through brown to yellow green and an off white precipitate was formed. After stirring overnight, removing solvent in vacuum, the yellowish residue was extracted with hot toluene. The toluene extract was concentrated under reduced pressure and anhydrous hexane added. An amorphous yellow solid was obtained and identified as diphenylmethyleneaminophenylmagnesium $(Ph_2CNMgPh)_n$, m.p. 170°(d).

Found: C = 78.1; H = 7.3; N = 4.9; Mg = 7.7%

$C_{19}H_{15}MgN$ requires C = 81.1; H = 5.3; N = 5.3; Mg = 8.6%

ν Max (Nujol Mull) 1618s, 1601w, 1592sh, 1583sh, 1579m, 1565sh, 1556sh, 1545sh, 1492w, 1448s, 1418w, 1403sh, 1372sh, 1316w, 1310sh, 1288w, 1250m.br, 1236w, 1231sh, 1198w, 1187w, 1177w, 1094w, 1081w, 1061m, 1032w, 1018w, 1007w, 997sh, 978w.br, 946m, 930sh, 912m, 857w, 840w, 794m, 780s, 725s, 725sh, 702s.br, 684m, 674sh, 655s, 627w, 608w, 591w, 534m.br, 510m, 472s, 457sh, 441s, cm^{-1}.

(xiii) Preparation of di-t-butylmethyleneaminophenylmagnesium

An ethereal solution of phenylmagnesiumbromide ($30.8cm^3$, 1.62M, 49.9 m.mol) was added to a solution of di-t-butylmethyleneaminolithium (49.9 m.mol) in about $100cm^3$ pentane-ether at -196°. A pale yellow suspension slowly formed on warming with stirring to room temperature. After stirring overnight, and removal of solvent the residual pale-yellow solid was extracted with hexane and filtered.

Crystallisation attempts proved fruitless and as a last resort all solvent was therefore removed. The yellow green amorphous solid so obtained was identified as di-t-butylmethyleneaminophenylmagnesium, $(Bu^t{}_2CNMgPh)_n$ n probably 2, m.p. 185° (d).

Found: C = 71.2; H = 8.8; N = 5.8; Mg = 10.1%

$C_{15}H_{23}MgH$ requires C = 74.6; H = 9.5; N = 5.8; Mg = 10.1%

ν Max (Nujol Mull): 1622sh, 1609s.br, 1576w, 1561sh, 1495sh, 1478sh, 1419s, 1390s, 1369s, 1307v.w, 1278w, 1268w, 1247sh, 1233m, 1216w.br, 1198w, 1157w.br, 1095w.br, 1078v.w, 1062m, 1052m, 1042m, 1029w, 1018w, 1009sh, 997m, 960s, 931m.br, 914sh, 900sh, 888sh, 857w, 838sh, 801w.br, 781w.br, 768w, 741m, 708s.br, 680m, 670m, 645sh, 634m, 607sh, 588m.br, 521w.v.br, 480m.v.br, 443m, 408m.br, cm^{-1}.

(xiv) Preparation of bis(diphenylmethyleneaminoethylmagnesium) TMED

Diethylmagnesium ($70cm^3$, 0.185M, 12.95 m.mol) in ether was mixed with tetramethylethylenediamine TMED ($1.95cm^3$, 12.95 m.mol). There was no evolution of heat and this mixture was cooled to -196° prior to the addition of diphenylmethyleneamine (2.34g, $2.16cm^3$, 12.95 m.mol) in $40cm^3$ ether.

As the stirred mixture warmed up the orange brown solution gradually deposited a pale yellow solid. The stirring was maintained overnight and filtered, the yellow residue was washed with ether and pumped solvent free. It was identified as bis(diphenylmethyleneaminoethylmagnesium)TMED,

$(Ph_2CNMgEt)_2TMED$, m.p. 125 - 35° (d), and showed immediate signs of reddening even in the glove box filled with nitrogen.

Found: C = 70.0; H = 7.4; N = 8.8; Mg = 8.6; hydrolysable; Et = 9.7% M (by cryoscopy) 561.

$C_{36}H_{46}Mg_2N_4$ requires C = 74.2; H = 7.9; N = 9.6; Mg = 8.3; hydrolysable Et = 10.3% M, 583.

ν Max (Nujol Mull): 1620v.s, 1605sh, 1580m, 1493m, 1448v.s, 1457w.br, 1372sh, 1316w, 1300v.w, 1263m, 1248m, 1185v.w.br, 1160v.w.br, 1127m, 1111w, 1079m, 1052v.w, 1033v.w, 1026v.w, 1008v.w, 995v.w.br, 976v.w.br, 946m, 935sh, 910m, 897m, 880s, 854v.w.br, 837v.w, 783s, 730w, 708v.s, 690w, 656s, 623m, 609m, 540sh, 512s.br, 470s, cm^{-1}.

(xv) Preparation of bis(di-p-tolylmethyleneaminoethylmagnesium)TMED

The above procedure was followed using diethylmagnesium ($38.8cm^3$, 0.35M, 13.59 m.mol), TMED ($2.05cm^3$, 13.59 m.mol) and di-p-tolylmethyleneamine (2.84g, 13.59 m.mol). The yellow product was identified as bis(di-p-tolylmethyleneaminoethylmagnesium)TMED, $\{(p\text{-tolyl})_2CNMgEt\}_2TMED$, m.p. 110-115° (d).

Found: C = 75.1; H = 10.2; N = 8.0; Mg = 7.6; hydrolysable Et = 9.2% M (by cryoscopy) 491.

$C_{40}H_{54}N_4Mg_2$ requires C = 75.2; H = 8.5; N = 8.7; Mg = 7.6; hydrolysable Et = 9.9% M, 639.

ν Max (Nujol Mull): 3260v.w, 1658w, 1617v.s. 1602v.s. 1574m, 1566sh, 1511m, 1450v.s, 1425v.w, 1419w, 1408w, 1371m, 1358w, 1316m, 1292m, 1284m, 1255sh, 1247s,br, 1216m, 1184s, 1177m, 1166v.w, 1147m, 1131w, 1119m, 1099v.w.br, 1080w, 1045w.br, 1031s, 1007s, 974w, 960m.br, 953m, 925v.s, 898m, 871w, 843s, 833v.s, 800m, 790s, 746v.s, 728v.w, 687m, 676m, 639m, 604v.s, 580m, 551s, 535m. br, 483v.s, 450w, 436w, 368m, 346 cm^{-1}.

An attempt was made to react di-t-butylmethyleneamine with diethylmagnesium and TMED, but unchanged methyleneamine was recovered and a solid thought to be an adduct, viz, $Et_2Mg.TMED$.

(xvi) A study of the controlled pyrolysis of $(Bu^t{}_2C=NMgBr)_2OEt_2$

A known mass of sample was heated for measured lengths of time at 100°C, 130°C, 155°C and 200°C. The evolved volatiles were separated and condensed out (and weighed) by standard vacuum-line techniques.

Mass of $(Bu^t{}_2C=NMgBr)_2OEt_2$ taken = 0.75g.

Temperature °C	Time min	Nature of product	Mass of product g.
100°	10	Et_2O	0.0747
130°	150	Et_2O	
155°	45	Et_2O	0.0142
200°	60	2-methyl-propane	-

Total mass of Et_2O evolved = 0.0889g

= 1.20 m.mol.

Alternative structures considered

(a) $(Bu^t{}_2C{=}NMgBrOEt_2)_2$ Mass taken = 0.75

= 1.177 m.mol.

Calculated mass (maximum) of Et_2O obtainable = 2.36m.mol

(b) $(Bu^t{}_2C{=}NMgBr)_2OEt_2$ Mass taken = 0.75g

= 1.33 m.mol.

Calculated mass (maximum) of Et_2O obtainable = 1.33 m.mol

Summary

(a) Calculated mass(max) Et_2O obtainable from 0.75g $(Bu^t{}_2C{=}NMgBrOEt_2)_2$ = 2.36 m.mol.

(b) Calculated mass (max) Et_2O obtainable from 0.75g $(Bu^t{}_2C{=}NMgBr)_2OEt_2$ = 1.33 m.mol.

(c) Mass of Et_2O obtained from 0.75g of compound = 1.20 m.mol.

(xvii) Estimations of hydrolysable ethyl in methyleneaminomagnesium derivatives, $\left[R_2C{=}NMgEt(OEt_2)\right]_x$, R = Ph, p-tolyl, Bu^t; x = 1, 1 and 0.

The ready hydrolysis of the Mg-C bond with hydrocarbon evolution was used as a basis for this analysis. Generally a weighed sample was hydrolysed under controlled conditions in a small two-necked flask attached to a vacuum line. The compounds were hydrolysed initially by a few cm^3 of methoxyethanol followed later by aqueous sulphuric acid. The liberated gases were fractionated and weighed.

Results:

(a) $(Bu^t{}_2C{=}NMgEt)_n$ n probably 2.

Mass of the methyleneaminomagnesium compound taken = 0.4600g.

Mass of ETHANE evolved = 0.0670g

Theoretical amount of ethane = 0.07138g.

Number of hydrolysable ethyl groups per mole of magnesium = 0.94

(b) $(Ph_2C{=}NMg(Et)OEt_2)_n$ n probably 2

Mass of methyleneaminomagnesium compound taken = 0.1740g

Mass of ETHANE evolved = 0.01473g

Theoretical amount of ethane = 0.01698g

Number of hydrolysable ethyl groups per mole of magnesium = 0.87

(c) $\left[(p\text{-tolyl})_2C{=}NMg(Et)OEt_2\right]_n$, n probably 2.

Mass of methyleneaminomagnesium compound taken = 0.2457g

Mass of ETHANE obtained = 0.01965g

Theoretical amount of ethane = 0.02198g

Number of hydrolysable ethyl groups per mole of Mg = 0.89

(d) Hydrolysable ethyl analyses also performed on $(R_2C{=}NMgEt)_2TMED$ (R = Ph, p-tolyl).

Results

Number of hydrolysable ethyl groups per mole of magnesium, in $(R_2C{=}NMgEt)_2TMED$ are 0.94 (R = Ph) and 0.93 (R = p-tolyl).

CHAPTER 3

METHYLENEAMINO DERIVATIVES OF ZINC

3.1 Introduction

This chapter seeks to repair some omissions which remained after earlier studies of the methyleneamino chemistry of zinc, such studies being duly acknowledged throughout the text (13, 50). It describes the preparation and properties of some new methyleneaminozinc derivatives, viz, (i) the adducts $(R_2C{=}NH)_nZnX_2$, R = Ph, p-tolyl, X = Cl, n = 2; R = Bu^t, X = Cl, n = 1; R = p-tolyl, X = Ph, n = 1; and p-tolylC≡N.$ZnPh_2$; and (ii) $(R_1R_2C{=}NZnX)_n$, (R_1 = Ph, p-tolyl, X = Cl, n = 2; R_1 = R_2 = p-tolyl, X = Ph, n = 2; R_1 = Ph, R_2 = p-tolyl, X = Ph, n = 2, and R_1 = R_2 = p-tolyl, X = $R_1R_2C{=}N$. The attempted reaction of di-t-butylmethyleneamine with diphenylzinc is also described.

Features of their infrared and ^{1}H-nuclear magnetic resonance spectra are discussed and compared - where such has not already been done in Chapter 2 - to related beryllium and magnesium compounds. The discussion (Section 3.3) begins on page 113

3.2 Experimental

3.2.1. Starting Materials

Anhydrous zinc chloride was made by refluxing commercial zinc chloride with thionyl chloride for about two hours, removing the latter by distillation and then eliminating final traces of thionyl chloride by pumping. Diphenylzinc, m.p. 105°C, was prepared by a metal aryl exchange reaction between zinc dust and diphenylmercury in boiling xylene (123). Manipulations were carried out in a conventional vacuum line, nitrogen- filled glove box, or nitrogen- filled apparatus as appropriate.

3.2.2. (i) Preparation of $R_2C{=}NH.ZnCl_2$ adducts (R = Ph, p-tolyl, Bu^t)

One description will serve to explain the general procedure. 3.05g of diphenylmethyleneamine (16.85 mmol) in $40cm^3$ diethyl ether was cooled to 196^o and $14.3cm^3$ 0.5892M zinc chloride solution in ether (8.42 mmol) added. The mixture was stirred overnight at room temperature and the white solid - which formed almost immediately - was washed with ether and pumped solvent - free. It was identified as the adduct, bis(diphenylmethyleneamine).zinc(II)chloride, $(Ph_2C{=}NH)_2ZnCl_2$, m.p. 225 - 230°C.

Found: C = 62.9; H = 4.6; N = 5.6; Zn = 13.3; Cl = 14.3%

$C_{26}H_{22}N_2ZnCl_2$ requires C = 62.6; H = 4.4; N = 5.6; Zn = 13.1; Cl = 14.2%

The same product was obtained by the above procedure using equimolar proportions (on a 12.32 mm scale).

ν max (Nujol mull) 3298s, 1604s.br, 1573s, 1565sh, 1493w, 1456v.s, 1422v.w, 1398s, 1382s, 1328w.br, 1305w.br, 1282w.br, 1267w.br, 1241s, 1210v.w.br, 1191w, 1181w, 1168m, 1161m, 1082m, 1036m, 1007m, 987w, 979w, 946m, 918m, 900w.br, 873s, 858m, 797s, 768s, 734m, 713s, 709s, 702s, 647s, 620w, 594w.br, 482w, 454w, 435w, cm^{-1}.

The adduct bis(di-p-tolymethyleneamine).zinc(II)chloride, $\{(p\text{-tolyl})_2C{=}NH\}_2.ZnCl_2$ m.p. 205 - 208°, was prepared similarly by using 1:1 molar proportions (16.93mmol scale) or 2:1 molar proportions of di-p-tolylmethyleneamine and zinc(II)chloride (14.17 and 7.09 mmol) respectively.

Found: C = 65.1; H = 5.3; N = 5.1; Zn = 11.8; Cl = 12.7%

$C_{30}H_{30}N_2ZnCl_2$ requires C = 64.9; H = 5.4; N = 5.1; Zn = 11.8; Cl = 12.8%

ν max (Nujol mull) 3300s, 1608s, 1596vs, 1560s, 1550sh, 1509m, 1424s, 1394m, 1380s, 1370sh, 1317w, 1290w, 1262w, 1244vs, 1212m, 1196w, 1187vs, 1162m, 1123m, 1094 w.br, 1043w.br, 1022m, 979w, 965m, 920s, 887m, 877m, 861w, 853w, 848w, 837vs, 828sh, 821s, 810sh, 774m, 745vs, 725w, 686w, 679m, 634m, 594s, 568w, 488sh, 483sh, 476s, 409w. cm^{-1}.

The adduct, di-t-butylmethyleneamine.zinc(II)chloride, $Bu^t_2C{=}NH.ZnCl_2$ m.p. 137 - 139°, was prepared by reacting together zinc(II)chloride and di-t-butylmethyleneamine as above in either 1:2 or 1:1 molar proportions respectively.

Found: C = 38.2; H = 6.0; N = 4.7; Zn = 23.9; Cl = 26.1%

$C_9H_{19}NZnCl_2$ requires C = 38.9; H = 6.8; N = 5.0; Zn = 23.6 Cl = 25.6%

ν max (Nujol mull) 3307s, 1613vs, 1597vs, 1487s, 1420m, 1412sh, 1402m, 1391m, 1376m, 1370m, 1360sh, 1262m, 1240, 1225s, 1202m, 1050m, 1045m, 1023w, 970vs, 936m, 880s, 867s, 857s, 843s, 794m, 728m-s, 661wbr, 595mbr, 550w, 485v.w, cm^{-1}.

(ii) Preparation of diphenylmethyleneaminozinc chloride dimer

An ethereal solution of diphenylmethyleneaminolithium (31.3mmol) was added to a frozen (-196°) solution of zinc chloride in ether (62.3cm^3 0.503M, 31.3mmol). On warming to room temperature with stirring a white suspension formed. The mixture was stirred overnight, solvent pumped off, and the pale-yellow residue refluxed briefly with toluene prior to the removal of lithium chloride by filtration. The toluene extract was concentrated under reduced pressure and anhydrous hexane added. A pale-yellow, woolly solid was formed and was identified as diphenylmethyleneaminozinc-chloride dimer, $(Ph_2C{=}NZnCl)_2$

Found: C = 55.0; H = 4.0; N = 5.0; Zn = 23.4; Cl = 11.9%M, by cryoscopy, 600

$C_{26}H_{20}N_2Zn_2Cl_2$ requires C = 55.5; H = 3.6; N = 5.0; Zn = 23.3; Cl = 12.6%M, 562

νmax (Nujol mull) 1622sh, 1604s.br, 1570m.br, 1562sh, 1543sh, 1492w, 1452vs, 1400sh, 1367s, 1320w.br, 1282w.br, 1263m.br, 1250sh, 1196m, 1183m, 1162m.br, 1077m.br, 1032m.br, 1005w, 975w.br, 938w.br, 912w, 891s, 855sh, 810sh, 793s, 758m.br, 742sh, 732m, 726w, 700vs, 673sh, 647m, 627m, 621sh, 595w.br, 574w.br, 471w.br, 452w.br, 430w.br, cm^{-1}.

(iii) Preparation of di-p-tolylmethyleneaminozinc chloride dimer

A solution of di-p-tolylmethyleneamine (3.31g, 15.84mmol) in 40cm^3 diethyl ether was cooled to -196^o and n-butyl lithium (10.6cm^3, 1.49M, 15.84mmol) in pentane was added. The mixture was allowed to reach room temperature with stirring and then stirred for about 30 minutes, before being added to a frozen solution (-196^o) of zinc chloride in ether (25.8cm^3, 0.6131M, 15.84mmol). On warming to room temperature with stirring a white suspension was formed. The mixture was stirred overnight, all solvent pumped off, lithium chloride being removed by filtration after brief reflux in toluene. The toluene extract was pumped free of solvent and the residual pale-yellow solid after recrystallisation from toluene/hexane was identified as dimeric di-p-tolylmethyleneaminozinc chloride, $\{(\text{p-tolyl})_2C{=}NZnCl\}_2$

Found: C = 56.7; H = 4.6; N = 4.5; Zn = 20.8; Cl = 11.8%M, by cryoscopy, 660

$C_{30}H_{28}N_2Zn_2Cl_2$ requires C = 58.3; H = 4.6; N = 4.5; Zn = 21.2, Cl = 11.5%M, 618

νmax (Nujol mull) 1600vsbr, 1570sh, 1565m, 1544sh, 1535sh, 1522sh, 1506m, 1422w, 1314w, 1290w, 1272s, 1247sh, 1215w, 1195sh, 1187m, 1182sh, 1160w, 1157vwbr, 1100sbr, 1022sbr, 960wbr, 932sh, 920m, 895m, 880sh, 830sh, 819s, 804s, 742s, 725w, 707vw, 679w.br, 635w, 600m, 570w, 502sh, 476m cm^{-1}.

(iv) Preparation of the di-p-tolylmethyleneamine.zinc diphenyl adduct.

$30cm^3$ of a toluene solution of diphenylzinc (3.915g; 17.84mmol) was added to 3.73g (17.84mmol) of di-p-tolylmethyleneamine in toluene ($30cm^3$) at 0°C. After mixing and stirring, the solution was warmed to about 40°. A small amount of pale-yellow solid was formed at this stage; this was removed and identified as di-p-tolylmethyleneamine-zinc diphenyl adduct, $(\text{p-tolyl})_2C{=}NH.ZnPh_2$.

Found: C = 75.6; H = 5.0; N = 3.1; Zn = 15.6%

$C_{27}H_{25}NZn$ requires C = 75.6; H = 5.8; N = 3.3; Zn = 15.3%

ν max (Nujol mull) 3261m, 1603vs br, 1565mbr, 1543sh, 1507w, 1420s, 1366sh, 1313m, 1300wbr, 1288w, 1246w, 1236vs, 1214m, 1193m, 1187s, 1173m, 1161s, 1157sh, 1122wbr, 1077s, 1050wvbr, 1027m, 999w, 981m, 958m, 915vs, 894vs, 873w, 853s, 848s, 832vs, 821vs, 807w, 788w, 743vs, 733vs, 727vs, 718vs, 711vs, 679s, 661m, 637m, 627w, 594s, 568m, 477s, 451vs, cm^{-1}

(v) Preparation of phenyl(di-p-tolylmethyleneamino)zinc.

After filtering off the di-p-tolylmethyleneamine.zinc diphenyl adduct, prepared as described in (iv) the filtrate was concentrated under reduced pressure whereupon off-white dimeric phenyl(di-p-tolylmethyleneamino)zinc was precipitated $\left\{(p\text{-tolyl})_2C{=}NZnPh\right\}_2$.

Found: C = 72.2; H = 4.7; N = 4.1; Zn = 18.6% M(by cryoscopy), 620

$C_{42}H_{38}N_2Zn_2$ requires C = 71.9; H = 5.4; N = 4.0; Zn = 18.7% M, 700

ν max (Nujol mull) 1615m, 1600s, 1564wvbr, 1509w, 1502w, 1495w, 1427m, 1410w, 1372w, 1316w, 1296m, 1271w.br, 1254w, 1217w, 1190w, 1184m, 1169w, 1121m, 1079m, 1026w.v.br, 1004wbr, 977w, 964w, 939m, 896w, 861w, 847w, 839s, 832m, 793m, 750s, 745m, 731m, 711m, 682w, 675w, 666w, 635wbr, 513w, 508w, 484m, 451m, cm^{-1}.

(vi) Reaction between diphenylmethyleneamine and diphenylzinc

1.65g (9.12mmol) of diphenylmethyleneamine in toluene was added to an ice cold toluene solution of diphenyl zinc (2.0g; 9.12mmol). The mixture was stirred and at room temperature a whitish suspension formed. The white solid was filtered off, washed with toluene, pumped solvent free and identified as dimeric phenyl(diphenylmethyleneamino)zinc, $(Ph_2C=NZnPh)_2$, m.p. = 130°.

Found: C = 70.3; H = 4.5; N = 3.94; Zn = 20.2%

$C_{38}H_{30}N_2Zn_2$ requires C = 70.7; H = 4.7; N = 4.3; Zn = 20.3%

Its infrared spectrum was identical to that reported earlier (13).

(vii) The effect of heat on Phenyl(di-p-tolylmethyleneamino)zinc.

Phenyl(di-p-tolylmethyleneamino)zinc, prepared as in (v) above, was dissolved in toluene and refluxed in a nitrogen atmosphere for 6-7 hours. There was no change in appearance, the solution maintaining its yellow colour, nor was any solid precipitated. The solution was concentrated under vacuum and the solid recovered, identified by its infrared spectrum, was starting material phenyl(di-p-tolylmethyleneamino)zinc, $[(p\text{-tolyl})_2C=NZnPh]_2$. The residue was further heated at about 200° for 5 hours. A small amount of solid formed at upper part of tube; it had a zinc content of 28.4% ($ZnPh_2$, an expected product of disproportionation has 29.8% of zinc; starting material has 18.6% zinc) but the residual substance was essentially unchanged.

(viii) Attempted preparation of bis(di-p-tolylmethyleneamino)zinc

An ethereal solution of di-p-tolylmethyleneaminolithium (20mm) was added to a frozen (-196°) solution of zinc chloride

(17.8 cm^3 of 0.5631M solution in ether, 10mm). On warming to room temperature a pale yellow suspension formed. The mixture was stirred overnight and then solvent was pumped off. The yellow solid left, after taking its infrared spectrum, was stirred with hot toluene and filtered hot. The yellow filtrate was concentrated under reduced pressure and ultimately all solvent was removed leaving a small amount of a yellow amorphous solid identified as *bis(di-p-tolylmethyleneamino)zinc* $\left[\left\{(\text{p-tolyl})_2C{=}N\right\}_2 Zn\right]_n$ (state of association uncertain). m.p. 270°d.

Found: C = 75.1; H = 5.3; N = 5.3; Zn = 12.6%

$C_{30}H_{28}N_2Zn$ requires C = 74.8; H = 5.8; N = 5.3; Zn = 13.6%

ν max (Nujol mull) identical to that of the above mixture of bis(di-p-tolylmethyleneamino)zinc and lithium chloride

1664w.br, 1623s, 1607s, 1573m, 1508m, 1416w, 1409w, 1345sh, 1312w, 1290w, 1250wbr, 1235sh, 1214w, 1200vw, 1183m, 1158wbr, 1118m, 1092w.v.br, 1042w.br, 1027m, 973w.br, 958w, 926m, 910w, 898w, 832s.br, 809w, 789m, 743s, 737sh, 701w, 678m, 645sh, 638w, 611mvbr, 580w.br, 480s.br, cm^{-1}.

Small equimolecular quantities (1.14mmol) of di-p-tolylmethyleneaminophenylzinc and di-p-tolylmethyleneamine dissolved in toluene were mixed at −196°, allowed to warm to room temperature and then refluxed for 5 hours. The pale yellow solution was concentrated under reduced pressure and finally all solvent removed leaving a gummy yellow residue identified by its infrared spectrum as bis(di-p-tolylmethyleneamino)zinc.

(ix) Preparation of p-tolunitrile zinc diphenyl adduct

10cm^3 of a toluene solution of p-tolunitrile (1.463g; 12.49mmol) was added to a suspension of diphenyzinc (2.74g; 12.49mm) in toluene (25cm^3) at -78°. The mixture was warmed to 20°, filtered, and toluene was removed under vacuum. The viscous residue was identified as the p-tolunitrile diphenylzinc adduct $pMeC_6H_4CN.ZnPh_2$.

Found: Zn = 19.8% $C_{20}H_{17}NZn$ requires Zn = 19.5%

ν max (Liquid film) 3058vs, 3007s, 2980m, 2930w, 2255vs, 1609vs, 1580w, 1512m, 1501w, 1450m.br, 1426vs, 1386w, 1337w.br, 1318w, 1300w, 1294sh, 1291sh, 1265wbr, 1252m, 1220w, 1212w, 1196w, 1183vs, 1160w, 1127m, 1107sh, 1084vs, 1062w, 1043w, 1028m, 1002m, 956wbr, 910wbr, 860wbr, 842sh, 820vs, 767w, 730vs 708vs 685w, 668wbr, 557vs, 473w, 457vs, 440w. cm^{-1}.

(x) Thermal decomposition of p-tolunitrile zinc diphenyl adduct; preparation of phenyl(phenyl-p-tolyl-methyleneamino)zinc.

A sample of the adduct, (p-tolyl)CN.ZnPh$_2$, was maintained at about 100°C under nitrogen for about five hours. After cooling to room temperature a yellow viscous liquid remained. It was washed several times with toluene and finally pumped free of solvent. The pale yellow residue was identified as phenyl(phenyl,p-tolylmethyleneamino)zinc, $[Ph(p\text{-}tolyl)C{=}NZnPh]_2$ m.p. 264°d.

Found: C = 71.7; H = 5.2; N = 3.7; Zn = 19.7%
M, by cryoscopy, 632

$C_{40}H_{34}Zn_2N_2$ requires C = 71.3; H = 5.1; N = 4.1;
Zn = 19.5% M, 672

ν max (Nujol mull) 1627sh, 1618sh, 1605s, 1580w, 1570wbr, 1511w, 1450sh, 1442sh, 1428w, 1372w.br, 1316w, 1296w, 1286vw, 1270w, 1253v.w, 1221w, 1190w, 1163w.br, 1080m, 1026w.br, 975w.br, 960w.br, 948w, 922w, 895w, 857w, 852w, 837m, 807w, 790m, 741m, 737m, 720sh, 712m, 707m, 681w, 666m, 651w, 637w, 601w.br, 518w, 495sh, 490w, 469m, 451w, cm^{-1}.

(xi) The attempted preparation of phenyl(di-t-butylmethyleneamino)zinc).

The mixing of toluene solutions of di-t-butylmethyleneamine and zinc diphenyl, in equimolar proportions, at room temperature and then heating to about 60° for three hours was followed by examination of the infrared spectrum of the mixture. The only evidence of any interaction was the sharper ν(N-H) at 3296 cm^{-1} but the intensity diminished with time.

The mixture was then refluxed for three hours and toluene removed under reduced pressure. The rather sticky pale yellow product smelled strongly of di-t-butylmethyleneamine and its infrared spectrum confirmed the presence of unchanged reactants.

3.3 Discussion

Reference has already been made (Chapter 2) to the comparability of the organometallic chemistry of zinc with that of magnesium and beryllium. As the most electronegative element of the triad, the organo-derivatives of zinc are rather less reactive than organoberyllium and organomagnesium compounds. Organometallic compounds of the type R_2M (M = Be, Mg + Zn) show significant differences, for whereas Me_2Be and Me_2Mg are polymeric species, dimethylzinc and all presently know dialkyl- and diarylzincs are monomeric and linear. Its structure has been studied by means of Raman spectroscopy (124) and X-ray diffraction (125). The latter shows a methyl group of a neighbouring molecule situated opposite the vacant p-orbitals of the zinc atom thereby not excluding some measure of intermolecular attraction like that observed for trimethylindium (125, 126) and trimethylaluminium (125,127). It has been suggested that in formally associated Me_2Zn the very acute Zn-C-Zn angle would cause serious repulsions because of the close proximity of neighbouring zinc atoms (125).

The first know organozinc co-ordination compounds were those of dimethyl zinc with dimethyl- and diethyl ethers (128) shown in more recent time to be 1:1 adducts, $Me_2Zn.OR_2$(R = Me, Et) (129). Dimethylzinc also forms adducts with cyclic ethers, $\overbrace{CH_2(CH_2)_nCH_2}^{O}$, which however dissociate when dissolved in benzene. As n increases the strength of the bond between zinc and the donor molecule also increases and the possibility of 1:2 complex formation, $Me_2Zn.2$(ether), becomes more likely. With ethylene- and trimethylene-oxides (n = 0, 1) 1:1 adducts are formed, but with tetramethylene- and pentamethylene-oxides (n = 2, 3), 1:2 adducts are formed with stronger co-ordinate links between zinc and oxygen (129).

Dialkyl and diarylzincs also form chelate complexes with, for example, 1,4 - dioxan, 1,4-thioxan (130), N,N,N^1,N^1-tetramethylenediamine, $2,2^1$-bipyridyl, 1,10-phenanthroline (131) and quinoline (132). Several of the co-ordination complexes can be exposed to the air for short periods without evident decomposition, in marked constrast, for example, to dimethylzinc. With trimethylamine, dimethylzinc forms both 1:1 and 2:1 adducts, $Me_3N.ZnMe_2$ and $(Me_3N)_2ZnMe_2$, the latter dissociating both at its boiling point, and when dissolved in benzene, to give the 1:1 adduct and free tertiary amine. A similar dissociation occurs when the analogous adducts of pyridine and triethylamine are dissolved in benzene (10). Furthermore whilst zinc forms relatively unstable complexes with sulphides, phosphines and arsines, attachment to electron attracting groups enhances its Lewis acidity, with consequent effect upon the stability of the complex produced. A study of the complexes formed between R_2Zn ($R = Bu^n$, Ph, C_6F_5) and various donor molecules (eg ethyleneglycoldimethyl ether, triphenylphosphine, o-phenylenebis(dimethylarsine) underwrites this. Di-n-butylzinc, $Bu^n{}_2Zn$, does not complex with triphenylphosphine, but bis(pentafluorophenyl)zinc, $(C_6F_5)_2Zn$, yields the expected adduct viz. $(C_6F_5)_2Zn.(PPh_3)_2$ (133). The increasing electronegativity of the R groups in R_2Zn causes a corresponding increase in the electron affinity of the vacant orbitals of the zinc atom thus increasing its electron acceptor character and presumably increasing the strength of the zinc σ-bond to the donor atom. However, an additional consideration must be allowed for. Complexes of phosphorus or arsenic containing ligands may also be stabilised by $d\pi - d\pi$ back bonding of electrons from the filled 3 d-orbitals of zinc to empty d-orbitals of phosphorus or arsenic. Such an effect would be decreased by the presence of more electronegative groups on zinc, strengthening the σ-bond from zinc to the donor atom, but consequently reducing the possibility of back-bonding. That the first effect appears the more dominant arise from the fact that diphenylzinc complexes are more stable than di-n-butylzinc complexes and whilst no complexes of $Bu^n{}_2Zn$ with triphenylphosphine/triphenylarsine are formed, the corresponding Ph_2Zn complexes are formed easily and are stable. Furthermore, complexes formed by bis(pentafluorophenyl)zinc are the most stable.

Not unexpectedly the order of stability of R_2Zn.TMED complexes is $Me > Et > Pr^i > Bu^t$ for such a sequence is justifiable either on steric grounds or because of the increasing electron <u>releasing</u> character of the alkyl groups so <u>weakening</u> the bond of co-ordination between zinc and the nitrogen containing donor. No further considerations are required because TMED can participate only in dative σ-bonding lacking the necessary vacant orbitals for back acceptance of electron density. A comparison of these dialkylzinc.TMED complexes with the corresponding $2,2^1$-bipyridyl complexes, however, shows a converse stability trend i.e. for R_2Zn.bipy ($R = Me, Et, Pr^i, Bu^t$), the order of stability is $Bu^t > Pr^i > Et > Me$ (134). Bipyridyl as well as being a σ-donor is also capable of π-bonding by accepting electron density from filled metal- π orbitals, with the appropriate symmetry, into the π-anti-bonding orbitals of the ring system. The view has been expressed that the role of $d\pi - d\pi$ bonding in di-tertiary arsine complexes of d^{10} metals, referred to earlier, is unimportant because of the high ionization potential of the non-bonding d^{10} shell of the metal atoms (135). A contradictory view, expressed to support the above data for R_2Zn.bipy complexes (134), suggests that since in dialkylzinc compounds the Zn-C bond is largely of covalent character there is likely to be but a formal positive change on zinc. In consequence the ionization energy of a 3d electron will be considerably less for R_2Zn than for Zn^{2+} complexes. Hence, because of synergism between σ and π bonding the occurrence of any significant back donation in organozinc complexes is likely to be reflected in the stablity of the complex. The relative stability of analogous complexes of $2,2^1$-bipyridyl and TMED illustrates such a feature. Other chelate complexes, also containing four-co-ordinate zinc - have been studied and of considerable interest are the coloured complexes of R_2Zn (R = alkyl, aryl) with $2,2^1$bi-pyridyl (136) and 1,10-phenanthroline (137). The long wave charge transfer bands are considered to arise from transitions of metal-d electrons to vacant π-type ligand orbitals. Whilst the reaction between secondary amines and dialkylzincs has not been studied in depth, several products of such systems have been characterised. Dimethylzinc and dimethylamine in (1:1) or (1:2) molar proportions respectively yield bis(dimethylamino) zinc, $[(Me_2N)_2Zn]_n$ probably polymeric in nature (138). Its likely mode of formation is via the disproportionation of methyl (dimethylamino)zinc, see equation 3.1, rather

$$n\left[Me(Me_2N)Zn\right]_2 \longrightarrow \left[(Me_2N)_2Zn\right]_n + n\ Me_2Zn \qquad 3.1$$

than by the interaction of methyl(dimethylamino)zinc and dimethylamine as formulated in equation 3.2, since it has

$$n(Me(Me_2N)Zn)_2 + 2nMe_2NH \longrightarrow 2\left[(Me_2N)_2Zn\right]_n + 2n(MeH) \quad 3.2$$

been reported that the related ethyl derivative viz ethyl (diethylamino)zinc is stable in the presence of diethylamine (139). Other compounds of a similar nature such as (alkyl or aryl) (diphenylamino)zinc, $RZnNPh_2$ (R = Me, Et, Pr^i, Bu^n, Ph), all stable solids, and ethyl(diethylamino)zinc are all dimeric in benzene and, since amino groups are better bridging groups than alkyl or aryl groups, are considered to have the structure shown in Figure 3.1. Such

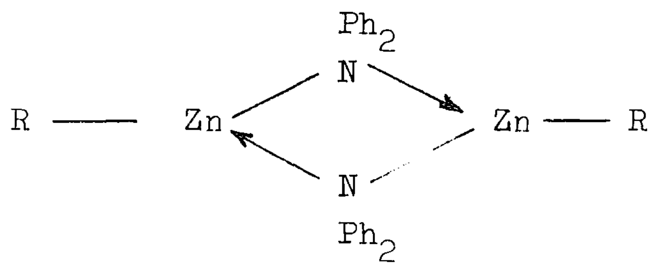


Figure 3.1

a structure with three-co-ordinate zinc and a four-membered $(ZnN)_2$ unit has been confirmed for methyl(diphenylamino) zinc, $[MeZn(NPh_2)]_2$ (Figure 3.1; R = Me) (140). The stability of these compounds is such as to imply that the valence angle strain, expected of such a structure can be withstood by the zinc atoms. Whilst a trimeric structure (Figure 3.2) based on a planar six-membered $(ZnN)_3$ ring would have allowed zinc and nitrogen to adopt a strain free

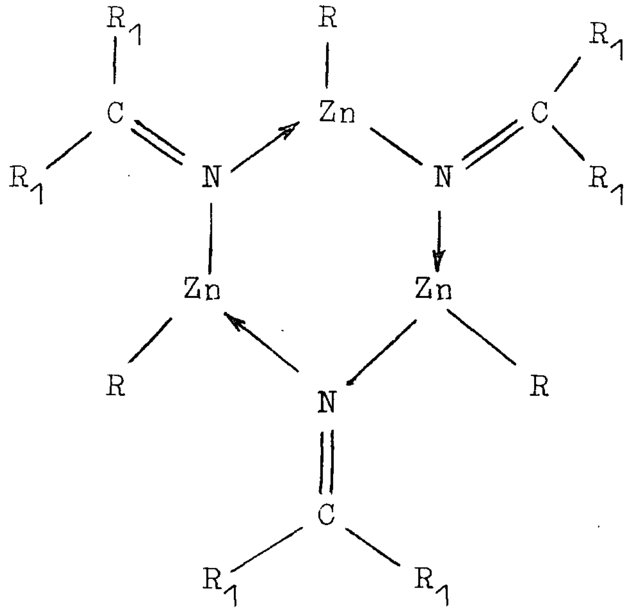


Figure 3.2

configuration, the controlling factor must presumably be the considerable crowding of the substituent groups concomitant with such a proposed structure. None the less, six-membered rings are believed to occur in derivatives of urea, $(RZnNPhCONR^1{}_2)_3$ and carbamates $(RZnNPh.COOR^1)_3$ (141) all trimeric in benzene although aminozinc alkyls, $(Ph_2NZnR)_2$ R = Me, Et, are dimeric, and four membered rings are a common feature of compounds of general description RZnX in which zinc is bonded to donor atoms such as oxygen (14, 138, 140), sulphur (138, 141) chlorine or bromine (142).

That three-co-ordinate zinc is a co-ordinatively - unsaturated condition is evidenced by the fact that when these compounds, $RZnNR^1{}_2$, whose structures are shown in

Figure 3.1, are heated or treated with pyridine, disproportionation occurs as shown in equations 3.1 and 3.3 the latter via $RZn(NPh_2)py$.

$$(RZnNPh_2)_2 + 2py \xrightarrow{\Delta} py_2Zn(NPh_2)_2 + ZnR_2 \qquad 3.3$$

The alkoxides of organozinc, $(RZnOR^1)_n$, so far reported are all associated species exemplified by dimeric ($R = Et$, $R^1 = C_6Cl_5$, C_6F_5, $n = 2$), trimeric ($R = R^1 = Bu^t$, $n = 3$) (143) or tetrameric ($R = Me$, $R^1 = Me$, Ph, $n = 4$) structures (138). They can be prepared by slow addition of the alcohol, or phenol, to the dialkylzinc - both in an inert solvent eg. hexane - at about -70^0 with negligible displacement of the second alkyl group. The product $RZnOR^1$ if monomeric would contain, bound to an oxygen atom of pronounced donor character, a co-ordinatively unsaturated zinc atom with enhanced acceptor character (by comparison with dialkylzinc). Consequently $RZnOR^1$ would be expected to be an associated species with relatively strong co-ordination. An X-ray examination of the methylzinc methoxide tetramer (140), $(MeZnOMe)_4$, has established it to have an eight-membered cubane structure with a $(ZnO)_4$ cage, the zinc and oxygen atoms occupying alternative corners of a distorted cube. An analogous cubane structure has been proposed for the structurally unstudied compounds $(MeZnOSiMe_4)_4$ and $(MeZnNPMe_3)_4$ (144-146). The methyl and ethyl alkoxides do not behave as though they were co-ordinatively unsaturated since for example they may be recovered unchanged from solutions to which pyridine has been added. They do however form co-ordination complexes with bis(2,2-dimethyl-3,5-hexanedionato)zinc, $(Bu^tCO.CH_2COMe)_2Zn$, for the β-diketonate oxygen atoms are very powerful electron donors, the vicinal zinc atom enhancing the electron density at the oxygens (147). Moreover in solution monomeric bis(2,2-dimethyl-3,5-hexanedionato)zinc contains a co-ordinatively-unsaturated zinc atom and therefore a synergic donor-acceptor behaviour can reasonably be expected. The relative strength of Ph_2N compared with Me_2N and OPh as bridging ligands may be seen in their different behaviours toward such donors as bipyridyl and TMED. Whilst $[Zn(NPh_2)_2]_2$ dissolves in bipyridyl giving a complex $Zn(NPh_2)_2$ bipy, (148), such does not happen with $[(Me_2N)_2Zn]_x$. Furthermore with TMED, the complex $EtZnNPh_2TMED$ is produced with $(EtZnNPh_2)_2$ but with $(EtZnOPh)_4$ the product $(EtZnOPh)_2TMED$ (143) retains two bridging OPh ligands. Representative sulphur-containing analogues of the alkylzinc alkoxides have been prepared and, in some cases, crystal structures have been obtained. Structures of methylzinc-isopropyl-and t-butylsulphides are of interest. The former is octameric, each zinc and carbon atoms lying near the corners of a truncated bisphenoid, giving rise to 4-, 6-, and 8-membered rings in contrast to the pentameric t-butyl system whose structure is based on a distorted square pyramid of zinc atoms and contains only 4- and 6- membered rings (141). The octameric methylzinc-isopropylsulphide arrangement can however be related to the cubane - type structure found in tetrameric methylzinc methoxide, $(MeZnOMe)_4$ (140), since the upper and lower parts of its polyhedra can each be obtained by the opening out of the cubane arrangement.

Over the years much attention has been devoted to the co-ordination chemistry of zinc and much of the reference material mentioned in this chapter, and the additional references quoted therein, reflect this feature. Reference (149) and various recent Organometallic Chemistry Reviews collate the relevant references. Reviews concerning the use of organozinc compounds in syntheses appear to be becoming more numerous, dealing, as they do, both with syntheses in a general sense and also majoring in monographic fashion on specific synthetic areas. So reference (150) (1975) deals solely with the Reformatsky reaction (151), a reaction of a carbonyl compound, usually an aldehyde or ketone, with an α-haloester in the presence of zinc metal to furnish after hydrolysis a β-hydroxyester. Subsequent dehydration is usually carried out to give an α,β-unsaturated ester. It summarises important advances in the understanding and use of the Reformatsky reaction - embracing discussion of studies on the nature of intermediates, side reactions, stereochemistry, and variations of the original reaction - since earlier accounts concerning various aspects of the reaction were written (152-156). The reaction of organic (and inorganic) substrates at a metal surface either in a catalytic fashion, or in an oxidative addition reaction with consumption of the metal, continues to represent an extremely important area of chemistry. Continuous attempts have been made to increase the reactivity of the metal in order to allow known reactions to be carried out under milder conditions, to improve yields, or to extend the reaction to less reactive substrates. Such objectives are being achieved in a variety of areas, including syntheses involving organozinc compounds, by the use of "activated metals". The "activated metals" are prepared by the reduction of metal salts (eg. anhydrous zinc chloride) in hydrocarbon or ethereal solvent (eg. tetrahydrofuran) with potassium (157). Other reviews of (i) organozinc compounds in syntheses, which discuss briefly the Reformatsky reaction, and also, among other things, describe in some detail features of the Simmons and Smith reaction by which cyclopropane derivatives can be made, and (ii) The structural chemistry of organic compounds of zinc (and mercury and cadmium) can be found in references 158 and 159.

Ethereal solutions of the methyleneamines $R_2C=NH$ ($R = Ph$, p-tolyl, Bu^t) were treated with a standardised solution of anhydrous zinc chloride, also in diethyl ether, in both 1:1 and 2:1 stoichiometric ratios respectively. In all three cases, whatever the stoichiometric ratios employed, white solid adducts were isolated and characterised as bis(diarylmethyleneamine)zinc (II)chloride, $(R_2C=NH)_2ZnCl_2$ ($R = Ph$, p-tolyl) and di-t-butylmethyleneamine.zinc (II) chloride, formally $Bu^t{}_2C=NH.ZnCl_2$ (equations 3.4 - 3.7)

$$R_2C=NH \quad + \quad ZnCl_2 \longrightarrow \tfrac{1}{2}(R_2C=NH)_2ZnCl_2 \quad + \quad \tfrac{1}{2}ZnCl_2 \qquad 3.4$$

$$2R_2C{=}NH \quad + \quad ZnCl_2 \longrightarrow (R_2C{=}NH)_2ZnCl_2 \tag{3.5}$$

$$R = Ph,\ p\text{-tolyl}$$

$$Bu^t{}_2C{=}NH \quad + \quad ZnCl_2 \longrightarrow Bu^t{}_2C{=}NH.ZnCl_2 \tag{3.6}$$

$$2Bu^t{}_2C{=}NH \quad + \quad ZnCl_2 \longrightarrow Bu^t{}_2C{=}NH.ZnCl_2 \quad + \quad Bu^t{}_2C{=}NH \tag{3.7}$$

Because of the inadequate solubility of the adducts in benzene, molecular weight values by cryoscopy were not obtained, but it seems likely that in all cases zinc is in a four co-ordinate condition and a tetrahedral configuration. The bis adducts of $R_2C{=}NH$ (R = Ph, p-tolyl) are presumably monomeric and the four membered co-ordinate state of zinc in the di-t-butylmethyleneamine-zinc chloride adduct is probably achieved not by the co-ordination of another molecule of the methyleneamine - which may not be easy because of steric problems - but by prefered dimerisation via chlorine bridges, like dimeric aluminium chloride (Figure 3.3).

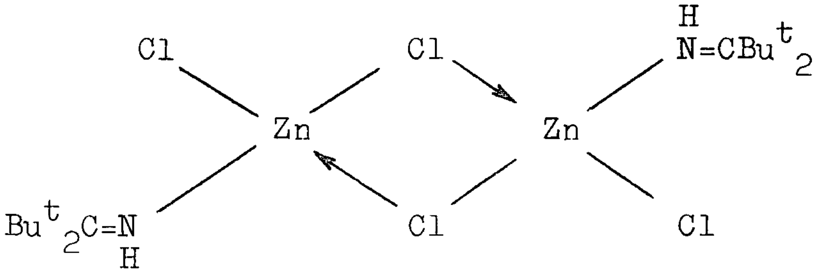
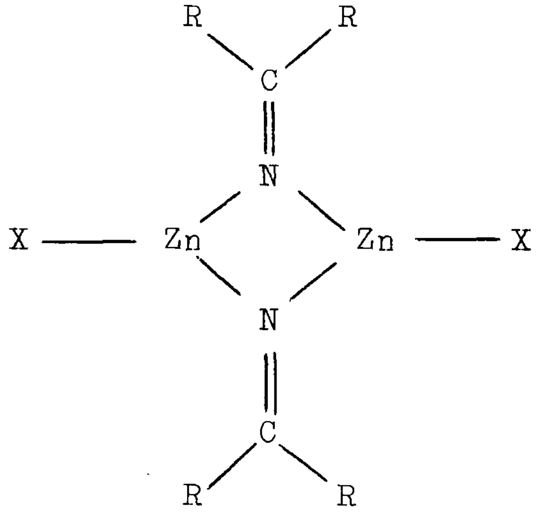


Figure 3.3

Diarylmethyleneaminozinc chlorides, $(R_2C{=}NZnCl)_2$ R = Ph, p-tolyl, were made by treating diarylmethyleneaminolithium in ether/pentane with a solution of zinc chloride in anhydrous ether in equimolar quantities (equation 3.8). The pale yellow, rather woolly solids isolated were shown to

$$R_2C{=}NLi \quad + \quad ZnCl_2 \longrightarrow \tfrac{1}{2}(R_2C{=}NZnCl)_2 \quad + \quad LiCl \qquad 3.8$$

be dimeric in benzene, resembling the corresponding di-t-butylmethyleneamino-derivative, $(Bu^t{}_2C{=}NZnCl)_2$ (50). The azomethine stretching frequencies, ν(C=N), of these compounds - see Table 3.1 - are appropriate for bridging methyleneamino units, and their most likely structure is shown in Figure 3.4 with four-membered $(ZnN)_2$ rings



R = Ph, p-tolyl, Bu^t. X = Cl, Me, Et, Ph

Figure 3.4

i.e. with bridging methyleneamino units, rather than chlorine atoms, as postulated for the analogous compounds of the Group II and Group III elements (24, 48, 75, 108). In this structure zinc is three co-ordinate. The preparation of bis(di-p-tolylmethyleneamino)zinc $\left[\left\{(p\text{-tolyl})_2C{=}N\right\}_2 Zn\right]_n$, proved very difficult and only small amounts of product was obtained by which ever route was followed. The corresponding bis(di-t-butylmethyleneamino)zinc, $\left[(\mathrm{Bu^t}_2\mathrm{C{=}N})_2\mathrm{Zn}\right]_2$, is dimeric and was prepared by treating the appropriate methyleneaminolithium derivative with anhydrous zinc chloride in ether solvent in a 2:1 molar ratio respectively (50). This route was followed (equation 3.9) for the corresponding p-tolyl derivative, but with small success

$$2n(\text{p-tolyl})_2\mathrm{C{=}NLi} \quad + \quad n\mathrm{ZnCl_2} \longrightarrow \left[\left\{(\text{p-tolyl})_2\mathrm{C{=}N}\right\}_2\mathrm{Zn}\right]_n + 2n\mathrm{LiCl} \qquad 3.9$$

for whilst the existence of the desired bis-derivative (mixed with lithium chloride) was evidenced, the separation of the mixture proved to be elusive. A sublimation technique was unsuccessful but a lengthy extraction employing refluxing toluene gave a small yield of product. Its involatility and sparingly soluble nature in toluene suggest that, like its phenyl-counterpart (13), $\left[\left\{(\text{p-tolyl})_2\mathrm{C{=}N}\right\}_2\mathrm{Zn}\right]_n$ it is probably polymeric. The corresponding bis(diphenylmethyleneamino)zinc derivative was prepared as illustrated in equations 3.10-3.13 (R = Ph) (13).

$$2\mathrm{R_2C{=}NH} \quad + \quad 2\mathrm{ZnPh_2} \longrightarrow (\mathrm{R_2C{=}NZnPh})_2 \quad + \ 2\mathrm{PhH} \qquad 3.10$$

$$n(\mathrm{R_2C{=}ZnPh})_2 \xrightarrow{80^{\circ}} \left[(\mathrm{R_2C{=}N})_2\mathrm{Zn}\right]_n \quad + \quad n\mathrm{ZnPh_2} \qquad 3.11$$

$$\mathrm{RC{\equiv}N} \quad + \quad \mathrm{ZnPh_2} \longrightarrow \mathrm{RC{\equiv}NZnPh_2} \qquad 3.12$$

$$2n\mathrm{RC{\equiv}N.ZnPh_2} \xrightarrow{100^{\circ}} \left[(\mathrm{RPhC{=}N})_2\mathrm{Zn}\right]_n \quad + \ n\mathrm{ZnPh_2} \qquad 3.13$$

The key feature of this scheme is the ready disproportionation of dimeric phenyl(diphenylmethyleneamino)zinc, $(\mathrm{Ph_2C{=}NZnPh})_2$ as shown in equations 3.11 , 3.13. In the latter case it seems reasonable to assume that the formation of the bis(diphenylmethyleneamino)zinc polymer involved $(Ph_2C{=}NZnPh)_2$ as an intermediate. This reaction pattern when applied to the attempted preparation of $\left[\left\{(p\text{-tolyl})_2C{=}N\right\}_2Zn\right]_n$ revealed certain points of difference. The reaction between di-p-tolylmethyleneamine and diphenylzinc (equation 3.9; R = p-tolyl) for example, as well as forming dimeric phenyl (di-p-tolylmethyleneamino)zinc also produced a small but characterisable amount of di-p-tolylmethyleneamine-diphenylzinc adduct, $(p\text{-tolyl})_2C{=}NH.ZnPh_2$. Furthermore the principal product of the reaction, phenyl(di-p-tolylmethyleneamino) zinc $\left\{(p\text{-tolyl})_2C{=}NZnPh\right\}_2$ disproportionates much less readily that the corresponding diphenyl- derivative (equation 3.11, R = Ph) and consequently only a very small amount of the desired $\left[(R_2C{=}N)_2Zn\right]_n$, R = p-tolyl, was obtained. The reaction between p-tolunitrile and diphenylzinc (equation 3.12 R = p-tolyl) yielded an adduct $RC{\equiv}N.ZnPh_2$, which when heated afforded dimeric phenyl(phenyl, p-tolylmethyleneamino)zinc, $(Ph(p\text{-tolyl})C{=}NZnPh)_2$ - equation 3.14. This product, formed

$$2(p\text{-tolyl})C{\equiv}NZnPh_2 \longrightarrow (Ph(p\text{-tolyl})C{=}NZnPh)_2 \qquad 3.14$$

by the insertion of nitrile into a Zn - C bond, did not disproportionate when heated to yield the corresponding bis(methyleneamino)zinc. It also corresponds to the proposed intermediate in the overall disproportionation of the benzonitrilediphenylzinc adduct (equation 3.13 , R = Ph) (13). Another attempt to make bis(di-p-tolylmethyleneamino)zinc used the reaction between the free methyleneamine, $R_2C{=}NH$, R = p-tolyl, and phenyl(di-p-tolylmethyleneamino)zinc (equation 3.15).

This also afforded a very low yield of the desired product.

$$n(\text{p-tolyl})_2C{=}NH + \frac{n}{2}\left[(\text{p-tolyl})_2C{=}NZnPh\right]_2 \rightarrow \left[\left\{(\text{p-tolyl})_2C{=}N\right\}_2 Zn\right]_n + nPhH$$

3.15

Table 3.1 shows infrared spectroscopic data of these new, and other previously reported, methyleneaminozinc compounds. In the infrared spectra of the methyleneamine zinc(II)chloride adducts, $(R_2C{=}NH)_2ZnCl_2$ (R = Ph, p-tolyl) and $R_2C{=}NH.\ ZnCl_2$ (R = Bu^t), the characteristic (N-H) band evidences a considerable sharpening and an increase in ν(N-H) compared with the parent methyleneamines. Little change was seen in the asymmetric stretch ν(C=N) on co-ordination of the methyleneamines to zinc(II)chloride, or indeed when the adduct $(\text{p-tolyl})_2C{=}NH.ZnPh_2$ was formed.

The bis(methyleneamino)zinc series, $\left[(R_2C{=}N)_2Zn\right]_n$ R = Ph, p-tolyl, Bu^t, reveals unsurprising differences in the degree of molecular association, being polymeric (R = Ph, p-tolyl) and dimeric (R = Bu^t). In the latter case, bis(di-t-butylmethyleneamino)zinc, the infrared spectrum shows two absorptions of significant difference ($1683cm^{-1}$ and $1585cm^{-1}$) which may be assigned to the stretching frequencies of terminal and bent methyleneamino ligands respectively. In the former case the relatively high value implies a considerable amount of $N \rightleftharpoons Zn$ dative bonding. The proposed structure of this compound is shown in Figure 3.5 and has been discussed in considerable detail in Chapter 2. The structure of the polymeric bis(diarymethyleneamino)zinc

Table 3.1

Methyleneamino Derivatives of Zinc

Compound	ν(C=N)* cm^{-1}	ν(C=N=Zn) terminal cm^{-1}	Reference
$(Ph_2C{=}NH)_2.ZnCl_2$	1602	-	a
$\{(p\text{-tolyl})_2C{=}NH\}_2ZnCl_2$	1608	-	a
$Bu^tC{=}NH.ZnCl_2$	1613	-	a
$(p\text{-tolyl})_2C{=}NH.ZnPh_2$	1607	-	a
$(Ph_2C{=}NZnCl)_2$	1604	-	a
$\{(p\text{-tolyl})_2C{=}NZnCl\}_2$	1600	-	a
$(Bu^t{}_2C{=}NZnCl)_2$	1608	-	50
$(Ph_2C{=}NZnMe)_2$	1624	-	13
$(Bu^t{}_2C{=}NZnMe)_2$	1592	-	50
$(Ph_2C{=}NZnEt)_2$	1611	-	13
$(Ph_2C{=}NZnPh)_2$	1607	-	13
$\{(p\text{-tolyl})_2C{=}NZnPh\}_2$	1615	-	a
$(Ph(p\text{-tolyl})C{=}NZnPh)_2$	1605	-	a
$[(Ph_2C{=}N)_2Zn]_n$	1600	-	13
$[\{(p\text{-tolyl})_2C{=}N\}_2Zn]_n$	1607	(1664)	a
$[(Bu^t{}_2C{=}N)_2Zn]_2$	1585	1683	50

*As Nujol Mulls; a:this work

compounds $\left[(R_2C{=}N)_2Zn\right]_n$ R = Ph, p-tolyl, is likely to be best represented as a co-ordination polymer with a high ratio of bridging to terminal methyleneamino units

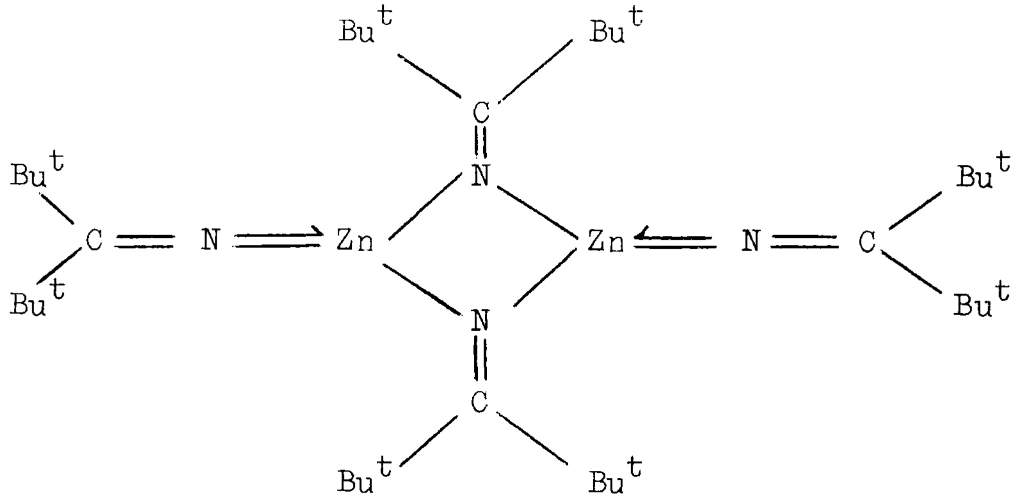


Figure 3.5

(Figure 3.6). In such a structure there must necessarily

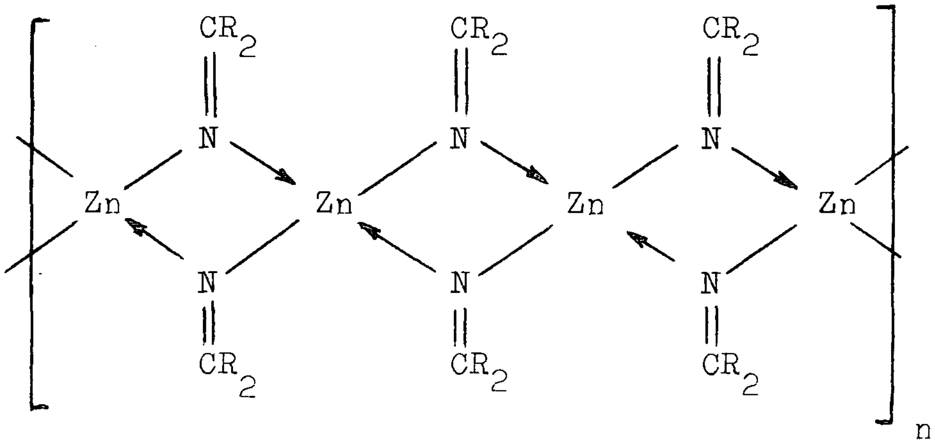


Figure 3.6

be two terminal methyleneamino group attached to a co-ordinatively unsaturated zinc atom, but the infrared spectrum, however, of the diphenyl compound shows only one azomethine stretching frequency at 1600cm^{-1} and this was assigned to the bridging ligand (13). The p-tolyl derivative also shows a very strong absorption, assigned to bridging ligands, ν(C=N) 1607cm^{-1}, and additionally a weak broad absorption is observed, ν(C=N) = 1660-1670, which may conceivably be assigned to the terminally - attached methyleneamino ligand.

All the methyleneaminozinc derivatives of general formula $(R_1R_2C{=}NZnX)_2$, $R_1 = R_2$ = Ph, p-tolyl, Bu^t, X = Cl; $R_1 = R_2$ = Ph, X = Me, Et; $R_1 = R_2$ = Ph, p-tolyl, X = Ph; R_1 = Ph, R_2 = p-tolyl, X = Ph, shown to be dimeric, by cryoscopy in benzene, have azomethine stretching frequencies, ν(C=N), in the range (1592 - 1624)cm^{-1} and these absorptions are assigned to bent/bridging C=N-Zn skeletons. The proposed structure of these dimeric compounds, with bridging methyleneamino ligands, four membered $(ZnN)_2$ rings and three - co-ordinate zinc is shown in Figure 3.4 (page 125). It seems very unlikely that back donation from the zinc 3d orbitals into the antibonding orbitals of the methyleneamino link plays any major part in the zinc-nitrogen bonding in these compounds because any interaction of zinc 3d orbitals and the $^*\pi$orbital of C=N- would be maximised when the C=N-Zn unit is linear, and would decrease as the C-N-Zn angle decreases.

The ^{1}H-NMR spectroscopic data for some of the new methyleneaminozinc compounds, together with other related examples, is shown in Table 3.2. The spectra, recorded on hexadeuteriobenzene solutions at about 40°C, were of somewhat poor resolution and consequently some assignments are rather imprecise. The interaction between $R_2C{=}NH$ (R = Ph, Bu^t and p-tolyl) and diphenylzinc is clearly very weak for in the cases of the diphenyl- and di-t-butylmethyleneamines no adduct is isolated - and indeed there is no evidence of any reaction, under the conditions employed, between di-t-butylmethyleneamine and diphenyzinc- and only a <u>small</u> amount of $(p\text{-tolyl})_2C{=}NH.ZnPh_2$ is isolable. The major product is almost exclusively dimeric $(R_2C{=}NZnPh)_2$, R = Ph, p-tolyl. Despite the fact that the $R_2C{=}NHZnPh_2$ adduct presumably decomposes slowly even at room temperature, evidence of interaction was obtained from the infrared (already referred to) and ^1H-NMR spectra of fresh samples. The spectrum of the adduct, in deuterated chloroform, although not well resolved, shows signals due to aromatic protons as a broad complex absorption τ(2.6 - 2.9), too broad to be particularly informative. The two signals τ,7.67 and 7.77, assigned to the tolyl-methyl protons, probably indicate both free and co-ordinated methyleneamine in the solution - a further index of the instability of the adduct - the former signal having the same chemical shift as a solution of the free methyleneamine $R_2C{=}NH$ (R = p-tolyl). Since the peak due to the (N-H) group in the free methyleneamine is at $\tau = -0.5$, it can be said that the peaks due to the methyl and nitrogen protons are shifted to higher fields - however slightly in the former case - on co-ordination to zinc. The more marked shift of the N-H peak is moreover in the direction opposite from that expected on electronic grounds in that co-ordination through nitrogen should reduce the

Table 3.2

^{1}H-NMR Results for Selected Methyleneaminozinc Compounds

Compound	τ ppm * (relative to Me_4Si τ =10.0)	Reference
$(Ph_2C{=}NZnCl)_2$	2.87 - 3.11c.	a
$\{(p\text{-tolyl})_2C{=}NZnCl\}_2$	2.80 - 3.14 c; 8.12s	a
$(Bu^t{}_2C{=}NZnCl)_2$	8.92s	50
$(p\text{-tolyl})_2C{=}NH.ZnPh_2$ [b]	0.7; 2.60 - 2.90c; 7.67, 7.77	a
$(Ph_2C{=}NZnPh)_2$	2.8s 2.9s	13
$\{(p\text{-tolyl})_2C{=}NZnPh\}_2$	2.8 - 3.1 (c); 8.05s	a
$[(Bu^t{}_2C{=}N)_2Zn]_2$	8.64(1),	50

*as external standard; s, singlet, c, complex, br, broad

a, this work. b in $CDCl_3$ and of poor resolution.

electron density in N - H bond. Complete interpretation of the spectrum is naturally obscured because of the difficulty in assigning resonances in the region τ = 2.6 - 2.9 to carbon-attached p-tolyl and zinc-attached phenyl groups. Similar findings have been made in systems involving adducts of R_3Al (R = Me, Et, Ph) and diphenylmethyleneamine in that all the peaks due to the donor molecule are shifted to higher fields in the presence of the organoalane (62). For the methyleneaminozinc chloride dimers, $(R_2C{=}NZnCl)_2$ R = Ph, p-tolyl, Bu^t, the resonances assigned to the aromatic protons, complex in outline, are in the approximate range τ = 2.8 - 3.1. The aryl methyl- and t-butyl protons are assigned to singlet peaks at τ 8.12 and 8.92 respectively. In all, the ^1H-NMR spectra of these methyleneaminozinc chloride dimers are consistent with the structure proposed for these derivatives. In the remaining compounds listed in Table 3.2 the bis(di-t-butylmethyleneamino)zinc data is quoted for the sake of completion, it having been discussed in Chapter 2, and also to highlight the absence of data for the other bis(diarymethyleneamino)zinc polymers, $\left[(R_2C{=}N)_2Zn\right]_n$, R = Ph, p-tolyl, whose insolubility prevented the recording of their spectra. The peaks due to the protons of the diphenylmethyleneamine residue in $(Ph_2C{=}NZnPh)_2$ appear as a singlet at τ = 2.8, the other singlet at τ = 2.9 was assigned to the protons of the Zn-Ph residue. This differs somewhat from the corresponding peaks in the spectra of aluminium and gallium compounds, $(Ph_2C{=}NMR_2)_2$ Me = Al, Ga; R = Me, Et, where the corresponding peaks due to protons of the diphenylmethyleneamine residue had two distinct complex features attributed to the ortho and meta/para sets of protons which are magnetically different (62, 63). The resonances observed due to aryl protons of $\{(p\text{-tolyl})_2\,C{=}NZnPh\}_2$ in the range $\tau = 2.8 - 3.1$ were insufficiently resolved for precise assignment to be made, and the absorption due to the aryl-methyl protons appeared as a singlet at $\tau = 8.05$, both signals being but little moved compared with the comparable absorptions of the parent methyleneamine.

3.4 Summary

New organozinc compounds have been made viz (i) methyleneamine adducts $(R_2C{=}NH)_2ZnCl_2$ (R = Ph, p-tolyl), $R_2C{=}NH.ZnX_2$ (R = Bu^t, X = Cl; R = p-tolyl, X = Ph), (ii) methyleneamino derivatives $(R_1R_2C{=}NZnX)_2$, $R_1 = R_2$ = Ph, p-tolyl, X = Cl; $R_1 = R_2$ = p-tolyl, X = Ph; R_1 = Ph, R_2 = p-tolyl, X = Ph and (iii) polymeric bis(di-p-tolylmethyleneamino)zinc $[\{(p\text{-tolyl})_2C{=}N\}_2Zn]_n$. Details of the azomethine stretching frequencies, ν(C=N), of these compounds are given (Table 3.1) and are assigned, as appropriate, to bridging or terminal methyleneamino ligands. The dimers $(R_1R_2C{=}NZnX)_2$ have azomethine stretching frequencies in the range (1600 - 1615) cm^{-1}, assigned to bridging methyleneamino ligands, and their structures have four membered $(ZnN)_2$ rings and three-co-ordinate zinc atoms. Dimeric phenyl(diarymethyleneamino)zinc $(R_1R_2C{=}NZnPh)_2$ $R_1 = R_2$ = p-tolyl, R_1 = Ph, R_2 = p-tolyl are much more stable to disproportionation when heated - unlike the related

$(Ph_2C{=}NZnPh)_2$ which affords the bis-product - and were obtained by the reactions of diphenylzinc with (i) di-p-tolylmethyleneamine and (ii) p-tolunitrile respectively. No evidence of reaction between di-t-butylmethyleneamine and diphenylzinc was observed.

Polymeric bis(di-p-tolylmethyleneamino)zinc was prepared only with considerable difficulty and in very low yield. Like its polymeric diphenyl analogue - but unlike dimeric bis(di-t-butylmethyleneamino)zinc, where there is unambiguous evidence of both terminal and bridging methyleneamino ligands - its infrared spectrum is dominated by the bridging units. Nevertheless the presence of a weak, broad absorption (ν ca $1664cm^{-1}$) is assigned tentatively to a terminally-attached methyleneamino ligand. In the polymeric structures of bis(diarymethyleneamino)zinc, $\left[(R_2C{=}N)_2Zn\right]_n$ R = Ph, p-tolyl, with both three and four co-ordinate zinc atoms, there must necessarily be terminally-attached methyleneamino ligands and, whether the assignment of the weak absorption to such is conclusive or not, such a C=N-Zn unit could well be near linear with substantial $(N\longrightarrow Zn)p\pi$ - $p\pi'$ bonding. The ^1H-NMR spectra of selected compounds, whilst generally of rather poor resolution, support the proposed structures of the new compounds.

CHAPTER 4

METHYLENEAMINO- AND ACETAMIDINO- DERIVATIVES OF TIN(II)

4.1 Introduction

This chapter, supplementing and extending some earlier work of D. G. Othen (80), describes the preparation and properties of (a) methyleneamine adducts and methyleneamino-derivatives and (b) N,N^{1}disubstituted acetamidine adducts and N,N^1-disubstituted acetamidino derivatives of two-covalent tin, viz.

$R_2C{=}NH.Sn^{II}Cl_2$ R = p-tolyl, Bu^t;
$(R_2C{=}NSn^{II}Cl)_2$ R = p-tolyl, Bu^t;
$\left[(R_2C{=}N)_2Sn^{II}\right]_n$ R = p-tolyl;
$MeC(NR)(NHR).Sn^{II}Cl_2$ R = Ph, p-tolyl;
$\left[MeC(NR)_2Sn^{II}Cl\right]_2$ R = p-tolyl;
$\left[MeC(NR)_2{}_2Sn^{II}\right]_n$ R = Ph, p-tolyl.

Their spectroscopic properties and proposed structures are described in the discussion section (Section 4.3), which starts on page 155 . As a preface to such discussion a short account is given of the stereochemistry of organotin(II) compounds; this is followed by the experimental section (Section 4.2).

4.1.1. Stereochemistry of Organotin(II) Compounds

(a) General features

The ground-state configuration of tin is $5s^2 5p_x{}^1 5p_y{}^1$ and covalent compounds in the II+ oxidation state could be formed

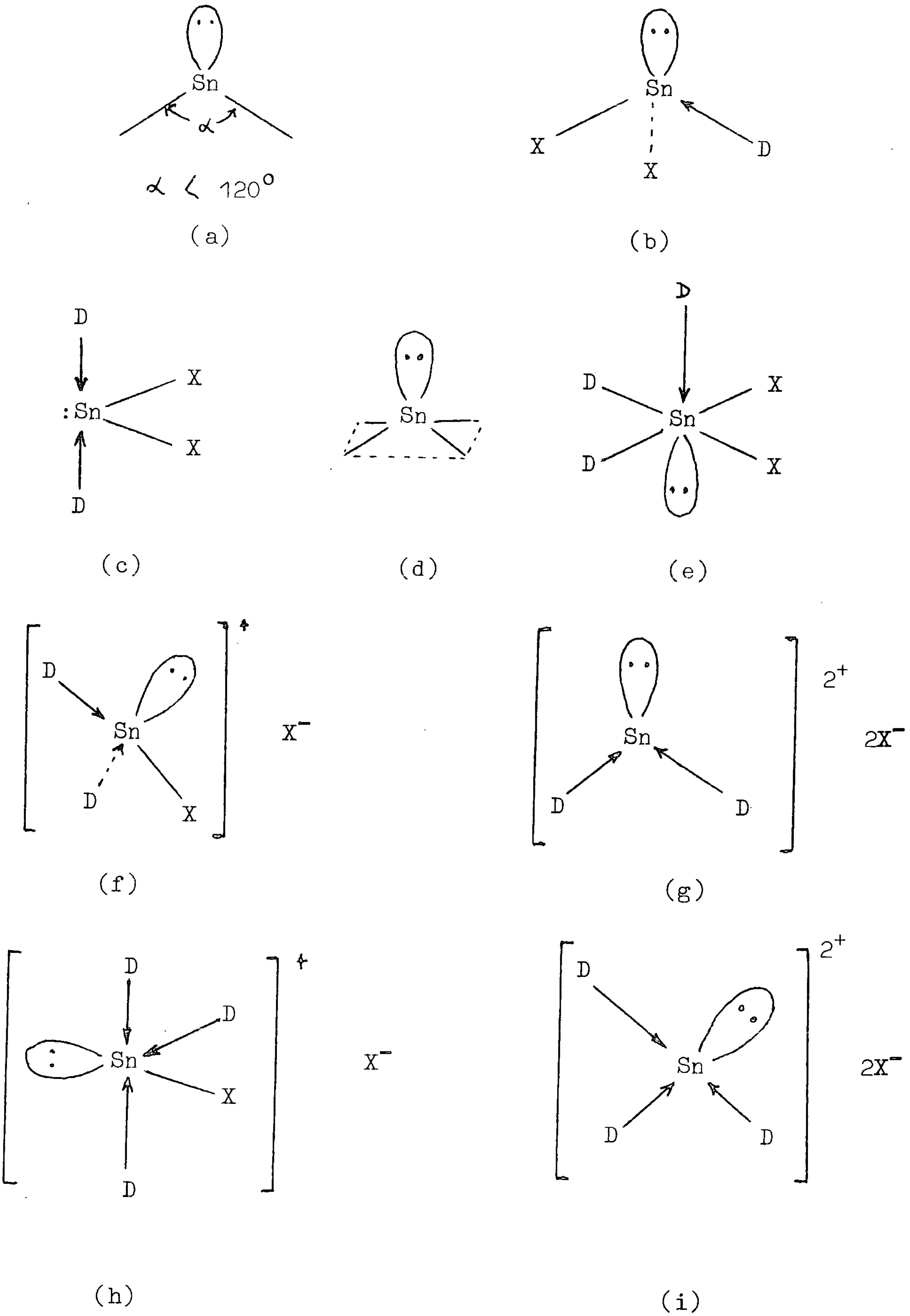

Sn
α
α < 120°
(a)
Sn
X
X
D
(b)
D
:Sn
X
X
D
(c)
Sn
(d)
D
D
D
Sn
X
X
(e)
D
Sn
D
X
+
X⁻
(f)
Sn
D
D
2+
2X⁻
(g)
D
D
Sn
X
D
+
X⁻
(h)
D
Sn
D
D
2+
2X⁻
(i)

Figure 4.1

simply by using the two unpaired electrons for bonding. The stereochemistry of the molecule so formed will depend upon the hybridisation of the valence shell electrons. Use of the two p orbitals would result in two covalent bonds mutually at right angles, but if the 5s electrons are incorporated in sp^2 hybridisation - and it is unusual for lone-pair electrons to be omitted from the hybridisation process (160)- the bond angle should approach 120^o, a trigonal planar arrangement of electron pairs (Figure 4.1 (a)). This could, however, be reduced significantly by repulsions between the bonds so formed and the very negative lone pair orbital. In the gas phase, compounds such as SnF_2 and $SnCl_2$ are of this type (161) with bond angle X - Sn - X ca 95^o. The bonding so far described, that of two-co-ordinate divalent tin, represents a situation where, because of the empty p-orbital on the tin atom, a state of co-ordinative unsaturation exists. Consequently such compounds are able to act as Lewis acids towards suitable donor ligands forming adducts which, at their simplest, are pyramidally shaped and based on sp^3 hybridisation (Fig. 4.1 (b)). Again lone pair - bond repulsions have the effect of lessening the bond angles below the tetrahedral value. Additionally there is a marked capacity for two-co-ordinate tin(II) compounds to polymerise via bridging constituents, the reaction involving overlap of the lone pair orbital of a monomer (the donor molecule) with an empty p orbital of an adjacent tin atom, so increasing the co-ordination number to three a very common value in divalent tin complexes. Anhydrous $SnCl_2$ (162), $SnCl_2.2H_2O$ (163), $Sn_2F_5^-$ (in $NaSn_2F_5$)

(164), $SnCl_2.py$ (165) and $(Me_2N)_2Sn.py$ (166) contain three co-ordinate tin(II). The stereochemically - important lone pair, conferring Lewis base activity may also be donated to other Lewis acids producing three co-ordinate tin(II) species such as $(C_5H_5)_2Sn^{II}\longrightarrow BF_3$ (167) and $\left[(Me_3Si)_2CH\right]_2Sn^{II}\longrightarrow Cr(CO)_5$ (168).

The extension of co-ordinate number beyond three is possible so long as the use of orbitals of higher energy (nd orbitals) is permitted and possible arrangements based on sp^3d and sp^3d^2 hybridisations, with one position in each case occupied by a lone pair of electrons, are illustrated in Figure 4.1 (c - e).

It has been suggested (169) that if two or more of the attached ligands are neutral donor molecules, and others are halogen atoms (or X groups of strong acids HX) then separation of halide ions may occur as shown in (Figure 4.1 f-i) being ionic versions of the molecular structures (Figure 4.1 c - e) Stoichiometrically (b) is a 1:1 adduct , (c), (f) and (g) are different 1:2 adducts whilst (e), (h) and (i) represent various 1:3 adducts. There are many known examples of tin(II) adducts, particularly of tin(II)halides, with oxygen donors such as dioxan (165) and water, with nitrogen donors such as amines (170), pyridine (171) and ammonia (172), and with sulphur donors such as thiourea and its derivatives. Evidence however concerning the structures of adducts of general description $SnX_2.x$(ligand) is somewhat incomplete and even scanty. Earlier, (173) structures such as $SnCl_2 9NH_3$ were rationalised by suggesting that additional ligand molecules beyond a certain number form a secondary shell around M^{n+}, but more recently the view seems to be that tin in its II+ compounds behaves primarily as a monofunctional acceptor, having a pyramidal primary co-ordination about tin, and that any donor molecules beyond the first may not be directly co-ordinated to tin. Whilst the structure of $SnCl_2 2H_2O$ (163) supports the latter rationale, and confirms the common three-co-ordinate state of tin, there is considerable uncertainty about adducts such as $SnCl_2$. $2,2^1$-bipyridyl (165) where it is unclear whether or not one or both nitrogen atoms are co-ordinated to tin. The higher co-ordination state would seem to exist in bis(8-quinolinolato)tin(II) (165) but several possibilities seem unresolved eg. only one ring might be chelated, tin-tin bonds might be present (174), or a four co-ordinate species with an electron pair in a fifth position could occur. In a study of $SnCl_2$ adducts with secondary amines and heterocyclic nitrogen-containing bases, such as quinoline, pyridine, β -picoline and piperidine, adducts of various molar proportions of donor: acceptor were made.

Such adducts as $2SnCl_2$.pip, $SnCl_2$.pip, and $SnCl_2$.2pip have been isolated and studied and on the basis of thermogravimetric, conductivity and infrared data a complete transitional series of $xSnCl_2y$ (ligand) has been postulated. Such species as $Sn^{II}ClL_2\ {}^{+}Cl^{-}$ preserve the three co-ordination of tin(II) and correspond to structure f (Figure 4.1) discussed earlier.

Much more convincing evidence of the use of d orbitals in hybridisation exists for the blue-black tin(II)oxide (176) with its square - pyramidal structure, described by sp^3d hybridisation of the available orbitals to give four covalent bonds to oxygen and a fifth orbital accommodating a lone pair of electrons.

Species of up to eight co-ordination have been characterised.

(b) Structural features of two-covalent organotin compounds

From information available on inorganic compounds of divalent tin, one would expect to find organotin(II) compounds of the type R_2Sn^{II}. Since the first compound of this type was made viz diethyltin(II) (177) a considerable number of such compounds has been reported. They are generally polymeric; in a few cases, monomeric compounds which slowly polymerise on standing have been obtained. So, for example, dimethyltin(II) has two molecular forms, linear chains of 10-100 catenated tin atoms and a six-membered ring of tin atoms (178). Diethyltin(II) is composed principally of $(Et_2Sn^{II})_7$, a seven-membered ring containing tin-tin bonds, but diphenyltin(II) has been described in a rich variety of ways, from colourless to bright red, from monomeric to polymeric, from a highly air sensitive to air stable material and with different solubilities (179). The position was clarified when, amongst other things, diphenyltin(II), as produced by the dehydrogenation of diphenyltin dihydride, was shown to consist of monomer units differing only in the degree and uniformity of polymerisation (180). With pyridine as catalyst the principal product was the hexamer, whilst employing dimethylformamide a good yield of pentamer was also obtained. The marked tendency of R_2Sn^{II} compounds to polymerise, caused by the presence of an empty p orbital on the tin(II) atom and its overlap with a lone pair orbital of an adjacent tin atom, results therefore in the formation of tin-tin bonds of tetravalent tin - $(Sn^{IV}R_2)_n$. Only a small number of monomeric organotin(II) derivatives are well established. They include dicyclopentadienyltin(II) (181) and its derivatives (182), also bis(phenyl-o-carboranyl)tin(II) viz. bis(2-phenyl-1,2-dicarba-closo-dodecaboran(12)-1-yl)tin(II) (183) a σ-bonded organotin(II) compound assumedly stabilised by steric effects. It is on this area - the stabilisation of divalent tin in a low co-ordinative state - that much recent interest has been focussed. Whilst bis(dimethylamido)tin(II) is dimeric in cyclohexane solution (Figure 4.2) and monomeric in the vapour phase (166) the 'self-reaction' can be blocked by using more sterically - demanding ligands, and as a consequence of

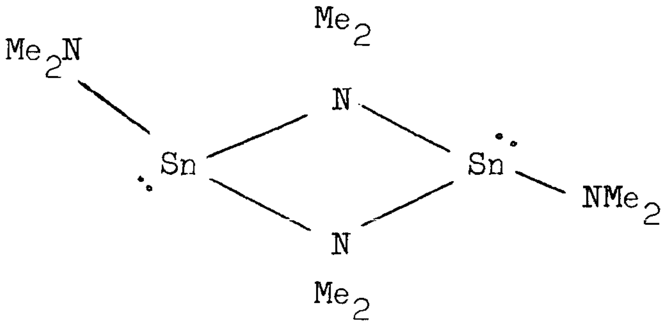


Figure 4.2

this the following compounds have been isolated and characterised: (a) bis(bis(trimethylsilyl)methyltin(II) - $\left[(Me_3Si)_2CH\right]_2Sn^{II}$, monomeric in both cyclohexane and benzene, but dimeric in the solid state (X-ray crystallography) (184); (b) bis(bis(trimethylsilylamido)tin(II) - $[(Me_3Si)_2N]_2Sn^{II}$, monomeric in solution (185) although elsewhere a dimeric structure is postulated (186); (c) bis(t-butyl, trimethylsilyl)tin(II)- (185) $[(Me_3C)(Me_3Si)N]_2Sn^{II}$ and (d) bis(2,2,6,6-tetramethylpiperidyl)tin(II) (187) (Fig. 4.3a) both of which are monomeric in solution. The molecular state of Sn^{II} (N(R)Si(Me$_2$)NR) (Figure 4.3 b) in solution depends

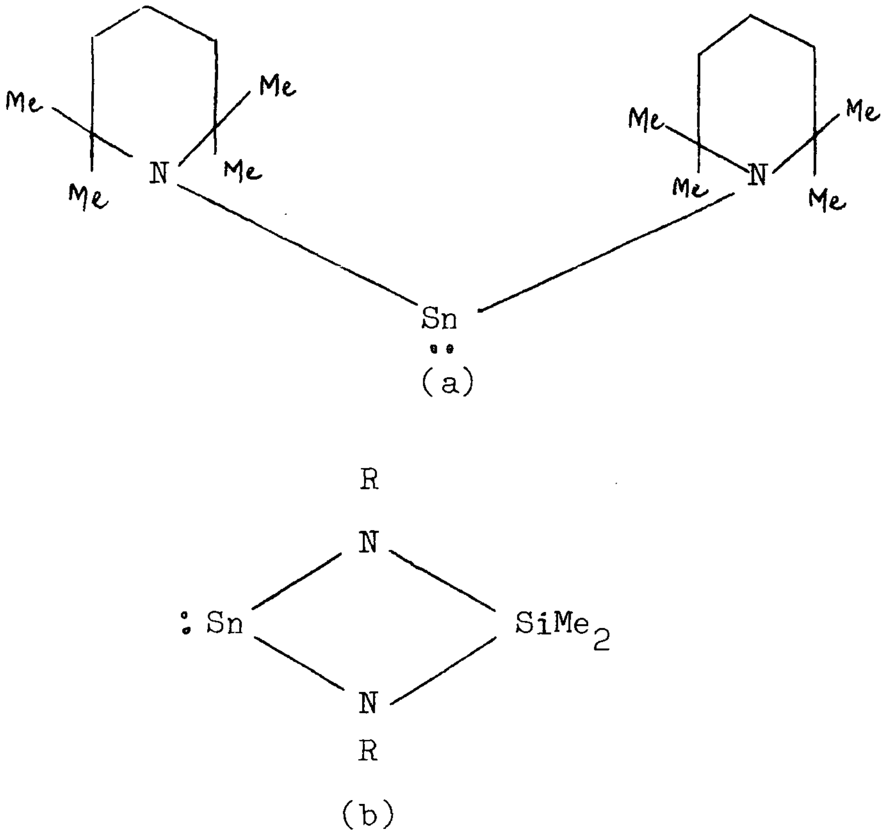


Figure 4.3

upon the nature of R. It is dimeric (R = Pr^i) and monomeric (R = Bu^t) and in the crystalline state has both a monomeric and dimeric phase (188). Other examples refer to a tin(II) carbamate (189), $2,2^1$-biphenylene-dicarbamatotin(II), presumed to be monomeric (Figure 4.4) obtained by the insertion of phenylisocyanate into the tin-oxygen bonds of 2,2^1-biphenylene-dioxytin(II), and a tin(II) diazole derivative (190), $[\mathrm{Sn\ N_2C_2Me_3}]_2$ which however polymerises

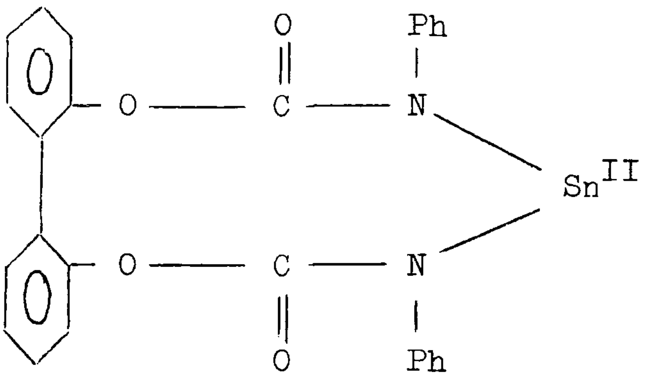


Figure 4.4

over a period of hours to give an (M-M) bonded tin(IV) polymer. Whilst two-co-ordinate divalent tin is not easily stabilised, three co-ordination is common and easily achieved by intermolecular bridging, and other means mentioned earlier, with tin acting as both a donor and acceptor atom. Such a common co-ordination state is also achieved by chelation as in the 1,3-diketonate halides (191) of tin(II) ($\mathrm{XSn^{II}O(CR)CHO(CR)}$; R = Me).

Two arrangements are possible for the four-co-ordinate state, one based on a trigonal bipyramid with the lone pair occupying an equatorial site eg. bis(N,N-diethyldithiocarbamato(tin(II) - $\mathrm{Sn^{II}[S_2CNEt_2]_2}$ (192), and bis(1-phenylbutane - 1,3-dionato)tin(II) - $\mathrm{Sn^{II}(PhCO.CH.COMe)_2}$ (193). The other possible four-co-ordinate arrangement, based on a tetragonal pyramid with an apical lone pair, is exemplified by tin(II) phthalocyanine (194) and tin(II) N,N^1- ethylenebis-acetylideneimine (195) (Figure 4.5). The tin atoms in the bis(thiourea)complex of tin(II) sulphate (196) are also four co-ordinate, linked to two sulphate-oxygen atoms and to two thiourea-sulphur atoms in distorted pyramidal sites.

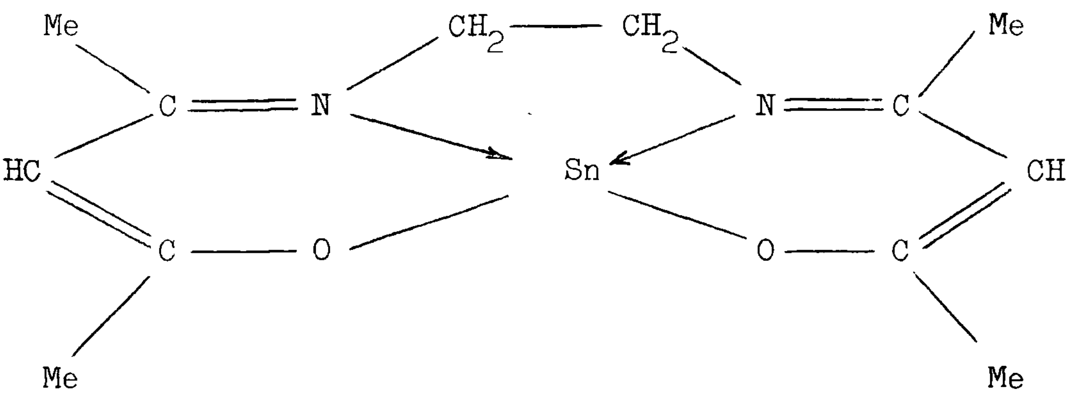


Figure 4.5

No less than three different types of six co-ordination have been characterised. In dihydrogenethylenediaminetetra-acetatostannate(II) the tin atom is centred in the rectangular face of a distorted trigonal prism, (197) whilst the tin(II) atoms of the mixed valency $Sn_2(O_2C.C_6H_4NO_2O)_4OTHF$ experience pentagonal pyramidal co-ordination, the tin's lone pair of electrons occupying the remaining axial position (198). In ditin(II)ethylenediamine-tetraacetate dihydrate (199) however, half the tin atoms are in similar pentagonal bi-pyramidal sites with an equat orial lone pair, but the remaining tin atoms are seven co-ordinate in a rather complex way in which the lone pair is again sterochemically active. Eight co-ordination has been observed in $Sn^{II}HPO_4$ (200).

4.2 Experimental

In general methyleneamino- and amidino- derivatives of tin(II), i.e. molecules possessing the Sn^{II}-N bond, are very sensitive to the presence of atmospheric moisture and oxygen, particularly when in solution. Whilst all reactions, and manipulations, were therefore performed under dry nitrogen, partial sample decomposition was evidenced in, for example, the molecular weights, - as determined by cryoscopy- of some of the tin(II) compounds.

(i) Preparation of di-p-tolymethyleneamine tin(II) dichloride adduct.

4.3089g. of di-p-tolylmethyleneamine (20.62)mm was dissolved in ca 40cm^3 dry toluene and added to a suspension of 3.9089g anhydrous tin(II) chloride (20.62mm) in 30cm^3 dry toluene, with stirring. The mixture was refluxed for 20 hours and the slightly cloudy pale yellow solution was filtered and cooled to ca -20°C. A mass of off-white solid was produced overnight, it was washed with cold dry toluene and then pumped solvent free. The product was identified as the adduct di-p-tolylmethyleneaminotin(II)dichloride $(p\text{-}CH_3C_6H_4)_2CNH.SnCl_2$, m.p. 138 - 140°.

Found: C = 44.1; H = 3.8; N = 3.3; Cl = 18.0%

$C_{15}H_{15}NSnCl_2$ requires C = 45.1; H = 3.8; N = 3.5; Cl = 17.8%

ν max (Nujol Mull) 3233s, 1606vs, 1580vs, 1548vs, 1540w, 1504m, 1415m, 1310w, 1290w, 1262vw, 1238vs, 1212m, 1192s, 1184vs, 1158s, 1120w, 1081wbr, 1019m, 972w, 957m, 916s, 893vs, 856w, 837vs, 822s, 807w, 782m, 743vs, 730w, 697w, 674w, 632m, 588s, 562w, 476vs, 417m cm^{-1}.

(ii) Preparation of di-t-butylmethyleneamintin(II)dichloride adduct.

5.86 cm^3 of di-t-butylmethyleneamine (32.72mm) was added to a suspension of 6.2037g of anhydrous tin(II)chloride (32.72mm) in 60 cm^3 dry toluene with stirring. The mixture was refluxed for 20 hours, filtered to remove a small amount of suspended material, and the filtrate cooled to ca -20°C. A mass of off-white solid was produced overnight and was identified as the adduct di-t-butylmethyleneaminetin(II)dichloride $^{t}Bu_2CNH.Sn^{II}Cl_2$, m.p. 70-72°.

Found: C = 34.0; H = 6.1; N = 3.9; Cl = 21.2%.

$C_9H_{19}NSnCl_2$ requires C = 32.7; H = 5.8; N = 4.2; Cl = 21.5%

ν max (Nujol Mull) 3290s, 3160s br, 1676s, 1634m, 1598vs, 1585vs, 1401s, 1360s, 1320w br, 1225vs, 1203m, 1155w, 1082w, 1047m, 1034w, 1023w, 972s, 926m, 908m, 865vs, 846m, 794m, 729vs, 1096w, 658w, 589m, 551m, 482w, 469m, 410br w, cm^{-1}.

(iii) Preparation of di-p-tolylmethyleneaminotin(II) chloride dimer.

20.86 mmol. of di-p-tolylmethyleneaminolithium in ca 30cm^3 ether/hexane was added to a suspension of 3.9543g. anhydrous tin(II)chloride (20.86mm) in 40cm^3 dry ether at -196°C. The mixture was allowed to warm to room temperature with stirring, then stirred at room temperature overnight.

All solvent was then removed under vacuum, replaced with ca 100cm^3 dry toluene, refluxed for 30 minutes and filtered whilst hot, giving a white solid (LiCl) and an orange solution. After cooling to room temperature, the filtrate deposited orange crystals of di-p-tolylmethyleneaminotin(II) chloride dimer, $[(pCH_3C_6H_4)_2CNSn^{II}Cl]_2$, m.p. 190-198^o.

Found: C = 49.6; H = 4.3; N = 3.6; Cl = 9.3%
M, by cryoscopy 646.

$C_{30}H_{28}N_2Sn_2Cl_2$ requires C = 49.7; H = 3.9; N = 3.9
Cl = 9.8%; M 724

ν max (Nujol Mull): 1606vs, 1577vs, 1550vs, 1501w, 1492w, 1405v w br, 1313w, 1308vw, 1297s, 1258s, 1211m, 1186s, 1181s, 1156w, 1117m, 1041w br, 1019m, 982m, 977w, 961w, 936s, 892w br, 858m, 823vs, 788m, 746vs, 732vs, 696m, 681m, 625s, 493s, 474s br, 407w, 362sh cm^{-1}.

(iv) Preparation of di-t-butylmethyleneaminotin(II)chloride

A solution of 32.53 mmol of di-t-butylmethyleneaminolithium in ca 30cm^3 ether/hexane was added to a suspension of 6.68g. anhydrous tin(II)chloride (32.53mm) in 40cm^3 dry ether at -196^{o}C. The mixture was allowed to warm to room temperature with stirring, and then stirred overnight. Solvent was removed under reduced pressure, replaced with 60cm^3 dry toluene, refluxed for 10minutes and then filtered when hot giving a grey solid (LiCl) and a dark brown solution. Cooling of the filtrate gave a yellow microcrystalline solid identified as di-t-butylmethyleneaminotin(II)chloride dimer,

$[Bu^{t}_{2}CNSn^{II}Cl]_{2}$ m.p. = 75 - 78°C,

Found: C = 36.9; H = 6.4; N = 4.5; Cl = 12.1%

M, by cryoscopy, 471.

$C_{19}H_{36}N_{2}Sn_{2}Cl_{2}$ requires C = 36.7; H = 6.1; N = 4.8;
Cl = 12.1% M, 589.

ν max (Nujol Mull) 1592w br, 1551vs br, 1390sh, 1376sh, 1261w, 1207s, 1040m, 962s, 923w, 832w, 795w, 733w, 721w, 656m, 600s, 490s, 383sh cm^{-1}.

(v) Preparation of bis(di-p-tolylmethyleneamino)tin(II) dimer.

A solution of 21.91 mmol di-p-tolylmethyleneaminolithium in ca 70cm^3 ether/hexane was added to a suspension of 3.1736g. of anhydrous tin(II)chloride (10.95mm) in 40cm^3 dry ether at -196°C. It was allowed to warm to room temperature with stirring, and then stirred overnight giving an orange-red suspension. All solvent was removed under reduced pressure replaced with 50cm^3 dry toluene, warmed to reflux temperature, and filtered whilst hot. The deep red filtrate was concentrated and cooled overnight at 20°C at which temperature it deposited a deep red microcrystalline solid, bis(di-p-tolylmethyleneamino)tin(II) dimer, $[\{(p\text{-}CH_3C_6H_4)_2CN\}_2Sn^{II}]_2$, m. p. 118 - 125°.

Found: C = 67.6; H = 5.3; N = 5.2; Sn = 21.9%

M, by cryoscopy, 865.

$C_{60}H_{56}N_{4}Sn_{2}$ requires C = 67.3; H = 5.2; N = 5.2;
Sn = 22.1; M, 1069.

ν max (Nujol Mull) 1609vs, 1589vs br, 1558 s br, 1502m, 1409m br, 1360s br, 1307m, 1288s, 1260s br, 1211s, 1193w, 1179vs, 1150m, 1112s, 1038m br, 1021s, 951m, 922s, 891s, 826vs br, 803s, 782s br, 734vs, 671s br, 630s, 604s br, 586m, 471vs, 365sh cm^{-1}.

(vi) Preparation of N,N^{1}diphenylacetamidinetin(II) dichloride adduct

2.92g. of anhydrous tin(II) chloride (15.45mm) was mixed with 3.2494g. N,N^1-diphenylacetamidine (15.45mm) in 40cm^3 dry toluene at room temperature with stirring. Whilst partial solution occurred, the reaction mixture was refluxed for 18 hours and the slightly cloudy solution was filtered hot. To the colourless filtrate 10cm^3 dry hexane was added and then cooled to -20^{o}C. A white solid was produced overnight and was identified as N,N^1-diphenylacetamidine-tin(II) dichloride, $CH_3C(NPh)(NHPh).SnCl_2$, m.p. 107-109^{o}C.

Found: C = 41.6; H = 4.0; N = 7.1; Cl = 17.6%

$C_{14}H_{14}N_2SnCl_2$ requires C = 42.0; H = 3.5; N = 7.0;
Cl = 17.8%

ν max (Nujol Mull) 3275vs, 1638s, 1602s, 1597s, 1570vs, 1500s, 1486s, 1423m, 1400vs, 1258w, 1226w, 1216m, 1172w, 1148vw, 1076w br, 1040m, 1025m, 1005m, 998vw, 969m, 856m, 822vw, 812m, 765s, 748s, 728w br, 698vs, 670m, 638v w br, 614w, 563w, 537w, 521w, 517w, 508vw, 495m, 452m, 430m, 397s, cm^{-1}.

(vii) Preparation of N,N^1-di-p-tolylacetamidinetin(II) dichloride adduct.

2.49g. of anhydrous tin(II) chloride (18.41mm) was mixed with 4.3858g. N,N^1-di-p-tolylacetamidine in 45cm^3 dry toluene at room temperature with stirring. The reaction mixture was refluxed for 20 hours, filtered whilst hot and the filtrate cooled to -20°C. A white solid was formed overnight and identified as N,N^1-di-p-tolylacetamidine-tin(II) dichloride, $CH_3C(NC_6H_4pCH_3)(NHC_6H_4pCH_3).\ SnCl_2$ m.p.= 127-131°C.

Found: C = 45.4; H = 4.6; N = 6.0; Cl = 17.0%

$C_{16}H_{18}N_2SnCl_2$ requires C = 44.9; H = 4.2; N = 6.5; Cl = 16.6%.

ν max (Nujol Mull) 3272vs, 1638m, 1608sh, 1588vs, 1564vsbr, 1512s, 1500s, 1408s, 1395s, 1347m, 1317w br, 1285vw, 1232m, 1204m, 1187w, 1175w, 1108w, 1037s, 1027m, 1019m, 972vs, 947w, 939m, 866s, 850s, 840m, 824s, 819vs, 806s, 780m, 757m, 730w, 714s, 696vw, 677s, 644m, 632m, 623vw, 617vw, 572m, 564m, 523vs, 502vs, 469w, 451s, 442s, 415vw cm^{-1}.

(viii) The Preparation of N,N^1-di-p-tolylacetamidinotin(II) chloride dimer.

20.20mmol of N,N^1-di-p-tolylacetamidinolithium in ca 100cm^3 ether/hexane was added to a suspension of 3.83g. anhydrous tin(II)chloride (20.20mm) in 30cm^3 dry ether at -196°C. The mixture was allowed to warm to room temperature with stirring, and stirring was continued overnight. Solvent was removed under pressure, replaced with 30cm^3 dry toluene, refluxed briefly and then filtered whilst hot. After cooling to room temperature, 15cm^3 dry hexane was added to the colourless filtrate which was then cooled to -20^{o}C. A white microcrystalline solid formed rapidly and was identified as N,N^1-di-p-tolylacetamidinotin(II)chloride, $\left[CH_3C(NC_6H_4p.CH_3)_2Sn^{II}Cl\right]_2$, m.p. = 250 - 270^o (d).

Found: C = 50.1; H = 4.2; N = 7.1; Cl = 9.2%

M, by cryoscopy, 656.

$C_{32}H_{34}N_2Sn_2Cl_2$ requires C = 49.1; H = 4.3; N = 7.1;

Cl = 9.1; M, 782.

ν max (Nujol Mull) 1638w, 1610w br, 1569w, 1502vs, 1491vs, 1410vs, 1364vs, 1312m, 1290s, 1271m br, 1250w br, 1220s, 1174w, 1110m, 1040w br, 1033w, 1078m, 986w, 960w, 939w, 854vs, 845m, 830w, 820w, 807s, 790w, 750w, 724w br, 710m, 662w, 654w, 642vw, 629w br, 587vw, 572m, 561m, 524s, 510w, 498w, 436w, 415w, 377w, cm^{-1}.

(ix) Preparation of bis(N,N^{1}diphenylacetamidino)tinII

20.01 mmol of N,N^1-diphenylacetamidinolithium in ca 100cm^3 dry ether/hexane was added to a suspension of 1.8979g. of anhydrous tin(II)chloride (10.00mm) in 30cm^3 dry ether at -196^{o}C. The mixture was allowed to warm to room temperature with stirring, and stirring was continued overnight. Solvent was removed under pressure from the buff-coloured suspension, replaced with 60cm^3 dry toluene and refluxed for 5 minutes prior to filtration. The pale-yellow filtrate was concentrated and a little anhydrous hexane added. A white microcrystalline solid was formed and identified as bis(N,N^1-diphenylacetamidino)-tin(II), $\left[\left\{CH_3C(NPh)_2\right\}_2Sn^{II}\right]_n$, m.p. = 220-226°.

Found: C = 62.2; H = 4.9; N = 10.0; Sn = 22.3%

$C_{28}H_{26}N_4Sn$ requires C = 62.6; H = 4.8; N = 10.4; Sn = 22.1%

ν max (Nujol Mull) 1630m, 1592vs, 1573w, 1530vs br, 1486vs br, 1414s br, 1355w, 1332w, 1306w, 1287m, 1268s, 1246w br, 1220vs, 1170m, 1167m, 1154m, 1112vw br, 1071s, 1026s, 1003m, 977m, 962w, 956w, 911w, 907s, 902s, 870vw br, 829vs, 812m, 772s, 753s, 743vs, 700vs, 694vs, 661m, 649w, 618w, 605vw br, 574w, 561m, 520vs, 486w, 425m cm^{-1}.

(x) The Preparation of bis(N,N^1-di-p-tolylacetamidino)tin(II)

22.62 mmol of N,N^1-di-p-tolylacetamidinolithium in ca 80cm^3 ether/hexane was added to a suspension of 2.1462g. anhydrous tin(II)chloride (11.31mm) in 20cm^3 dry ether at -196°C. The mixture was allowed to warm to room temperature with stirring, and stirring was continued overnight. Solvent was removed under reduced pressure, replaced with 40cm^3 dry toluene, refluxed for a few minutes and then filtered whilst hot. The yellow filtrate was cooled to -20° and off-white crystals were formed overnight, identified as bis(N,N^1-di-p-tolylacetamidino)tin(II), $\left[\left\{CH_3C(NC_6H_4pCH_3)_2\right\}_2Sn^{II}\right]_n$, m.p. = 205 - 213°C.

Found: C = 64.7; H = 5.7; N = 9.6; Sn = 20.0%

$C_{32}H_{34}N_4Sn$ requires C = 64.8; H = 5.7; N = 9.4; Sn = 20.0%

ν_{max} (Nujol Mull) 1635w br, 1610m, 1566m, 1528s br, 1510vs br, 1498vs br, 1352s, 1357s, 1300s, 1245sh, 1219vs, 1173m, 1104s, 1015w br, 978w, 955w, 933w, 852vs, 839vs, 826w, 815m, 798m, 778w br, 747m, 727w, 722w br, 707m, 650w, 622w, 546s, 516vs, 493m, 450w br, 417w br, 365m cm^{-1}.

4.3. Discussion

4.3.1. Preparation and stability of the new tin(II) compounds.

Compared with other main group 4 elements, the chemistry of tin(II) compounds has been a relatively neglected area of research. Literature perusal reveals few well-defined covalent tin(II) compounds and in particular the tin(II)-nitrogen bond has been very elusive. Indeed the first unequivocal identification and characterisation of the tin(II) - nitrogen bond was claimed when bis(dimethylamido)tin(II) was synthesised in 1974 (166). The principal cause of inactivity in the field of tin(II) compounds is considered to be, in the first major review of the chemistry of bivalent tin, the preparative and analytical difficulties arising from the ease of oxidation of the element in its lower oxidation state (161).

Despite the extreme care taken in the handling of the new compounds which comprise this present work, the evidence of partial decomposition, whilst at a variable rate, was compelling. Sensitivity to atmospheric oxidation is enhanced in solution, and molecular weight determinations, by cryoscopy, where such were possible, gave rise to values which were consistently low although greater than the value attributable to the monomeric species. Some of the compounds were highly coloured eg $(R_2CN)_2Sn^{II}$, R = Ph, p-tolyl) caused presumably by the interaction of the Sn^{II}-N bond with the C=N group and subsequent modification of the π-system of the attached aromatic rings, rather than an N ⟶ Sn (p ⟶ d) electronic transition. Exposure to the air for short periods of time caused hydrolysis to the parent methyleneamine or amidine, indeed the isolation of $Ph_2CNH(Ph_2CNSn^{II}Cl)_2C_7H_8$ whilst preparing the dimeric diphenylmethyleneaminotin(II)chloride, $(Ph_2CNSn^{II}Cl)_2$, was a consequence of such partial hydrolysis (80). During exposure to air coloured compounds rapidly whiten, and after longer exposure there is evidence in some instances of a very broad band in the infrared spectrum at (520-560)cm^{-1}, assignable to a tin-oxygen stretching vibration (201). In addition to the hydrolysis of the highly reactive tin^{II}-nitrogen bond, some direct oxidation by oxygen may also occur, a behaviour typical of dialkylamido-tin(II) compounds eg $\left[(Me_3Si)_2N\right]_2 Sn^{II}$ (186).

With the exception of the simple adducts of tin(II) dichloride and the appropriate methyleneamines and amidines, the new compounds were prepared exclusively by reacting the corresponding lithio derivative with tin(II) dichloride, usually in anhydrous ether, with the elimination of lithium chloride (<u>equation 4.1 - 4.2</u>).

$$SnCl_2 \;+\; n\,AmLi \longrightarrow Am_nSnCl_{2-n} \;+\; nLiCl \qquad 4.1$$

(Am represent the N,N^1-diphenylacetamidino group $MeC(NPh)_2$)

$$SnCl_2 + nR_2C{=}NLi \longrightarrow (R_2CN)_nSnCl_{2-n} + nLiCl \qquad 4.2$$

Such a route employing N-lithiated reagents has been used quite extensively as a means of synthesising Metal - nitrogen bonds and examples of these include $PhC(NMe)_2MPh_3$ (202) (M = Sn^{IV}, Si), $\left[(CH_3)_2N\right]_2Sn^{II}$ (166), $\underset{\ddot{Sn}}{Me_3SiN\text{-}(CH_2)_n\text{-}NSiMe_3}$ (n = 2,3,4) (186), $\left[(CH(SiMe_3)_2\right]_2Sn^{II}$ (184) and $Sn^{II}\left[\overline{NCMe_2(CH_2)_3CMe_2}\right]_2$ (187).

It was hoped that in the new compounds synthesised, the ligands employed, i.e. methyleneamino and amidino groups, would have a steric requirement sufficient to stabilise divalent tin in a two-co-ordinate condition but this was not achieved. All the new derivatives in fact attain a co-ordination state greater than two by means which include the use of nitrogen bridges. The new compounds are listed in Table 4.1 and to facilitate discussion they are arranged in two groups.

Table 4.1

The New Tin(II) Compounds

Group A: Methyleneamino- derivatives

$(p\text{-tolyl})_2CNHSn^{II}Cl_2$	White Solid
$Bu^t{}_2CNH.Sn^{II}Cl_2$	White Solid
$\left[(p\text{-tolyl})_2CNSn^{II}Cl\right]_2$	Orange Crystals
$\left[Bu^t{}_2CNSn^{II}Cl\right]_2$	Yellow Microcrystalline Solid
$\left[\left\{(p\text{-tolyl})_2CN\right\}_2Sn^{II}\right]_2$	Red Microcrystalline Solid

Group B: N,N^1-diaryacetamidino- derivatives

$CH_3C(NPh)NHPh.Sn^{II}Cl_2$	White Solid
$CH_3C(NC_6H_4pMe)NHC_6H_4pMe.Sn^{II}Cl_2$	White Solid
$\left[CH_3C(NC_6H_4pMe)_2Sn^{II}Cl\right]_2$	White Solid
$\left[\left\{CH_3C(NPh)_2\right\}_2Sn^{II}\right]_n$	Off-White Micro-crystalline Solid
$\left[\left\{CH_3C(NC_6H_4pMe)_2\right\}_2Sn^{II}\right]_n$	Off-White Micro-crystalline Solid

4.3.2. Characterisation and spectroscopic properties of methyleneamine adducts and methyleneamino derivatives of tin(II)chloride

The adducts $R_2C{=}NH.SnCl_2$ (R = Ph, (80) p-tolyl, Bu^t) were prepared by refluxing (in toluene) equimolar mixtures of the appropriate methyleneamine and anhydrous tin(II) chloride for about 24 hours, followed by cooling to about -20^o. Whilst no evidence of their molecular state was obtained, they are likely to be monomers with three-co-ordinate tin.

A previous study, of a series of di- and tri-substituted methyleneamines ($R^1R^2C{=}NR^3$), (8) on the effect of co-ordination to a proton or boron(III) fluoride has shown that the azomethine stretching frequencies, ν(C=N), increased noticeably by amounts which depended upon the nature of R^1, R^2 and R^3. The shift of the C=N stretching frequency upon co-ordination is in the opposite sense to that observed with co-ordinated phosphine oxides, sulphoxides, ketones and other donor groups. Indeed the co-ordination of ketones R^1_2CO, (203-205) or other carbonyl compounds RCOX, (204-206) to Lewis acids MX_n through the carbonyl oxygen is usually accompanied by a marked *decrease* in the carbonyl stretching frequency $\nu(C=O)$. The generality of this finding has been used not only to identify the co-ordination site in compounds with more than one potential donor atom (204,207), but also as a guide to the relative acidities of a series of Lewis acids (206). The increase in $\nu(C=N)$ of methyleneamines on co-ordination may be compared with the increase which invariably occurs in $\nu(C\equiv N)$ of nitriles (6) on the formation of adducts $RC\equiv NMX_n$. Although this increase is thought to arise in part from the mechanical constraint applied to the nitrogen of the co-ordinated nitrile (208), there is X-ray crystallographic evidence (209) to suggest that co-ordination is accompanied by a shortening of the $C\equiv N$ bond i.e. a fractional increase in its bond order. There may well be a comparable fractional increase in the $C=N$ bond order of methyleneamines on co-ordination.

When methyleneamines are co-ordinated to *weak* Lewis acids, the change in the azomethine stretching frequency $\nu(C=N)$ is much less pronounced. Co-ordination of diphenylmethyleneamine, $Ph_2C=NH$, to boron (59), aluminium (62) or gallium (63) alkyls revealed insignificant changes in $\nu(C=N)$, results which were considered to be consistent with very weak co-ordination.

Similar observations are made with the adducts of various methyleneamines with tin(II)chloride (*see Table 4.2*).

Table 4.2

Methyleneamine Stretching Frequencies ν (C=N) of the Parent Methyleneamine, their Hydrochlorides and their Boron(III) Chloride and Tin(II) Chloride Adducts

$R_2C=NH$	$R_2C=NH.HCl$	$R_2C=NHBF_3$	$R_2C=NHSnCl_2$
R = Ph 1603[a]cm^{-1}	1653cm^{-1}	1628cm^{-1}	1594cm^{-1}
R = p-tolyl 1610cm^{-1}	1643cm^{-1}	1626cm^{-1}	1606cm^{-1}
R = Bu^t 1604[a]cm^{-1}	1670cm^{-1}	1672cm^{-1}	(1670)* 1598cm^{-1}

a liquid film; all other figures refer to Nujol Mulls.

* caused by $Bu^t{}_2C=NH_2{}^+$

It may be seen that ν (C=N) for co-ordinated molecules differs but slightly from the parent methyleneamine and may conceivably be regarded as arising from the different physical state of the samples. Small, but unspecified, changes are also reported for corresponding adducts of tin(II)chloride and quinoline, pyridine, β-picoline and piperidine, whilst in the compound $(Ph_2C=N)_3HSn_2Cl_2C_7H_8$ (80) the stretching frequency ν (C=N) assigned to the co-ordinated methyleneamine molecule is 1600cm^{-1}. In all, situations in which the weak Lewis acids tin(II)chloride co-ordinates to nitrogen-containing bases, as outlined above, contrast sharply with the change of ν(C=N) to higher energies as observed when strong Lewis bases, including tin(IV)chloride, are similarly co-ordinated.

Whilst the greatest attention has been given to the effect of co-ordination on the azomethine stretching frequency, ν(C=N), the band assignable to the N-H stretching frequency also undergoes change.

Co-ordination to tin(II)chloride causes this band to sharpen and move to slightly lower frequency, but the broadness of these bands in some of the parent methyleneamines prevents precise measurements of such changes.

Whilst the ^{1}H-NMR spectra of the adducts seemed unlikely to provide further structural information they were recorded as solutions in $CDCl_3$ at about 42°C (Table 4.3)

The H^1-NMR spectra of the methyleneamine-tin(II) chloride adducts are relatively simple. All the peaks in the methyleneamine spectra referred to appear to be moved to lower fields on co-ordination to tin(II)chloride, the changes being, in general, most marked in the case of the N-H peak. These chemical shifts on co-ordination are in the direction expected on electronic grounds since co-ordination through nitrogen should result in deshielding of the nitrogen-attached proton and, to a lesser extent, the adjacent protons, but in a different direction to that observed in the organoaluminium- (62) and organogallium-diphenylmethyleneamine (63) systems already mentioned. Mass spectra were obtained for each of these compounds but no tin- containing fragements were generated.

Table 4.3

^{1}H-NMR Spectroscopic Data For Some Methyleneamino-tin(II) Chloride Adducts

Compound	τ^a values ppm.		
	Ar——H	CH_3	N——H
$Ph_2C=NH$	2.07, 2.14, 2.18, 2.3, 2.4(m) (10)	-	-0.16s (1)
$Ph_2C=NH.SnCl_2$	1.90, 2.0, 2.08, 2.2 (m) (10)	-	-0.45s (1)
(p-tolyl)$_2$C=NH	2.07, 2.18, 2.52, 2.83 (m) (8)	7.27s(6)	0.12s (1)
(p-tolyl$_2$C=NH.SnCl$_2$	1.80, 1.93, 2.03, 2.28, m (8)	7.12s(6)	-0.53sbr(1)
$Bu^t{}_2C=NH$	-	8.10s (18)	-0.15sbr(1)
$Bu^t{}_2C=NH.SnCl_2$	-	8.07s (18)	-0.30sbr(1)

Relative intensities in parentheses; a: relative to τ (TMS) = 10ppm (external reference)

s = singlet; br = broad

m = unresolved multiplet

For the methyleneaminotin(II) derivatives, $(R_2C{=}NSn^{II}X)_n$ R = Ph, (80) p-tolyl, Bu^t, X = Cl, the evidence taken overall suggests that they are probably dimeric. In all cases the determination of molecular weight, by cryoscopy in benzene, was hampered by sample decomposition. Nevertheless the values obtained, although less than that required by the dimeric molecules, were significantly greater than the monomeric values. The infrared spectra of these compounds shows only one azomethine stretching frequency ν (C=N), and this is assigned to a bridging methyleneamino unit (Table 4.4). The ^{1}H-NMR spectrocopic data for these compounds are recorded in Table 4.5 and are in accordance with their proposed structure (Figure 4.6 ; R = Ph, p-tolyl, Bu^t, X = Cl) in which stability has been gained by intermolecular Sn-N bridging bonds (cf Sn = halogen bridges in the associated cyclopentadienyl-tin (II)- chloride and - bromide)(210). Such bridging bonds

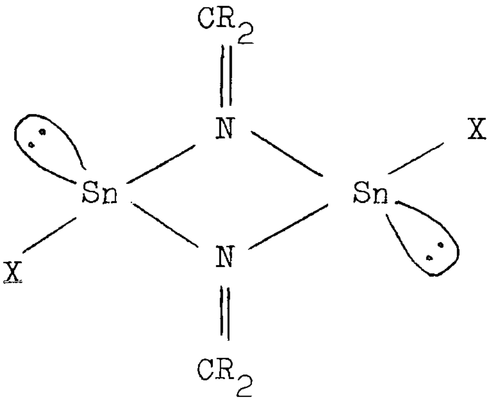


Figure 4.6

preclude polymerisation via tin-tin bonds with the formation of tin(IV) species. Such a structure has been confirmed for dimeric diphenylmethyleneaminotin(II)chloride.

Table 4.4

Azomethine Stretching Frequencies, ν (C=N), For Some New Methyleneamino Derivatives of Tin(II)

Compond	ν (C=N) cm^{-1}	
	Terminal	Bridging
$[Ph_2CNSn^{II}Cl]_2$ (80)	-	1564
$[(p\text{-tolyl})_2CNSn^{II}Cl]_2$	-	1578
$[Bu^t{}_2CNSn^{II}Cl]_2$	-	1551
$[(Ph_2CN)_2Sn^{II}]_2$ (80)	1600	1570
$[\{(p\text{-tolyl})_2CN\}_2Sn^{II}]_2$	1608	1589
$[(Bu^t{}_2CN)_2Sn^{II}]_n$ (80)	1628	1560

All spectra were recorded as Nujol Mulls

$(Ph_2C{=}NSn^{II}Cl)_2$, by X-ray crystallography (211). It reveals in particular a basic four-membered $(SnN)_2$ ring, a three-co-ordinate pyramidal environment of the tin atoms and the absence of metal-metal bonds. The mass spectra of the methyleneaminotin(II) compounds are discussed later, but in general they were disappointingly unproductive.

The bis(methyleneamino)tin(II)derivatives, $(R_2C{=}NSnX)_n$ R = Ph (80), p-tolyl, Bu^t (80), X = R_2CN, also showed evidence of partial sample decomposition. Nevertheless the determined molecular weights, by cryoscopy, suggest a dimeric structure exists in solution for $\left[(R_2C{=}N)_2Sn\right]_n$ R = Ph, p-tolyl, but the very low value for bis(di-t-butylmethyleneamino)tin^{II} - consistently below the monomeric formula weight - allows the feasibility of a monomeric state for this compound. However, the infrared spectra of these bis(methyleneamino)tin(II) derivatives show two azomethine stretching frequencies, ν(C=N), which are assigned to bridging and terminal methyleneamino ligands (Table 4.4) observations which are quite consistent with the proposed associated structure for the compounds $\left[(R_2C{=}N)_2Sn\right]_2$, R = Ph, p-tolyl, Bu^t, in the solid state (Figure 4.6. page 163). Few assignments for Sn^{II}-N stretching frequencies have been reported. For bis(dimethylamido)tin(II), $\left[(Me_2N)_2Sn^{II}\right]_2$, a band at 440cm^{-1} has been assigned to Sn^{II}-N stretching (166), and it has been suggested that for $\left[\{(Me_3Si)_2N\}_2Sn^{II}\right]_2$ and some related compounds, $\nu_{as}(Sn^{II}{-}N)$ lies at (350-400) cm^{-1} with the symmetric vibration some 10-22cm^{-1} below this.(186). Whilst $Li(Bu^t{}_2CN)_3Sn^{II}$, $\left[(Bu^t{}_2CN)_2Sn^{II}\right]_n$ (80)

and $\left[(\text{p-tolyl})_2\text{CNSn}^{\text{II}}\text{Cl}\right]_2$ do show reasonably well defined absorptions at 406, 388 and 407 cm^{-1} respectively, no such bands were found in the spectra of the other methyleneamino derivatives of tin(II). For $(\text{Bu}^t{}_2\text{CNSn}^{\text{II}}\text{Cl})_2$ and $\left[\left\{(\text{p-tolyl})_2\text{CN}\right\}_2\text{Sn}^{\text{II}}\right]_2$ shoulders are seen at 383 and 365 cm^{-1} respectively. Absorptions of medium intensity would be consistent with the considerable polarity expected for the Sn^{II}-N bond and therefore the inconsistency of the data prevents the derivation of firm conclusions concerning the position of $\nu(\text{Sn}^{\text{II}}\text{-N})$ in these compounds. The ^{1}H-NMR data for these bis- compounds support the proposed structures, for as Table 4.5 shows, the bis(di-p-tolymethyleneamino)tin(II) dimer gives but one methyl resonance at ambient temperature (ca 42°) and temperatures down to -45°. Clearly the structure described, with both terminal and bridging methyleneamino groups, possesses moieties in non-equivalent sites. Presumably, exchange is occurring at a high enough rate, compared with the NMR time scale, for the inequivalence of the p-tolyl groups not to be detected. The spectrum of the di-t-butylmethyleneamino compound $(\text{Bu}^t{}_2\text{CN})_2\text{Sn}^{\text{II}}$, already shown to be associated (probably dimeric) in the solid state, with bridging and terminal methyleneamino units, but feasibly in a monomeric state when dissolved in benzene (cryoscopy), evidences a single t-butyl resonance at 42° similar to the spectrum of $\left[(\text{Bu}^t{}_2\text{CN})_2\text{Mg}\right]_2$ - see Chapter 2. This contrasts, however, with the results obtained for the compounds $\left[(\text{Bu}^t{}_2\text{CN})_2\text{M}\right]_2$ (M = Be, Zn) whose spectra detect the non-equivalence of bridging

Table 4.5

^{1}H-NMR Spectroscopic Data for Methyleneaminotin(II) Derivatives $[R_2CNSn^{II}X]_n$, R = Ph, p-tolyl, Bu^t; X = Cl, R$_2$CN

Compound	τ^a values ppm
$[Ph_2CNSn^{II}Cl]_2$ (80)	Ar - H 1.95m br
$[(p\text{-tolyl})_2CNSn^{II}Cl]_2$	Ar - H 2.15m br (4) CH$_3$ 7.05s br (3)
$[Bu^t{}_2CNSn^{II}Cl]_2$	C - H 7.94br
$[\{(p\text{-tolyl})_2CN\}_2Sn^{II}]_2$	Ar - H 2.41m (4) CH$_3$ 7.24s br (3)
$[(Bu^t{}_2CN)_2Sn^{II}]_n$ (80)	C - H 8.77s ^{b}

Relative intensities in parentheses

a: relative to τ(TMS) = 10ppm (external reference)

b: partially resolved (d^8toluene) at -100°C as doublet separation 0.10ppm^1

All other spectra in CDCl$_3$ solution

s: singlet; m: unresolved multiplet; br: broad and terminal methyleneamino groups even at ambient temperatures(50). For the tin(II) compound the t-butyl resonance is partially resolved into two signals at -100°C and these may be probably assigned to terminal and bridging methyleneamino groups. This thermal dependence of the spectrum is similar to that observed for dimeric bis(dimethylamido)tin(II) (166) which gives a methyl signal resolvable into a doublet at -40° corresponding to the bridging and terminal dimethylamido groups. These groups undergo exchange at too rapid a rate for their inequivalence to be detected at a temperature of 42°, but at -40° the reduced rate of exchange is detectable. This is likely to be the explanation of the ^{1}H-NMR spectrum of $(Bu^{t}_{2}C{=}N)_{2}Sn^{II}$ rather that the existence of a dimer$\rightleftharpoons$monomer equilibrium, particularly when $[(Bu^{t}_{2}CN)_{2}Be]_{2}$ is dimeric in both the solid state and in solution.

It seems likely therefore that bis(di-t-butylmethyleneamino)tin(II) is associated (probably dimeric) in both the solid state and in solution.

For the few mass spectra of compounds containing an Sn^{II}-N bond so far reported, the fragmentation patterns would seem to arise predominantly via cleavage of the tin-nitrogen bonds. In the mass spectrum of dimeric bis(bis(trimethylsilyl)amido)tin(II) for example, $[\{(Me_{3}Si)_{2}N\}_{2}Sn^{II}]_{2}$, the highest observed ion (at 70eV) is $2P^{+}$ with several polyisotopic ditin fragments between P^{+} and $2P^{+}$ corresponding to the loss, in various combination of Me, $Me_{3}Si$, and $N(Me_{3}Si)_{2}$ (166). The spectrum of dimeric bis(dimethylamido) tin(II), $\left[\mathrm{Sn^{II}(NMe_2)_2}\right]_2$ however showed no peaks beyond $\mathrm{Sn(NMe_2)_2}^+$ but consisted also of two clusters of overlapping peaks. These correspond to $\mathrm{HSnNMe_2}^+$, $\mathrm{SnNMe_2}^+$ and $\mathrm{SnN(CH_3)CH_2}^+$ and also to the overlap of $\mathrm{SnH^+}$ and $\mathrm{Sn^+}$ (1660), the evidences of SnH ions being evidently well known for organotin compounds (212).

In general terms, the mass spectra of the new methyleneamino tin(II) compounds were disappointingly unproductive. For the adducts $\mathrm{R_2CNH.Sn^{II}Cl_2}$ (R = Ph (80), p-tolyl, $\mathrm{Bu^t}$), and the bis(methyleneamino)tin(II) dimers, $\left[\mathrm{(R_2CN)_2Sn^{II}}\right]_2$ R = Ph, p-tolyl, the mass spectra did not show any tin-containing fragments even when recorded using a low source temperature and low accelerating potential. However, the reported mass spectra of $\left[\mathrm{(Bu^t{}_2CN)_2Sn^{II}}\right]_n$ and $\left(\mathrm{Ph_2CNSn^{II}Cl}\right)_2$ do have tin-containing fragments (80). In the case of bis (di-t-butylmethyleneamino)tin$^{\mathrm{II}}$, the tin-containing fragments generated were monotin-species and included $\mathrm{(Bu^t{}_2CN)_2Sn^+}$, $\mathrm{Bu^t{}_2CN.Bu^t{}_2Sn^+}$, $\mathrm{Bu^t{}_2CN.Bu^tCNSn^+}$ and subsequent break-down fragments. Whilst there were peaks with m/e ratios greater than the monomeric value, eg. $\mathrm{(Bu^t{}_2CN)_3Sn^+}$, these were assumed to be the result of recombinative processes rather than being confirmative of the dimeric or associated state of the compound. In the spectrum of diphenyl-methyleneaminotin(II)chloride dimer however, $\left(\mathrm{Ph_2CNSn^{II}Cl}\right)_2$ the strong evidence of its dimeric nature was further reinforced by its mass spectrum, and furthermore the presence of four di-tin fragments (one of considerable intensity) was regarded as reflecting the stability of the Sn-N-Sn bridge when tin is bonded to electron withdrawing groups such as chlorine. Whilst the infra-red and ^{1}H-NMR data for di-p-tolylmethyleneaminotin(II) chloride, together with its cryoscopically determined molecular weight, support its dimeric nature, the evidence from its mass spectrum was much less conclusive. The ditin fragments, particularly, are uniformly of low intensity and the m/e values quoted (Table 4.6) are necessarily imprecise.

Although fragments such as $(p\text{-tolyl})_2CNSn_2Cl_2^+$ support the existence of methyleneamino- bridging species, their low relative intensities cannot be used to support the view that the Sn-N-Sn bridge is stable when tin is bonded to an electronegative element such as chlorine. The mass spectrum therefore of dimeric di-p-tolylmethyleneaminotin(II) chloride, contained fewer ditin species than reported for its phenyl analogue, and no fragments corresponding to the dimeric ion were generated. However, subsequent attempts to reproduce the mass spectrum of this compound were unsuccessful, the only tin- containing fragments being $SnCl_2^+$ and $SnCl^+$. This suggests that the difference between the phenyl and p-tolyl compounds, $(R_2C{=}NSn^{II}Cl)_2$ R = Ph, p-tolyl, may be apparent rather than real, and might be caused by different degrees of partial decomposition.

4.3.3. N,N^1-disubstituted acetamidino derivatives of two-covalent tin

Before the characterisation and spectroscopic properties of the new acetamidinotin(II) derivatives are described

Table 4.6

Major Metal-Containing Fragments in the Mass Spectrum of Di-p-tolylmethyleneaminotin(II)chloride dimer, $[(\text{p-tolyl})_2\text{CNSn}^{\text{II}}\text{Cl}]_2$

m/e	Relative Intensity	Assignment
518	0.5	$(\text{p-tolyl})_2\text{CNSn}_2\text{Cl}_2^+$
363	0.5	$(\text{p-tolyl})_2\text{CNSnCl}^+$
211	20	$(\text{p-tolyl})\text{Sn}^+$
208	100	$(\text{p-tolyl})_2\text{CN}^+$
190	5	SnCl_2^+
132	100	p-tolyl.NC.CH_3^+
120	5	Sn^+

m/e values refer to the peaks containing ^{120}Sn and ^{35}Cl the most abundant isotopes.

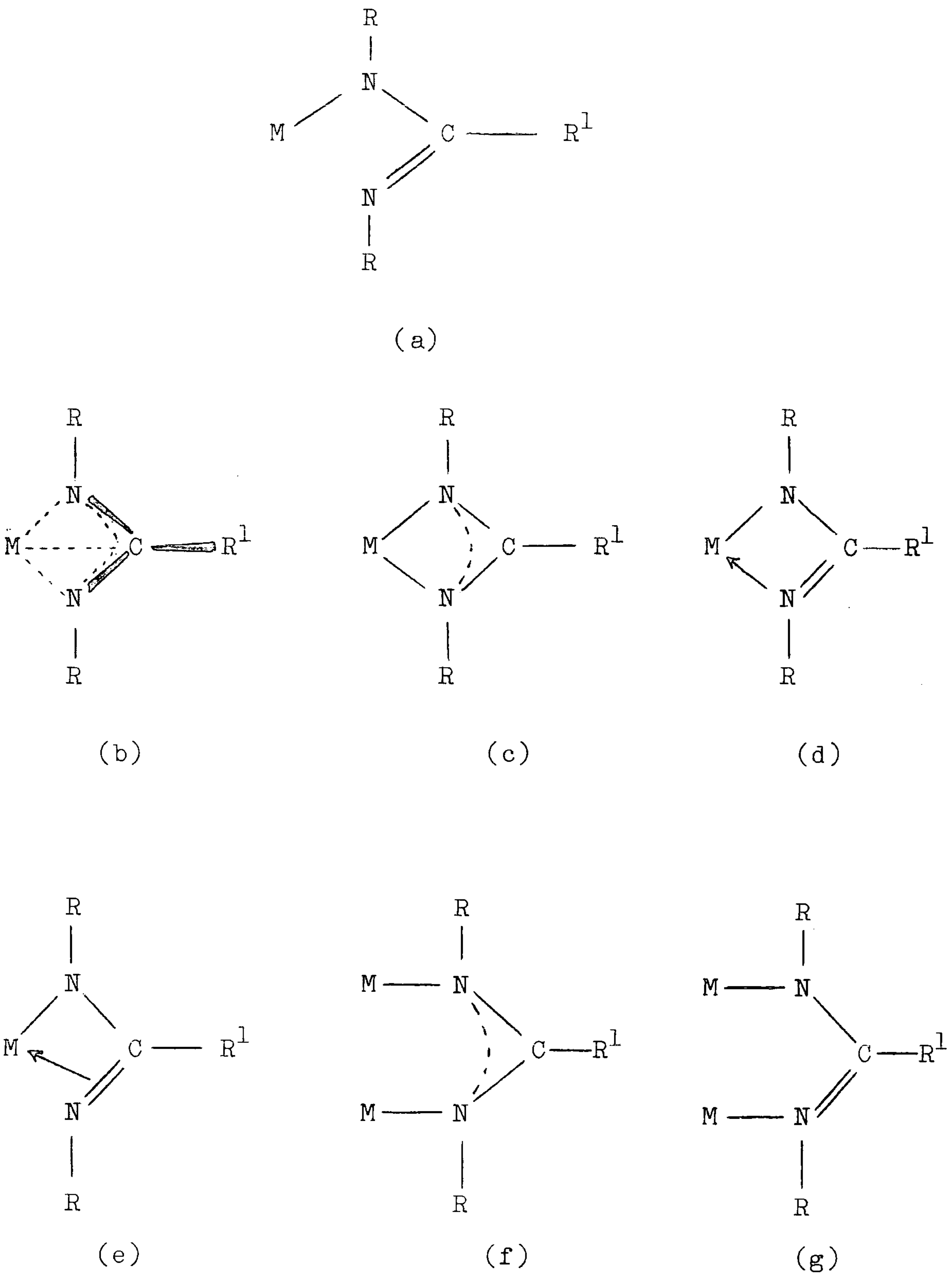
(part (b) begins on page 179), a brief description is given of the structures of selected metallo derivatives which contain the symmetrically disubstituted amidino ligand. This introduction is also intended to serve as a background to the next chapter (Chapter 5) concerned with new N,N^1-diarylacetamidino derivatives of Group IV elements, principally tin, in an oxidation state of +4.

(a) Introduction

By comparison with the methyleneamino ligand the symmetrically N,N^1-disubstituted amidino ligand ($RNCR^1NR$) has available a greater variety of bonding possibilities. Of interest is its isoelectronic realtionship with both allyl and carboxylato- groups and its ability to adopt bidentate or bridging bonding modes characteristic of both of these groups. The range of bonding possibilities is summarised in Figure 4.7 (a - g).

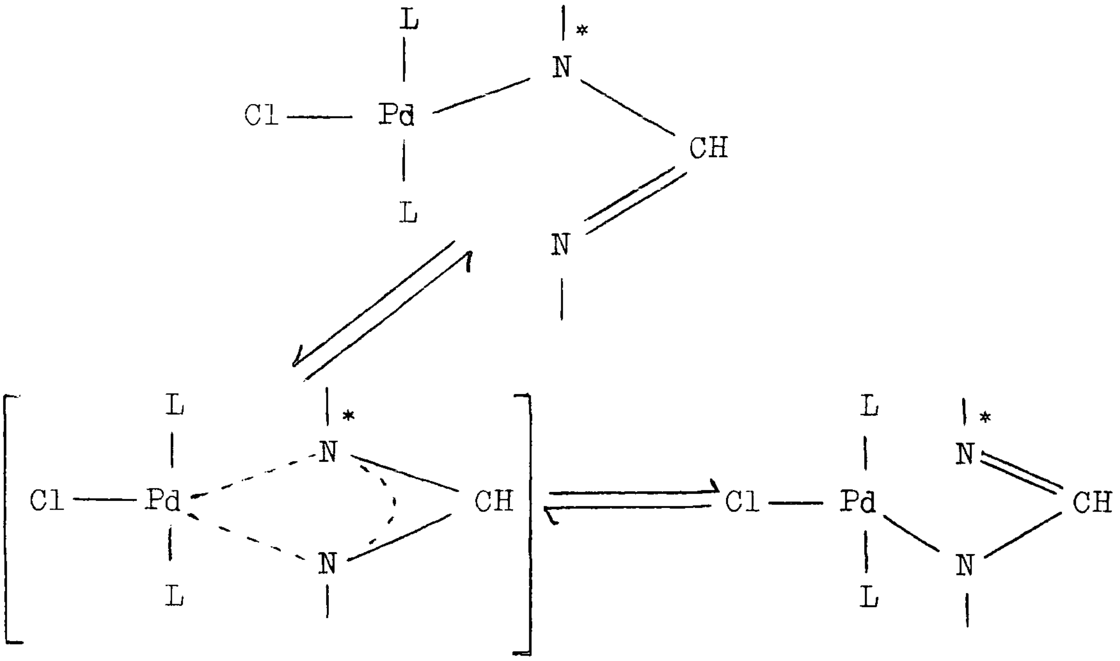
The ligand can fulfil a one electron or three electron donor role to a single metal atom, or may bridge between two atoms, as Figure 4.7 shows, both localised and delocalised arrangements being known. Structures involving the ligands in monodentate derivatives (a), proposed on the basis of spectroscopic data, include $M(PPh_3)_2(pMeC_6H_4NCH{=}NC_6H_4pMe)Cl$ where M = Pd, Pt, apparently stable in the solid state but decomposing in solution (213). Proton-NMR spectra suggest a reversible fluxional behaviour such as that shown in equation 4.3. Another interpretation proposes a localised σ, π - bonding in which an M-N σ-bond is supported by an

Bonding possibilities for N,N^1-disubstituted amidino ligands



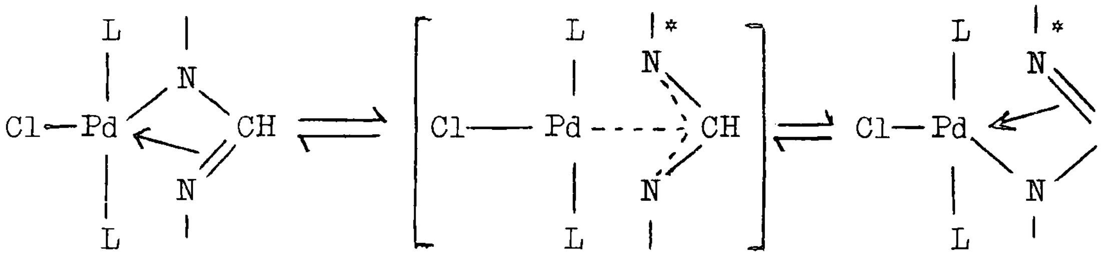
(a) (b) (c) (d) (e) (f) (g)

Figure 4.7



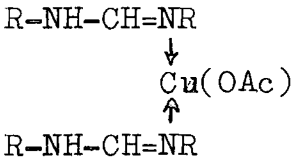
4.3

olefinic-type bonding through the C=N double bond (equation 4.4) This violates however the preferred four-co-ordination of Pd (II) in its complexes, and also contrasts with a rationale proposed for the closely-related triazenido complex, Pt(PPh$_3$)$_2$ (pMeC$_6$H$_4$N-N=NC$_6$H$_4$Mep)$_2$ (56).



4.4

Whilst another example in which the ligand may be acting in a monodentate manner (Figure 4.7a) is the unstable adduct (R-NH-CH=NR)$_2$ Cu(OAc)$_2$(R = Ph, p-tolyl) (Figure 4.8), a structure proposed purely on the basis of molecular weight



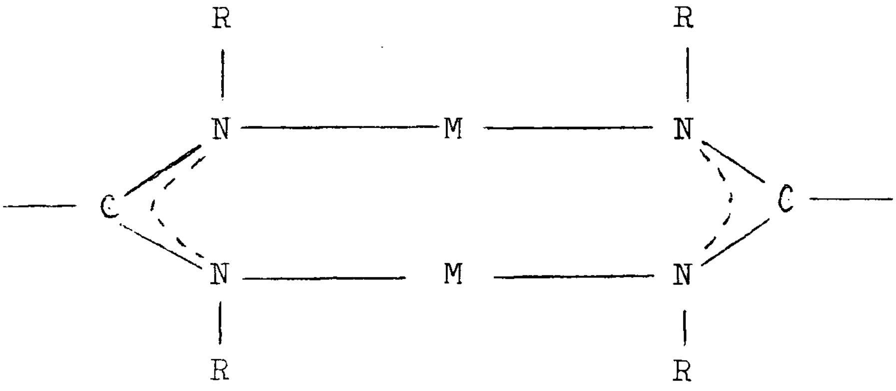
$$\begin{array}{l} \text{R-NH-CH=NR} \\ \qquad\quad\;\downarrow \\ \qquad\quad\;\text{Cu(OAc)} \\ \qquad\quad\;\uparrow \\ \text{R-NH-CH=NR} \end{array}$$

Figure 4.8

determination and chemical reactivity without any spectroscopic evidence (214), it would seem that unidentate amidine groups are generally formed only with reluctance. This presents a sharp distinction between amidino and carboxylato groups, despite their electronic and structural resemblances, for the latter seems to prefer to adopt a monodentate or bridging conformation as in $Mn(CO)_3OCOR$ (215, 216) and $Rh(CO)_2(OCOR)_2$ (60) respectively. The few examples of bidentate carboxylato groups bonded to transition metals in low valent complexes seem to be mostly confined to the heaviest metals of the series eg. Ir or Os (218).

Most of the reported N-metallated amidino derivatives are of transition metals and the majority of these compounds contain chelate bidentate ligands, probably of the σ,σ-type with the metal atom in the plane of the CN_2 unit (Figure 4.7, c and d) although the precise mode of attachment may not be absolutely certain. The favoured structure for $(\pi\text{-}C_5H_5)M(CO)_2R^1NC(R)NR^1$ (219) (M = Mo, W; R = Ph; R^1 = H, Ph, p-tolyl) is the delocalised one (Figure 4.7c) with the ligand strictly comparable with bidentate carboxylate groups. Further examples of transition metal amidine derivatives include those of Pt and Pd (219), Mn (220), Fe and Co, (221) Ni (219, 222), Mo (219, 223), W (219), Cr (223), Rh (224), Ta and Nb (225) and Cu and Ag (222, 226).

The amidine groups can also act as a bridging ligand between two metal atoms (Figure 4.9) similar to the closely related triazinido (227-228) or carboxylate ligands (229).



$R = pMeC_6H_4$

Figure 4.9

Examples of such derivatives include $\left[Pd(pMeC_6H_4N\ \ CH\ \ NC_6H_4Mep)\right]_2$ (230) and $Mo_2\left\{PhNCPhNPh\right\}_4$ (223) but the nickel derivative $\left[(C_5H_5)Ni\ \ PhN.C(Ph)NPh\right]_n$ might well be polymeric via bridging amidino groups (219). Derivatives of copper (I) and silver, eg copper(I)N,N^1-di-p-n-butoxyphenylformamidine, are known which are tetrameric in benzene and may also have bridging amidino ligands (Figure 4.10) (222). Some molybdenum

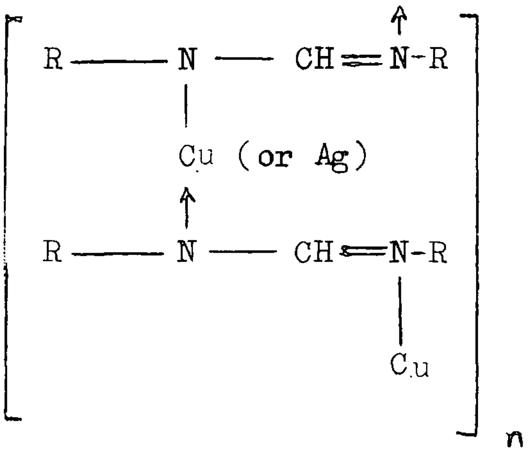
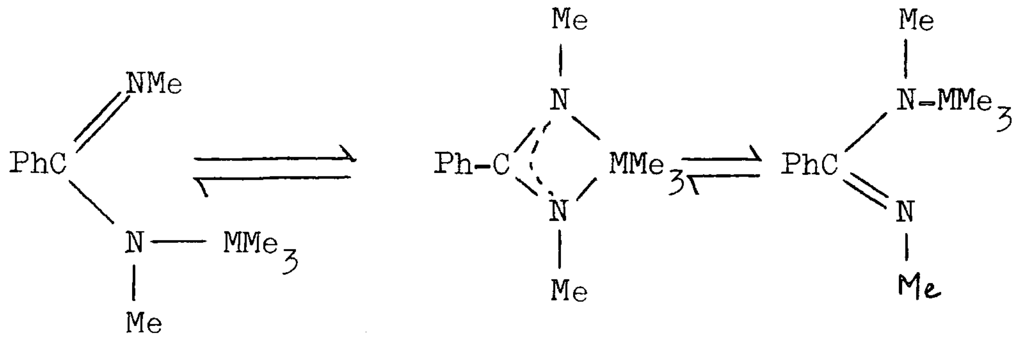


Figure 4.10

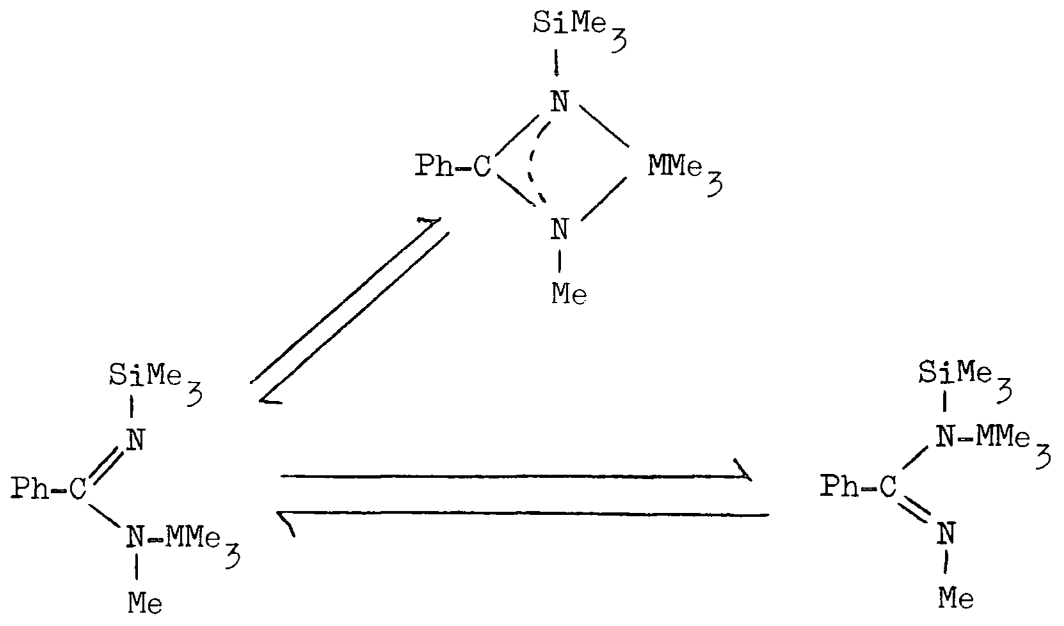
and rhenium (224) derivatives exist where a metal-metal bond is bridged by two or more amidine groups.

The Group IV derivatives of N,N^1-disubstituted benzamidine which have been reported are MeNC(Ph)NMe.MMe$_3$ (M = Si, Sn) and Me$_3$SiNC(Ph)NMeMMe$_3$ (M Si, Ge, Sn, Pb) (202). In the former compounds the amidino group is predominantly a one electron donor, but whilst ^{1}H-NMR shows the equivalence of the N-methyl groups at ambient conditions, the N-methyl signal is resolvable into two components at -60°C. This result was interpreted in favour of a very rapid equilibrium (equation 4.5) rather that the existence of one delocalised species. In the latter series of compounds, Me$_3$SiNC(Ph)NMe.MMe$_3$ (M = Si, Ge, Sn, Pb) an



4.5

equilibrium also appears to exist giving rise to a mixture of isomers (equation 4.6). Again, localised and delocalised



4.6

forms are in evidence, the former being preferred for M = Si, and the latter for M = Ge, Sn, Pb.

Considerable interest has also been shown in the chemical properties and mode of co-ordination of the isoelectronic 1,3-diaryltriazenido (ArNNNAr) ligand. The bonding possibilities for this ligand (Figure 4.11) are similar to those already described and discussed for the N,N^1-disubstituted amidino ligand, and structures involving the 1,3-diaryltriazenido ligand in monodentate (231), chelate (232) and bridging derivatives (231, 233) (Figure 4.11 a,b-d and e respectively) have been proposed on the basis of spectroscopic data. X-ray studies on mononuclear Co(PhNNNPh)$_3$C$_7$H$_8$ (227) and binuclear $\left[Ni(PhNNNPh)_2\right]_2$ (227)

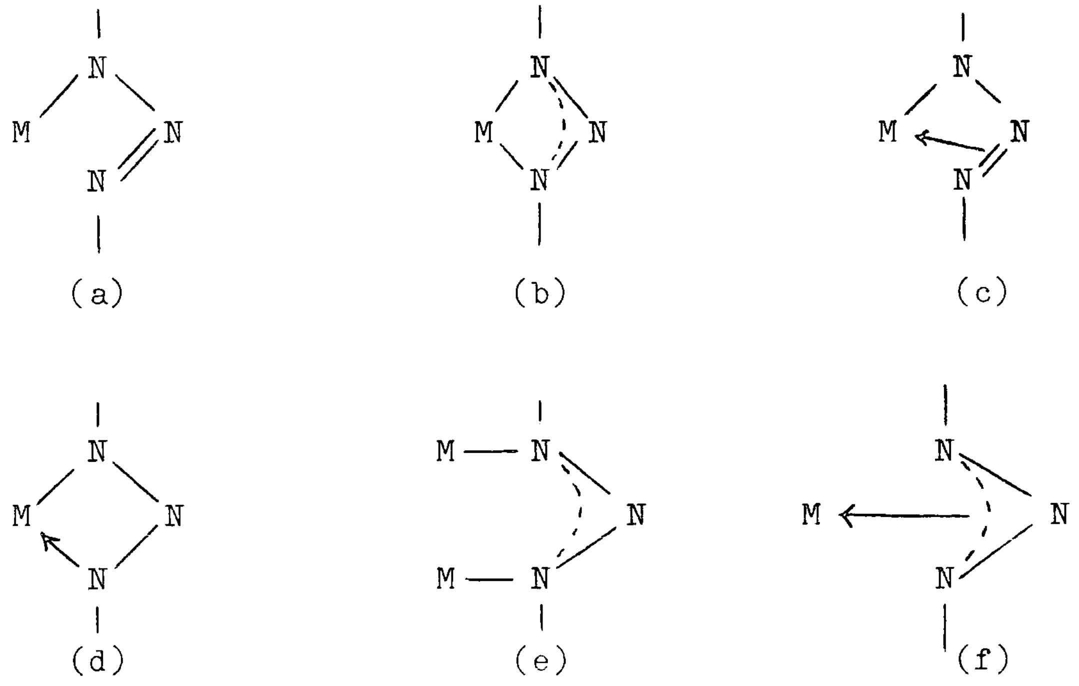


Figure 4.11

and Cu$_2$(PhNNNPh)$_2$ (234) have confirmed the presence of chelate and bridging σ-bonded ligands (Figure 4.12 b and e) respectively. Furthermore, structures (a) (213, 230, 235) and (c) (236) have been suggested for the triazenido complexes of the platinum metals, their fluxional behaviour being interpreted as occurring through a type (b) or (f) intermediate (213, 235-237). The triazinidotin derivatives $Me_2Sn(dpt)_2$, $PhSn(dpt)_2Cl$, and Ph_3Sndpt (dpt = 1,3-diphenyltriazine) are monomeric and proabably contain bidentate ligands (238).

(b) The characterisation and spectroscopic properties of the new amidine adducts and amidino derivatives of tin(II)chloride

The compounds discussed in this section comprise $MeC(NR)NHR.Sn^{II}Cl_2$ (R = Ph, p-tolyl), $\left[MeC(NR)_2Sn^{II}X\right]_n$ R = p-tolyl, X = Cl, n = 2; R = Ph, p-tolyl, X = RNC(Me)NR.

The simple 1:1 adducts of tin(II) chloride and N,N^1-diarylacetamidine, viz $MeC(NR)NHR.SnCl_2$ R = Ph, p-tolyl, were prepared by refluxing a mixture of the reagents (in 1:1 or 1:2 molar proportions respectively) in toluene for about 24 hours followed by the addition of anhydrous hexane and cooling to ca $-20^{o}C$. No evidence of their molecular state was obtainable by cryoscopic measurements because of their sparing solubility in benzene, and their proposed structure is based almost entirely on features of their infrared spectra. Their infrared spectra, together with those of the parent amidines, and their adducts with hydrogen chloride and boron(III)fluoride- made for reference purposes - are recorded in Table 4.7. Because of hydrogen bonding, the infrared spectra of the parent amidines show a very broad, and therefore imprecise, absorption assignable to the(N-H) stretching frequency. Hence although co-ordination to Lewis acids causes a considerable sharpening of the absorption band and indeed an increase in ν (N-H) - the (N-H) absorption in the adduct N,N^1-diphenylbenzamidine . $Cr(CO)_3$, compared to the parent amidine, is higher by 100cm^{-1} (223) - in these instances $\Delta\nu$(N-H) could not be measured. Attention therefore was focused on the change in stretching frequency of the (NCN) unit, ν(NCN), upon co-ordination, and Table 4.7 reflects this emphasis. Various values have been assigned to ν(NCN) and, for example, derivatives of tantalum and niobium such as $MCl_4\left[NR\text{-}C(Me)\text{=}NR\right]$ ($R = Pr^i$, C_6H_{11}), have ν(NCN) values which range from 1635 - 1647 cm^{-1} (of weak to medium intensity) often with two or three other bands in the 1500 - 1600 cm^{-1} region (225). A medium intensity absorption at 1630cm^{-1}, found for (π-C_5H_5)$M(CO)_2R^1NC(R)NR^1$ (M = Mo, W; R^1 = H, Ph, p-tolyl; R = Ph), a band little removed from that of the free amidines, was assigned to a bidentate delocalised (NCN) attachment (219). For a number of transition metal carbonyl systems the relevant vibrations, both symmetric and asymmetric, were considered to lie in the region 1300 - 1500 cm^{-1} (239). Consequently, in the examination of the infrared spectra of amidine derivatives of tin(II), any bands which vary from derivative to derivative, in the range (1300 - 1645) are assumed to be associated with the (NCN) stretching frequencies.

The general pattern which emerges from the infrared spectra of the adducts (Table 4.7) parallels the findings for the methyleneamine adducts and endorses the relative weakness of tin (II) chloride as a Lewis acid. Because the amidine ligand can co-ordinate in many varied ways (Figure 4.7), its precise mode of co-ordination is not easily resolved. Boron(III)fluoride is necessarily a monobasic Lewis acid and therefore the amidine.BF_3 adducts must have amidine units co-ordinated as monodentate ligands. Inthe parent amdines the highest ν(NCN) is assigned to ν(C=N) and the presence of such a band in metallated derivatives, little removed from those in the free amidine, may reflect either the presence of free N,N-disubstituted

Table 4.7

ν(NCN)* of the N,N^1-Disubstituted Amidines and Their Adducts With HCl, BF_3 and $Sn^{II}Cl_2$

R-N=C(Me)-NR	Amidine	Amidine.HCl	Amidine.BF_3	Amidine.$SnCl_2$
R = Ph	1629vs 1535vs 1338vs	1640vs 1568m 1347m	1640vs 1570sh 1355w	1637m 1568m 1334vwbr
R = p-tolyl	1635vs 1532vsbr 1323s	1641vsbr 1570vsbr 1355sbr	1645vs 1570sh 1355w	1638m 1564m 1318w

*As Nujol mulls

amidines or, in the absence of associated (N-H) absorptions, some vestiges of remaining delocalised (C=N). The latter may of course be realised by the co-ordination of the amidine or amidino ligand in a mono- or bidentate manner.

The spectra of the amidine- Lewis acid adducts are all very similar, and this could mean that the amidine-tin(II) chloride adducts also possess monodentate amidine ligands. Such an arrangement would preserve the commonly preferred three-co-ordinate state of two-covalent tin.

The ^{1}H-NMR spectra of the adducts were recorded, together with the parent N,N^1-disubstituted amidines, as solutions in $CDCl_3$ at ambient temperatures (Table 4.8). As with the methyleneamine.$Sn^{II}Cl_2$ adducts, the above adducts yield relatively simple spectra at 42°, unchanged on cooling to about -40°, revealing downfield movement of all peaks on co-ordination to tin(II) chloride. The most significant shift is that of the (N-H) peak, the size of such shift being considerably greater than in the corresponding methyleneamine-tin(II)chloride adducts, suggesting stronger co-ordination between the amidine-nitrogen and tin. These chemical shifts, as a whole, on co-ordination are in the direction expected on electronic grounds reflecting in particular the strong deshielding of the nitrogen-attached proton, because of co-ordination through nitrogen to tin.

Mass spectra were obtained for the amidine-tin(II) chloride adducts but no tin- containing fragments were generated.

Table 4.8

^{1}H-NMR Spectra of Some Amidine-tin(II)chloride Adducts

Compound	τ^a values ppm			
	Ar-H	Amidine-Me	p-tolyl-Me	N-H
AmH	2.29 br	7.64sbr	-	3.2s
AmH.Sn^{II}Cl$_2$	2.2 2.3 br (10)	7.50s (3)	-	0.17s(1)
Am^{1}H	2.43, 2.45, 2.48, 2.50	7.63s	7.27s	3.91s
Am^{1}H.Sn^{II}Cl$_2$	2.23sbr (8)	7.45s (3)	7.07s (6)	0.05s(1)

a: relative to τ(TMS) = 10 ppm (external reference); relative intensities in parentheses;

s = singlet; m = unresolved multiplet;

br = broad.

Am = PhNC(Me)NPh; Am^1 = pMeC$_6$H$_4$NC(Me)NC$_6$H$_4$pMe.

As mentioned earlier, compounds of general formula $[\mathrm{RNC(Me)NRSnX}]_n$ R = p-tolyl, X = Cl, n = 2; R = Ph, p-tolyl, X = RNC(Me)NR, were prepared by reacting the appropriate amidinolithium with anhydrous tin(II) chloride (in diethyl ether) at liquid nitrogen temperatures in mole ratios 1:1 or 2:1 respectively (equation 4.1). After warming to room temperature, with stirring, separation of the metallated amidine from lithium chloride was effected by brief refluxing with toluene and subsequent filtration. The amidinotin(II) derivatives crystallise on cooling. The bis(amidino)tin(II) compounds, $[\{\mathrm{MeC(NR)_2}\}_2\mathrm{Sn}]_n$ R = Ph, p-tolyl, were too insoluble for molecular weight determinations, by cryoscopy, to be made. The values obtained, by cryoscopy, for the chloro-compounds, $[\mathrm{MeC(NR)_2Sn^{II}Cl}]_n$ R = Ph, p-tolyl however, were somewhat lower than the dimeric formula weights, yet significantly higher than the monomeric values $[\mathrm{MeC(NR)_2SnCl}]_n$ R = Ph;M, by cryoscopy 551 - monomeric value 363.5 (80); R = p-tolyl; M by cryoscopy 656 (monomer, 391). These amidinotin(II)chlorides are therefore regarded as being dimeric in solution. Furthermore it seems that an associated molecular condition, evidenced in solution, persists in the solid state, for on steric grounds a monomeric structure for these amidinotin(II)chlorides seems most unlikely. Such a structure for $\mathrm{RNC(Me)NRSn^{II}Cl}$ with three-co-ordinate tin and a terminally attached, presumably bidentate, amidino ligand would require a very small NSnN angle - the NSnN angles in the monomeric $\mathrm{PhNC(Me)NPhSn^{IV}Cl_3}$ and $\mathrm{(Ph_2C{=}NSn^{II}Cl)_2}$ are about 61° and 75° respectively (211). Hence a dimeric structure with bridging amidino ligands is more probable. The infrared evidence concerning $(RNC(Me)NRSn^{II}Cl)_n$, R = Ph, p-tolyl, shows that absorptions assignable to the stretching frequencies of the (NCN) group are confined to the regions $(1520-1530)cm^{-1}$ and $(1312-1332)cm^{-1}$. These frequency ranges are assigned to amidine bridging ligands since the spectrum of monomeric N,N^1diphenylacetamidinotin (IV)trichloride, $PhNC(Me)NPh.Sn^{IV}Cl_3$, known to have terminally attached bidentate ligands has no such absorptions (80). The infrared spectroscopic date (Table 4.9) therefore endorses the associated nature of these chloro-derivatives.

Their ^{1}H-NMR spectra (Table 4.10)in deuterated chloroform showed no changes whether run at ambient or sub-ambient temperatures and are in accord with an associated, probably dimeric, structure. The magnetic equivalence of the p-methyl substituents in $(p\text{-tolylNC(Me)Np-tolyl.}Sn^{II}Cl)_2$, down to ca - 50°C, may mean that the molecule is symmetrical. The structure proposed for these dimeric chloro- derivatives, RNC(Me)NRSnCl - R = Ph, p-tolyl, is shown in a simplified form in Figure 4.12, with bridging amidino ligands and three co-ordinate tin. The extent of delocalisation of the bridging (NCN) units is very difficult to gauge, but the

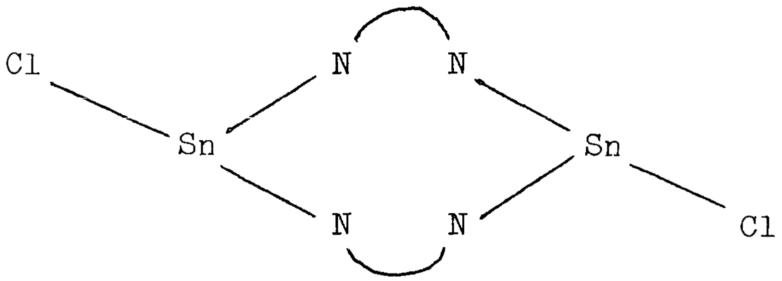


Figure 4.12

Table 4.9

$^*\nu$(NCN) for $\left[\mathrm{RNC(Me)NRSn^{II}X}\right]_n$ R = Ph, p-tolyl; X = Cl, RNC(Me)NR.

Compound	ν(NCN)cm^{-1}
$(\mathrm{PhNC(Me)NPhSn^{II}Cl})_2$	1523vs, 1332vw
$\left\{(\mathrm{pMeC_6H_4})\mathrm{NC(Me)N}(\mathrm{C_6H_4pMe})\mathrm{Sn^{II}Cl}\right\}_2$	1530vs br, 1312m
$\left[(\mathrm{PhNC(Me)NPh})_2\mathrm{Sn^{II}}\right]_n$	1630m, 1530vs br, 1332w
$\left[\left\{(\mathrm{pMeC_6H_4})\mathrm{NC(Me)NC_6H_4pMe}\right\}_2\mathrm{Sn^{II}}\right]_n$	1635m br, 1528s br, 1300w
PhNC(Me)NHPh	1629vs, 1535vs, 1338vs
$(\mathrm{pMeC_6H_4})\mathrm{NC(Me)NH}(\mathrm{C_6H_4pMe})$	1635vs, 1532vs br, 1323s

* as Nujol mulls

Table 4.10

^{1}H-NMR Spectra For Some N,N^{1}disubstituted Acetamidino-tin(II) Derivatives

Compound	τ^a values ppm		
	Ar - H	Amidine Me	p-tolyl Me
$(AmSn^{II}Cl_2$	2.33c (10)	7.63s (3)	-
$(Am^1SnCl)_2$	2.33, 2.38 2.5m (8)	7.55s (3)	7.12s (6)
$(Am_2Sn^{II})_n$	2.33, 2.43c (10)	7.58s (3)	-
$(Am^1{}_2Sn)_n$	2.25, 2.42, 2.55, 2.69 (8)	7.62s (3)	7.16s (6)
AmH	2.29 br	7.64s br	-
Am^1H	2.43m 2.45, 2.48, 2.50	7.63s	7.27s

a: relative to TMS (external reference); relative intensities in parentheses. All spectra run on $CDCl_3$ solution at about 42°C; s = Singlet; m = multiplet; c = complex; br = broad. Am = PhNC(Me)NPh; Am^1 = $(pMeC_6H_4)NC(Me)N(C_6H_4pMe)$

eight-membered bridging ring would be expected to be considerably puckered to reduce bond angle strain and steric interactions with the tin(II) lone pairs of electrons to acceptable levels. This means that the C=N π-systems would be highly localised, for delocalisation would demand the existence of a planar SnNCNSn framework and such would provoke severe angle strain because of the nearness of the two tin atoms.

The mass spectrum of dimeric N,N^1-di-p-tolylacetamidinotin(II)chloride was somewhat dissimilar to that reported for the analogous phenyl derivative (80). Fewer tin-containing fragments were generated and no fragments were obtained which could be assigned to the dimeric ion (similar to the mass spectrum of dimeric p-tolylmethyleneaminotin(II) chloride discussed earlier). Again the major factor in this disparity may be the varying degrees of decompositions of the two samples. The principal fragments in the mass spectra of $(RNC(Me)NRSnCl)_2$, R = p-tolyl, are shown in Table 4.11.

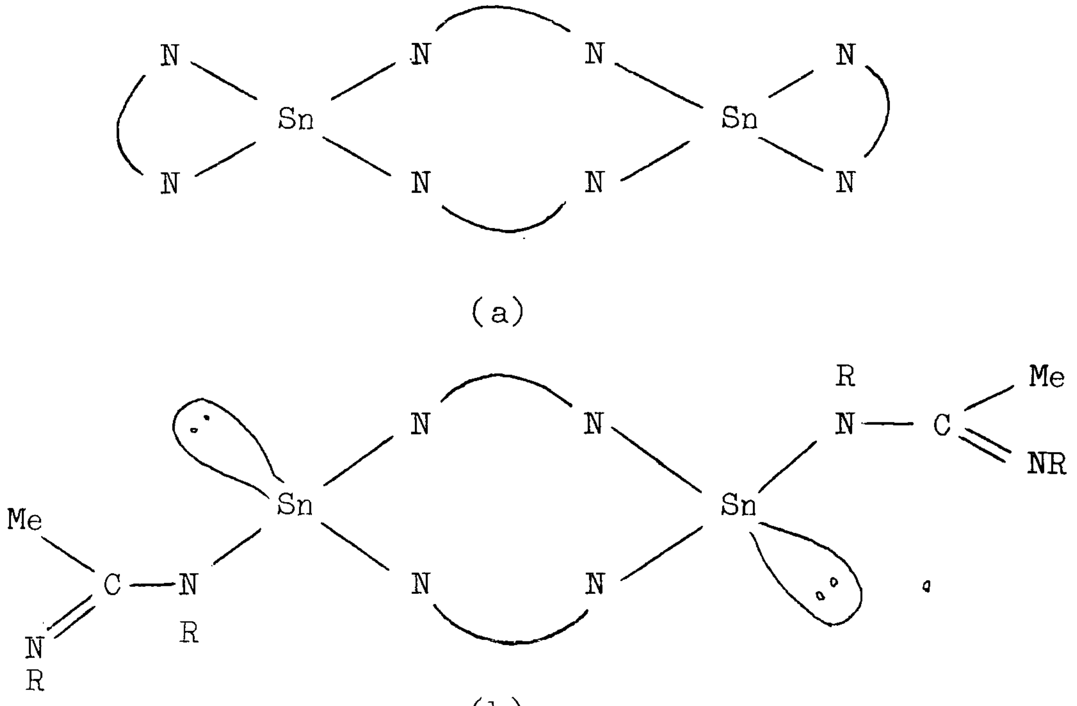
Because of the insolubility of the bis(N,N^1-diarylacetamidino)tin(II) compounds, $\left[(RNC(Me)NR)_2Sn^{II}\right]_n$ R = Ph, p-tolyl, no evidence for their molecular state was obtained by cryoscopy. Their infrared spectra (Table 4.9) show absorptions which are appropriate to the presence of both bridging and terminally attached amidino ligands. The absorptions of medium intensity, little removed from the ν(NCN) in the parent amidine, are not regarded as being due to amidine impurity because of the absence of absorptions

Table 4.11

Mass Spectrum of N,N^{1}di-p-tolylacetamidinotin(II)chloride Dimer

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
664	0.1	$Am^1{}_2SnCl_2{}^+$	190	2	$SnCl_2{}^+$
392	37	Am^1SnCl^+	132	100	$C_7H_7NCMe^+$
237	21	Am^{1+}	119	0.8	$C_7H_7N_2{}^+$/ $C_7H_7NCH_2{}^+$
208	0.9	$C_7H_7NCC_7H_7{}^+$	105	1	$C_7H_7N^+$
196	1	$(C_7H_7)_2N^+$	91	32	$C_7H_7{}^+$

associated with the (N-H) stretching vibration. The infrared spectrum of N,N^1-diphenylacetamidinotin(IV)trichloride, $PhNC(Me)NPhSn^{IV}Cl_3$ (80), shows an absorption of very weak intensity at ca 1645 cm^{-1} not far removed from the highest energy absorptions evidenced in these bis(amidino) tin(II) compounds. The former compound is known, by X-ray crystallography (211), to have a terminally attached chelating amidine ligand, and consequently the absorptions at 1630cm^{-1} and 1635cm^{-1} for phenyl and p-tolyl derivatives respectively, $\left[(RNC(Me)NR)_2Sn^{II}\right]_n$ R = Ph, p-tolyl are assigned to terminally attached amidino units. Since PhNC(Me)NPhSn^{IV}Cl$_3$ has no absorptions in the region 1300-1600cm^{-1} due to amidine groups then the absorptions of the bis derivative in the ranges (1528-1530)cm^{-1} and (1300-1332) cm^{-1} are assignable to bridging amidino units. The bis-derivatives therefore are associated molecules with both bridging and terminal amidino ligands. Possible structures for such molecules include those shown in simplified dimeric form in Figure 4.13.



(a)

(b)

Figure 4.13

No unambiguous assignment of Sn^{II}-N stretching frequencies for the amidinotin(II) derivatives was possible. Tin - nitrogen stretching frequencies for the analogous amidinotin(IV) compounds (Chapter 5) fall in the range

(653-677)cm^{-1} but a comparison of these spectra with compounds of the lower oxidation state gave unrealistic results.

The ^{1}H-NMR spectra of these bis(amidino)tin(II) derivatives (Table 4.10) showed small chemical shifts when compared with those of the parent amidine. At both ambient and sub-ambient temperatures, singlet signals corresponding to the methyl protons whether acetamidino, in the range τ (7.58-7.62), or tolyl, at τ = 7.16, were obtained. A slight broadening of the signals at about -50°C was regarded as being caused by the precipitation of some solid complex. A possible implication is that throughout this temperature range the amidine groups co-ordinated to tin have identical magnetic and chemical environments, such being inconsistent with one possible structure, viz Figure 4.13 (b), where the bridging and terminal ligands, bidentate and monodentate respectively, have very different environments. Cooling to about -50° should freeze out any inversion processes which could conceivably be operating at ambient conditions - so making dissimilar environment appear to be identical. Whilst the evidence is not compelling, it seems likely that the structures of these bis(acetamidino)tin(II) compounds, $\left[(RNC(Me)NR)_2Sn^{II}\right]_n$ R = Ph, p-tolyl are associated molecules, probably polymeric, with a symmetrical structure such as shown in Figure 4.13 (a), having both bridging and terminal bidentate amidino ligands and four-co-ordinate tin atoms.

The mass spectra of these compounds gives no help in the formulation of their state of association for neither generated identifiable fragments containing more than one tin atom or amidine unit. In the spectra of the methyleneamino tin(II) compounds discussed earlier, relatively few tin-containing fragments were evidenced and overall the spectra were dominated by the methyleneamino ligands or their breakdown products, the most abundant of which were often R^+, $RCNH^+$ and R_2CN^+. The fragment patterns of the amidinotin(II) derivatives are similarly swamped by amidino ligands and their extensive breakdown products, because of the greater variety of decomposition courses open to such ligands. The major primary processes could well involve stepwise loss of amidino groups, cleavage of such groups at nitrogen with loss of R• or RN•, loss of Me and the formation of R_2N fragments by the elimination of the stable molecule acetonitrile. Not all of these possible processes have been observed in these amidinotin(II) compounds and it is possible that the state of decomposition of the materials has been of considerable influence. The major fragments for the bis(amidino)tin(II) compounds are recorded (after Section 4.4) in Table 4.12 (a and b).

4.4 Summary

(a) Methyleneamino derivatives of tin(II)

All the new methyleneaminotin(II) compounds referred to in this chapter viz $R_2C{=}NH.Sn^{II}Cl_2$ (R = p-tolyl, Bu^t), and $\left[R_2C{=}NSn^{II}X\right]_n$ R = p-tolyl, Bu^t, X = Cl, n = 2; R = p-tolyl, X = $R_2C{=}N$, contain two-covalent tin in a co-ordination state of three or more. The compounds

$(R_2C{=}NSn^{II}X)_n$ R = p-tolyl, Bu^t, are similar to the analogous phenyl derivative both in association number (80) and structure (211). They are probably dimeric both in the solid state and in solution, and their proposed structure contains bridging methyleneamino ligands and four-membered $(SnN)_2$ rings. Bis(di-p-tolylmethyleneamino) tin(II) is probably dimeric in both the solid state and in solution, and like its phenyl and t-butyl analogues $\left[R_2C{=}NSn^{II}X\right]_2$ R = Ph, Bu^t, X = R_2C has both bridging and terminally co-ordinated methyleneamino ligands. In the latter case there is little evidence of a linear $C{=}N \Rightarrow Sn^{II}$ skeleton with its associated $(p{\rightarrow}d)N \longrightarrow Sn^{II}$ dative π-bonding presumably because π-overlap between the 2p orbitals of the N-atom and 5d orbitals of tin is too small.

(b) Acetamidino derivatives of tin(II)

The preferred co-ordination states of two-covalent tin in the N,N^1-diarylacetamidino derivatives discussed above are three - in the simple adducts $RNC(Me)NHR.SnCl_2$ R = Ph, (80) p-tolyl and in the amidinotin(II) chloride dimers $(RNC(Me)NRSn^{II}Cl)_2$ R = Ph, p-tolyl - and four as in bis(acetamidino)tin(II). The N,N^1-diarylacetamidinotin(II) chloride dimers, $(RNC(Me)NRSn^{II}Cl)_2$ R = Ph, (80) p-tolyl, are dimeric species with bridging amidino ligands and probably an eight membered $Sn_2C_2N_4$ ring. The bis-amidino derivatives, $\left[(RNC(Me)NR)_2Sn^{II}\right]_n$ R = Ph, p-tolyl, are probably polymeric and have both bridging and terminally attached bidentate amidino ligands.

Table 4.12

The Mass Spectra of bis(N,N^1-diarylacetamidino)tin(II)

$(RNC(Me)NR)_2Sn^{II}{}_n$ R = Ph, p-tolyl

(a) $\left[(PhNC(Me)NPh)_2Sn\right]_n$

m/e	Relative Intensity	Assignment
329	10	$AmSn^+$
210	100	Am^+
194	65	$PhNCNPh^+$
168	100	Ph_2N^+
118	100	$PhNCMe^+$
105	100	$PhN_2{}^+$
91	100	PhN^+
77	100	Ph^+

Am = PhNC(Me)NPh

(b) $\left[(pMeC_6H_4NC(Me)NC_6H_4pMe)_2Sn^{II}\right]_n$

m/e	Relative Intensity	Assignment
512 *	0.2	$(C_7H_7)_2N)_2Sn^+$
357	40	Am^1Sn^+
237	60	Am^{1+}
232	100	$C_7H_7NCNC_7H_7^+$
196	100	$(C_7H_7)_2N^+$
132	70	$C_7H_7NCMe^+$
119	80	$C_7H_7N_2^+$
105	90	$C_7H_7N^+$
91	90	$C_7H_7^+$

Am^1 = $pMeC_6H_4NC(Me)NC_6H_4pMe$

* a very tentative estimation/assignment, of very low intensity

CHAPTER 5

SOME N,N^{1}-DIARYLACETAMIDINO DERIVATIVES OF SILICON, GERMANIUM AND TIN

5.1. Introduction

This chapter extends earlier work in this field (80) and describes the synthesis of new tin(IV) and, to a much lesser extent, germanium and silicon derivatives of symmetrical N,N^1-disubstituted acetamidines, MeC(:NR).NHR viz: N,N^1-di-p-tolylacetamidinotin(IV)trichloride $MeC(NC_6H_4pMe)_2Sn^{IV}Cl_3$

bis(N,N^1-diphenylacetamidino)dichlorostannane,

$$\left[MeC(NPh)_2\right]_2 Sn^{IV}Cl_2$$

bis(N,N^1-di-p-tolylacetamidino)dichlorostannane,

$$\left[MeC(NC_6H_4pMe)_2\right]_2 Sn^{IV}Cl_2,$$

bis(N,N^1-di-p-tolylacetamidino)dichlorosilane,

$$\left[MeC(NC_6H_4pMe)_2\right]_2 SiCl_2$$

bis(N,N^1-di-p-tolylacetamidino)dichlorogermane,

$$\left[MeC(NC_6H_4pMe)\right]_2 GeCl_2$$

tris(N,N^1-diphenylacetamidino)chlorostannane,

$$\left[MeC(NPh)_2\right]_3 Sn^{IV}Cl$$

tris(N,N^1-di-p-tolylacetamidino)chlorostannane,

$$\left[MeC(NC_6H_4pMe)_2\right]_3 Sn^{IV}Cl$$

tetrakis(N,N^1-diphenylacetamidino)tin,

$$\left[MeC(NPh)_2\right]_4 Sn^{IV}$$

tetrakis(N,N^1-di-p-tolylacetamidino)tin,

$$\left[MeC(NC_6H_4pMe)_2\right]_4 Sn^{IV}$$

The infrared spectra, ^{1}H-nuclear magnetic spectra and mass spectra of these derivatives are interpreted, so far as it is possible, in terms of their structural implications. A brief discussion of the structural chemistry of organotin(IV) derivatives precedes the experimental and discussion sections of this chapter (the latter, Section 5.4 begins on page 208). A more detailed and extensive account of this may be found in various reviews (80, 169, 240-243) and other more comprehensive works (244-246).

5.2. Stereochemistry of Organotin(IV) Derivatives

The ground state outer electronic configuration of tin viz $5s^2$, $5p^2$, allows tin to form compounds in both the +II and +IV oxidation states - the former having been discussed in Chapter 4. A qualitative description of the way in which the +IV oxidation state is formed involves the uncoupling of the *s* electrons and the promotion of one of these to a higher energy level so affording an sp^3 configuration. Thus the four equivalent covalent bonds of tin(IV) can arise from this, the first excited state of the tin atom. Expansion of the co-ordination state beyond four may arise by making use of the empty 5d orbitals which are of similar energy to the valence-electron orbitals, and therefore may be included with ease in the hybridisation process. Examples of co-ordination states from four to eight are known.

<u>Four-co-ordinate</u> tin with a tetrahedral configuration occurs for example in R_4Sn (R = alkyl, aryl), the tin(IV)-halides (not SnF_4 which has a structure based on octahedral tin (247)) and -hydrides. But whilst the Lewis acidity of tin in R_4Sn is weak, it is enhanced when attached to electron withdrawing groups. Therefore the possibility of association exists, with attendant increase in co-ordination number, and this is reflected in the structure of such compounds. Nevertheless some vestige of a tetrahedral molecular unit

may still prevail, as for example in dimethyltin dichloride where the polymeric structure formed by the bridging of a chlorine atom to tin, shows an octahedral configuration at tin, but distorted sufficiently to allow the molecular unit to be evidently derived from a tetrahedral arrangement (248). Many examples of compounds with <u>penta-co-ordinate</u> tin are known, for autocomplex formation (when a group attached to tin acts as a Lewis base to another tin atom, with accompanying association and increase in co-ordination number) is very common in compounds of the type R_3SnX. The trigonal bipyramidal configuration in this pentaco-ordinate condition often has the more electronegative substituent X and the organic groups R in axial and equatorial positions respectively. Examples include trimethyltin(IV)fluoride (249) and trimethyltin carboxylates (250). It is however, of interest that association in the trialkyltin carboxylates, $R_3SnO_2CR^1$, is inhibited when the alkyl groups R are bulky or when the carboxylate oxygen atoms are replaced by sulphur. Hence $R_3Sn(XY)CR^1$ ($R = Pr^i$, $R^1 = Me$, $X = Y = O$; $R = R^1 = Me$, $X = S$, $Y = O$; $R = R^1 = Me$, $X = Y = S$) is monomeric with tin reverting to its four-co-ordinate state, but a number of compounds of the type ClR_2SnO_2CMe, which are also monomeric, contain a chelating carboxyl group and five-co-ordinate tin (251). Other examples of monomeric five co-ordinate tin include the simple adducts formed between an organotin compound and a donor molecule. In general compounds $RSnX_3$, for example, readily form such complexes, the lowering in the acceptor strength of tin only becoming at all striking when weak donors are involved, alkyl sulphides giving adducts with $SnCl_4$ but not with $PhSnCl_3$ (252-3). Typical of a large number of 1:1 adducts with five-co-ordinate tin is $Me_3SnCl.py$, an X-ray crystal study of which has shown that the molecule is a trigonal bipyramid with the pyridine unit and the chlorine atom lying on either side of the plane of the three methyl groups (254). For compounds of the general formula R_2SnX_2 where X has donor properties, the possibility of tin achieving a <u>six-co-ordinate</u> state by autocomplex formation arises. The polymeric fluorides R_2SnF_2 (eg. R = Me (255)) have octahedral co-ordination at tin and the structure of dimethyltin bis(fluorosulphate), $Me_2Sn(FSO_3)_2$, is based on a distorted form of the Me_2SnF_2 structure having fluorosulphate bridges. The dicarboxylates, $R_2Sn(O_2CR^1)_2$, alternatively, are monomeric and it is suggested that the six-co-ordination state of tin is achieved by the two chelating carboxyl groups (251,256). A simple six-co-ordinate structure is possible for many adducts of tinIV compounds with bidentate (1:1) or monodentate (2:1) donor molecules. One exception to this is bipy. $\left[Ph_2Sn(NCO)_2\right]_2$ in which tin is five - co-ordinate and bipyridine is acting as a bridging group (257). There are fewer examples of compounds containing tin in a co-ordination state greater than six. Compounds of general formula $RSnX_3$ where X is a chelating ligand and tin is seven-co-ordinate might be expected to have a structure based on a pentagonal bipyramid. Such a structure has been proposed for the alkyltin tricarboxylates, $RSn(O_2CR^1)_3$ (242) and has been established for $MeSn(NO_3)_3$ (258), tris(tropolonato)monochlorotin (259) and the ethylenediaminetetracetic acid complex $Sn^{IV}(EDTA).H_2O$ (260).

Eight-co-ordinate tin is a much rarer condition, but exists in bis(phthalocyaninato)tin(IV), which has a structure based on a square anti-prisom of nitrogen atoms (261), and tin(IV) nitrate, having a structure based on a dodecahedron of oxygen atoms, the four nitrate groups being arranged symmetrically and bidentate to the central tin atom (262).

The experimental work about to be described involves almost exclusively the systems MCl_4(M = Sn, Ge, Si) and lithio-amidines, $MeC(NR)_2Li$ (R = Ph, p-tolyl). The nature of the N,N^1-disubstituted amidine ligand and a brief review of symmetrically substituted N-metallated amidines has already been presented in Chapter 4 - Section 4.3.3(a) pages 170 to 179.

5.3. Experimental

All the reactions were carried out under an atmosphere of dry nitrogen. The tetrahalides of tin and silicon were purified by vacuum distillation but germanium(IV) chloride was used directly as a fresh commercial sample.

(i) Reaction of N,N^1-di-p-tolylacetamidinolithium with tin tetrachloride, (mole ratio (1:1))

21.78 mmol of N,N^1-di-p-tolylacetamidinolithium (made by reacting 5.16g, 21.78 mmol of N,N^1-di-p-tolylacetamidine in 100cm^3 anhydrous ether with 12.1 cm^3 of 1.8M Bu^nLi at -

-196^{o}, and stirring to room temperature for about 30-45 minutes) suspended in about $100-120cm^{3}$ ether/hexane was cooled to $-196^{o}C$. Tin(IV) chloride was added ($2.55cm^{3}$, 21.78 mmol) and the mixture was allowed to warm to room temperature being stirred continuously. It was stirred overnight, and all solvent was then removed under reduced pressure from the creamy suspension. Anhydrous toluene was added ($50cm^{3}$) and refluxed for 20 minutes followed by filtration of the hot suspension. The yellow filtrate after concentration deposited a yellow powdery solid identified as $\underline{N,N^{1}}$-di-p-tolylacetamidinotin(IV)trichloride, $MeC(NC_6H_4pMe)_2Sn^{IV}Cl_3$, mp 170-175°.

Found: C = 42.4; H = 3.5; N = 5.9; Cl = 23.0%
M, 441

$C_{16}H_{17}N_2SnCl_3$ requires C = 41.5; H = 3.7; N = 6.1;
Cl = 23.0% M, 462

ν max(Nujol Mull) 1638v.w, 1579m, 1504v.s, 1489v.s, 1408v.s, 1370v.s, 1318m, 1300m, 1280w, 1211m, 1118sh, 1106m, 1033m, 1021s, 937s, 859v.s, 804v.s, 773s, 764w, 723w.br, 708s, 665s, 643w, 633m, 583s, 518vs, 502m, 456s, 387s, 368sh, 337m cm^{-1}.

(ii) Reaction of N,N^{1}-diphenylacetamidinolithium and tin tetrachloride (mole ratio 2:1)

The procedure as outlined in (i) was followed in most of the reactions conducted, and consequently only essential details are subsequently offered. This reaction employed 21.92 mmol of N,N^{1}-diphenylacetamidinolithium and 10.96mmol of tin(IV)chloride. The work-up procedure was as above and the concentrated toluene extract was cooled overnight to about -20°. A white amorphous solid was obtained and identified as bis(N,N^1-diphenylacetamidino)tin(IV)dichloride, $\left[\left\{MeC(NPh)_2\right\}_2 Sn^{IV}Cl_2\right]_x$ m.p. 228-230°C.

Found: C = 54.1; H = 4.4; N = 8.7; Cl = 12.1%

M, by cryoscopy 691

$C_{28}H_{26}N_4SnCl_2$ requires C = 55.3; H = 4.3; N = 9.2;
Cl = 11.7% M, 608

ν max(Nujol Mull) 1660vwbr, 1595s, 1580m, 1563sh, 1540sbr, 1519s, 1508sh, 1496vsbr, 1445s, 1417vs, 1376s, 1320m, 1304s, 1281s, 1219s, 1182w, 1175w, 1160m, 1075m, 1031m, 1019m, 1005w, 963w, 918m, 909m, 846m, 835m, 768m, 745vs, 740sh, 725sh, 704m, 690vs, 672m, 630vwbr, 588m, 582m, 518s, 480vw, 428m, 380sh, 350sh, 340w cm^{-1}.

(iii) Reaction of N,N^{1}di-p-tolylacetamidinolithium with tin tetrachloride (mole ratio 2:1)

The above procedure was followed using 32.57 mmol amidinolithium and 16.28 mmol tin(IV)chloride. A white microcrystalline solid was obtained and identified as bis(N,N^1-di-p-tolylacetamidino)tin(IV)dichloride, $\left[\left\{MeC(NC_6H_4pMe)_2\right\}_2 Sn^{IV}Cl_2\right]_x$ m.p. 300°d.

Found: C = 57.6; H = 5.4; N = 8.4; Cl = 10.3%

M, by cryoscopy 827

$C_{32}H_{34}N_4SnCl_2$ requires C = 57.9; H = 5.1; N = 8.4;
Cl = 10.7% M, 764

ν max(Nujol Mull) 1645vwbr, 1578w, 1550sh, 1543sh, 1538s, 1510vs br, 1495vs, 1412vs, 1379s, 1368s, 1312m, 1300s, 1278w, 1246w, 1219s, 1178w, 1126vwbr, 1108s, 1042wbr, 1025m, 1011m, 939w, 864s, 853m, 837wbr, 818w, 804s, 790w, 757w, 732w, 710m, 700w, 658m, 633w, 580s, 522vs, 499w, 470vw, 430vw, 385m, 358sh, 322wbr, cm^{-1}.

(iv) Reaction of N,N^1-di-p-tolylacetamidinolithium with silicon tetrachloride (mole ratio 1:1 or 2:1)

The above procedure was followed on a molar ratio of 1:1 (17.7 mmol of each reagent) and 2:1(25.3 mmol of amidinolithium - 12.6 mmol of silicon(IV) chloride). The white microcrystalline product was identified, in both systems, as bis(N,N^1-di-p-tolylacetamidino)silicon(IV)dichloride, $\left[\left\{MeC(NC_6H_4pMe)_2\right\}_2 SiCl_2\right]_x$ m.p 242°-246°.

Found: C = 65.7; H = 6.4; N = 9.9; Cl = 12.3%

M, by cryoscopy, 658.

$C_{32}H_{34}N_4SiCl_2$ requires C = 67.0; H = 5.6; N = 9.8;

Cl = 12.4% M, 573.

ν max(Nujol Mull) 1646w, 1610w, 1578sh, 1560vsbr, 1508vsbr, 1412vs, 1378s, 1368s, 1320s, 1311s, 1305s, 1278w, 1226vs, 1212m, 1174m, 1108vs, 1042sh, 1034m, 1028s, 1011s, 968vw, 944s, 886s, 860s, 846vw, 832vw, 822m, 809vs, 798sh, 770w, 733w, 720w, 711s, 700vw, 662w, 650m, 620sh, 600vs, 560vs, 525vs, 505m, 476vs, 460s, 430s, 408s, 388m, cm^{-1}.

(v) Reaction of N,N^1-di-p-tolylacetamidinolithium with germanium tetrachloride (mole ratio 1:1 or 2:1)

The above procedure was followed on both a 1:1 and a 2:1 molar ratio basis (18.1 mmol of each and 25.2 mmol amidinolithium: 12.6 mmol germanium IV chloride respectively). The white solid isolated in both cases was identified as bis(N,N^1-di-p-tolylacetamidino)germanium(IV)dichloride, $\left\{\left[MeC(NC_6H_4pMe)_2\right] GeCl_2\right\}_y$ m.p. 240° - 245° d.

Found: C = 62.0; H = 5.1; N = 9.0; Cl = 11.3%

M by cryoscopy 770

$C_{32}H_{34}N_4GeCl_2$ requires C = 62.2; H = 5.5; N = 9.1;
Cl = 11.5% M, 617.5

ν max(Nujol Mull) 1646m, 1608w, 1575m, 1561sh, 1552vs, 1510vs br, 1480vs br, 1412s br, 1380s, 1368s, 1314s, 1303, 1281w, 1265w, 1250vw, 1220vs, 1173w br, 1107s, 1024s, 1011m, 940m, 870vs, 852s, 818m, 804vs, 790m, 760m, 734m br, 717m, 709s, 697w, 659w, 647w, 586vs, 524vs, 509m, 500w, 462m, 438m, 400vs, 338w, 322w, cm^{-1}.

(vi) Reaction of N,N^1-diphenylacetamidinolithium and tin tetrachloride (mole ratio 3:1)

The above procedure was followed employing 29.7 mmol of amidinolithium and 9.9 mmol of tin(IV)chloride. The white powder obtained was identified as tris(N,N^1-diphenylacetamidino)tin(IV)monochloride, $\left[\left\{MeC(NPh)_2\right\}_3 Sn^{IV}Cl\right]_x$ mp. 183° - 193°

Found: C = 63.2; H = 5.4; N = 10.4; Cl = 4.8%

$C_{42}H_{39}N_6SnCl$ requires C = 64.8; H = 5.0; N = 10.8;
Cl = 4.6%

ν max(Nujol Mull) 1653m br, 1590s, 1574s, 1563sh, 1538s br, 1520m br, 1492v s br, 1445m, 1417vs, 1378s, 1318w, 1303m, 1280m, 1262w, 1218m, 1182w, 1173w, 1156w, 1070m br, 1030m, 1015m, 1005w br, 960w, 916m, 907m, 840m, 768m, 746vs, 738w, 728w, 700sh, 690vs, 670m,br, 615v w br, 586m, 518m, 468w, 428w, 405w, 332w, cm^{-1}.

(vii) Reaction of N,N^1-di-p-tolylacetamidinolithium and tin tetrachloride (mole ratio 3:1)

A similar procedure to that established above was followed using 26.87mmol of amidinolithium and 8.96mmol tin(IV) chloride. The white powder obtained was identified as tris(N,N^1-di-p-tolylacetamidino)tin(IV)monochloride, $\left[\left\{MeC(NC_6H_4pMe)_2\right\}_3Sn^{IV}Cl\right]_x$ m.p. 235 - 245 d.

Found: C = 66.1; H = 6.6; N = 9.3; Cl = 4.0%

$C_{48}H_{51}N_6SnCl$ requires C = 66.6; H = 5.9; N = 9.7; Cl = 4.1%

ν max(Nujol Mull) 1645m br, 1610w br, 1580sh, 1560s br, 1512vs br, 1483vs, br, 1413s br, 1378s, 1369s, 1221m, 1312m, 1305m, 1226m, 1210w, 1172w, 1105m, 1040w, 1030w, 1025m, 1010m, 940m, 883s, 858m, 820m, 806s, 795w br, 765w.br, 730vw br, 708m, 698vw, 658m br, 646vw, 598s, 588w, 568s, 522s, 517w, 502m, 473s br, 458w, 426m, 405s, 400w, 384m, 363sh, 350sh, 330sh, 310sh cm^{-1}.

(viii) Reaction of N,N^1diphenylacetamidinolithium and tin tetrachloride (mole ratio 4:1)

The standard procedure outlined was followed using 33.53 mmol of amidinolithium and 8.38 mmol of tin(IV)chloride. The white solid produced was identified as tetrakis(N,N^1-diphenylacetamidino)tin(IV), $\left[\left\{MeC(NPh)_2\right\}_4Sn^{IV}\right]_x$ m.p 245-255°d.

Found: $C = 71.5$; $H = 6.1$; $N = 11.9$; $Sn = 11.9\%$

$C_{56}H_{52}N_8Sn$ requires $C = 70.4$; $H = 5.5$; $N = 11.7$; $Sn = 12.4\%$

ν max(Nujol Mull) 1655s br, 1625sh, 1592vs, 1572vs, 1550vs br, 1490vs, 1445sh, 1412vs br, 1379vs, 1366vs, 1324m br, 1312w, 1290m, 1268s, 1255sh, 1221vs, 1212sh, 1182vw, 1171m, 1154w, 1100w, 1085sh, 1072 , 1028vs, 1019sh, 1004m, 975v w br, 962w, 908s, 837vs, 802m, 790vw, 767m, 746vs, 726m, 693vs, 653m br, 617w br, 575m, 520vs, 488w, 467w, 424w, 380sh, 360sh, 332sh, 310vw cm^{-1}.

(ix) The reaction of N,N^1-di-p-tolylacetamidinolithium and tin tetrachloride (mole ratio 4:1)

Using 29.59 mmol of amidinolithium and 7.39 mmol of tin (IV)chloride the white powder isolated was identified as tetrakis(N,N^1-di-p-tolylacetamidino)tinIV, $\left[\left\{MeC(NC_6H_4pMe)_2\right\}_4 Sn^{IV}\right]_x$ m.p. 260°-280°d.

Found: $C = 70.6$; $H = 6.4$; $N = 10.3$; $Sn = 11.1\%$

$C_{64}H_{68}N_8Sn$ requires $C = 72.0$; $H = 6.4$; $N = 10.5$; $Sn = 11.1\%$

ν max(Nujol Mull) 1652m br, 1635v w br, 1597m, 1572w, 1535sh, 1507vs, 1493vs, 1414s br, 1378s, 1366s, 1331m, 1311m, 1298m, 1275w br, 1242w br, 1218s, 1172m, 1107s, 1035w br, 1022m, 937w, 863s, 850m, 818w, 806s, 790w, 657m, 631vw, 575s, 579vs, 490w, 396w, 386m, 322m br, cm^{-1}.

(x) Attempted preparations of $\left[MeC(NR)_2\right]_n MCl_{4-n}$ ($M = Si$, Ge, $n = 3, 4$).

Following the procedure already outlined in reactions of amidinolithium and silicon/germanium (IV)chloride in 3:1 and 4:1 molar ratios were studied. In all cases, products were obtained which were identified, by means of their infrared spectra, as the bis-amidino-derivatives $\left[MeC(NR)_2\right]_2MCl_2$. There was no evidence of higher substitution products.

(xi) Reaction between N,N^1-di-p-tolylacetamidine and tin tetrachloride

4.7875g of N,N^1-di-p-tolylacetamidine (20.09 mmol) in 60cm^3 anhydrous toluene was mixed with 5.2314g tin(IV) chloride (20.09 mmol) and the yellow solution was refluxed for about 24 hours. The off-white suspension formed was filtered off, washed with toluene and pumped solvent free, and isolated as product A. The yellow filtrate after cooling formed a yellow amorphous mass B, recognised by its infrared spectrum as being N,N^1-di-p-tolylacetamidinotin(IV)trichloride, $MeC(NC_6H_4pMe)_2SnCl_3$.

The analysis of A gave the following data:

C = 46.5; H = 4.7; N = 7.0; Cl = 26.3%

The infrared spectrum suggest A is a mixture of N,N^1-di-p-tolylacetamidinium chloride, $MeC(NHC_6H_4pMe)_2^+Cl^-$ and N,N^1-di-p-tolylacetamidine.tin(IV)chloride adduct, $MeC(=NC_6H_4pMe)NHC_6H_4pMe.SnCl_4$, in the approximate molar ratio of 2:3

Found C = 46.5; H = 4.7; N = 7.0; Cl ≠ 26.3%

$C_{16}H_{19}N_2Cl$ requires C = 69.9; H = 6.9; N = 10.2; cl = 12.9%

$C_{16}H_{18}N_2SnCl_4$ requires C = 38.5; H = 3.6; N = 5.6; Cl = 28.5%

A mixture of these two products with the stoichiometry suggested would have a composition C = 46.7; H = 5.0; N = 6.8; Cl = 24.3%.

Section 5.4 Discussion

(a) Preparation and stability of the new N-metallated -acetamidino derivatives

The new compounds are tabulated in Table 5.1, the abbreviations Am and Am^1 being used to represent the N,N^1-diphenylacetamidino, $MeC(NPh)_2$, and the N,N^1-di-p-tolyl-acetamidino, $MeC(NC_6H_4pMe)_2$, units respectively.

Table 5.1

New N,N^1-diarylacetamidino Compounds of Silicon, Germanium and Tin.

$Am_n\ Sn^{IV}Cl_{4-n}$	n = 2, 3, 4	White solids
$Am^1{}_nSn^{IV}Cl_{4-n}$	n = 1	Yellow solid
	n = 2, 3, 4	White solids
$(Am^1{}_2SiCl_2)_x$		White solid
$(Am^1{}_2GeCl_2)_y$		White solid

The only successful preparative route to these compounds was the reaction of the appropriate acetamidinolithium with the metal halide (equation 5.1).

$$n\ Am(or\ Am^1)Li + MCl_4 \longrightarrow nLiCl + Am(or Am^1)_nMCl_{4-n} \qquad 5.1$$

The reaction between the acetamidinolithium, AmLi (80) or Am^1Li, and MCl_4 (M = Si, Ge) in 1:1 molar proportions yields the bis(acetamidino) metal dichlorides, Am_2MCl_2 or $Am^1{}_2MCl_2$, feasibly by a route involving the disproportionation of the initially formed acetamidino metal trichloride (eg. Equation 5.2). These bis-derivatives were also the

$$2Am^1MCl_3 \longrightarrow Am^1{}_2MCl_2 + MCl_4 \qquad 5.2$$

product of the reaction (equation 5.1) whatever the relative molar proportions of the reagents.

The direct aminolysis of MCl_4(M = Sn) by N,N^1-diphenylacetamidine (AmH) (80) and N,N^1-di-p-tolylacetamidine (Am^1H) afforded a mixture of the amidinium chloride and amidinotin (IV)-trichloride (equations 5.3 - 5.4)

$$Am^1H + SnCl_4 \longrightarrow Am^1H.SnCl_4 \qquad 5.3$$

$$2\ Am^1H.SnCl_4 \longrightarrow Am^1Sn^{IV}Cl_3 + Am^1H_2^+Cl^- + SnCl_4 \qquad 5.4$$

As with the methyleneamino and acetamidino tin(II) compounds discussed in Chapter 4, all the new compounds are air and moisture sensitive. Decomposition is indicated by the appearance in the infrared spectrum of bands at (3200-3400)cm^{-1} and (1629 - 1635)cm^{-1} corresponding to ν(N-H) and ν(C=N) of the free amidines respectively. Molecular weights as determined cryoscopically - where such was possible - gave values which were consistently low, presumably a consequence of sample decomposition.

(b) Characterisation and spectroscopic properties of the new N,N^1-disubstituted acetamidino derivatives

N, N^1-diphenylacetamidinotin(IV)trichloride, $AmSn^{IV}Cl_3$, has been shown to be monomeric both in solution and in the solid state (80). A crystal structure determination (213) shows it to contain five-co-ordinate tin with a chelating amidino group. A molecular weight determination by cryoscopy also confirms the monomeric nature of $Am^1Sn^{IV}Cl_3$ in solution (M, 441; monomer requires 462). Its infrared, ^{1}H-NMR and mass spectra - all discussed in greater detail later are similar to those of the phenyl analogue and is therefore judged to have a similar structure (Figure 5.1).

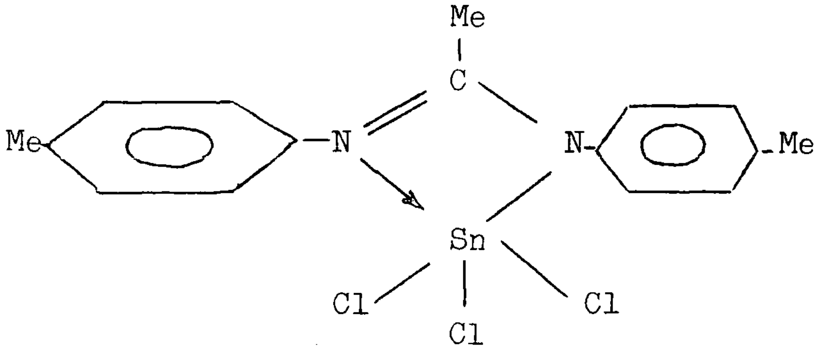
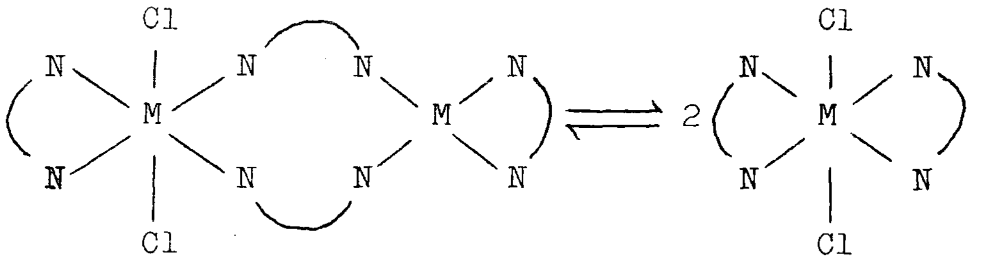


Figure 5.1

Molecular weight determinations, by cryoscopy, of $(Am^1{}_2MCl_2)_n$ (M = Si, Ge, Sn) and $(Am_2MCl_2)_n$ (M = Sn) are rather ambiguous, the determined values being 658, 770, 691 and 827 (monomeric values required are 573, 617.5 608 and 764) respectively. It may be that allowing for sample decomposition, all of these bis-amidino derivatives are dimeric in solution. However whilst the ^{1}H-NMR spectrum - taken at about 42° - of $(Am^1{}_2MCl_2)_n$ (M = Si) can be interpreted in terms of a dimeric structure, the other spectra do not show the presence of distinguishable amidino groups even when cooled to ca -50°. It is possible therefore that, if $(Am^1{}_2GeCl_2)n$ and $(Am_2(\text{or } Am^1{}_2)SnCl_2)_n$ are dimeric in solution, an equilibrium between dimeric and monomeric forms could exist (equation 5.5). Such an equilibrium could offer additional explanation for the apparent



5.5

anomalies in the determined molecular weights of these compounds. The infrared spectra of $(Am^1{}_2MCl_2)_n$ M = Si, Ge are very similar and presumably they have similar structures in the solid state. Both bis-derivatives have two absorptions which may be assigned to the M-Cl stretching frequency, ν(M-Cl), corresponding to symmetric and asymmetric stretching vibrations. A structure involving a linear unit Cl-M-Cl is necessarily excluded therefore because its symmetrical stretching vibration would be inactive in the infrared. Both spectra show absorptions of medium intensity at about $1640cm^{-1}$ i.e. in the region appropriate to ν(C=N) - absorptions which are absent from the infrared spectra of $AmSn^{IV}Cl_3$ (80), $Am^1Sn^{IV}Cl_3$, $(Am_2Sn^{IV}Cl_2)_n$ and $(Am^1{}_2Sn^{IV}Cl_2)_n$. This suggests that a different mode of bonding for the amidino-ligands is possible. Indeed the presence of such an absorption, of medium intensity, could reflect a monodentate group, the need of which might be expected to be inversely proportional to the size of M, and directly proportional to the number of co-ordinated amidine groups. So whilst a distorted six-co-ordinate structure, shown in simplified form in Figure 5.2 - analogous to that found for $Me_2M(CN)_2$, M = Si, Ge, Sn (263) - cannot be excluded completely, an alternative proposal - discussed more fully later - for $(Am^1{}_2MCl_2)_2$

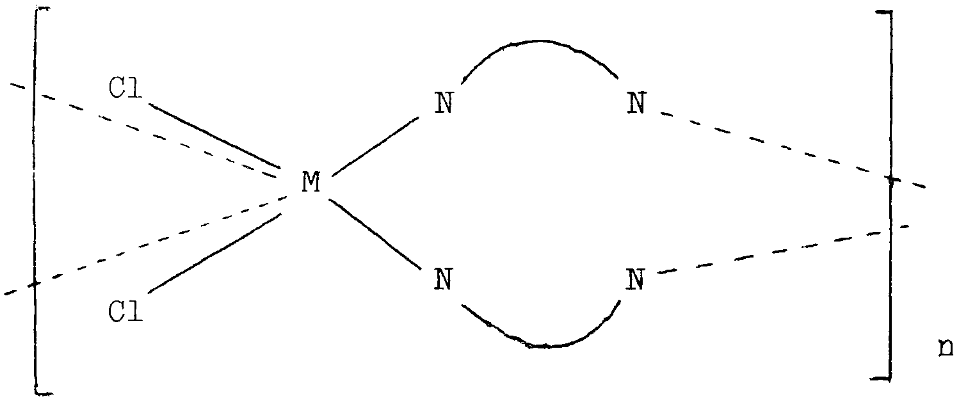


Figure 5.2

shown in Figure 5.3 has bidentate bridging amidine groups, monodentate terminal amidine groups and five co-ordinate atoms of M (M = Si, Ge).

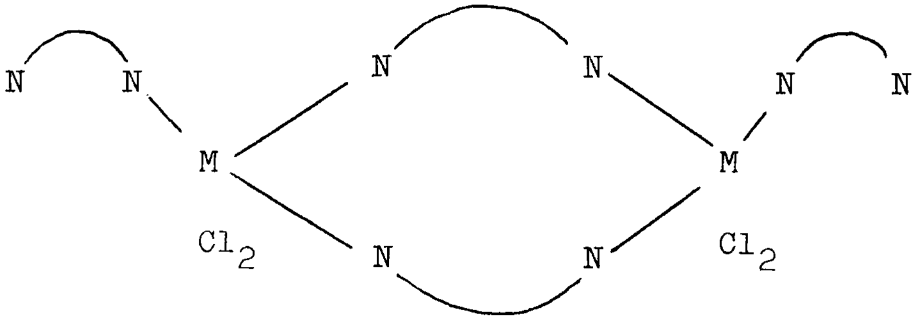
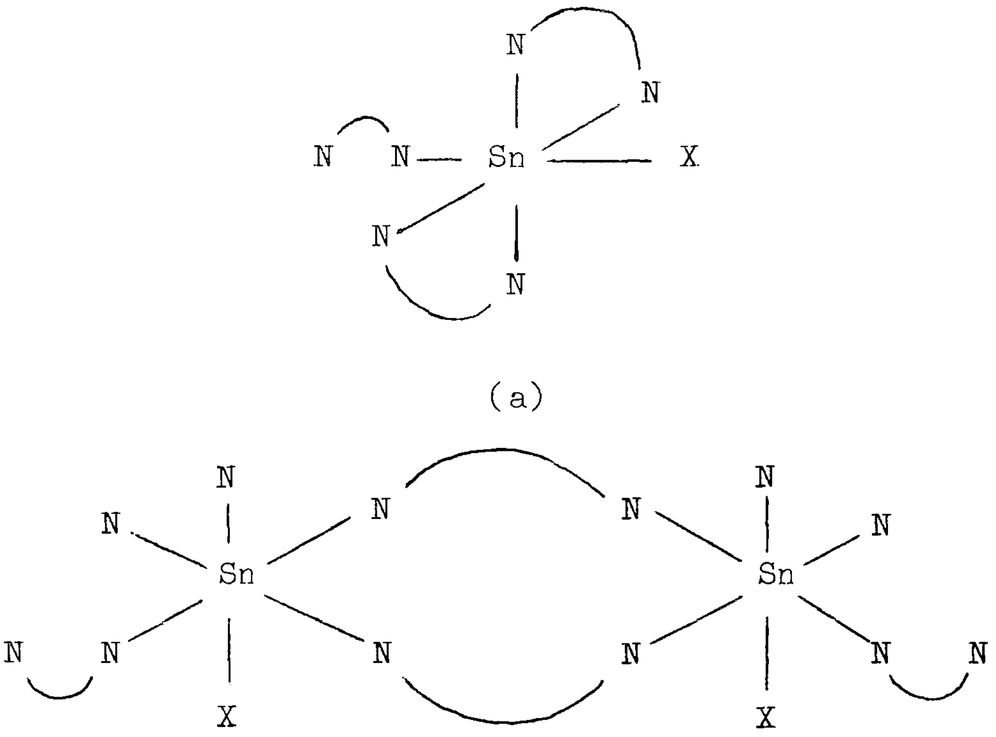


Figure 5.3

No evidence for the molecular state of the tris- and tetrakis- amidinotin(IV) compounds ($Am_3Sn^{IV}Cl$, $Am^1{}_3Sn^{IV}Cl$, Am_4Sn and $Am^1{}_4Sn$) was obtained by cryoscopy or from ^{1}H-NMR and mass spectral data. Proposals therefore concerning their structures are necessarily tentative. All the spectra have absorptions of medium intensity in the range (1645-1655) cm^{-1} which may reflect the presence of a monodentate amidino ligand. A possible structure for these derivatives, if they are monomeric, is shown in simplified form in Figure 5.4 (a) the group X representing a chloride atom or monodentate



(a)

(b)

Figure 5.4

amidine group. If the compounds are associated, a possible structure expressed in dimeric terms, again with six-co-ordinate tin, is shown in Figure 5.4 (b). Whilst the infrared data-presented in greater detail later - is difficult to interpret precisely, it would seem to favour an associated state for tris- and tetrakis- amidino derivatives of tin.

The ^{1}H-NMR spectra of the new N,N^{1}-diarylacetamidino compounds of tin(IV), silicon and germanium in CDCl$_3$ solution at about 42^{o} are tabulated in Table 5.2

Table 5.2

^{1}H-NMR Spectra of Some N,N^1-diarylacetamidino Derivatives of Group 4 Elements

Compound	Chemical Shifts τ ppm ^{a}			
	Ar-H	amidine-CH_3	tolyl-CH_3	N-H
$AmSn^{IV}Cl_3$ *	2.1, 2.2c	7.3s	-	-
Am^1SnCl_3	2.63c (8)	7.73s(3)	7.33s (1)	-
Am_2SnCl_2	2.28,2.48c(10)	7.63s(3)	-	-
$Am^1{}_2SnCl_2$	2.62,2.75c(8)	7.79s(3)	7.33s(6)	-
$Am^1{}_2SiCl_2$	2.38sbr(8)	7.68sbr(3)	7.12, 7.17(6)	-
$Am^1{}_2GeCl_2$	2.32, 2.44 2.52c (8)	7.70s(3)	7.18s (b)	-
$Am_3Sn^{IV}Cl$	2.18,2.36c(10)	7.57s(3)	-	-
$Am^1{}_3Sn^{IV}Cl$	2.78,3.13c(8)	8.03s(3)	7.31s (b)	-
Am_4Sn	2.43,2.89 2.93,3.02c(10)	7.87s(3)	-	-
$Am^1{}_4Sn$	2.28,2.52 2.67,3.08, 3.16c(8)	7.93s(3)	7.25s (b)	-
AmH	2.29c	7.64s br	-	3.07s
Am^1H	2.43,2.45, 2.48,2.50m	7.63s	7.27s	3.91s

* very poor resolution; s: singlet; d: doublet; m: multiplet; c: complex

a: relative to TMS as external reference τ = 10.0 ppm

All the spectra, but one, showed two sharp singlets when recorded on $CDCl_3$ solutions at about 42°C, one attributable to the amidino-methyl protons and the other to the p-tolyl-methyl protons. Both showed signs of slight broadening when the spectra were recorded at -50°C. Bis(N,N^1-diphenylacetamidino)silicon dichloride, $(Am_2SiCl_2)_n$ n probably 2, is reported as showing two peaks of relative intensities 1:1 which probably correspond to bridging and non-bridging amidino groups (80). Furthermore on cooling to -40°, the lower of the two methyl resonances was resolved into a doublet. This was explained by assuming the terminal ligand to be monodentate (<u>Figure 5.3</u>) the appearance of two-methyl signals, corresponding to the resolution of the syn-anti isomers, being consequential upon the freezing of the inversion process at the imine nitrogen. The ^{1}H-NMR spectrum of bis(N,N^1-di-p-tolylacetamidino)silicon dichloride, $(Am^1{}_2SiCl_2)_n$ n probably 2, also differs from the spectra of the bis(amidino)tin(IV) derivatives in showing at ambient temperatures two signals corresponding to p-tolyl-methyl protons, although only one signal - a broad singlet - corresponding to the amidine-methyl protons. It would seem that even at 42°C the amidino ligands are distinguishable and correspond to non-bridging and bridging units. Cooling to ca-50° did not freeze out the syn-anti isomers, but the singlet assignable to the amidine-methyl protons broadened noticeably. It seems possible therefore that $(Am^1{}_2SiCl_2)_2$ has the structure suggested in <u>Figure 5.3</u> with five co-ordinate silicon, bridging-bidentate and terminal-monodentate ligands. Since the infrared spectra of $(Am^1{}_2MCl_2)_2$ Me = Si, Ge, are very similar then such a structure cannot be ruled out (despite the absence of supporting ^{1}H-NMR data) for the corresponding germanium compound.

The other spectral data (Table 5.2) provides little further information concerning the structures of these compounds. It shows that in almost all cases the methyl group of the parent amidines is slightly more deshielded, i.e. farther downfield, than the amidine methyl protons of the metallated compounds. The chemical shift of the tolyl-methyl protons, on the other hand, is very small when the parent amidine, N,N^1-di-p-tolylacetamidine, is metallated.

The bands in the infrared spectra associated with NCN stretching vibrations, ν(NCN), are given in Table 5.3. Various assignments have been made for the stretching vibrations of the NCN unit in N-metallated amidines. A weak band at about 1640cm^{-1} together with other bands in the region (1500-1600)cm^{-1} were assigned to ν(NCN) for a series of tantalum or niobium chloride derivatives of a number of bidentate N,N^1-disubstituted amidines. On the other hand the symmetric and asymmetric modes of the (NCN) unit were considered to lie in the region (1300-1500)cm^{-1} for a number of transition metal-carbonyl systems (239). Some molybdenum and tungsten derivatives of N,N^1-diphenyl-acetamidine show an absorption of medium intensity at ca. 1630cm^{-1} and this was attributed to ν_{as}(NCN) and was considered to be consistent with a bidentate chelating amidino group (219). In general terms, any bands present in the infrared spectra of these new compounds in the range (1300–1660)cm^{-1}, which show variation from derivative to derivative, are regarded as candidates for assignment as (NCN) stretching frequencies. Table 5.3 shows the results of applying such a principle. The NCN stretching frequencies of these derivatives fall into three regions, viz (1310–1332)cm^{-1}, (1533–1566)cm^{-1} and (1645–1656)cm^{-1}. An X-ray crystallographic study of monomeric N,N^1-diphenylacetamidino-tin(IV) trichloride, $AmSnCl_3$ (213), shows that the molecule contains a bidentate chelating amidino group only. Its infrared spectrum shows no absorptions in the (1533–1566)cm^{-1} region and only a very weak absorption at 1326cm^{-1}. It may be therefore that the absorptions of significant intensity at (1533–1566) and (1310–1322)cm^{-1} may be assigned to those of bridging amidino ligands. In the infrared spectrum of $AmSnCl_3$ the weak absorption at 1645cm^{-1} – in the absence of absorptions which would indicate hydrolysis had occurred may then feasibly be assigned to a bidentate chelating amidino unit, but this is uncertain. The infrared spectrum of monomeric N,N^1-di-p-tolylacetamidino-tin(IV)trichloride, Am^1SnCl_3, together with its other characteristics already described, is consistent with its structure being similar to that of $AmSnCl_3$.

If the absorptions at (1310–1332)cm^{-1} and (1533–1566)cm^{-1} are assigned to bridging amidino ligands, then it would seem that the bis-amidino compounds $(Am_2MCl_2)_n$, $(Am^1{}_2MCl_2)_n$ M = Si, Ge, Sn, the tris-amidino compounds $(Am_3SnCl)_n$ and $(Am^1{}_3SnCl)_n$, and the tetrakis amidino derivatives Am_4Sn amd $Am^1{}_4Sn$ are

Table 5.3

ν(NCN) for Some N,N^1-diphenyl- and N,N^1-di-p-tolyl-acetamidino Derivatives of the Group IV Elements Silicon, Germanium and Tin

Compound	ν(NCN)cm^{-1} [a]	Reference
$AmSnCl_3$	1645w	80
Am^1SnCl_3	1645w	b
$(Am_2SnCl_2)_n$	1540s, 1319m	b
$(Am^1{}_2SnCl_2)_n$	1538s, 1312m	b
$(Am_2SiCl_2)_n$	1647w, 1566vs, 1332m	80
$(Am^1{}_2SiCl_2)_n$	1646m, 1560vs, 1320s	b
$(Am_2GeCl_2)_n$	1650w, 1554vs, 1324w	80
$(Am^1{}_2GeCl_2)_n$	1646m, 1553vs, 1314s	b
$(Am_3SnCl)_m$	1650m, 1538s, 1319m	b
$(Am^1{}_3SnCl)_m$	1645m, 1540m, 1310m	b
$(Am_4Sn)_m$	1655m, 1545s v br 1320w	b
$(Am^1{}_4Sn)_m$	1656m, 1533s, 1311m,	b
AmH	1629vs, 1535vs, 1338vs	b
Am^1H	1635vs, 1532vs, 1323s	b

a: Nujol Mulls, n, probably 2; b: this work all associated in the solid state. The infrared spectra of the derivatives Am_2MCl_2, $Am^1{}_2MCl_2$ (M = Si, Ge) and Am_nSnCl_{4-n}, $Am^1{}_nSnCl_{4-n}$ (n = 3, 4) show an absorption of medium intensity at (1646-1656)cm^{-1}. Whilst the ^{1}H-NMR spectrum of dimeric Am_2SiCl_2, discussed earlier, indicates the non-bridging amidino ligands to be monodentate in this compounds (80) such evidence could not be reproduced for $Am^1{}_2SiCl_2$. None the less it seems reasonable to postulate that the appearance of an absorption at (1646-1656)cm^{-1}- appearing as it does when the steric demands of the system intensify, (either as the number of amidino ligands increases, ot the size of the central atom decreases) may evidence a monodentate amidino ligand. In the infrared spectra of Am_2SnCl_2 and $Am^1{}_2SnCl_2$ the apparent absence of a high energy band, even of low intensity, at (1645-1656)cm^{-1} corresponding to a localised monodentate amidino group (or to a bidentate chelating)amidino group indicate that the solid is polymeric. In such a situation, all the amidino ligands could then be bridging (Figure 5.5).

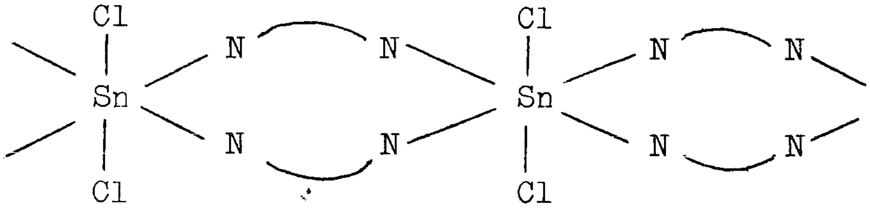


Figure 5.5

Metal-chlorine stretching frequencies for the compounds Am_nSnCl_{4-n}, $Am^1{}_nSnCl_{4-n}$ (n = 1, 2, 3), Am_2MCl_2 and $Am^1{}_2MCl_2$ (M = Si, Ge) are given in Table 5.4. Only one band is

Table 5.4

ν(M-Cl) For Some N,N^1-diarylacetamidino Derivatives of Silicon, Germanium and Tin

Compound	ν(M-Cl) cm^{-1}	
	as	s
$AmSnCl_3$ (80)	353	-
Am^1SnCl_3	336	-
Am_2SnCl_2	335	310
$Am^1{}_2SmCl_2$	323	298
Am_2SiCl_2 (80)	492	436
$Am^1{}_2SiCl_2$	476	429
Am_2GeCl_2 (80)	360	340
$Am^1{}_2GeCl_2$	340	322
Am_3SnCl	334	
$Am^1{}_3SnCl$	332	

quoted for each of the monomeric N,N^1-diarylacetamidinotin(IV)trichlorides, the two other bands expected are probably outside the range studied. Two bands are quoted for the bis-amidino derivatives Am_2MCl_2 and $Am^1{}_2MCl_2$ (M = Si, Ge, Sn) and this implies that their molecules (probably dimeric) contain a non-linear Cl-M-Cl arrangement. The trend in frequencies viz Si $>$ Ge $>$ Sn is consistent with the predominance of the mass effect.

In Table 5.5 are listed the frequencies of bands assignable to M-N stretching vibrations. The assignment must be regarded as tentative and mostly relate to only one of the M-N stretching absorptions expected for these compounds. The frequencies show the expected variation with M and appear to be in line with other M-N absorptions (264).

Whilst $AmSnCl_3$ and Am_2MCl_2 (M = Si, Ge) gave good mass spectra, each showing parent peaks corresponding to the monomeric units and several peaks containing one metal atom, the mass spectra of the new compounds were disappointingly unproductive. Several decomposition courses are open to amidino ligands, eg $(MeC(NR)_2$, the principal ones probably involving cleavage at nitrogen with loss of R· or RN·, loss of Me, and the formation of R_2N by elimination of acetonitrile. The major fragments for the new compounds are given in Table 5.6 a - f. Three of the new amidino derivatives, $Am^1{}_2MCl_2$ (M = Si, Ge) and Am_3SnCl, generated no metal-containing fragments and the other spectra showed only a small number of metal-containing fragments each with one

Table 5.5

ν(M-N) For Some N,N^1-diarylacetamidino Derivatives of Silicon, Germanium and Tin

Compound	ν(M-N) cm^{-1}
$AmSnCl_3$	677
Am^1SnCl_3	665
Am_2SnCl_2	672
$Am^1{}_2SnCl_2$	658
Am_2GeCl_2	(734)
$Am^1{}_2GeCl_2$	717, (509)
Am_2SiCl_2	868, 566
$Am^1{}_2SiCl_2$	860, 560
Am_3SnCl	675
$Am^1{}_3SnCl$	658
Am_4Sn	653
$Am^1{}_4Sn$	657

Table 5.6

Major Fragments in the Mass Spectra of Some N,N^{1}diarylacetamidino Derivatives of Silicon, Germanium and Tin

(a) Am^{1}SnCl$_3$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
629	2	$Am^1{}_2SnCl^+$	238	100	Am^{1+}
532	0.2	$Am^1SnCl_2NC_7H_7{}^+$	225	100	$SnCl_3{}^+$
497	0.2	$Am^1SnClNC_7H_7{}^+$	208	25	$C_7H_7NCC_7H_7{}^+$
463.5	20	$Am^1SnCl_3{}^+$	196	31	$(C_7H_7)_2N^+$
427	15	$Am^1SnCl_2{}^+$	155	63	$SnCl^+$
392	17	Am^1SnCl^+	132	100	$C_7H_7NCMe^+$
357	10	Am^1Sn^+	105	52	$C_7H_7N^+$
351	8	$(C_7H_7)_2NSnCl^+$	91	100	$C_7H_7{}^+$
260	1	$SnCl_4{}^+$			

m/e values refer to the peaks containing the most abundant isotopes (^{120}Sn, ^{35}Cl).

(b) Am_2SnCl_2

m/e	Relative Intensity	Assignment
608	3	$Am_2SnCl_2^+$
573	14	Am_2SnCl^+
210	2.2	AmH^+
209	67	Am^+
194	5	$PhNCNPh^+$
155	27	$SnCl^+$
118	100	$PhNCMe^+$
92	6	$PhNH^+$
91	10	PhN
77	91	Ph^+

(c) $Am^{1}{}_{2}SnCl_{2}$

m/e	Relative Intensity	Assignment
664	6	$Am^{1}{}_{2}SnCl_{2}$
237	30	$Am^{1}{}^{+}$
222	2	$C_7H_7NCNC_7H_7{}^+$
155	12	$SnCl^+$
132	100	$C_7H_7NCMe^+$
106	18	$C_7H_7NH^+$
91	24	$C_7H_7{}^+$

(d) $Am^{1}{}_{3}SnCl$

m/e	Relative Intensity	Assignment
664	5	$Am^{1}{}_{2}SnCl_{2}{}^{+}$
392	30	$Am^{1}SnCl^{+}$
237	25	Am^{1+}
222	2	$C_7H_7NCNC_7H_7{}^+$
155	30	$SnCl^+$
132	100	$C_7H_7NCMe^+$
119	7	$C_7H_7NCH_2{}^+$
106	3	$C_7H_7NH^+$
91	74	$C_7H_7{}^+$

(e) Am_4Sn

m/e	Relative Intensity	Assignment
329	6	$AmSn^+$
209	84	Am^+
194	2	$PhNCNPh^+$
168	9	Ph_2N^+
118	100	$PhNCMe^+$
104	5	$PhNCH^+$
91	4	PhN^+
77	100	Ph^+

(f) $Am^1{}_4Sn$

m/e	Relative Intensity	Assignment
357	5	Am^1Sn^+
237	19	Am^{1+}
132	100	$C_7H_7NCMe^+$
118	5	$C_7H_7NCH^+$
105	3	$C_7H_7N^+$
91	87	$C_7H_7{}^+$

metal atom. Parent peaks corresponding to monomeric units were obtained for Am_2SnCl_2 and $Am^1{}_2SnCl_2$but generally the spectra are swamped by the amidino ligands and their breakdown products. The spectra therefore are generally uniformative, their inconsistency and frequent irreproducibility probably being due to varying degrees of sample decomposition.

5.5 Summary

Several new metallated- N,N^1diarylacetamidine derivatives, (I; $\left[\left\{ MeC(NR)_2 \right\}_n MCl_{4-n}\right]_x$, R = Ph, p-tolyl, M = Si, Ge, Sn), have been prepared. Whilst mono-acetamidino derivatives of tin (IV) are stable(I; R = Ph, p-tolyl, M = Sn, n = 1), the analogous silicon and germanium compounds are not because they are unstable to disproportionation, affording the bis(acetamidino)metal-dichlorides (I; R = Ph, (80) p-tolyl; M = Si, Ge, n = 2). Attempts to prepare tris(acetamidino)- and tetrakis(acetamidino)-silicon and germanium derivatives (I; R = Ph, p-tolyl; M = Si, Ge; n = 3, 4) were unsuccessful, but the whole range of acetamidino derivatives (I; R = Ph, p-tolyl; M = Sn; n = 1-4) of the larger tin atom are isolable. Both the monoacetamidino derivatives of tin, $AmSn^{IV}Cl_3$ (80) and $Am^1Sn^{IV}Cl_3$ are monomeric and presumably of similar structure. A crystal structure of the former (213) shows it to contain five-co-ordinate tin, and a bidentate chelating amidino group which occupies one axial and one equational position in a distorted bipyramidal structure.

All the bis-amidino derivatives (I; R = Ph, p-tolyl; M = Si, Ge Sn; x probably 2) appear to be associated in both the solid state and in solution. In the latter instance an equilibrium between monomeric and dimeric forms is feasible. The solid silicon and germanium compounds may also be dimeric with five-co-ordinate metal atoms, and furthermore the non-bridging amidino group is probably monodentate to the metal. The solid bis-amidino-tin compounds may well be polymeric with bidentate-bridging amidino groups and six co-ordinate tin atoms. No firm evidence was obtained for the structures of the tris- and tetrakis- amidino derivatives of tin, but they are probably associated in the solid state, and appear to have bidentate-(terminal and bridging) and terminal monodentate-amidino ligands.

CHAPTER 6

THE RELATIVE LEWIS ACIDITIES OF SILICON-, GERMANIUM- AND TIN-TETRACHLORIDES TOWARDS ACETONITRILE, ACRYLONITRILE, ETHYL ACETATE, DIETHYL ETHER AND TETRAHYDROFURAN: A VAPOUR PRESSURE: COMPOSITION STUDY

6.1 Introduction

Whilst carbon tetrachloride shows no tendency to function as a Lewis acid, the other tetrachlorides of Group IV elements are able to co-ordinate with one or two molecules of Lewis bases (equation 6.1). Indeed

$$MCl_4 \underset{}{\overset{L}{\rightleftharpoons}} MCl_4.L \overset{L}{\rightleftharpoons} MCl_2 2L \qquad 6.1$$

a well established feature of their co-ordination chemistry is the fact that their Lewis acidity increases in the sequence $SiCl_4$, $GeCl_4$, $SnCl_4$ (6, 265-273). Calorimetric studies (265, 266), for example, of their reactions with pyridine and isoquinoline have shown that the heat evolved increases progressively in that sequence and that the tin(IV) chloride forms a wide range of relatively stable adducts, $SnCl_4.2L$, with bases such as ethers (267, 268) or nitriles (6, 82, 83, 273 - 276). These adducts are commonly isolable as crystalline solids soluble in inert solvents with varying degrees of dissociation (82, 83, 276, 277). The related silicon and germanium analogues, however, $SiCl_4.2L$ and $GeCl_4.2L$ are much fewer in number and, where they exist, dissociate more readily or are formed with the evolution of less heat (265, 266, 271, 273, 278). Whilst adducts of germanium- or silicon-tetrachlorides with nitriles or ethers have never been isolated, a feeble interaction between the chloride and weak donors such as nitriles and ether molecules has been assumed, such as would cause the acid-base mixtures to have relatively low vapour pressures. However, vapour pressure composition studies on liquid binary mixtures of silicon- or germanium-tetrachlorides with a range of Lewis bases (all of which were known to co-ordinate with tin tetrachloride but not with silicon- or germanium-tetrachlorides) have shown this assumption to be false. Indeed, with the exceptions of germanium tetrachloride (the stronger Lewis acid) and tetrahydrofuran (the strongest Lewis base), positive deviations have been found rather than the negative deviations expected.

These findings are discussed in Section 6.4 which begins on page 248 after the experimental section. The discussion also includes an evaluation of the use of the deviation from ideality of silicon tetrachloride- Lewis base systems as a criterion by which relative Lewis basicity can be established.

6.2 Experimental

6.2.1. Reagents

The Group IV tetrachlorides were purified by vacuum distillation. Acetonitrile was repeatedly distilled from P_2O_5 until little or no colour change occurred in the P_2O_5. Acrylonitrile was purified by being twice distilled from calcium hydride. Diethyl ether and tetrahydrofuran were dried over sodium wire and molten potassium respectively and ethyl acetate was purified by fractional distillation. The nitriles and the ester were stored over 3A molecular sieve.

6.2.2. Vapour pressure measurements

Rigorously anhydrous conditions were maintained throughout the experimental work by working under an atmosphere of dry nitrogen or by standard vacuum line techniques. Vapour pressures were determined manometrically. Acid-base mixtures of known composition were made by distilling weighed portions of base into a flask containing a measured quantity of the acid, and the vapour pressures of such mixtures were measured after vigorous stirring at 0°C. The values reported are constant equilibrium values, normally reached after stirring at 0°C for about one hour. Reproducibility was checked by conducting independent runs starting with fresh samples of MCl_4. Care was taken to avoid the accumulation of the volatile products of side reactions such as HCl and chloroethane. In the system $SiCl_4$ and Et_2O, for example, known to react slowly at or about room temperature to give EtCl and $SiCl_3OEt$ (279), careful monitoring was performed, by low temperature vapour pressure measurement and by taking gas-phase infra-red spectra, to ensure that no such side reactions had occurred.

The mixtures were then allowed to expand into a line of known volume (ca. $3dm^3$) and the partial pressures of acid and base in vapour samples were determined by measuring their vapour densities (known volumes were weighed under established temperatures and pressures), calculating their apparent molecular weights, M_{App} which were then used to compute the mole fractions of acid and base (equation 6.2).

$$M_{App} = (M_L \cdot mf_L) + (M_{MCl_4} \cdot mf_{MCl_4}) \qquad 6.2$$

M = molecular weight, mf = mole fraction, L = Lewis base and MCl_4 is $SiCl_4$ or $GeCl_4$.

The partial pressure of base, P_L was then calculated using (equation 6.3).

$$P_L = mf_L.P \qquad 6.3$$

P = total pressure

The reliability of this method, which depends upon there being negligible interaction of the components in the gas phase was established by a comparison with totally gaseous mixtures made from measured quantities of L and MCl_4, when the total pressure was found to be the sum of the partial pressures. An alternative method of determining P_L, the partial pressure of Lewis base, by measuring the intensities of characteristic bands in the infrared spectrum of a sample of the vapour, had been tried for the acrylonitrile- MCl_4 systems (280) but was found to be inadequate, and much less informative than vapour density measurements.

6.3 Results

The raw results for the eight binary systems studied in this work are given in Table 6.1 - 6.8 and the vapour pressure-composition curves for the ten systems studied, including the systems MCl_4 and CH_2CHCN (280), are given in Figures 6.1 - 6.5. The deviations from ideality, summarised in Table 9 are found by listing (i) the experimentally observed vapour pressures, P_{Expt}, of 1:1 mixtures of MCl_4 and L, (ii) the vapour pressures, P_{IDEAL}, expected for ideal 1:1 mixtures ($2P_{IDEAL} = P_{MCl_4} + P_L$), and (iii) the percentage deviation from ideality (equation 6.4).

$$\% \text{ deviation} = \frac{100(P_{EXPT} - P_{IDEAL})}{P_{IDEAL}} \qquad 6.4$$

All four nitrile systems $MCl_4.CH_2CHCN$ (Figure 6.1) and MCl_4 - MeCN (Figure 6.2) show pronounced positive deviations from ideality. The nitriles differ in their behaviour toward silicon- and germanium-tetrachlorides in that whilst acrylonitrile is miscible with both the Group IV tetrachlorides over the whole composition range despite their evident lack of mutual affinity- acetonitrile and MCl_4 form two liquid phases at 0^oC over the approximate composition ranges 15-80 mole % (M = Si) and 10-70 mole % (M = Ge). Between such limits the measured vapour pressures correspond to saturated solutions of MeCN in MCl_4 (the Group IV chloride is the more volatile component in both the acrylonitrile systems although this is somewhat marginal in the system $GeCl_4$ - MeCN).

The ethyl acetate systems, $SiCl_4/MeCO_2Et$ and $GeCl_4/MeCO_2Et$ (Figure 6.3) also show positive deviations from ideality, although such deviations are considerably less than in the nitrile systems (Figure 6.1).

Toward the ethers, Et_2O and THF, the different affinities of $SiCl_4$ and $GeCl_4$ reflect the greater Lewis acidity of the latter. Whilst $SiCl_4$ and Et_2O show a slight positive deviation from ideality, $GeCl_4$ and Et_2O exhibit ideal behaviour (Figure 6.4). In the tetrahydrofuran systems (Figure 6.5), the slight positive deviation evidenced by $SiCl_4$ may be contrasted with the slight negative deviation shown by $GeCl_4$.

Table 6.1

Vapour Pressure: Composition Data for the System $SiCl_4$-MeCN

Mole % MeCN	T K	Mass Condensate g	M_{App}	P mm	P_L mm
0	-	-	-	76.9	0
2.4	293	2.5896	165.09	82.21	3.07
5.78	293	2.7135	156.80	90.70	9.2
10.85	292.6	2.8446	151.27	98.42	14.23
15.5	292	2.8514	150.10	99.22	15.24
24.7	292	2.8385	148.68	99.72	16.42
35.4	292.6	2.8156	147.93	99.62	16.98
58.8	292.6	2.7999	147.02	100.2	17.8
70.2	291	2.7690	146.0	98.74	18.31
82.6	293.6	2.7107	143.84	98.97	20.01
89.9	293.2	1.9727	137.09	75.47	19.22
93.6	292.6	1.5963	130.67	63.94	19.5
96.2	293.3	1.2572	117.47	56.15	22.85
100	-	-	-	23.43	23.43

Table 6.2

Vapour Pressure: Composition Data for the System $GeCl_4$-MeCN

Mole % MeCN	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	24.3	0
4.3	296.3	1.1338	170.33	35.28	8.97
7.4	296.5	1.2668	159.21	42.20	13.43
11.6	296.5	1.2655	143.69	46.71	19.05
25.7	296.5	1.2544	142.49	46.69	19.36
39.3	296.3	1.2310	140.43	46.46	19.82
58.1	296.6	1.2075	138.16	46.37	20.4
71.9	296.4	1.2045	137.63	46.40	20.55
84.1	296.3	1.1429	135.18	44.81	20.48
91.4	296.2	1.0101	128.23	41.75	20.75
95.8	296	0.7075	104.7	35.78	22.64
100	-	-	-	23.43	23.43

Table 6.3

Vapour Pressure: Composition Data for the System $SiCl_4$-$MeCO_2Et$

Mole % Ester	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	76.79	0
11.45	288	2.4038	162.5	76.20	6.89
16.81	289	2.3864	162.32	76.00	7.04
24.57	290	2.3220	159.79	75.38	9.31
36.00	288	2.2270	157.81	72.70	10.75
45.27	292	2.0545	152.88	70.19	14.60
58.33	292.6	1.8046	148.74	63.50	16.43
71.50	292.3	1.5561	144.26	56.40	17.70
82.40	293.5	1.2666	134.20	49.55	19.46
89.40	292.5	0.9318	125.50	38.85	21.1
97.01	292.6	0.6017	105.29	29.91	23.63
100	-	-	-	24.10	24.10

Table 6.4

Vapour Pressure: Composition Data for the System $GeCl_4$-$MeCO_2Et$

Mole % Ester	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	24.30	0
6.99	291	1.0888	204.54	27.71	2.17
16.39	291.3	1.0422	188.63	28.79	5.87
25.72	291.3	1.0155	176.32	30.01	9.05
40.25	291.7	1.0082	170.19	30.91	10.82
54.5	291.7	1.0017	165.87	31.51	12.11
65.43	292.1	0.8927	149.07	31.29	16.18
83.47	292.1	0.6777	125.85	28.03	19.66
92.05	291	0.5871	112.45	27.27	22.02
100	-	-	-	24.10	24.10

Table 6.5

Vapour Pressure: Composition Data for the System $SiCl_4$-Et_2O

Mole % Ether	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	79.90	0
10.17	295.6	2.4376	140.48	91.75	28.18
15.90	296	2.5054	133.91	99.06	37.23
21.3	294.8	2.5231	125.52	106.00	49.11
33.15	295.1	2.8711	123.72	122.50	59.06
46.59	294.8	2.8650	111.25	135.80	83.15
58.75	294.7	2.9087	102.40	149.74	105.53
71.35	295.9	2.8720	94.25	161.29	127.39
81.90	296.4	2.8473	86.21	175.12	153.01
87.02	296	2.8704	84.67	179.50	159.73
96.06	296	2.7384	79.81	181.66	170.87
100	-	-	-	183.23	183.23

Table 6.6

Vapour Pressure: Composition Data for the System $GeCl_4$-Et_2O

Mole % Ether	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	24.3	0
10.04	295.8	1.1683	153.28	40.33	17.60
11.50	295.2	1.1844	147.16	42.50	20.40
13.42	295.5	1.2590	144.80	45.96	22.83
15.55	297	1.3001	137.15	50.36	27.79
22.34	295.2	1.5507	130.14	62.92	37.86
29.45	295.2	1.5591	114.30	72.03	51.50
32.06	295.6	1.5560	109.52	75.12	56.27
34.62	295.6	1.6151	108.10	79.00	59.98
48.78	294.7	1.9005	98.22	102.00	84.64
57.40	294.5	1.9485	89.24	115.02	102.82
66.55	294.7	2.1894	88.08	131.03	118.22
74.00	296.5	2.4009	87.78	145.06	131.18
81.04	296	2.4220	82.63	155.20	146.06
87.4	296	2.5242	81.01	164.98	157.18
93.86	296	2.4732	75.75	172.88	171.20
100	-	-	-	183.23	183.23

Table 6.7

Vapour Pressure: Composition Data for the System $SiCl_4$-THF

Mole % THF	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	76.90	0
7.7	292	2.4200	164.43	76.87	4.30
18.7	292	2.3515	159.09	77.20	8.53
33.1	292	2.1125	148.61	74.25	16.16
52.6	292	1.7098	128.96	69.25	28.29
65.6	292	1.4430	117.86	64.17	34.15
77.0	292.1	1.3237	110.06	62.84	38.46
85.5	292.1	1.1439	100.86	59.26	41.84
91.2	292.6	1.0045	92.28	56.97	45.22
95.1	292.1	0.8498	81.88	54.23	48.82
100	-	-	-	50.29	50.29

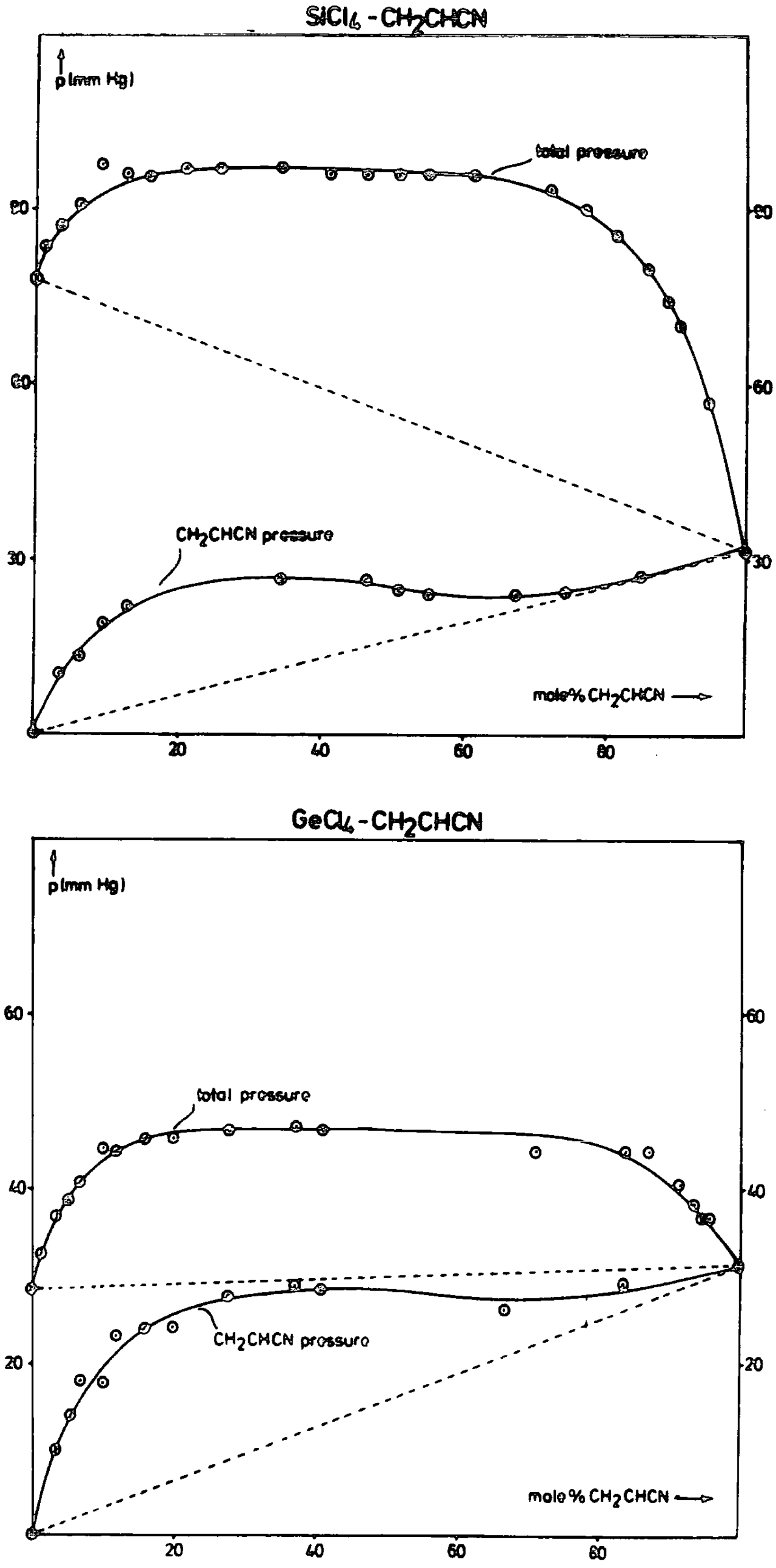
Table 6.8

Vapour Pressure: Composition Data for the System $GeCl_4$-THF

Mole % THF	T K	Mass Condensate g	M_{App}	P_{mm}	P_L mm
0	-	-	-	24.3	0
7.9	293	0.9664	202.60	25.00	2.07
14.9	293	0.9686	188.65	26.91	4.87
25.9	294.2	0.9174	168.10	28.72	9.35
37.1	293.3	0.9576	159.49	31.50	12.16
47.8	293.3	0.8740	140.66	32.60	16.90
57.9	293.7	0.8246	122.12	35.47	23.00
68.9	293	0.7143	97.13	38.54	31.77
82.1	294.3	0.6786	83.72	42.67	39.19
94.5	291	0.7372	78.79	48.64	46.32
100	-	-	-	50.29	50.29

NB The volume of the vac-line used was 3.486 dm^3

Figure 6.1

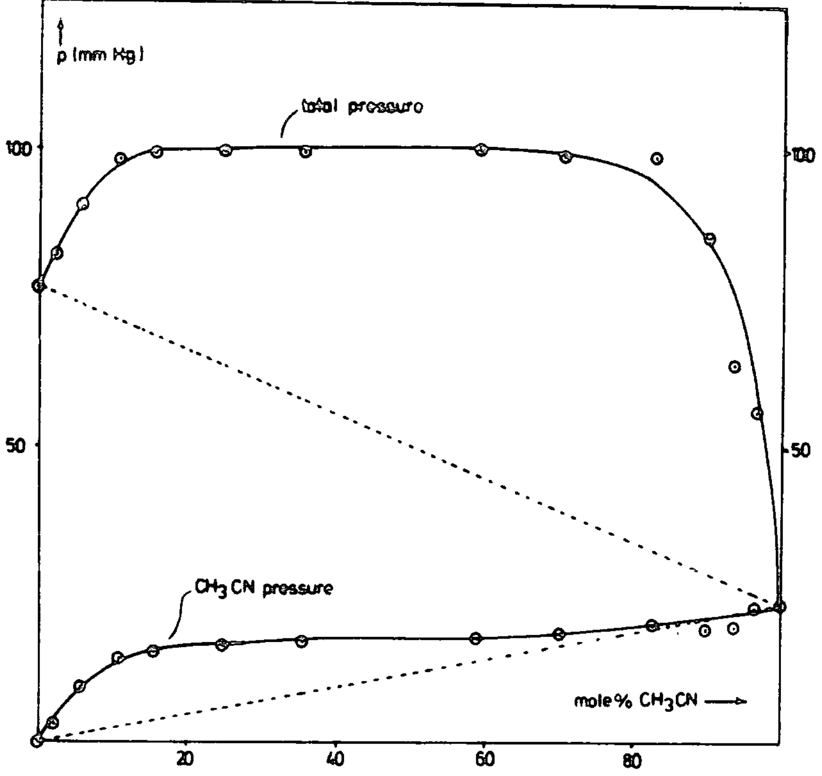


$SiCl_4$ - CH_2CHCN

$GeCl_4$ - CH_2CHCN

Figure 6.2.

SiCl$_4$-MeCN



GeCl$_4$-MeCN

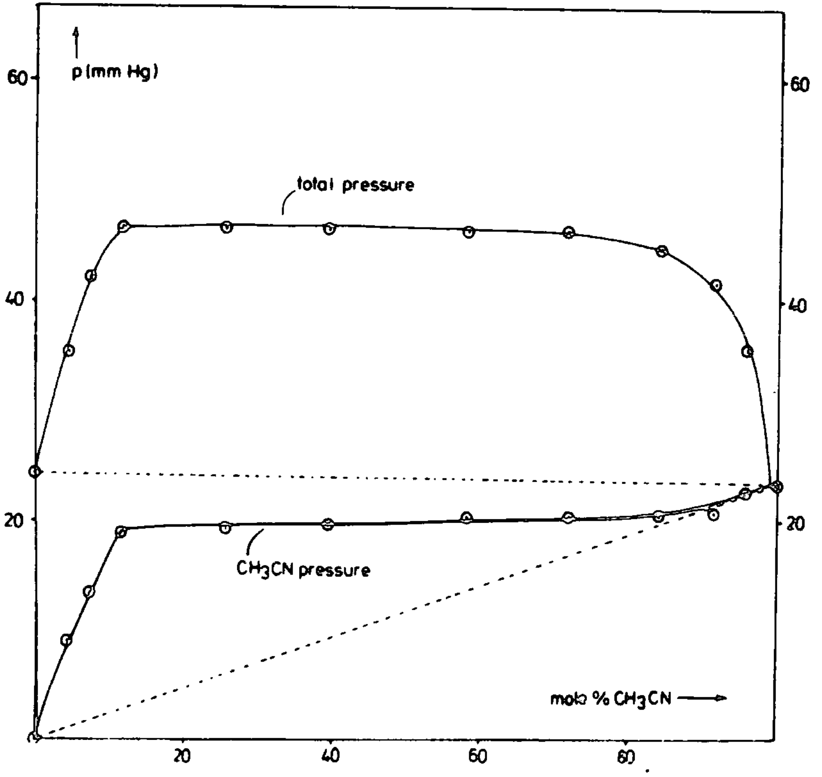


Figure 6.3

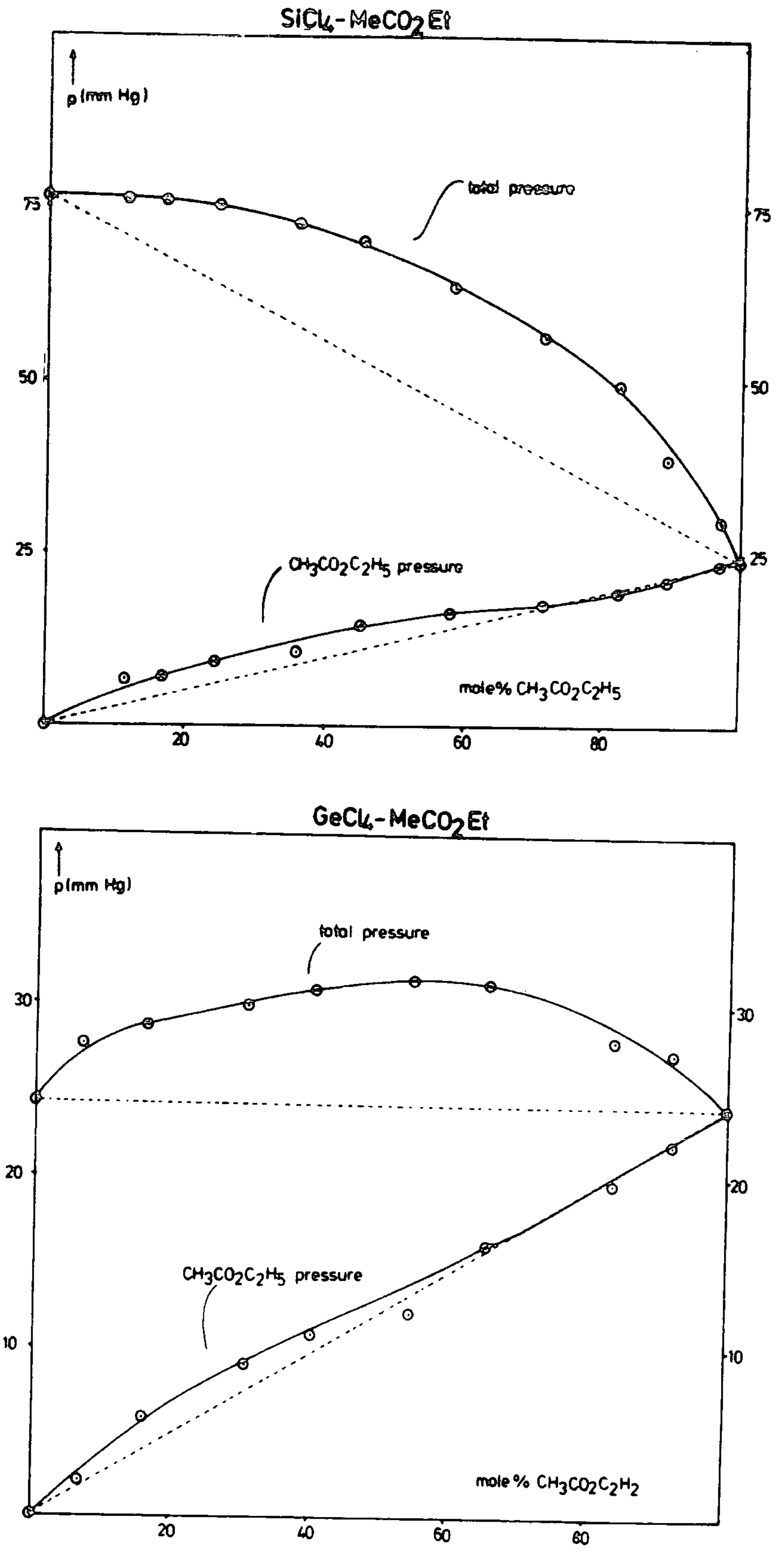
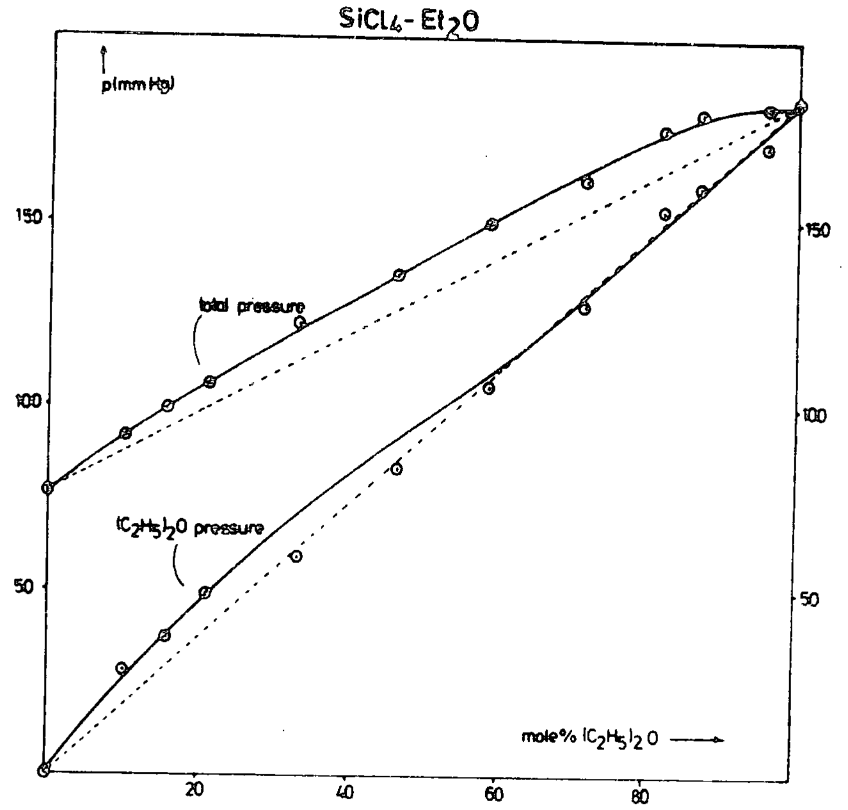

SiCl4-MeCO2Et
p (mm Hg)
total pressure
CH3CO2C2H5 pressure
mole% CH3CO2C2H5
75
50
25
75
50
25
20
40
60
80
GeCl4-MeCO2Et
p(mm Hg)
total pressure
CH3CO2C2H5 pressure
mole % CH3CO2C2H2
30
20
10
30
20
10
20
40
60
80

Figure 6.4.


SiCl$_4$-Et$_2$O
p(mm Hg)
total pressure
(C$_2$H$_5$)$_2$O pressure
mole% (C$_2$H$_5$)$_2$O
150
100
50
20
40
60
80
150
100
50

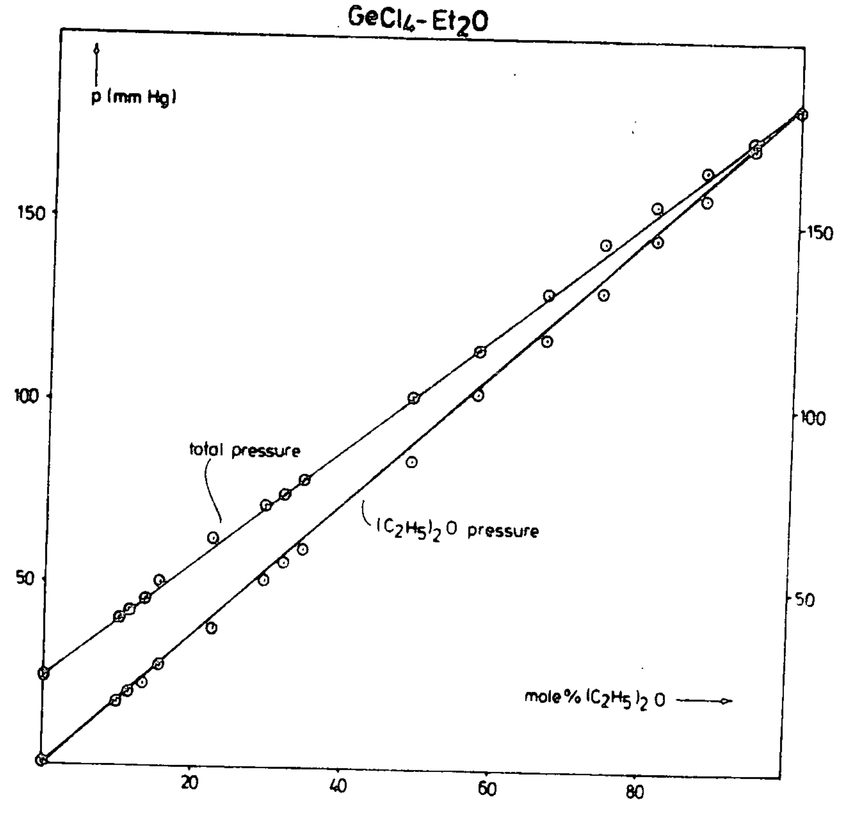
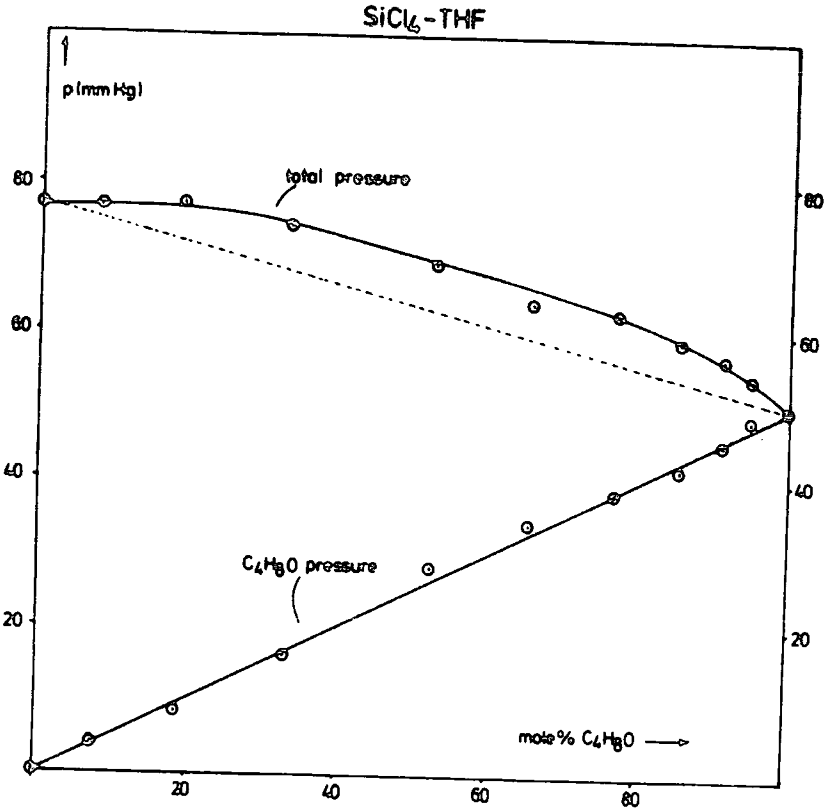

GeCl$_4$-Et$_2$O
p (mm Hg)
total pressure
(C$_2$H$_5$)$_2$O pressure
mole% (C$_2$H$_5$)$_2$O
150
100
50
20
40
60
80
150
100
50

Figure 6.5.


SiCl$_4$-THF
p(mm Hg)
total pressure
C$_4$H$_8$O pressure
mole% C$_4$H$_8$O
80
60
40
20
80
60
40
20
20
40
60
80

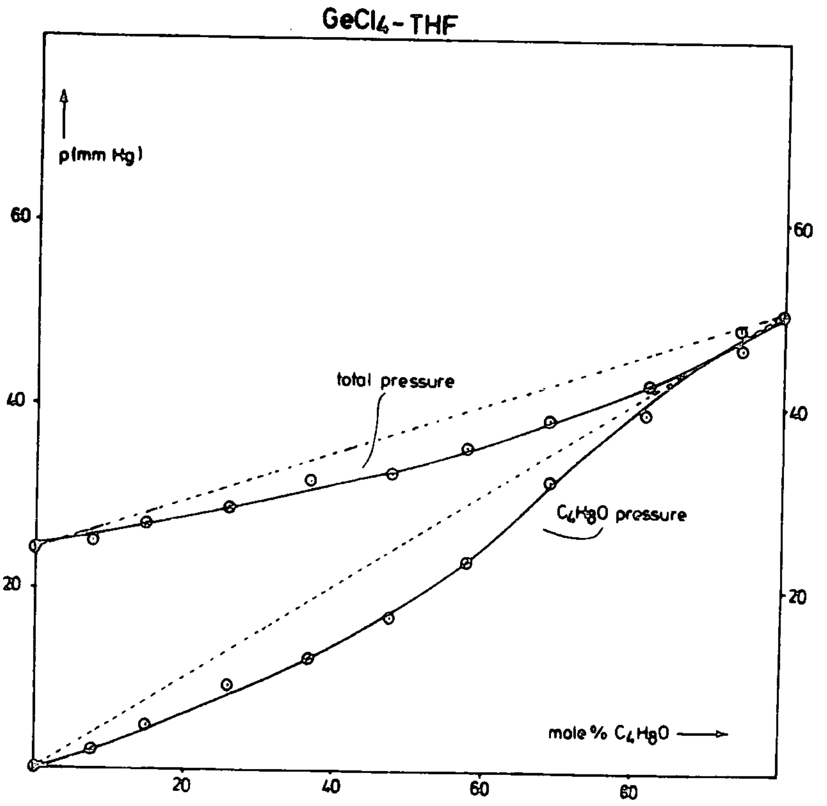

GeCl$_4$-THF
p(mm Hg)
total pressure
C$_4$H$_8$O pressure
mole% C$_4$H$_8$O
60
40
20
60
40
20
20
40
60
80

Table 6.9

Vapour Pressures of 1:1 Mixtures of MCl_4 and L at 0°C

Deviations from Ideality

Mixture	P_{Expt} mm	P_{IDEAL} mm **	% Deviation ***
$SiCl_4$, CH_2CHCN	96.6	54.4	+ 76.92
$GeCl_4$, CH_2CHCN	46.8	30	+ 56.0
$SiCl_4$, MeCN *	100	50	+ 100
$GeCl_4$, MeCN *	46.43	24	+ 93.45
$SiCl_4$, $MeCO_2Et$	67.5	50.05	+ 34.86
$GeCl_4$, $MeCO_2Et$	31.2	24.2	+ 28.92
$SiCl_4$, Et_2O	141.5	130	+ 8.84
$GeCl_4$, Et_2O	104	104	0
$SiCl_4$, THF	69.5	64	+ 8.59
$GeCl_4$, THF	33.4	37.4	- 10.69

*immiscible at this composition (at 0°C);

**$P_{ideal} = \frac{1}{2}(P_{MCl_4} + P_L)$;

***% deviation = $100\,(P_{Expt} - P_{ideal})/P_{IDEAL}$ (equation 6.4)

6.4 Discussion

This study of the value of the vapour pressure - composition curves as a criterion for the assessment of the degree of interaction between Group IV tetrachlorides and a series of Lewis bases was sparked off by the observation that whilst $SnCl_4$ evolves heat when mixed with acrylonitrile (forming the crystalline adduct $SnCl_4.2CH_2CHCN$) (276, 280) $SiCl_4$ and $GeCl_4$ by contrast have such a small affinity for this base that they absorb heat when mixed with it. The resulting mixtures have vapour pressures at 0^o greater than would be predicted from Raoult's Law - i.e. the Lewis acid and base molecules have less affinity for their opposite numbers than they have for molecules of their own kind. A preliminary report of these observations has already been made (280) within which it was suggested that positive enthalpies of mixing and positive deviations from ideality might characterise binary systems of $SiCl_4$ or $GeCl_4$ with other Lewis bases such as nitriles, esters or ethers. The present work summarised graphically in Figures 6.2 - 6.5 and also in Table 6.9 fully substantiate this prediction, and show furthermore that in all the systems explored, $SiCl_4$ is a weaker Lewis acid than $GeCl_4$. All the five bases studied form stable adducts with $SnCl_4$ (6, 268, 270-273, 82, 83, 274-277, 281-284) and the results therefore confirm the gradation of Lewis acidities, $SiCl_4 < GeCl_4 < SnCl_4$, already indicated by earlier work (6, 265-273). The results are also consistent with increasing donor character towards MCl_4 in the sequence MeCN, CH_2CHCN, $MeCO_2Et$, Et_2O and THF.

The positive deviations from ideality observed in most of these binary systems are not totally without precedent, for similar positive deviations from ideality have been reported without comment in some $SiCl_4$-ether systems (eg di-n-propylether), and $SiCl_4$ (or $SiHCl_3$)-β-chloroethyl ether (285), but the deviations from ideality in the systems reported herein are novel. Other phase studies have tended to focus attention on the solid-liquid rather that the liquid-gas transitions as in earlier studies on ether systems (267, 268) and some more recent studies on phosphoryl chloride-MCl_4 systems (286-288) from which the attractive or repulsive nature of the interactions in the liquid phase is very difficult to assess, particularly in the absence of data relating to interactions in the solid state eg. lattice energies.

The observed departure from ideality may be rationalised in the following way. In their unco-ordinated state, the Group IV tetrachlorides have too little space between their chlorine atoms to allow easy access of L to M without distortion of MCl_4 - the space between the chlorine atoms of MCl_4 has a diameter of 24pm, 32pm and 80pm (M= Si, Ge, Sn) respectively. In order to co-ordinate a Lewis base L to form an adduct $MCl_4.L$ (i.e. to allow a bond $L \longrightarrow M$ to form) a Group IV tetrachloride must change from a tetrahedral to a pyramidal arrangement (Figure 6.6). Unless the energy of this new $L \longrightarrow M$ dative bond, $E(L \rightarrow M)$, exceeds the reorganisation energy required to deform MCl_4, ΔH_{reorg} (see Figure 6.7) adduct formation will not occur. Such binary liquid mixtures will then have vapour pressures

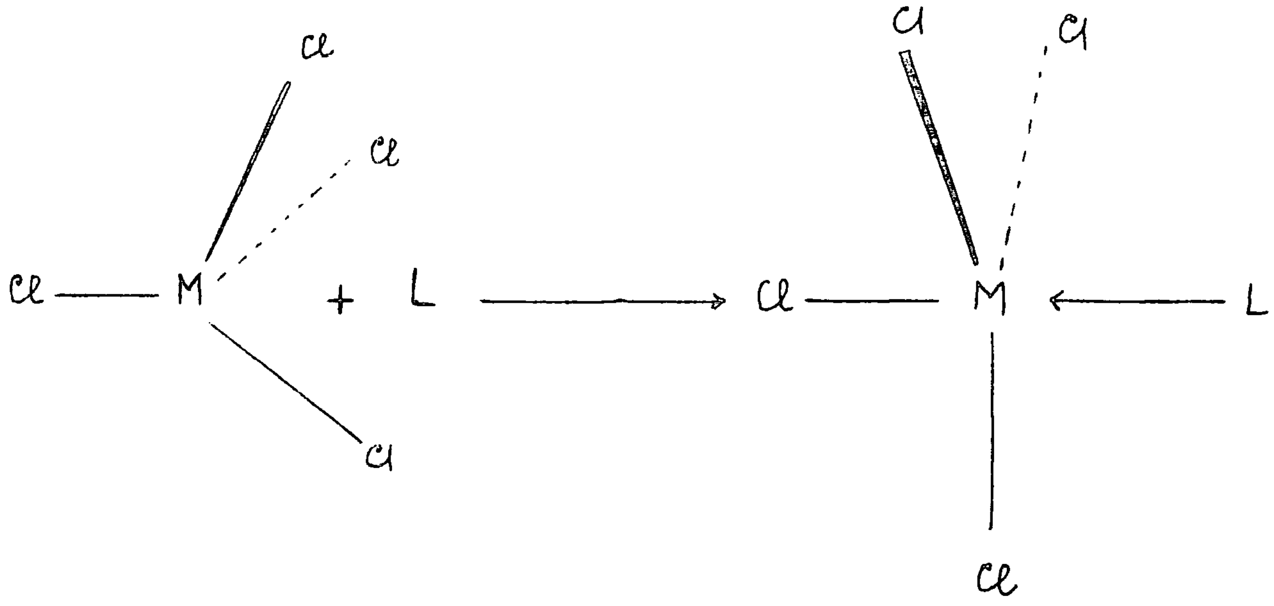


Figure: 6.6.

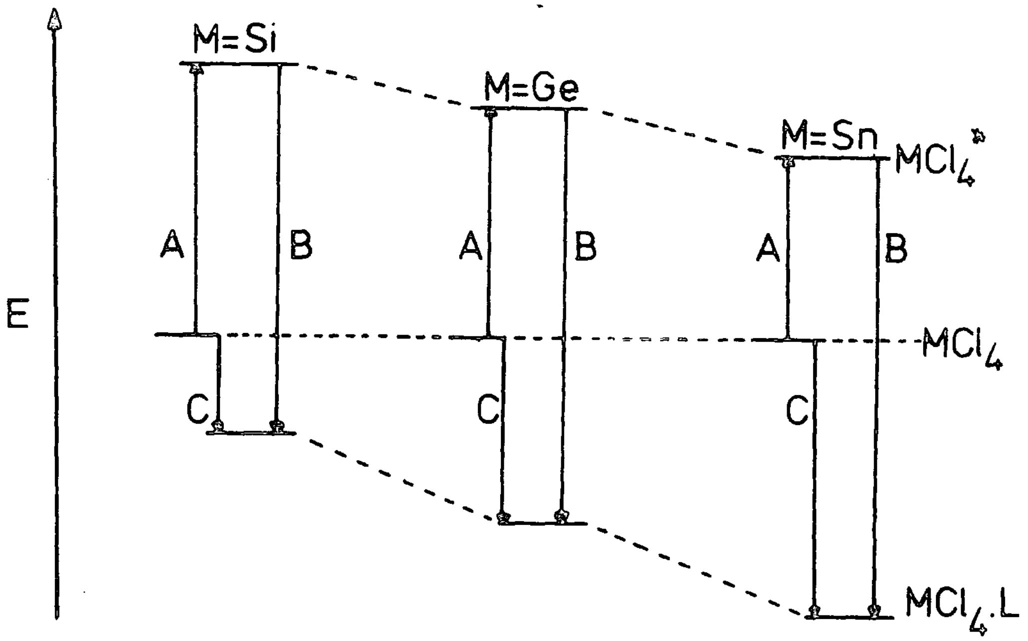
which fully reflect the lack of mutual distortion or of mutual affinity which non-polar, tetrahedral or pseudo-spherical MCl_4 molecules are likely to have for polar, non-spherical base molcules L.

Figure 6.7 illustrates qualitatively the difference between $SiCl_4$, $GeCl_4$ and $SnCl_4$ in their behaviour (265, 266) towards strong Lewis bases such as pyridine or isoquinoline. All the Lewis acids form adducts with these bases although the enthalpy change, ΔH_{coord}, for the co-ordination reaction is progressively less exothermic in the sequence $SnCl_4$, $GeCl_4$ and $SiCl_4$ (265, 266) - see Table 6.10.

This enthalpy change may be represented as shown in equation 6.5.

$$\Delta H_{coord} = E(L \longrightarrow M) - \Delta H_{reorg} \qquad 6.5$$

Enthalpy changes in the formation of $MCl_4.L$



MCl_4^*=the reorganised [trigonal pyramidal] MCl_4 molecule

A=ΔH_{reorg}

B=E[L→M]

C=ΔH_{coord}

Figure: 6.7.

Table 6.10

Physico-chemical Data for the Group IV Chlorides, MCl_4

Data	Sn	Ge	Si	Reference
Electronegativity (Pauling)	1.72	2.02	1.74	289
d(M-Cl)pm	231	208	201	290-292
ΔH_f(M-Cl)KJmol^{-1}	414	343	476	289
ΔH_{coord}KJmol^{-1}$MCl_4$2py*	100	83	76	278
ΔH_{coord}KJmol^{-1}$MCl_4$2iq**	95	85	79	278

* py = pyridine; ** isoquinoline

The energy of the new $L \rightarrow M$ dative bond, $E(L \rightarrow M)$ may be expected to increase with the electrophilic character of M in MCl_4, i.e. in the sequence M = Si < Ge < Sn, whilst ΔH_{reorg} is expected to decrease as the M-Cl bonds become longer and weaker i.e. in the sequence $SiCl_4 > GeCl_4 > SnCl_4$. Consequently the enthalpy change, ΔH_{coord}, represented by the difference between $E(L \rightarrow M)$ and ΔH_{reorg} becomes less exothermic in the sequence M = Sn, Ge, Si.

The stepwise changes in ΔH_{coord}, going from $SnCl_4$ to $GeCl_4$, and from $GeCl_4$ to $SiCl_4$, are likely to vary with the nature of the Lewis base, L. For instance, when L = pyridine the steps are about 17 and 7 kJmol^{-1} respectively

($\Delta H_{coord} \sim 100$ kJ. mol^{-1} for $SnCl_4$, 83 kJ mol^{-1} for $GeCl_4$ and 76 kJ mol^{-1} for $SiCl_4$) whilst when L = isoquinoline the steps are about 10 and 6 kJ mol^{-1} respectively ($\Delta H_{coord} \sim 95$ kJ mol^{-1} for $SnCl_4$, 85 kJ mol^{-1} for $GeCl_4$ and 79 kJ mol^{-1} for $SiCl_4$) (266). Nevertheless it appears tha, unless the formation of a tin tetrachloride adduct $SnCl_4$ L, is accompanied by the evolution of at least 20 kJmol^{-1} possible considerably more, than the co-ordination of the same base L to $GeCl_4$ or $SiCl_4$, i.e. the formation of adduct $GeCl_4L$ and $SiCl_4L$, is unlikely.

Binary systems such as $SiCl_4$ or $GeCl_4$ with some base L (THF or $MeCO_2Et$), which when mixed with $SnCl_4$ evolves less than about 40 kJ mol^{-1}, are likely to exhibit virtually ideal behaviour or positive deviations from Raoult's Law. The reported values of ΔH_{coord} for the formation of the adducts $SnCl_4 2THF$ and $SnCl_4 2MeCO_2Et$ are 59 kJ mol^{-1} and 44 kJ mol^{-1} respectively (282). Furthermore it may follow that a negative deviation from Raoult's Law can only be expected in the systems MCl_4 - L (M=Si, Ge) when L mixed with $SnCl_4$ evolves 50 - 60 kJ mol^{-1} or thereabouts. It should be noticed, however, that all the available thermochemical data for these systems is related to solid adducts. The implications of this may help to reconcile the disparity between the above values, for examination of a relevant Born- Haber cycle indicates that ΔH_{coord} is a composite term incorporating the Lattice Energy of the adduct (Figure 6.8).

Accurate comparisons can only be made, therefore, by using the values of ΔH_{coord} (g), the heat of formation of the gaseous adduct, derivable by means of (equation 6.6)

$$\Delta H_{coord}(g) = \Delta H_{EA} + 2\Delta H_{EB} + \Delta H_{coord} - \Delta H_{LE} \qquad 6.6$$

Figure 6.8

$$\begin{tikzcd}
MCl_4(g) & + & 2L(g) \arrow[r, "\Delta H_{coord}(g)"] & MCl_4 2L(g) \arrow[d, "\Delta H_{LE}"] \\
MCL_4(l) \arrow[u, "\Delta H_{EA}"] & + & 2L_{(l)} \arrow[u, "\Delta H_{EB}"'] \arrow[r, "\Delta H_{coord}"] & MCl_4 2L_{(s)}
\end{tikzcd}$$

ΔH_{EA}, ΔH_{EB} = Heat of Vapourisation of the Lewis acid(A) or base (B)

ΔH_{LE} = Lattice Energy

Whilst Latent Heats of Vapourisation of Lewis acids and bases (ΔH_{EA} and ΔH_{EB} respectively) are usually known, the Lattice Energy parameter is but rarely determined. Hence a comparison of ΔH_{coord} seems allowable only when the adducts concerned have closely similar structures. The extent to which such an assumption is valid in this situation may well explain the disparity in the estimated values of the minimum enthalpy change necessary in the $SiCl_4$-L systems as a criterion for predicting the behaviour of the binary systems $SiCl_4$-L and $GeCl_4$-L. In view if the limitations placed upon the usefulness of ΔH_{coord}

values as criteria for interpretation and prediction, as outlined above, a study of 1:1 molar mixtures of $SiCl_4$-Lewis bases has been made. The degree of deviation from ideality (cf. Table 6.9) has been quantified, and used as a basis for the establishment of the relative basic character of a series of Lewis bases. These results, summarised in Table 6.11, illustrate the uncertainity of the method particularly when applied to a number of bases of widely-different structures. Whilst there seems to be insufficient comparative data, it has to be admitted that the method does not discriminate correctly between two similar bases Et_2O and the stronger base THF, nor does the apparent greater basic strength of $POCl_3$ over $MeCO_2Et$ agree with the deductions made from thermochemical data.

6.5 Summary

The extent of the difference in the behaviour of $SnCl_4$ and its silicon and germanium analogues has been demonstrated by vapour pressure measurements of binary liquid systems MCl_4-L (L = acetonitrile, ethyl acetate, diethyl ether or tetrahydrofuran). Whilst all five Lewis bases form adducts with $SnCl_4$ the $SiCl_4$ and $GeCl_4$ systems show generally positive deviations from ideality, although $GeCl_4$-Et_2O (ideal) and $GeCl_4$-THF (negative) are exceptions. The deviations from ideality are consistent with the acid sequence $SiCl_4 < GeCl_4 < SnCl_4$ and base sequence $MeCN < CH_2CHCN < MeCO_2Et < Et_2O <$ THF. An attempt, however, to establish relative Lewis basicities of a wide range of donor molecules, by their degree of deviation from ideality, was unsuccessful affording anomalous values.

Table 6.11

Vapour Pressures of 1:1 Mixtures of $SiCl_4$ & Lewis Base at 0°C. Deviations from Ideality

Rank Order ‡	Lewis Base	Pressure Expt. mm	Pressure Ideal mm	% Deviation *
1	Me_3N	336	380	-12
2	Et_2O	141.5	130	9
3	THF	69.5	64	9
4	$POCl_3$	56	48	17
5	$MeCO_2Et$	68	50	36
6	Bu^tCN	64	47	36
7	$CH_2{:}CHCN$	97	55	76
8	PhCN	69	37	86
9	MeCN	100	50	100 **
10	EtCN	107	46	133 **
	C_5H_5N	formation of adduct occurred		
	Me_2SO	evidence of chemical reaction		

‡ in descending Lewis base strength

$$* \ \% \text{ deviation} = \frac{P_{obs} - P_{ideal}}{P_{ideal}} \times 100$$

** immiscible liquids

CHAPTER 7

A BRIEF STUDY OF SOME NITRILE-TIN (II) CHLORIDE - HYDROGEN CHLORIDE - SYSTEMS

7.1 Introduction

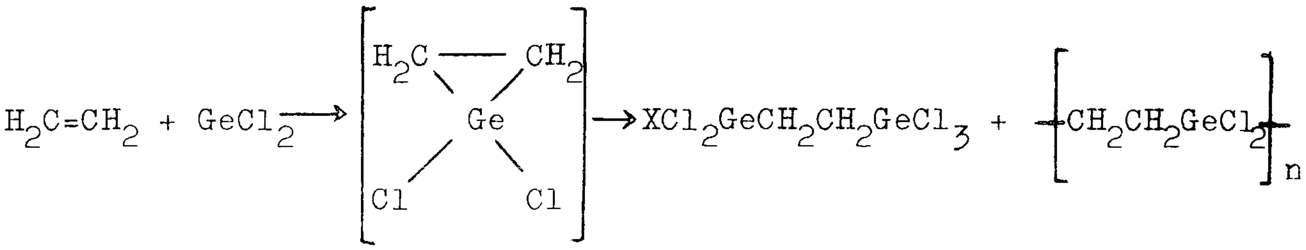
The proposed product of the reaction between tin(II) chloride and hydrogen chloride is a solvated trichlorostannane species, formally represented as $HSnCl_3 . L$ (L = solvent). Such a product, $HSnCl_3.3H_2O$ (obtained by cooling an aqueous solution of tin(II) chloride, already saturated with hydrogen chloride) has been reported (293), and conductivity studies have also evidenced other species including H_2SnCl_4. (294). The determination of the formation constants of chlorostannate (II) ions (295) (equation 7.1), by means of emf data from concentration cells, shows favourable thermodynamic data for the existence of the trichlorostannate (II) ion $SnCl_3^-$, but suggests that the concentration of tetrachlorostannate (II) ion, $SnCl_4^{2-}$

$$Sn^{2+} + nCl^{-} \longrightarrow SnCl_n^{2-n} \qquad 7.1$$

is likely to be small unless the temperature and chloride ion concentration are high. The presence of $SnCl_3^-$ in the ethereal extract of a tin(II) chloride-hydrochloric acid solution is also proposed on the basis of Raman spectral data (296).

Workers studying the behaviour of $HGeCl_3.2Et_2O$, trichlorogermane-dietherate, towards alkenes and alkynes (297-299), have proposed the initial formation of an electron deficient species, a pseudo-carbene, (equation 7.2) which subsequently reacts as summarised in (equation 7.3).

$$HGeCl_3 . n\left(OEt_2\right) \overset{-HCl}{\rightleftharpoons} GeCl_2 + Et_2\overset{+}{O}H + Cl^- \qquad 7.2$$



X = H, Cl 7.3

However, the claim that the analogous trichlorostannate etherate is unreactive toward unsaturated hydrocarbons, explicitly contradicts a report that α-alkenes do indeed afford adducts (300) (equation 7.4).

$$HSnCl_3 + H_2C{=}CHR \longrightarrow Cl_3SnCH_2CH_2R \qquad R = H, \text{alkyl} \qquad 7.4$$

The reaction of the system tin(II) chloride-hydrogen chloride in ether with bifunctional molecules possessing two potentially - reactive sites is also of interest. With acrylonitrile, for example, the preferred product is β-cyanoethyltin trichloride (301) (equation 7.5), a similar preferred addition across the carbon-carbon double bond being observed in the reactions with $\alpha\beta$-unsaturated compounds such

$$HSnCl_3 + CH_2{=}CH{-}C{\equiv}N \longrightarrow Cl_3SnCH_2{-}CH_2C{\equiv}N \qquad 7.5$$

as acrylic esters and amides (302, 303) (equation 7.6), the

$$HSnCl_3 + CH_2{=}CHCO_2Me \longrightarrow Cl_3SnCH_2CH_2CO_2Me \qquad 7.6$$

β- substituted tin trichlorides being formed in high yield. The preparation of substituted dialkyltin dichlorides, using tin, hydrogen chloride and acrylic esters, has also been described (equation 7.7) (303-305), H_2SnCl_2 or HSnCl being postulated as reactive intermediates.

$$5HCl + 3Sn + 3CH_2{=}CHCO_2Me \rightarrow Cl_3SnCH_2CH_2CO_2Me + Cl_2Sn(CH_2CH_2CO_2Me)_2 + H_2$$

7.7

Recent work (306) has confirmed the results of earlier findings (297-299) that anhydrous tin(II) chloride dissolves rapidly in a saturated solution of hydrogen chloride to give an etherate $H_nSnCl_{2+n}.xEt_2O$ which separates out as a yellow oily liquid (equation 7.8) insoluble in the clear colourless supernatant liquid. A thermodynamically controlled

$$nHCl + SnCl_2 + x\ Et_2O \rightleftharpoons H_nSnCl_{2+n}x\ Et_2O \tag{7.8}$$

equilibrium is indicated by the fact that addition of diethyl ether causes precipitation of tin(II) chloride which redissolves on passing hydrogen chloride. Similarly, addition of inert polar substances such as toluene or tetramethylsilane, or evaporation of diethyl ether and/or hydrogen chloride, immediately induces the precipitation of tin(II) chloride. ^{1}H-NMR spectrometry of the supernatant suggest a composition similar to that of hydrogen chloride etherates, whilst the data for $H_nSnCl_{2+n}.xEt_2O$ show a strongly ionised proton with a chemical shift, relative to tetramethylsilane $\tau = 10$, varying between τ (-2.8 to -0.8). Interaction of this proton with the diethylether oxygen atom is reflected by the downfield shift of the methylene and methyl protons. Comparison with the data for $HCl.Et_2O$ and $HCl.2Et_2O$ (298) ($\tau = 3.2$) shows the considerably increased ionization caused by the interaction with tin(II) chloride. It seems most likely that $H_nSnCl_{2+n}xEt_2O$ is not a single well-defined substance, but rather a mixture arising from a set of equilibria described by (equation 7.9) with approximately one molecule of diethyl ether per proton.

$$HCl + SnCl_2 + Et_2O \rightleftharpoons HSnCl_3.Et_2O \xrightleftharpoons{HCl/Et_2O} H_2SnCl_4.2Et_2O \tag{7.9}$$

No (Sn-H) stretching frequency could be detected in the infrared spectrum at (1700-2200)cm^{-1} - $EtCl_2SnH$ shows an (Sn-H) absorption band (307) at 1934cm^{-1} - and furthermore ^{119}Sn Mössbauer data show that the product to be a tin(II) compound rather than a tin(IV) species. Overall, therefore, the products of interaction between hydrogen chloride and tin(II) chloride in ether seems to be best described as being strongly ionized etherated hydrogen trichlorostannate(II) and dihydrogen tetrachlorostannate(II) rather than trichlorostannane(II), $HSnCl_3$, or tetrachlorostannane(II), H_2SnCl_4. This is summarised in (equation 7.10).

$$\begin{tikzcd}
HCl + SnCl_2 + xEt_2O \arrow[r, shift left] & HSnCl_3.xEt_2O \arrow[l, shift left] \arrow[r, "HCl"] \arrow[d, shift left] & H_2SnCl_4.Et_2O \arrow[d, shift left] \\
& Et_2OH^+ + SnCl_3^- \arrow[u, shift left] & Et_2OH^+ + SnCl_4^{2-} \arrow[u, shift left]
\end{tikzcd} \tag{7.10}$$

This chapter describes a study of the reactions of monofunctional nitriles RC≡N (R = Me, Et, Bu^t, Ph) with tin(II) chloride and hydrogen chloride in anhydrous ethereal solvent. Such systems undergo hydrostannation but in a manner different to that already descibed for alkenes. The principal product from these systems is probably dimeric and is formulated as

$Cl_3Sn^{IV}C(R):NC(R):NH_2^+\ Sn^{II}Cl_3^-$ (I; R = Me, Et, Bu^t, Ph).

A more detailed discussion of these systems (Section 7.3) follows the experimental section, and begins on page 264.

7.2 Experimental

All compounds were handled under nitrogen. Hydrogen chloride was used directly from a cylinder without further purification. Anhydrous tin(II) chloride (B.D.H.) was also used directly, its infrared spectrum having shown, and continuing to show, the absence of moisture. All other reagents and solvents employed were dried by standard methods. The estimation of tin(II) depends upon its oxidation, in aqueous solution, by iodine to tin(IV) according to equation 7.11. It was not possible to estimate

$$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^- \qquad 7.11$$

tin(II) in the product of the system tin(II) chloride-hydrogen chloride- 2,2- dimethylpropionitrile because of its insolubility in concentrated HCl. The estimation of total tin involves the initial reduction of any tin in oxidation state (+IV) by boiling the acidified solution with a reducing agent such as lead and then estimating all the tin (II) as above. The total tin values as estimated in this way were uniformly low, presumably because of the loss of some tin as volatile tin(IV) chloride.

(i) The propionitrile-tin(II)chloride-hydrogen chloride system.

3.17g $SnCl_4$(16.7 m.mol) was added to 10cm^3 propionitrile and HCl gas was passed into the mixture kept at 0°C for some 12 hours. Dissolution of $SnCl_2$ was complete after about 3 hours, a straw coloured solution being obtained. The mixture was allowed to stand for a week at about 0°C by which time a yellow precipitate had formed which, after filtering, washing with propionitrile and pumping solvent free appeared as a waxy solid. It was identified as being

N(ethyl,trichlorostannylmethylene)propanamidinium-trichlorostannate(II), $(C_3H_6NSnCl_3)_n$ n probably 2, m.p. 84° (d).

Found: C = 12.6; H = 2.6; N = 4.9; Cl = 39.4; Sn(total)=35.3; Sn^{II} = 20.9%

$C_3H_6NSnCl_3$ requires C = 12.8; H = 2.2; N = 5.0; Cl = 38.9; Sn(total) = 42.2; Sn^{II} = 21.1%

ν Max (Nujol Mull) 3510sh, 3320s, 3220s, 1678s, 1648s, 1612m, 1570m, 1480m, 1455m, 1405s, 1390s, 1360s, 1308m, 1245w, 1175w, 1150m, 1125m, 1100m, 1070sh, 1010sh, 1000m, 875w, 835m, 800m, cm^{-1}.

The example outlined above is to illustrate the method employed for each of the four systems used. Accordingly therefore only essential detail is now given for each of the remaining systems.

(ii) The 2,2-dimethylpropionitrile-tin(II)chloride-hydrogen chloride system.

The same reaction scheme to (i) was followed employing 15.3 m.mol of $SnCl_2$ and passing HCl gas for about 6 hours, then filtering etc, after standing at about 0°C overnight. The pale brown powder isolated was identified as N(2,2-dimethylpropyl,trichlorostannylmethylene)2,2-dimethylpropanamidinium-trichlorostannate(II), $(C_5H_{10}NSnCl_3)_n$ n probably 2, m.p. 185° (d)

Found: C = 19.7; H = 3.8; N = 4.5; Cl = 35.6; Sn(total)=27.7% Sn^{II} not obtained.

$C_5H_{10}NSnCl_3$ requires C = 19.4; H = 3.2; N = 4.5; Cl = 34.4; Sn(total) = 38.5%

ν Max (Nujol Mull). 3320s.br, 3220s, 3180s.br, 1690s, 1540m, 1480m, 1400s, 1118m, 1080w, 1040w, 1025w, 870s, 728w, cm^{-1}.

(iii) The benzonitrile-tin(II)chloride-hydrogen chloride system.

A similar procedure was employed as in (ii) the white powder isolated being identified as N(phenyl,trichlorstannylmethylene)benzamidinium trichlorostannate(II), $(C_7H_6NSnCl_3)_n$ n probably 2, m.p. 180° (d).

Found: C = 23.6; H = 1.7; N = 4.3; Cl = 32.7; Sn(total)=32.6; Sn^{II} = 17.9%

$C_7H_6NSnCl_3$ requires C = 25.5; H = 1.8; N = 4.3; Cl = 32.4; Sn(total)= 36.0; Sn^{II} = 18.0%

ν Max (Nujol Mull). 3310s,br, 3160s.br, 2215w, 1720s.br, 1660s.br, 1600s, 1580w, 1545m.br, 1460sh, 1450s, 1445sh, 1330m, 1315m, 1220s, 1185m, 1162w, 1055w, 845sh, 838s, 790s, 765w, 710w, 700w, 685w, 588w, 550w, 450m, 435w, cm^{-1}.

(iv) The acetonitrile-tin(II)chloride-hydrogen chloride system.

By a procedure common to that described already, the product obtained, a white solid was identified as N(methyl, trichlorostannylmethylene)acetamidinium-trichlorostannate(II), $(C_2H_4NSnCl_3)_n$ n probably 2, m.p. = 92° (d).

Found: C = 9.2; H = 2.3; N = 5.3; Cl = 39.7; Sn(total)=40.1; Sn^{II} = 21.4%.

$C_2H_4NSnCl_3$ requires C = 9.0; H = 1.9; N = 5.2; Cl = 39.7; Sn(total)= 44.2; Sn^{II}= 22.1%

ν Max (Nujol Mull) 3340s.br, 3180s,br, 1675s.br, 1550s, 1480s, 1420s, 1388s, 1370m, 1350s, 1300m, 1260m, 1230w, 1140m, 1115s, 1040m, 1028m, 990s, 922m, 792m, 750s, 680s, 525s cm^{-1}.

7.3 Discussion

(i) Characterisation and Spectroscopic Properties

The products of the systems RCN(R = Me, Et, Bu^t, Ph)-$SnCl_2$ - HCl are solids which are extremely moisture sensitive. They are waxy, difficult to mull and their stability varies considerably - the methyl and t-butyl derivatives, for example, darkened slowly yielding obscure decomposition products. Their insolubility in benzene prevented the determination of molecular weights by cryoscopy. Analytical data (C,H,N and Cl) are consistent with their formulation as 1:1 adducts of trichlorostannane and RCN, and tin estimations showed the metal to be both two - and four covalent. Analysis of total tin gave low results, but tin(II) estimations on all products, except the t-butyl derivative, show the ratio tin(IV): tin(II) to be almost 1:1. Therefore, half the tin present is in the lower oxidation state either as $SnCl_2$ or, more likely, $Sn^{II}Cl_3^-$. The products at their simplest are regarded as being dimeric, and of general formula $Cl_3SnC(R)=NC(R)NH_2^+$ $SnCl_3^-$ (I; R = Me, Et, Bu^t, Ph). Their proposed structures are shown in Figure 7.1.

The infrared spectroscopic data is much less helpful than other spectral detail to be presented shortly. Because of extreme mulling difficulties and therefore poorly-resolved

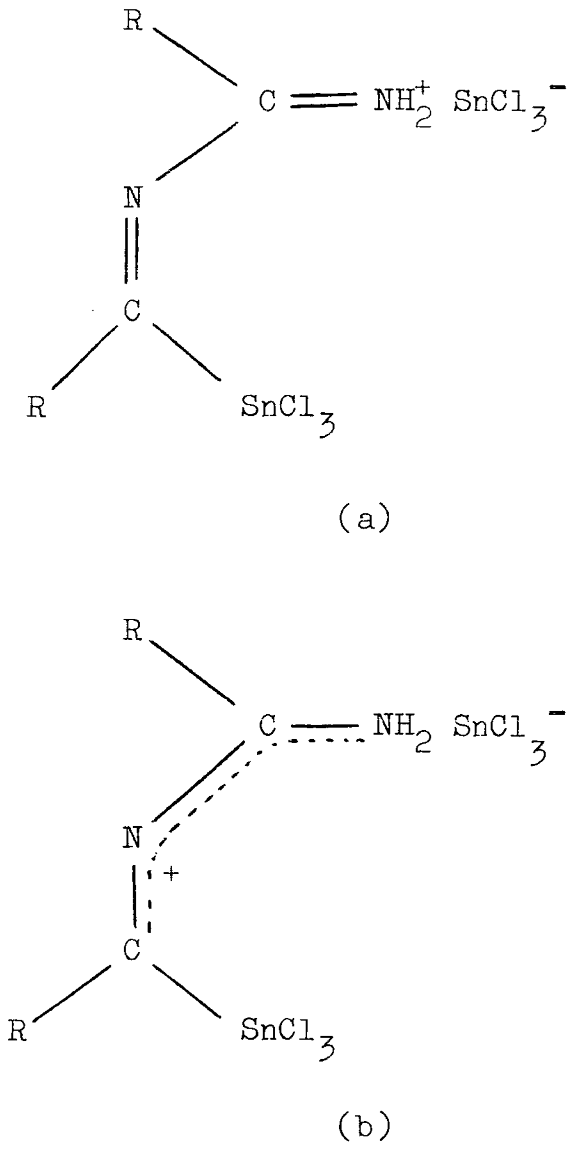
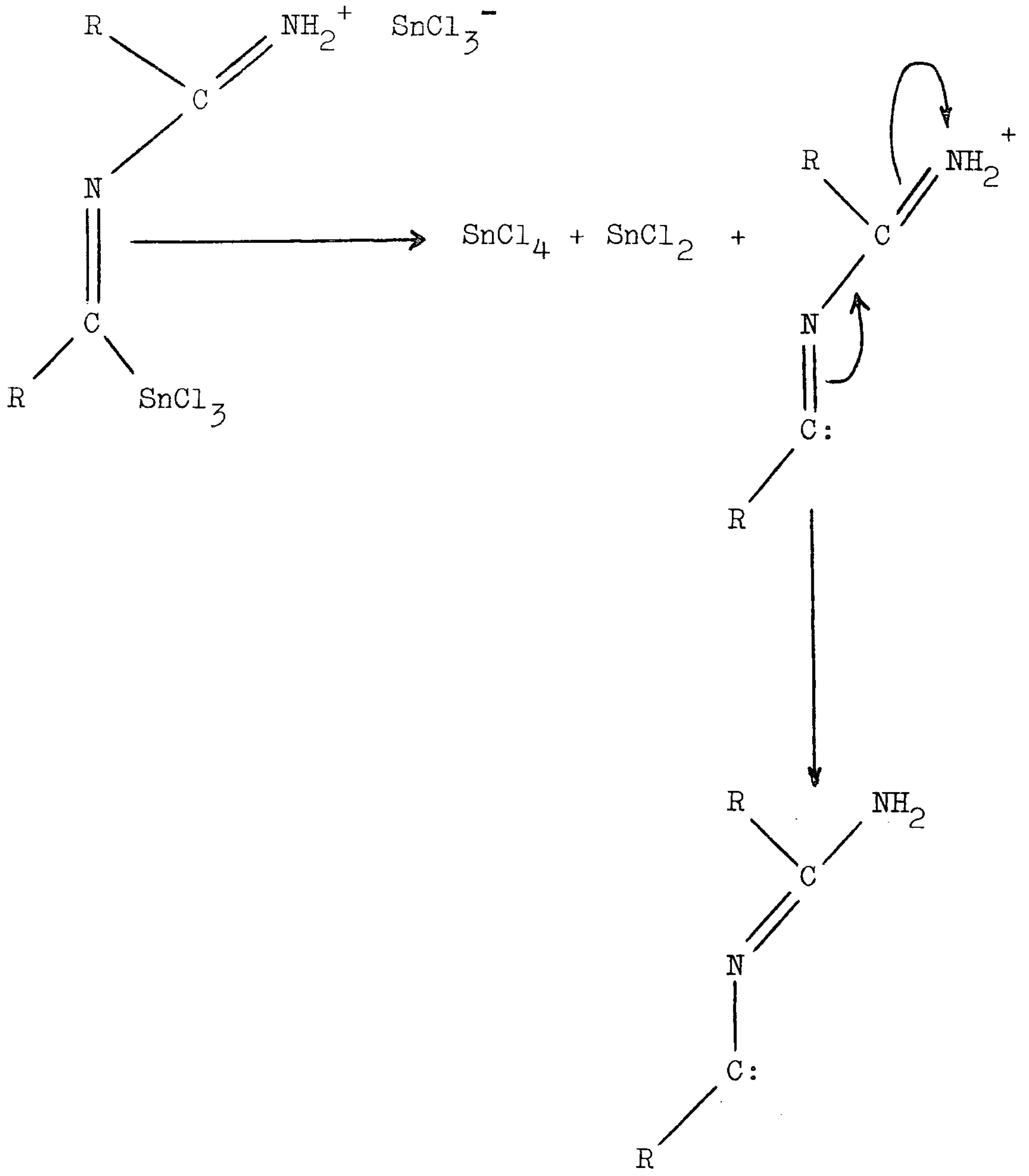


Figure 7.1

spectra, only general structural inferences are permissible. All spectra show two or three broad, high intensity absorptions at ν (3200-3500)cm^{-1}, similar to the spectra of aniline (308) and some dialkylamine hydrochlorides (309). These absorptions are assigned to (N-H) stretching frequencies of strongly hydrogen-bonded species. In the range ν (1400-1700)cm^{-1} three bands are assigned to ν(C=N) stretch and δ(NH$_2$) scissoring. Whilst it would be tempting to regard the localised structure more favourably than the delocalised structure (Figure 7.1) (a) and (b) respectively), because the latter might conceivably have a greater number of bands in this region, the poor quality of the spectra makes such a distinction unjustifiable. Absorptions assignable to the $SnCl_3$ groups should be at $\nu(200-400)cm^{-1}$ (80, 310) but this is outside the range scanned in this study.

The mass spectroscopic data listed in Table 7.1 a-d, show neither peaks corresponding to parent ions nor organo-tin fragments. The highest peaks are assigned to $SnCl_3^+$ or $SnCl_4^+$, and are both present in the spectra of two of the products (R = Me, Et, Table 7.1 a,b). The $SnCl_4^+$ fragment could arise by an ion-ion recombination process and/or by sample decomposition with the elimination of tin(II)- and tin(IV) chlorides (equation 7.12). The carbenoid species ($RC(NH_2)=N\ddot{C}R$) which may accompany such an elimination reaction would be a very reactive electron-deficient moiety. Whilst a fragment corresponding to such a species is found in the mass spectrum of the methyl derivative, Figure 7.1 (a), no fragments related to its combination products were identified. The spectra do not offer firm evidence in support of the proposed structure for in only one instance, that of the methyl derivative (Table 7.1 a), is there observed a 'dimeric' backbone ($RC(:NH_2)CN(R)^+$; R = Me). In fact the general breakdown pattern evidences loss of organic fragments before loss of chloride ions a feature also observed in the spectra of methyleneamino- and acetamidino- tin(II and IV) derivatives (Chapter 4 and 5), β- cyanoethyltin trichloride and tri-n-butyltin trichloride (301).



7.12

The ^{1}H-NMR data is summarised in Table 7.2. Since the compounds are insoluble in weakly polar solvents such as chloroform, tetrachloromethane and toluene, the spectra were recorded at ambient temperatures as solutions of perdeuterodimethyl sulphoxide. The ^{14}N nucleus has a spin number I = 1 and accordingly should cause a proton attached to it to show three (i.e. 2I + 1) peaks of equal

Table 7.1

Principal Fragments in the Mass Spectra of $RC(SnCl_3): NC(R): NH_2^+ \; SnCl_3^-$

(a) R = Me

m/e	Relative Intensity	Assignment
260	4	$SnCl_4^+$
225	5	$SnCl_3^+$
190	3	$SnCl_2^+$
155	11	$SnCl^+$
120	4	Sn^+
84	2	$MeC(NH_2)NC\ Me^+$
59	68	$MeC(NH_2)NH_2^+$
58	41	$MeC(NH_2):NH^+$
42	100	$MeCNH^+$

(b) R = Et

m/e	Relative Intensity	Assignment
260	3	$SnCl_4^+$
225	32	$SnCl_3^+$
218	6	-
190	34	$SnCl_2^+$
155	70	$SnCl^+$
120	10	Sn^+
110	1	$(EtC{=}N)_2$
73	5	$EtC(NH_2): NH_2^+$
57	5	$EtCNH_2^+$
56	8	$EtCNH^+$
36	100	HCl^+

(c) R = Bu^t

m/e	Relative Intensity	Assignment
225	3	$SnCl_3^+$
190	3	$SnCl_2^+$
155	17	$SnCl^+$
120	7	Sn^+
98	6	$Bu^tC(N): NH^+$
84	2	Bu^tCNH^+
70	38	Bu^tCH^+
57	51	Bu^{t+}

(d) R = Ph

m/e	Relative Intensity	Assignment
225	4	$SnCl_3^+$
190	1	$SnCl_2^+$
155	4	$SnCl^+$
121	3	$PhC(NH_2): NH_2^+$
120	2	Sn^+
105	80	$PhCNH_2^+$
104	100	$PhCNH^+$
78	36	PhH^+
36	48	HCl^+

intensity because of spin-spin coupling. The projected theoretical picture is however complicated by two features viz. the rate of exhange of the proton on the nitrogen atom and the electrical quadrupole moment of the ^{14}N nucleus. If the protons on a nitrogen atom undergo rapid exchange, then they are decoupled from the N atom and a sharp singlet- such as is the case for many aliphatic amines- for the (N-H) peak results. At a somewhat slower rate of exchange, partial decoupling can occur with the consequent appearance of a broad singlet N-H peak. Only if a slow rate of exchange pertains, might the evidence of ^{14}N spin coupling be seen. This chance is further reduced because of the electrical quadrupole moment of the ^{14}N nucleus. Nuclei with a spin number of 1 have a non-spherical charge distribution and this asymmetry is described by an electrical quadrupole moment which induces a moderately efficient spin relaxation and thus an intermediate lifespan for the three spin states of the nitrogen nucleus. The three spin states of N changing at a moderate rate tend to cause a broad singlet peak to be observed.

The compounds under discussion here, viz $Cl_3SnC(R):N.C(R):NH_2^+\ SnCl_3^-$ (I; R = Et, Bu^t, Ph), surprisingly reveal triplet absorptions of equal intensity assignable to the protons of the $C:NH_2^+$ unit. Such absorptions of the appropriate relative intensities appear at or about the same τ values - Table 7.2 - whatever the compound. The three peaks are relatively widely separated (J = 50.7, R = Et; J = 52, R = Bu^t, Ph) suggesting very

Table 7.2

^{1}H-NMR Spectra of $RC(SnCl_3):NC(R):\overset{+}{N}H_2\ SnCl_3^-$

Compound	τ values ppm ^{a}
R = Me	Sample decomposed in the solvent
R = Et	1.96, 2.80, 3.54t (2); 5.50, 5.58, 5.64, 5.75q (2) 8.51, 8.63, 8.75t (3); 7.16, 7.28, 7.40, 7.52q (2) 8.73, 8.85, 8.97t (3)
R = Bu^t	1.85, 2.72, 3.59t (2) 8.97s.br. (9)
R = Ph	2.0, 2.87, 3.74t (2) 2.20 - 2.30 complex (20)

a relative to internal standard, TMS τ = 10

t = triplet; q = quartet; relative intensities parenthesised.

effective coupling - the coupling constants compare favourably with those of secondary amines or trialkylammonium salts (308, 311) (J(N-H)being 40 - 68). Whereas chemical shift is dependent on the strength of the applied magnetic field, spin - spin coupling is, by contrast, independent of changes in the magnetic field. The spectra were recorded at different fields and the coupling constant J remained unchanged. The inevitable inference must be that (despite the likelihood of strong hydrogen bonding in these compounds, which would facilitate proton exchange, and the nuclear quadropole of ^{14}N, already referred to, both of which would cause broadening and coalescence of the lines) the triplet observed is caused by coupling between the ^{14}N nucleus and protons of the $C{=}NH_2^+$ unit. For the ethyl derivative, $Cl_3SnC(R){:}N.C(R){:}NH_2^+\ SnCl_3^-$ (R = Et), two magnetically different ethyl groups are evidenced, the signal (a quartet) due to the methylene groups, of appropriate relative intensities, being farther downfield than the related methyl triplet signal (Table 7.2). Of the two remaining compounds, each possessing either alkyl (Bu^t) or aryl (Ph) groups without α-hydrogen atoms, the spectrum of the phenyl derivative is poorly resolved, the phenyl absorption being a rather broad complex signal at τ(2.20 - 2.30). Hence by comparison with the ethyl compound already maintained, the evidence neither confirms nor disproves the anticipated magnetic inequivalence of the phenyl groups; a similar spectrum was also recorded for the t-butyl derivative.

The product of the systems RCN - $SnCl_2$ - HCl (R = Me, Et, Bu^t, Ph) in anhydrous ethereal solvent, corresponding analytically to the adduct RCN. $HSnCl_3$, has been formulated as $RC(Sn^{IV}Cl_3)$: NC(R): NH_2^+ $Sn^{II}Cl_3^-$ - with tin in oxidation states + II and + IV - and some evidence has been presented already to justify such a proposal. A possible mechanism by which such a species can arise is now to be discussed.

(ii) A mechanistic rationale

The reaction between methyl acrylate and a saturated ethereal solution of tin(II) chloride and hydrogen chloride to give β-carbomethoxyethyltin trichloride, $Cl_3SnCH_2CH_2CO_2Me$ (equation 7.6), has been explained in terms of a hydrostannation (302-304), i.e. a reaction in which an unsaturated unit inserts into a tin-hydrogen bond. In view of the earlier discussion concerning the nature of the active species in the tin (II) chloride-hydrogen chloride- ether system (Section 7.1) the presence of a tin-hydrogen bond in the active species (equation 7.8 and 7.10) appears to be very unlikely. Consequently in the systems RCN - $SnCl_2$ - HCl in anhydrous ether, a reaction following a hydrostannation mechanism appears to be equally improbable. An alternative mechanism for the methyl acrylate - tin(II) chloride - hydrogen chloride system could, at first sight, be based upon the reaction of tin(II) chloride with the adduct initially formed by the methyl acrylate hydrogen chloride reaction (equations 7.13 - 7.14. However, whilst the adduct $ClCH_2CH_2CO_2Me$ is known to be a substantial by-product, it has no reaction

$$HCl + CH_2{=}CHCO_2Me \longrightarrow ClCH_2CH_2CO_2Me \qquad 7.13$$

$$SnCl_2 + ClCH_2CH_2CO_2Me \not\longrightarrow Cl_3SnCH_2CH_2CO_2Me \qquad 7.14$$

with tin(II) chloride under these conditions. It seems probable therefore that, notwithstanding the ready formation of the initial adduct of RCN and HCl - an imidoyl chloride (equation 7.15), (312 - 314) an analogous mechanism for systems RCN-$SnCl_2$ - HCl (equations 7.15 - 7.16)

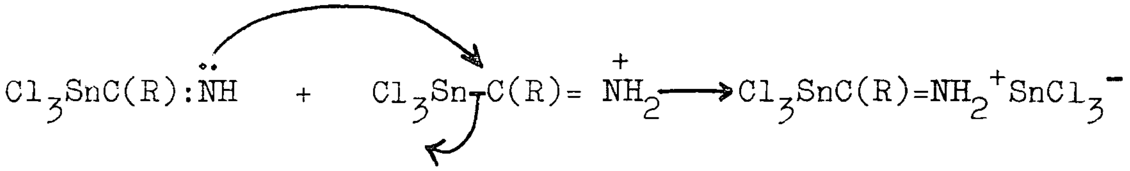
$$RC{\equiv}N + HCl \longrightarrow R{-}C(Cl){:}\,NH \xrightarrow{HCl} RC(Cl){:}NH_2^{+}Cl^{-} \qquad 7.15$$

$$SnCl_2 + RC(Cl){:}NH_2^{+}\ Cl^{-} \not\longrightarrow Cl_3SnC(R){:}NH_2^{+}\ Cl^{-} \qquad 7.16$$

is unlikely. Furthermore, no dimerisation products of such imidoyl chlorides, RC(Cl):NH, - discussed in greater detail later - are evidenced in the systems studied. The mechanism proposed for these RCN - $SnCl_2$ - HCl systems involves the highly ionized species of hydrogen trichlorostannate(II), viz $Et_2OH^{+}\ SnCl_3^{-}$ (equation 7.10). The initial step involves a 1,2-addition which affords a nitrilium ion(II) and subsequently an alkyl (or aryl) trichlorostannylimine(III). The latter may then be protonated to give an iminium salt(IV). This is shown in (equation 7.17). However, the proposed

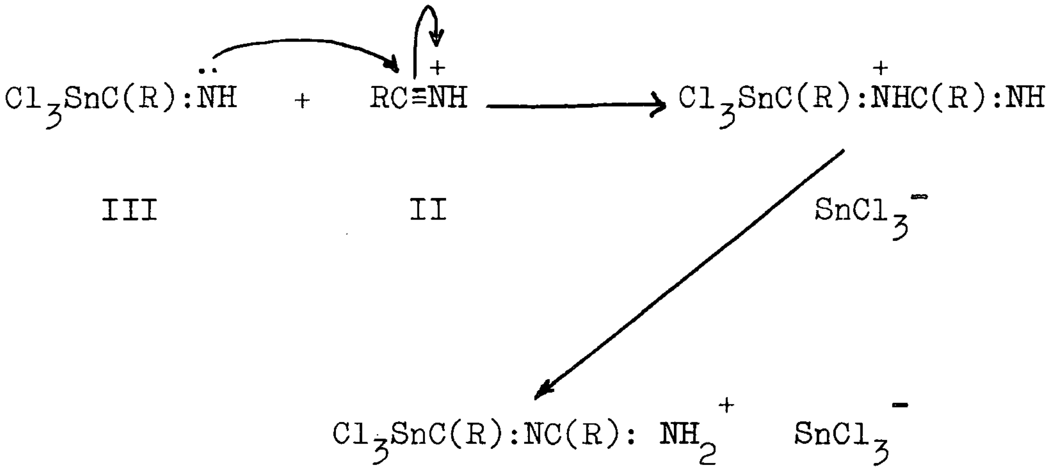
$$RC{=}N \overset{H^{+}}{\rightleftharpoons} \underset{II}{\overset{+}{RC{=}NH}} \xrightarrow{SnCl_3^{-}} \underset{III}{Cl_3SnC(R){:}NH} \overset{H^{+}}{\rightleftharpoons} \underset{IV}{Cl_3SnC(R){:}NH_2^{+}} \qquad 7.17$$

products of these systems are dimeric with two- and four-covalent tin. Such dimers could arise by involvement of the nucleophilic species alkyl (or aryl) trichlorostannylimine(III) as shown in equations 7.18 - 7.19. The product as formulated,



$$\mathrm{Cl_3SnC(R){:}\ddot{N}H} \quad + \quad \mathrm{Cl_3Sn{-}C(R){=}\overset{+}{N}H_2} \longrightarrow \mathrm{Cl_3SnC(R){=}NH_2{}^+SnCl_3{}^-} \qquad 7.18$$

III IV

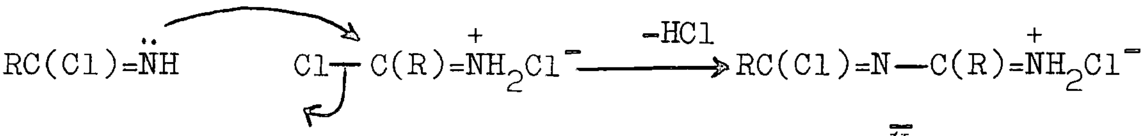


$$\mathrm{Cl_3SnC(R){:}\ddot{N}H} \quad + \quad \mathrm{RC{\equiv}\overset{+}{N}H} \longrightarrow \mathrm{Cl_3SnC(R){:}\overset{+}{N}HC(R){:}NH} \xrightarrow{\mathrm{SnCl_3^-}} \mathrm{Cl_3SnC(R){:}NC(R){:}\overset{+}{N}H_2\ \ \overset{-}{SnCl_3}} \qquad 7.19$$

III II

I

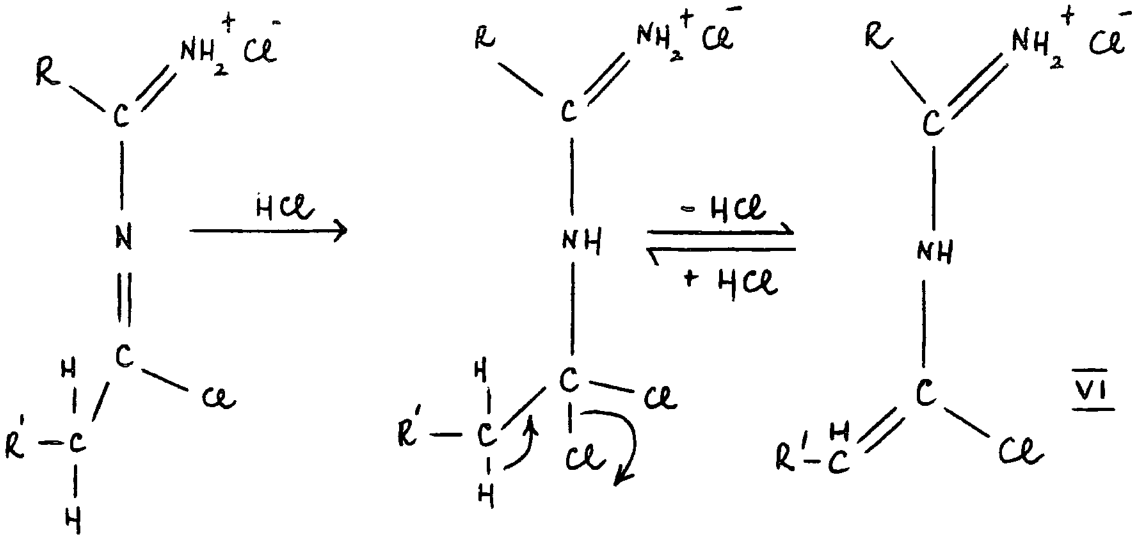
$\mathrm{Cl_3SnC(R){:}NC(R){:}\overset{+}{N}H_2\ SnCl_3^-}$ (I) represents the terminal compound for all the systems studied, and overall the mechanism proposed bears a close similarity to proposals made concerning the dimerization of nitriles in the presence of hydrogen chloride (313 - 316). Here imidoyl chlorides, RC(Cl):NH (equation 7.15) dimerise under relatively mild conditions yielding N(alkylchloromethylene) alkyl amidinium salts (V Equation 7.20). For nitriles without α -hydrogen



$$\mathrm{RC(Cl){=}\ddot{N}H} \qquad \mathrm{Cl{-}C(R){=}\overset{+}{N}H_2Cl^-} \xrightarrow{-\mathrm{HCl}} \mathrm{RC(Cl){=}N{-}C(R){=}\overset{+}{N}H_2Cl^-} \qquad 7.20$$

V

atoms, RCN (R = Ph, MeC_6H_4, EtS, (315) Me_2N (317)) V is the terminal product, but when α -hydrogen exists then V undergoes rearrangement (equation 7.21) to give an N(α-chloroalkenyl) amidinium chloride (VI) (313). Acetimidoyl chloride, MeC(Cl): $\overset{+}{NH_2}$ $\bar{Cl}$, for example, changes slowly on standing



7.21.

to give N(chloroethylidene)- acetamidinium chloride (VI; R^1 = H, R = Me) (42) presumably via the dimer V (R = Me) as shown. In the present study, two of the four systems examined contained nitriles, RCN, with α-hydrogen atoms (R = Me, Et) and whilst analogues of VI are formally possible, no such comparable rearrangement product has been characterised. In all cases the terminal product was $Cl_3SnC(R){:}\ NC(R){:}\ \overset{+}{NH_2}\ \overset{-}{SnCl_3}$ (I; R = Me, Et, Bu^t, Ph) being the analogue of V (Cl = $SnCl_3$). If such rearrangement does not occur it may be that the trichlorostannate(II) ion, $Sn^{II}Cl_3^-$, is a better nucleophile (i.e. poorer leaving group) than Cl^-. Consequently the mechanism by which such dimers (I) arise is more likely to be that which does not postulate $Sn^{II}Cl_3^-$ as a leaving group, equation 7.19 being preferred therefore to equation 7.18.

7.4 Summary

In its reaction with nitriles the system tin(II) chloride-hydrogen chloride in ethereal solvent behaves as ionized hydrogen trichlorostannate(II) and effectively the reactive species are H^+ and $SnCl_3^-$. Reaction takes place by addition across C≡N to give a molecule which subsequently dimerises to give an N(alkyl(or aryl)trichlorostannylmethylene)alkyl(or aryl)amidinium trichlorostannate(II), $Cl_3Sn^{IV}C(R){:}NC(R){:}\overset{+}{NH_2}\ \overset{-}{SnCl_3}$ (I; R = Me, Et, Bu^t, Ph). It contains tin in oxidation state (II) and(IV) and is the terminal product in all the systems studied, there being no evidence of any further rearrangement reactions even when the nitriles possessed α-hydrogen atoms. Their infrared, mass and ^1H-NMR spectra are discussed and the latter recorded for the ethyl, t-butyl and phenyl derivatives evidenced coupling between ^{14}N and protons of the $C{=}\overset{+}{NH_2}$ unit.

APPENDIX

EXPERIMENTAL DETAILS

1. General

Most of the reactions described in this thesis involved the handling of air- and moisture-sensitive compounds. All reactions therefore were carried out in an atmosphere of pure dry nitrogen in a two-necked round-bottomed flask. Air-sensitive solids were handled in a glove box and liquids and solutions were transferred as necessary using a syringe against a counter current of nitrogen.

2. Nitrogen Supply

Nitrogen was drawn off from a tank containing liquid nitrogen, removing traces of oxygen by passing through a furnace containing reduced wire-form copper at about 400^{o}. Water was removed by a trap cooled by liquid air and a P_2O_5 tower. The gas was then delivered to a multiplet outlet system.

3. Glove Box

The nitrogen was purified as described above and when not in use its purity was maintained by continuous recycling through hot (400^{o}) copper towers, and cooling traps, at -196^{o}, a P_2O_5 tower and a KOH tower. Phosphorus pentoxide was also placed in the glove box.

4. Infrared Spectra

Infrared spectra in the range (4000 - 250)cm^{-1} were recorded on a Perkin Elmer 457 spectrometer. Samples were in the form of Nujol mulls or neat liquids between KBr plates.

5. ^{1}H- Nuclear Magnetic Resonance Spectra

There were recorded at 60 MHz on a Varian A56/60D spectrometer. Samples were prepared as solutions in benzene, deuterobenzene, deuterochloroform and deuterated dimethylsulphoxide as appropriate. Tetramethylsilane (TMS) was commonly used as an external reference standard. Sample tubes were filled by syringe against a counter current of nitrogen and were sealed under nitrogen.

6. Mass Spectra

These were recorded on an AEI MS9 mass spectrometer at 70 ev and an accelerating potential of 8kv with a source temperature at 150° - 250° and electromagnetic scanning. Samples were introduced by direct insertion into the ion source and protected from atmospheric moisture by a nitrogen filled tube attached to the probe.

7. Molecular Weights

These were determined cryoscopically in benzene using a Beckman apparatus of conventional type. The benzene, of analytical reagent purity, was dried over sodium wire and calibrated using biphenyl. All measurements were taken while a slow stream of nitrogen was passed through the apparatus.

8. Solvents

Hydrocarbon solvents and diethyl ether were dried and stored over extruded sodium wire. Tetrahydrofuran was dried over KOH followed by potassium metal, and was freshly distilled before use. Deuterated solvents for ^{1}H-NMR work were commercial samples stored under dry nitrogen.

9. Starting Materials

Anhydrous tin (II) chloride and germanium (IV) chloride were fresh commercial samples. Tin (IV) - and silicon (IV) chlorides were purified by vacuum distillation. Solutions of alkyl lithium and diethylmagnesium were standardised against a molar solution of sec-butanol in xylene using 1,10-phenanthroline as indicator (122). The methyleneamines (68, 318) and N,N^1-diarylacetamidines (319) were prepared as described in the literature.

10. Analytical Methods

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Nitrogen was also determined by the Kjeldahl method.

Chlorine was determined by (i) fusion of the compound with potassium followed by volumetric determination of the chloride ion or (ii) oxygen flask combination followed by potentiometric titration of the chloride ion.

Tin was determined gravimetrically by a procedure which basically involved the decompostion of a sample to tin (IV) oxide.

Zinc and magnesium were determined by decomposing samples using a mixture of concentrated nitric and perchloric acids. The liquids were heated until clear, diluted with water, and then the metal content of the solution determined using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer.

REFERENCES

1. E. E. Blaise, Compt. Rend, 1901, 132, 38; J. Chem. Soc, 1901, 80(1), 133.

2. H. Gilman and K. E. Marple, Rec. Trav. Chem, 1936, 55, 133.

3. R. H. Anker and A. H. Cook, J. Chem. Soc, 1941, 323.

4. L. I. Zakharkin and I. M. Khorlina, Dokl. Akad. Nauk. S.S.S.R., 1957, 116, 442.

5. J. R. Jennings, J. E. Lloyd, and K Wade, J. Chem. Soc, 1965, 5083.

6. R. A. Walton, Quart. Rev., 1965, 19, 125.

7. I Pattison, K. Wade and B. K. Wyatt, J. Chem. Soc. (A), 1967, 857.

8. B. Samuel, R Snaith, C. Summerford and K. Wade, ibid., 1970, 2019.

9. H. J. Anderson, N. C. Wang, and E. T.P. Jwili, Canad. J. Chem, 1971, 49, 2315.

10. H. M. Rowe-Anderson, Ph.D. Thesis, University of Nebraska, U.S.A., 1971.

11. E. A. Petch, Ph.D. Thesis, University of Durham, 1974.

12. G. E. Coates and D. Ridley, J. Chem. Soc.(A), 1967 56.

13. I. Pattison and K. Wade, ibid., 1968, 57.

14. G. E. Coates and D. Ridley, ibid., 1966, 1064.

15. E. Frankland and J. Evans, J. Chem. Soc. 1880, 37, 563.

16. S. Pasynkiewicz and S. Maciaszek, J. Organometal. Chem. 1968, 15, 301.

17. W. Kuran and S. Pasynkiewicz, J. Organometal Chem, 1970, 23, 343.

18. W. Kuran, S. Pasynkiewicz, and J. Muszynski, ibid., 1970, 25, 23.

19. H. Hoberg and J. Barluenga-Mur, ibid., 1969, 17, 28.

20. G. E. Coates and G. L. Morgan, Adv. Organometal Chem., 1970, 9, 195.

21. H. J. Leffler. Inorg. Chem., 1964, 3, 145.

22. M. F. Hawthorne. Tetrahedron, 1962, 17, 117.

23. J. E. Lloyd and K. Wade, J. Chem. Soc., 1964, 1649.

24. J. R. Jennings, I Pattison and K. Wade, J. Chem. Soc.(A), 1969, 565.

25. J. R. Jennings and K. Wade. ibid., 1967, 1222.

26. J. E. Lloyd and K. Wade, J. Chem. Soc., 1965, 2662.

27. B. Bogdanovic and S. Konstantinovic, Annalen, 1970, 738, 202.

28. K. Wade and B. K. Wyatt, J. Chem. Soc., 1969, 1121.

29. H. Hoberg and J. Barluenga-Mur, J. Organometal Chem., 1969, 17, 30.

30. H. Hoberg and J. Barluenga-Mur, Annalen, 1970, 733, 141.

31. T. Hirabayashi, K. Itoh, S. Sakai and Y. Ishii, J. Organometal Chem., 1970, 21, 273.

32. R. Calas, E. Frainnet and A. Bazonin, Compt. Rend., 1961, 252, 420.

33. D. Martin, K. Witke, P. Reich and N. Nadolski, Chem. Ber., 1968, 101, 3185.

34. M. F. Lappert, J. McMeeking and D. E. Palmer, J. Chem. Soc.(D), 1973, 151.

35. T. A. George, K. Jones and M. F. Lappert, J. Chem. Soc., 1965, 2157.

36. A. J. Bloodworth and A. G. Davies, Proc. Chem. Soc., 1963, 315.

37. W. P. Neumann and K. Künlein, Tetrahedron Letters, 1966, 29, 3423.

38. A. G. Davies and R. J. Puddephat, J. Organometal Chem., 1966, 5, 590.

39. F. C. Schaefer - "The Chemistry of the Cyano-group", Ed. Zvi Rappoport, Interscience, 1970 Chapter 6.

40. E. N. Zil'berman, Russian Chem. Rev., 1962, 31, 615.

41. I. Hechenbleikner, Chem. Abstr., 50, 1902f, 8718i, 1956; 51, 16544d, 1957.

42. L. E. Hinkel and G. J. Treharne, J. Chem. Soc., 1945, 866.

43. A. Ya. Lazaris, E. N. Zil'berman and O. D. Strizhakov, J. Gen. Chem. U.S.S.R. 1962, 32, 890.

44. F. C. Schaefer, I. Hechenbleikner, G. A. Peters and V. P. Wystrach, J. Amer. Chem. Soc., 1959, 81, 1466 and refs. therein.

45. R. N. Johnson and H. M. Woodburn, J. Org. Chem., 1962, 27, 3958 and refs. therein.

46. P. Oxley and W. F. Short, J. Chem. Soc., 1949, 49 and earlier papers cited therein.

47. F. C. Schaefer and A. P. Krapcho, J. Org. Chem., 1962, 27, 1255.

48. C. Summerford, K. Wade, and B. K. Wyatt, J. Chem. Soc., 1970. 2016.

49. J. Keeble, D. G. Othen and K. Wade, J. Chem. Soc.,(D), 1974, 1.

50. J. B. Farmer, Ph.D. Thesis, University of Durham, 1973.

51. B. Hall, J. Keable, R. Snaith and K. Wade, J. Chem. Soc. (D)., 1978, 986.

52. O. J. Scherer, Organometal Chem. Rev., 1968, 3, 281.

53. C. Summerford and K. Wade, J. Chem. Soc., 1969, 1487.

54. B. Hall, J. B. Farmer and K. Wade, J. Chem. Soc.,(D), 1979, 102.

55. G. E. Coates and A. H. Fishwick, J. Chem. Soc.(A)., 1967, 1199.

56. W. S. Middleton and C. G. Krespan, J. Org. Chem., 1965, 30, 1398.

57. R. Snaith, Ph.D. Thesis, University of Durham, 1971.

58. R. Snaith, K. Wade and B. K. Wyatt, J. Chem. Soc(A)., 1970. 380.

59. I. Pattison and K. Wade, J. Chem. Soc., 1967, 1098.

60. R. W. Layer, Chem. Rev., 1963, 63, 489.

61. I. Pattison and K. Wade, J. Chem. Soc., 1968, 842.

62. K. Wade, and B. K. Wyatt, ibid., 1967, 1339.

63. J. R. Jennings, I. Pattinson, K. Wade and B. K. Wyatt, ibid., 1967, 1608.

64. A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem., 1958, 5, 264.

65. N. Davidson and M. C. Brown, J. Amer. Chem. Soc., 1942, 64, 316.

66. G. E. Coates, J. Chem. Soc., 1951, 2003.

67. E. Wiberg and P. Buchhert, Inorg. Chem., 1949, 1. 288.

68. P.L. Pickard and D. J. Vaughan, J. Amer. Chem. Soc., 1950, 72, 5017.

69. B. Samuel and K. Wade, J. Chem. Soc(A)., 1969, 1742.

70. C. Summerford and K. Wade, ibid., 1970, 2010.

71. D. Y. Curtin, E. J. Grubbs and C. G. McCarty, J. Amer. Chem. Soc., 1966, 88, 2775.

72. D. Y. Curtin and C. G. McCarty, Tetrahedron Letters, 1962, 1269.

73. D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck and H. A. Staab, Annalen, 1967, 708, 36.

74. D. Wurmb-Gerlich, F. Vögtle and A. Mannschreck, Tetrahedron Letters, 1965, 12, 697.

75. R. Snaith, C. Summerford, K. Wade and B. K. Wyatt, J. Chem. Soc(A)., 1970, 2635.

76. E. A. V. Ebsworth. Chem. Comm., 1966, 530.

77. J. B. Farmer, H. M. M. Shearer, J. D. Sowerby and K. Wade ibid., 1976, 160.

78. L. H. Chan and E. G. Rochow, J. Organometal Chem., 1967, 9, 231.

79. P.L. Pickard and G. W. Polly, J. Amer. Chem. Soc., 1954, 76, 5169.

80. D. G. Othen, Ph.D, Thesis, University of Durham, 1977.

81. J. Spencer, Ph.D. Thesis, University of Durham, 1973.

82. H. J. Coerver and C. Curran, J. Amer. Chem. Soc., 1958, 80, 3522.

83. H. C. Brown and M. Kubota, ibid., 1961, 83, 4175.

84. D. Cook, Canad. J. Chem., 1962, 40, 480.

85. J. L. Hoard, T. B. Owen, A. Buzzell and O. N. Salmon, Acta Crystallogr. 1950, 3, 130.

86. B. Swanson, D. F. Shriver and J. A. Ibers, Inorg. Chem., 1969, 8, 2182.

87. K. Manning, E. A. Petch, H. M. M. Shearer, K. Wade and R. G. Whitehead, Chem. Comm. 1976, 107.

88. G. J. Bullen, K. Wade, ibid, 1971, 1123.

89. C. G. McCarty "The Chemistry of the C=N Group". Ed. S. Patai Interscience 1970, Wiley (Chapter 9).

90. R. J. Cook, and K. Mislow, J. Amer. Chem. Soc., 1971, 93, 6703.

91. R. D. Baechler and K. Mislow, ibid., 1971, 93, 773.

92. M. R. Collier, M. F. Lappert, R. Snaith, and K. Wade, J. Chem. Soc(Dalton), 1972, 370.

93. N. W. Alcock, M. Pierce-Butler and G. R. Willey, Chem. Comm. 1975, 183.

94. G. R. Whitehead, Ph.D. Thesis, University of Durham 1979.

95. P. T. Moseley and H. M. M. Shearer, Chem Comm., 1968, 279.

96. V. Magnusson and G. D. Stucky, Inorg. Chem., 1969, 8, 1427.

97. J. Toney and G. D. Stucky, J. Organometal Chem., 1971, 28, 5.

98. J. Toney and G. D. Stucky, Chem. Comm., 1967, 1168.

99. G. D. Stucky and R. E. Rundle, J. Amer. Chem. Soc., 1964, 86, 4825.

100. E. Weiss, J. Organometal Chem., 1965, 4, 101.

101. E. Weiss, ibid., 1964, 2, 314.

102. A. Bondi, J. Phys. Chem., 1964, 68, 441.

103. N. W. Alcock, Adv. Inorg. Chem. Radiochem., 1972, 15, 1

104. M. Vallino, J. Organometal Chem., 1969, 20, 1.

105. W. Theilacker and K. Fauser, Annalen, 1939, 539, 103.

106. G. R. Whitehead, Personnel Communication, University of Durham.

107. A. Fratiello, T. P. Onak and R. E. Schuster, J. Amer. Chem. Soc., 1968, 90, 1194.

108. I. Pattison, Ph.D. Thesis, University of Durham, 1967.

109. N. R. Fetter and F. M. Peters, Canad. J. Chem., 1965, 43, 1884.

110. R. A. Cover and G. L. Morgan, J. Amer. Chem. Soc., 1970, 92, 5067.

111. J. L. Atwood and G. D. Stucky, ibid., 1969, 91, 4426.

112. G. E. Coates and J. A. Heslop, J. Chem. Soc., 1968, 631.

113. G. E. Coates, J. E. Heslop, M. E. Redwood and D. Ridley, J. Chem. Soc(A)., 1968, 1118.

114. L. E. Zakharkin, Zh. Obsh. Khim., 1964, 34, 3125.

115. L. Pauling- "Nature of the Chemical Bond" 3rd Edition, Cornell U.P. New York, 1960.

116. G. E. Coates and S. I. E. Green, J. Chem. Soc., 1962, 3340.

117. G. E. Coates and P. D. Roberts, J. Chem. Soc(A)., 1968, 265.

118. G. E. Coates and J. A. Heslop, ibid., 1968, 514.

119. G. E. Coates and P. D. Roberts, ibid., 1969, 1008.

120. G. E. Coates and B. R. Francis, ibid., 1971, 1305.

121. U. Bleinheim, G. E. Coates and R. C. Srivastava, J. Chem. Soc(D)., 1972, 2302.

122. S. C. Watson and J. F. Eastham, J. Organometal Chem., 1967, 9, 165.

123. K. A. Kozeschkow, A. N. Nesmeyanov and W. J. Petrosow, Ber., 1934, 63, 1138.

124. K. S. Ras, B. P. Stoicheff and R. Turner, Canad. J. Phys., 1960, 38, 1516.

125. R. E. Rundle, Survey Prog. Chem., 1963, 1, 81.

126. E. L. Amma and R. E. Rundle, J. Amer. Chem. Soc., 1958, 80, 4141.

127. S. K. Byram, J. K. Fawcett, S. C. Nyburg and R. J. O'Brien, Chem. Comm., 1970, 16.

128. E. Frankland, Annal., 1859, 111, 62.

129. K. H. Thiele, Z. Anorg. Chem., 1962, 319, 183.

130. N. I. Sheverdina, L. V. Abramova and K. A. Kocheskov, Dokl. Akad. Nauk, U.S.S.R. 1959, 128, 320.

131. K. H. Thiele, Z Anorg. Chem., 1963, 325, 156.

132. K. H. Thiele and S. Schröder, ibid., 1965, 337, 14

133. J. G. Noltes and J. W. G. van den Hurk, J. Organometal. Chem., 1964, 1, 377.

134. J. G. Noltes and J. Boersma, ibid., 1967, 9, 1.

135. J. Lewis, R. S. Nyholm and D. J. Philips, J. Chem. Soc., 1962, 2177.

136. K. H. Thiele and H. Raw, Z. Anorg. Chem., 1967, 353, 127.

137. J. G. Noltes, and J. W. G. van den Hurk, J. Organometal Chem., 1965, 3, 232.

138. G. E. Coates and D. Ridley, J. Chem Soc., 1965, 1870.

139. J. G. Noltes, Rec. Trav. Chim., 1965, 84, 126.

140. H. M. M. Shearer and C. B. Spencer, Chem. Comm., 1966, 194.

141. J. W. Adamson and H. M. M. Shearer, ibid., 1969, 897.

142. J. Boersma and J. G. Noltes, Tetrahedron Letters, 1966, 14, 1521.

143. J. G. Noltes and J. Boersma, J. Organometal Chem., 1968, 12, 425.

144. F. Schindler and H. Schmidbaur, Angew Chem., 1967, 79, 697.

145. F. Schindler, H. Schmidbaur and U. Krüger, Angew, Chem.(Int. Ed.)., 1965, 4, 876.

146. F. Schindler, H. Schmidbaur and G. Jones, Angew. Chem., 1967, 79, 413.

147. J. Boersma, A. L. Spek and J. G. Noltes, J. Organometal Chem, 1974, 81, 7.

148. J. G. Noltes and J. Boersma, ibid., 1969, 16, 345.

149. G. E. Coates, M. L. H. Green and K. Wade in "Organometallic Compounds" Vol. 1. London, Methuen 1974.

150. M. W. Rathke. Org. Reactions, 1975, 22, 423.

151. S. N. Reformatsky, Ber., 1887, 20, 1210.

152. D. G. M. Diaper and A. Kuksis, Chem. Rev., 1959, 59, 89.

153. M. Gandemar, Organometal Chem. Rev., 1972, A8, 183.

154. A. Sementsov, J. Chem. Ed., 1957, 34, 530.

155. H. O. House, "Modern Synthetic Reactions" 2nd Edition. W. A. Benjamin, New York 1972 p671.

156. R. L. Shriner, Org. Reactions 1942, 1, 1.

157. R. D. Rieke, Accts. of Chem Res., 1977, 10, 301.

158. J. Furukawa and N. Kawabata, Adv. Organometal Chem., 1974, 12, 83.

159. L. G. Kuz'mina, N. G. Bokii and Yu. T. Struchkov, Uspekhi Khimii 1975, 44, 134.

160. R. J. Gillespie and R. S. Nyholar, Quart. Rev., 1957, 11, 339.

161. J. B. Donaldson, Progr. Inorg. Chem., 1967, 8, 287.

162. J. M. Van der Berg, Acta Crystallogr. 1961, 14, 1002.

163. B. Kamenar and D. Grdenic, J. Chem. Soc., 1961, 3954.

164. R. R. McDonald, A. C. Larson, and D. T. Cromer, Acta Crystallogr., 1964, 17, 1104.

165. J. S. Morrison and H. M. Haendler, J. Inorg. Nucl. Chem., 1967, 29, 393.

166. P. Foley and M. Zeldin, Inorg. Chem., 1975, 14, 2264.

167. P. G. Harrison and J. J. Zuckerman, J. Amer. Chem. Soc., 1970, 92, 2577.

168. J. D. Cotton, P. J. Davidson and M. F. Lappert, J. Chem. Soc(D)., 1976, 2275.

169. B. J. Aylett, Progress in Stereochemistry 1969, 4, 213.

170. S. Prasad, K. S. R. Krishnaiah, and V. Hariharan, J. Ind. Chem., Soc., 1960, 37, 347.

171. P. Pascal "Nouveau Traite' de Chemie Minerale Vol. 8" Maison et Cie, Paris, 1963.

172. J. F. Lefelhoez, M. A. Desky and C. Curran Abstr., of 19th Meeting of American Chem. Soc., Paper 1408, 1965.

173. Clark G. L. American Journal of Science 1921, 7, 1.

174. R. E. Rundle and D. H. Olsen, Inorg. Chem., 1964, 3, 596.

175. T. H. Sumarkova and D. E. Surpina, Roznick Ann. Soc. Chem. Polonorum, 1970, 44, 947.

176. W. J. Moore and L. Pauling, J. Amer. Chem. Soc., 1941, 63, 1392.

177. C. Löwig, Annal., 1852, 84, 308.

178. T. L. Brown and G. L. Morgan, Inorg. Chem., 1963, 2, 736.

179. R. K. Ingham, S. D. Rosenberg, and H. Gilman, Chem. Rev., 1960, 60, 459.

180. W. P. Newman and K. König, Angew Chem., 1962, 74, 215.

163. B. Kamenar and D. Grdenic, J. Chem. Soc., 1961, 3954.

164. R. R. McDonald, A. C. Larson, and D. T. Cromer, Acta Crystallogr., 1964, 17, 1104.

165. J. S. Morrison and H. M. Haendler, J. Inorg. Nucl. Chem., 1967, 29, 393.

166. P. Foley and M. Zeldin, Inorg. Chem., 1975, 14, 2264.

167. P. G. Harrison and J. J. Zuckerman, J. Amer. Chem. Soc., 1970, 92, 2577.

168. J. D. Cotton, P. J. Davidson and M. F. Lappert, J. Chem. Soc(D)., 1976, 2275.

169. B. J. Aylett, Progress in Stereochemistry 1969, 4, 213.

170. S. Prasad, K. S. R. Krishnaiah, and V. Hariharan, J. Ind. Chem., Soc., 1960, 37, 347.

171. P. Pascal "Nouveau Traite' de Chemie Minerale Vol. 8" Maison et Cie, Paris, 1963.

172. J. F. Lefelhoez, M. A. Desky and C. Curran Abstr., of 19th Meeting of American Chem. Soc., Paper 1408, 1965.

173. Clark G. L. American Journal of Science 1921, 7, 1.

174. R. E. Rundle and D. H. Olsen, Inorg. Chem., 1964, 3, 596.

175. T. H. Sumarkova and D. E. Surpina, Roznick Ann. Soc. Chem. Polonorum, 1970, 44, 947.

176. W. J. Moore and L. Pauling, J. Amer. Chem. Soc., 1941, 63, 1392.

177. C. Löwig, Annal., 1852, 84, 308.

178. T. L. Brown and G. L. Morgan, Inorg. Chem., 1963, 2, 736.

179. R. K. Ingham, S. D. Rosenberg, and H. Gilman, Chem. Rev., 1960, 60, 459.

180. W. P. Newman and K. König, Angew Chem., 1962, 74, 215.

181. E. O. Fischer and S. Schriner, Ber., 1959, 92, 938.

182. L. D. Dane, D. F. Evans and G. Wilkinson, J. Chem. Soc., 1959, 3684.

183. L. I. Zakharkin, O. Yu. Okllobystin and V. V. Khrapov, Dokl, Akad, Nauk, S.S.S.R. 1965, 165, 593; Chem. Abstr. 1966, 64, 9106b.

184. D. E. Goldberg, D. H. Harris, M. F. Lappert and K. M. Thomas, Chem. Comm., 1976, 261.

185. D. H. Harris and M. F. Lappert, ibid., 1974, 895.

186. C. D. Schaefer and J. J. Zuckerman, J. Amer. Chem. Soc., 1974, 96, 7160.

187. M. F. Lappert, P. P. Power, M. J. Slade, L. Hedberg, K. Hedberg and V. Schomaker, Chem. Comm., 1979, 369.

188. M. Zeith, Z. Naturforsch, 1978, 33b, 1, 7.

189. P. G. Harrison and J. J. Zuckerman, Inorg. Nucl. Chem., Letters, 1969 5(7), 545.

190. P. G. Harrison and S. R. Stobart, J. Chem. Soc(D)., 1973, 940.

191. P. F. R. Ewings, D. E. Fenton, P. G. Harrison ibid., 1975, 821.

192. J. Potenza and D. Mastropaolo, Acta. Crystallogr., 1973, B29, 1830.

193. P. F. R. Ewings, P. G. Harrison and T. J. King, J. Chem. Soc(D)., 1975, 1455.

194. M. K. Friedel, B. F. Hoskins, R. L. Martin and S. A. Mason, Chem., Comm., 1970, 400.

195. P. F. Ewings, P. G. Harrison and A. Mangria, J. Organometal Chem., 1976, 114, 35.

196. J. D. Donaldson, D. A. Nicholson, D. C. Puxley, and R. A. Howie, J. Chem. Soc(D), 1973, 1810.

197. K. G. Shields, R. C. Seccombe and C. H. L. Kennard, ibid., 1973, 741.

198. P. F. R. Ewings, P. G. Harrison, T. J. King and A. Morris, Chem. Comm., 1974, 53.

199. F. P. van Remoortere, J. J. Flynn, F. P. Boer and P. P. North, Inorg. Chem., 1971, 10, 1511.

200. A. F. Berndt and R. Lambert, Acta Crystallogr., 1971, B.27, 1092.

201. L. J. Bellamy and H. E. Hallam, Trans. Farad. Soc., 1959, 55, 220.

202. D. J. Scherer and P. Hornig, Ber., 1968, 101, 2533.

203. B. P. Susz and I. Cooke, Helv. Chim. Acta., 1954, 37, 1273.

B. P. Susz and P. Chalandon, ibid., 1958, 41, 1332.

R. C. Paul and S. L. Chadha, J. Inorg. Nucl. Chem., 1969, 31, 1679.

204. D. Cook, Friedel Crafts and related reactions, Ed. G. Olah, Interscience, New York, 1963 I p.806.

205. L. J. Bellamy, Adv. in Infrared Group Frequency, Methuen, London. 1968.

206. M. F. Lappert, J. Chem. Soc., 1962, 542.

207. D. E. H. Jones and J. L. Wood, J. Chem. Soc.(A), 1967, 1140.

208. H. J. Coerver and C. Curran, J. Amer. Chem. Soc., 1958, 80, 3522.

H. C. Brown and M. Kubota, ibid., 1961, 83, 4175.

D. Cook, Canad. J. Chem., 1962, 40, 480.

209. J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, Acta. Crystallogr., 1959, 3, 130. B. Swanson, D. F. Shriver and J. A. Ibers, Inorg. Chem., 1969, 8, 2182.

210. K. D. Bos, E. J. Bulten and J. G. Noltes, J. Organometal Chem, 1972, 39, C52.

211. M. M. Mahmoud, Ph.D. Thesis, University of Nottingham. 1976.

212. D. B. Chambers, F. Glocking and M. Weston, J. Chem. Soc(A)., 1967, 1759.

213. K. R. Laing, S. D. Robinson and M. F. Uttley, J. Chem. Soc.,(D), 1974, 1205.

214. W. Bradley and I. Wright, J. Chem. Soc., 1956, 640.

215. M. L. H. Green, A. G. Massey, J. J. Moelwyn-Hughes and P. L. I. Nagy, J. Organometal Chem., 1967, 8, 511.

216. D. N. Lawson and G. Wilkinson, J. Chem Soc., 1900, 1965.

217. W. Rigby, R. Whyman and K. Wilding, J. Phys. E. 1970, 3, 572.

218. W. R. McClellan, H. H. Hocha, H. N. Cripps, E. L. Muetterties, and B. W. Hawk, J. Amer. Chem. Soc., 1961, 83, 1601.

219. T. Inglis and M. Kilner, J. Chem. Soc(D)., 1975, 730.

220. T. Inglis, M. Kilner, T. Reynoldson and E. E. Robertson, ibid., 1975, 925.

221. W. Hieber and K. Kaiser, Z. Anorg. Chem., 1968, 362, 1969.

222. W. Bradley and I Wright, J. Chem. Soc., 1956, 640.

223. F. A. Cotton, T. Iglis, M. Kilner and T. R. Webb, Inorg. Chem., 1975, 14, 2023.

224. F. A. Cotton and L. W. Shire, ibid., 1975, 14, 2027.

225. J. D. Wilkins, J. Organometal Chem., 1974, 80, 349.

226. W. Bradley and E. Leete, J. Chem. Soc., 1951, 2147.

227. M. Corbett and B. F. Hoskins, J. Amer. Chem. Soc., 1967, 1530; Chem. Comm., 1968, 1602.

228. S. Candeloro, De Sanetis, L. Toniolo, T. Boschi and G. Deganello, Inorg. Chim. Acta., 1975, 12, 251.

229. L. S. Sutton, Chem. Soc. Spec. Publ., 1958, 11 and 1965, 18.

230. L. Toniolo, G. Deganello, P. L. Sandrini and G. Bambieri, Inorg. Chim. Acta., 1975, 15, 11.

231. C. M. Harris, B. F. Hoskins and R. L. Martin, J. Chem. Soc., 1959, 3728.

232. F. P. Dwyer and D. P. Mellor, J. Amer. Chem. Soc., 1941, 63, 81.

233. L. Toniolo, T. Boschi and G. Deganello, J. Organometal. Chem., 1975, 93, 405.

234. I. D. Brown and J. D. Dunitz, Acta Crystallogr., 1961, 14, 480.

235. L. Toniolo, G. de Luca and C. Panattioni, Synth. Inorg. and Metal Org. Chem., 1973, 3, 221.

236. W. H. Knoth, Inorg. Chem., 1973, 12, 38.

237. L. Toniolo, G. Deganello, P. L. Sandrini and G. Bambieri, Inorg. Chem. Acta., 1975, 15, 11.

238. F. E. Brinkman and H. S. Haiss, Chem. and Ind., 1963, 1124.

239. T. Inglis, Inorg Chem. Acta. Rev., 1973, 7, 35.

240. R. C. Poller, J. Organometal Chem., 1965, 3, 321.

241. N. Gielen and N. Sprecher, Organometal Chem. Rev., 1966, 1, 455.

242. R. Okawara and M. Wada, Adv. Organometal Chem., 1967, 5, 137.

243, B. Y. K. Ho and J. J. Zuckerman, J. Organometal Chem., 1973, 48, 1.

244. A. G. Macdiarmid(Ed), "Organometallic Compounds of the GroupIV element" Marcel Dekker, New York, 1972.

245. R. C. Poller, "The Chemistry of Organotin Compounds" Academic Press, 1970.

246. A. K. Sawyer "Organotin Compounds" Marcell Dekker, New York, 1971.

247. R. Hopper and W. Dähne, Naturwissenschaften, 1962, 49, 254.

248. A. G. Davies, H. J. Millidge and D. C. Pusley and P. J. Smith, J. Chem. Soc(A)., 1970, 2862.

249. H. C. Clark, R. J. O'Brien and J. Trotter, J. Chem. Soc., 1964, 2332.

250. M. J. Janssen, J. G. A. Luijten and G. J. M. Van der Kerk, Rec. Trav. Chim., 1963, 82, 90.

251. M. Wada, M. Shindo and R. Okawara, J. Organometal Chem., 1963, 1, 95.

252. I. P. Gol'dshtein, E. N. Gur'yanova and K. A. Kocheshkov, Dokl. Akad, Nauk, S.S.S.R., 1961, 138, 1099.

253. I. P. Gol'dshtein, E. D. Delenskaya and K. A. Kocheshkov, ibid. , 1961, 136, 1079.

254. R. Hulme, J. Chem. Soc., 1973, 1524.

255. E. O. Schlemper and W. C. Hamilton, Inorg. Chem., 1966, 5, 995.

256. I. R. Beattie and T. Gibson, J. Chem. Soc., 1961, 2585.

257. A. S. Mufti and R. C. Poller, J. Organometal Chem., 1965, 3, 99.

258. G. S. Brownlee, A. Walker, S. C. Nyburg, J. T. Szymanski, Chem. Comm., 1971, 1073.

259. J. J. Park, D. M. Collins and J. L. Hoard, J. Amer. Chem. Soc., 1970, 92, 3636.

260. F. P. van Remoortere, J. J. Flynn and F. P. Boer, Inorg. Chem., 1971, 10, 2313.

261. W. E. Bennett, D. E. Broberg, and N. C. Baenziger, ibid., 1973, 12, 93.

262. C. D. Garner, D. Sutton and S. C. Wallwork, J. Chem. Soc(A)., 1967, 1949.

263. J. Konnert, D. Britten and Y. M. Chow, Acta. Crystallogr., 1972, B28, 180.

264. Chem. Soc. Spec. Periodic Reports - "Spectroscopic Properties of Inorganic and Organometallic Compounds" Vols. 1 - 7.

265. J. M. Miller and M. Onyszchuk, J. Chem. Soc., 1967, 1132.

266. G. Vandrish and M. Onyszchuk, J. Chem. Soc(A)., 1970, 3327.

267. H. H. Sisler, W. J. Wilson, B. J. Gribbins, H. H. Batey, B. Pfahler, and R. Mattair, J. Amer. Chem. Soc., 1948, 70, 3818.

268. H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, J. Amer. Chem. Soc., 1948, 70, 3821.

269. V. V. Udovenko and Yu Yu Fialkov, Zhur. Neorg. Khim, 1957, 2, 434, 868.

270. Yu. N. Vol'nor Zhur. Neorg. Khim., 1959, 4, 2287.

271. M. F. Lappert, J. Chem. Soc., 1962, 542.

272. I. R. Beattie, G. P. McQuillan, L. Rule and M. Webster, ibid., 1963, 1514.

273. I. R. Beattie, Quart. Rev. Chem. Soc., 1963, 17, 382.

274. I. P. Gol'dshtein, E. N. Gur'yanova and E. S. Shcherbakova, J. Gen. Chem. U.S.S.R., 1970, 40, 166.

275. H. Ulich, E. Hertel and W. Nespital, Z. Phys. Chem., 1932, B17, 21.

276. M. F. Farona and J. G. Grasselli, Inorg. Chem., 1967, 6, 1675.

277. S. J. Ruzicka and A. E. Merbach, Inorg. Chim. Acta., 1976, 20, 221.

278. E. N. Gur'yanova, I. P. Gol'shtein and I. P. Roman "The Donor-Acceptor Bond" Wiley New York, 1975.

279. F. S. Kipping and A. G. Murray, J. Chem. Soc., 1928, 2734.

280. J. A. Daniels, J. R. Jennings, P. G. Huggett and K. Wade, Inorg. Nucl. Chem. Letters, 1978, 14, 445.

281. S. T. Zenchelsky and P. R. Segatto, J. Amer. Chem. Soc., 1958, 80, 4796.

282. F. J. Cioffi and S. T. Zenchelsky. J. Phys. Chem., 1963, 67, 357.

283. J. J. Myher and K. E. Russell, Canad. J. Chem., 1964, 42, 1555.

284. A. Kenula and R. J. Iwanoto, J. Phys. Chem., 1968, 72, 1334.

285. I. I. Lapidus and N. A. Nisel'son, Russ. J. Phys. Chem., 1968, 42, 733 (trans).

286. J. C. Sheldon and S. Y. Tyree, J. Amer. Chem. Soc., 1958, 80, 4775.

287. B. F. Markov, B. A. Voitovich and A. S. Barabanova, Russ. J. Inorg. Chem. 1961, 6, 616(trans).

288. R. B. Shirts, R. J. Goates and J. B. Ott, J. Chem. Thermodynamics, 1974, 6, 493.

289. H. J. Gordon and R. A. Ford "The Chemist's Companion" Wiley Interscience New York, 1972.

290. E. W. Abel, Comp. Inorg. Chem. Vol. 2 Pergamon, London 1973

291. E. G. Rochow, ibid, idem.

292. Gmelin Handbuch, Silicon Teil 8, 1959.

293. J. Engel, Ann. Chim. Phys., 1889, 17, 338.

294. W. H. Young, J. Amer. Chem. Soc., 1901, 23, 450.

295. C. E. Vanderzee and D. E. Rhodes, ibid., 1952, 74, 3552.

296. L. A. Woodward and M. J. Taylor, J. Chem. Soc., 1962, 407.

297. O. M. Nefedov, S. P. Kolesnikov, V. I. Sheichencho and N. D. Zelinsky, Ang. Chem. Int. Ed., 1964, 3, 508.

298. O. M. Nefedov, S. P. Kolesnikov, V. I. Sheichencho and Yu. N. Sheinkner, Dokl. Akad. Nauk, S. S. S. R., 1965, 162, 589.

299. O. M. Nefedov and S. P. Kolesnikov, Bull. Acad. Sci, U.S.S.R. Chem., 1966, 201.

300. G. Reifenberg and W. J. Considine, Ger. Offen. 1968, 1, 963589.

301. P. G. Huggett, Personal Communication, University of Durham, 1979.

302. J. W. Burley, R. E. Hutton and B. R. Iles. Ger. Offen., 1976, 2, 540210.

303. J. W. Burley, R. E. Hutton, V. E. Oakes, Chem. Comm., 1976, 803.

304. R. E. Hutton and V. E. Oakes, Adv. Chem. Series, 1976, 157, 123.

305. J. W. Burley, P. Hope, R. E. Hutton and G. J. Groenboom, J. Organometal Chem., 1979, 170, 21.

306. E. J. Bulten and J. W. G. Van den Hurk, ibid., 1978, 162, 161.

307. E. J. Bulten and H. A. Budding, Unpublished results mentioned in ref. 306.

308. J. C. Muller, Bull. Soc. Chim. France 1964, 2027.

309. J. C. Evans, Spectrochim. Acta., 1966, 16, 428.

310. K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", Wiley, New York, 1963.

311. L. M. Jackson and S. STernhell, Application of NMR-Spectroscopy in Organic Chemistry, 2nd Edition, Perganon.

312. J. M. Williams, Inorg. Chem., 1968, 7, 2577.

313. S. Yanagida, T. Fugita, M. Ohoka, K. Katagiri and S. Komori, Bull. Soc. Japan, 1973, 46, 292.

314. S. Yanagida, T. Fugita, R. Kumagai and S. Komori, ibid., 1973, 46, 299.

315. S. Yamagida, T. Fugita, K. Katagori and S. Komori, ibid., 1973, 46, 303.

316. S. Yamagida, T. Fugita, K. Katagari and S. Komori, ibid., 1973, 46, 306.

317. I. Heichenbleikner, U. S. 2704297, 2719174 (1955) and 2768204 (1956).

318. P. L. Pickard and T. L. Tolbert, J. Org. Chem., 1961, 26, 4886.

319. E. E. Taylor and W. A. Ehrhart, ibid., 1963, 28, 1108.