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STUDIES IN THE ORGANONITROGEN CHEMISTRY OF TIN AND NEIGHBOURING ELEMENTS

by

DAVID GEORGE OTHEN B.Sc.

Van Mildert College

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

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April 1977
To my parents.
The copyright of this thesis rests with the author. No quotation from it should be published without his prior written consent and information derived from it should be acknowledged.
Chapter 1. Introduction and Background

1.1 Introduction

1.2 Stereochemistry of Organic Derivatives of Tin
   A. General Considerations
   B. Structural Characteristics of Organic Derivatives of Divalent Tin
   C. Structural Characteristics of Organic Derivatives of Tetravalent Tin
      i) Tetra-coordinate Tin(IV)
      ii) Penta-coordinate Tin(IV)
      iii) Hexa-coordinate Tin(IV)
      iv) Higher coordination numbers

1.3 Compounds containing the Tin-Nitrogen Bond
   A. Historical Background
   B. Organonitrogen Derivatives of Divalent Tin
   C. Organonitrogen Derivatives of Tetravalent Tin
      i) Compounds containing Tin bonded to 3-covalent Nitrogen
         a) Preparative Aspects
         b) Reactions
         c) Physical and Structural Properties
      ii) Compounds containing Tin bonded to 2-covalent Nitrogen
      iii) The Tin-Nitrogen Bond in the Organotin Pseudohalides

2.1 Introduction 75
2.2 Bonding and Structure in Methyleneamino-derivatives 75
2.3 Spectroscopic Studies on Methyleneamino-derivatives
   A. Nuclear Magnetic Resonance Spectroscopy 80
   B. Infra-red Spectroscopy 82
   C. Ultra-violet Spectroscopy 87
2.4 Experimental
   A. Diphenylmethyleneamine derivatives
      i) Reaction of \( \text{Ph}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (4:1) 90
      ii) Reaction of \( \text{Ph}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (3:1) 91
      iii) Reaction of \( \text{Ph}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (2:1) 91
      iv) Reaction of \( \text{Ph}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (1:1) 92
      v) Reaction of \( \text{Ph}_2\text{CNLi} \) with \( \text{GeCl}_4 \) (1:1) 92
      vi) Reaction of \( \text{Ph}_2\text{CNH} \) with \( \text{SiCl}_4 \) in the presence of \( \text{Et}_3\text{N} \) (1:1:1) 94
      vii) Reaction of \( \text{(Ph}_2\text{CN})_2\text{SiCl}_2 \) with \( \text{SiCl}_4 \) 94
   B. Di-t-butylmethyleneamino derivatives
      i) Reaction of \( \text{tBu}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (4:1) 95
      ii) Reaction of \( \text{tBu}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (3:1) 96
      iii) Reaction of \( \text{tBu}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (2:1) 96
      iv) Attempted reaction of \( \text{tBu}_2\text{CNLi} \) with \( \text{SnCl}_4 \) (1:1) 97
      v) Reaction between \( \text{Li}^{\text{tBu}_2\text{CN}}\text{Sn}^{\text{II}} \) and \( \text{Li}^{\text{tBu}_2\text{CN}}\text{Sn}^{\text{IV}}\text{Cl} \) 98
      vi) Thermal decomposition of \( \text{(tBu}_2\text{CN})_2\text{SnCl}_2 \) 99
      vii) Reaction of \( \text{tBu}_2\text{CNH} \) with \( \text{SnCl}_4 \) (1:1) 100
      viii) Reaction of \( \text{tBu}_2\text{CNH} \) with \( \text{SnCl}_4 \) (2:1) 101
2.5 Discussion
   A. Preparation and Stability of Methyleneamino derivatives of Group IVB 102
   B. Spectroscopic and Structural Data
      i) Mass Spectra 109
ii) Proton nuclear magnetic resonance spectra

iii) Infra-red spectra
   a) Azomethine stretching frequencies
   b) Metal-nitrogen stretching frequencies

iv) Basicity measurements on \((tBu_2CN)_n\)SnCl \(_{4-n}, n = 2,3\)

v) Crystallographic studies

C. Summary

Chapter 3. Methyleneamine derivatives of tin(II)

3.1 Introduction

3.2 Experimental

A. Diphenylmethyleneamine derivatives
   i) Reaction of Ph\(_2\)CNH with SnCl\(_2\) (1:1)
   ii) Attempted reaction of Ph\(_2\)CNH with SnCl\(_2\) in the presence of Et\(_3\)N (1:1:1)
   iii) Reaction of Ph\(_2\)CNLi with SnCl\(_2\) (1:1)
   iv) Reaction of Ph\(_2\)CNLi with SnCl\(_2\) (2:1)
   v) Attempted reaction of Ph\(_2\)CNLi with SnCl\(_2\) (3:1)
      (performed by B. Hall)
   vi) Attempted reaction of (Ph\(_2\)CNSn\(^{II}\)Cl)\(_2\) with NaC\(_5\)H\(_5\)
   vii) Attempted preparation of a (Ph\(_2\)CNSn\(^{II}\)Cl)\(_2\)-THF adduct

B. Di-t-butylmethyleneamine derivatives
   i) Reaction of \(^tBu_2\)CNLi with SnCl\(_2\) (2:1)
   ii) Reaction of \(^tBu_2\)CNLi with SnCl\(_2\) (3:1)

3.3 Discussion

A. Preparation and stability of methyleneamine derivatives of tin (II)

B. Spectroscopic and Structural Properties
   i) Group A. Compounds of the type \((R_2CNSnX)_n,\)
      \(X = R_2CN, Cl.\)
      The crystal structure of (Ph\(_2\)CNSn\(^{II}\)Cl)\(_2\)
   ii) Group B. The methyleneamine adducts,
      \(R_2CNH.(R_2CN)_nSnCl\(_m(2m-n)\)
      The crystal structure of Ph\(_2\)CNH.(Ph\(_2\)CNSn\(^{II}\)Cl)\(_2\)C\(_7\)H\(_8\)
iii) Group C. \((^t\text{Bu}_2\text{CN})_3\text{H}_2\text{Sn}_3\text{Cl}_5\)  
iv) Group D. \(\text{Li} (^t\text{Bu}_2\text{CN})_3\text{Sn}\)  
v) General Considerations

C. Summary

Tables

Chapter 4. Some Amidino-derivatives of the Group IVB elements

4.1 Introduction

4.2 Experimental

i) Reaction of N,N'-diphenylacetamidinolithium ('AmLi') with SiCl\(_4\) (1:1)  
ii) Reaction of AmLi with GeCl\(_4\) (1:1)  
iii) Reaction between AmLi and SnCl\(_4\) (1:1)  
iv) Reaction between N,N'-diphenylacetamide ('AmH') and SnCl\(_4\) (1:1)  
v) Reaction of AmLi and SnCl\(_2\) (1:1)

4.3 Discussion

A. Preparative and structural aspects

B. Spectroscopic and structural data

i) Mass spectra  
ii) Proton nuclear magnetic resonance spectra  
iii) Infra-red spectra  
iv) Crystallographic studies

C. Summary

Chapter 5. Ortho-metallation reactions of diarylmethyleneamino tin(IV) trichlorides

5.1 Introduction

5.2 Experimental

A. Metallations involving diarylmethyleneamine derivatives

i) Reaction of \(\text{Ph}_2\text{CNLi}\) and SnCl\(_4\) (1:1)  
ii) Reaction of \(\text{Ph}_2\text{CNSiMe}_3\) with SnCl\(_4\) (1:1)  
iii) Reaction of \((p-\text{ClC}_6\text{H}_4)_2\text{CNLi}\) with SnCl\(_4\) (1:1)  
iv) Reaction of \((p-\text{toly})_2\text{CNLi}\) with SnCl\(_4\) (1:1)  
v) Reaction of \(2-\text{SnCl}_3\text{-}4-\text{MeC}_6\text{H}_3\text{C}(p-\text{toly})=\text{NH}\) with THF
vi) Attempted reaction of $\text{SnCl}_3 - 4\text{MeC}_6\text{H}_3\text{C(p-tolyl)=NH}$ with iodine

vii) Reaction of $(\text{p-tolyl})_2\text{CNLi}$ with $\text{SnCl}_4$ (2:1)

viii) Rearrangement of $(\text{Ph}_2\text{CN})_3\text{SnCl}$

B. Attempted metallations of other related systems by $\text{SnCl}_4$

i) Reaction of $\text{Ph}_2\text{C=NMe}$ with $\text{SnCl}_4$ in the presence of $\text{Et}_3\text{N}$ (1:1:1)

ii) Reaction of $\text{Ph}_2\text{C=NPh}$ with $\text{SnCl}_4$ in the presence of $\text{Et}_3\text{N}$ (1:1:1)

iii) Reaction of azobenzene with $\text{SnCl}_4$ in the presence of $\text{Et}_3\text{N}$ (1:1:1)

5.3 Discussion

A. Preparation and structure of ortho-metallated derivatives of tin(IV)

B. Spectroscopic and structural data

i) Mass spectra

ii) Proton nuclear magnetic resonance spectra

iii) Infra-red spectra
   a) Azomethine stretching frequencies
   b) Other vibrations

iv) Crystallographic data

C. Summary

Appendices

Appendix 1. Mössbauer Data

Appendix 2. Experimental Details

References
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I should like to express my gratitude to Dr K. Wade, under whose supervision this work was carried out, for his unfailing encouragement and invaluable advice. I also wish to thank Mr B. Hall for his valuable technical assistance, and many other members of the Department of Chemistry for useful discussions.

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

The work described in this thesis was carried out in the University of Durham between October 1973 and September 1976. It has not been submitted for any other degree, and is the original work of the author except where acknowledged by reference. Some aspects of this work have formed the basis of the following publications:

'Azomethine Derivatives. Part XVII. Some New Methyleneamino-derivatives of Silicon, Germanium and Tin'.
By J. Keable, D.G. Othen, and K. Wade.

'New route to aryltin(IV) halides by spontaneous cyclometallation of benzylideneaminotin(IV) halides; structure of the ortho-metallated ketimine $\text{o-SnCl}_6\text{p-MeC}_6\text{H}_3\text{C}(=\text{NH})\text{p-C}_6\text{H}_4\text{Me.}$.'
By B. Fitzsimmons, D.G. Othen, H.M.M. Shearer, K. Wade and G. Whitehead.

Parts of this work have also been presented at the following conferences:

'Some Ketimino Derivatives of Group IVB Elements'
By D.G. Othen and K. Wade. 10th University of Strathclyde Inorganic Club Conference, Ayr, June 1975 (No abstracts published)

'Ketimino complexes of tin'
By K. Manning, D.G. Othen and K. Wade. 17th International Conference on Coordination Chemistry, Hamburg, September 1976, Abstract 76.
'Ortho-metallation reactions of arylketiminotin(IV) chlorides'

'Studies in the Organonitrogen Chemistry of Tin and Neighbouring Elements'  

By D.G. Othen, B.Sc.

Abstract

This thesis describes the preparation and properties of some new organonitrogen derivatives of silicon, germanium, and tin. The structural implications of their I.R., $^1$H-NMR., and mass spectra are discussed with X-ray crystal structures in some cases. A survey of species containing tin-nitrogen bonds, and a discussion of the stereochemistry of tin are also presented.

New methyleneamine derivatives of the type $(R_2CN)_nSn^{IV}Cl_{4-n}$ $(n = 2-4)$, $(Ph_2CN)_2GeCl_2$, $[(R_2CN)_2Sn^{II}]_n$, $(Ph_2CNSn^{II}Cl)_2$, and Li$(^tBu_2CN)_3Sn^{II}$ were prepared from the metal chlorides and N-lithioketimines. The adducts $Ph_2CNH.Sn^{II}Cl_2$, $(^tBu_2CNH)_nSn^{IV}Cl_4$ $(n = 1,2)$, $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2$. $C_7H_8$, and $^tBu_2CNH.^tBu_2CNSn^{II}Cl_3$ are described. Attempts to prepare $^tBu_2CNSn^{IV}Cl_3$ led to $^tBuCN$ and $Sn^{II}Cl_2$. Similar decomposition of $(^tBu_2CN)_nSn^{IV}Cl_{4-n}$ $(n = 2,3)$ led to the imino-tin(II) complexes $^tBu_2CNH.\cdot^tBu_2CNSn^{II}Cl_3$ and $^tBu_2CNH.\cdot^tBu_2CNSn^{II}Cl_3$. $(^tBu_2CN)_2Sn^{II}Cl_5$.

The new $Sn^{IV}$ derivatives are monomeric, except for the iminotin chlorides $[(Ph_2CN)_nSn^{IV}Cl_{4-n}]_m$ $(n = 2,3; m \geq 2)$. The $Sn^{II}$ derivatives appear to involve bridging methyleneamino groups. The adducts $R_2CNH.(R_2CN)Sn^{II}_n2Cl_{4-n}$ appear to contain one three-coordinate and one four-coordinate tin atom. The C=N-M skeletons of those compounds containing terminal methyleneamino groups are probably bent with little or no N→M (p→d) $\pi$-bonding.
The N,N'-diphenylacetamidino ('Am') derivatives (Am₂SiCl₂)₂, (Am₂GeCl₂)₂, AmSnCl₃ and (AmSnCl)₂ are described. Attempts to prepare AmMCl₃ (M = Si, Ge) afforded Am₂MCl₂, apparently by disproportionation. AmSnIVCl₃ is monomeric, containing 5-coordinate tin. The associated amidino species are believed to contain bridging amidino groups.

Evidence was found for formation of Ph₂CNMCl₃ (M = Si, Ge), but attempts to prepare Ar₂CNSnIVCl₃ led to ortho-metallated products 2-SnIVCl₃-4-XC₆H₃C(p-XC₆H₄)=NH, apparently by electrophilic attack on the aromatic ring by the SnCl₃ group. The products (containing five-coordinate tin) readily form adducts with Lewis bases. Initial attempts to form similar ortho-metallated species from Ph₂C=NR (R = Me, Ph) and azobenzene were unsuccessful.

Experimental techniques and preliminary Mössbauer data on some of the new tin compounds are presented in appendices.
Nomenclature

The Chemical Society has recommended that compounds containing the \(\text{C} = \text{N}\) group should be named as derivatives of the (unknown) parent compound methyleneamine, \(\text{CH}_2\text{=NH}\). Thus compounds of the type \(\text{RCH}=\text{N-M}\) would be alkyl- or arylmethyleneamino (also known as 'aldimino') derivatives of M, and \(\text{R}_2\text{C} = \text{N-M}\), dialkyl- or diarylmethyleneamino ('ketimino') derivatives.

The recommended nomenclature has been used in Chapter headings and throughout the experimental sections. For simplicity in discussion, however, the alternative terms 'imino', 'aldimino', 'ketimino', and 'azomethine' have often been used where this does not cause confusion.

Current practice in the naming of organotin compounds is based upon use of the suffix -tin, rather than deriving the name from the parent stannane, as in the older system. Both systems have been used in this work, since both have advantages, the former being more logical but often more cumbersome.

In chemical formulae, particularly in Chapter 4, the contraction 'Am' has been used to represent the \(\text{N,N}'\text{-diphenylacetamidino}\) group, \(\text{Ph-N=CCH}_3\text{=NPh}\).

Particularly in the early chapters, to avoid continual repetition of the terms 'tin(II)' and 'tin(IV)', the expressions 'divalent' and 'tetravalent' have been used to refer to formal oxidation states (II) and (IV). Similar expressions, used by some authors to refer to the number of bonds formed by the element, are here replaced by the alternative 'di-(or 2-) covalent', etc.
CHAPTER ONE

INTRODUCTION AND BACKGROUND
1.1 **Introduction**

This thesis describes the synthesis of methyleneamino and amidino derivatives of tin (iv) and tin (ii), together with some parallel silicon and germanium systems. Their infra-red, nuclear magnetic resonance and mass spectra are interpreted in terms of their structural implications, and where the crystal structure has been investigated, this too is discussed. Some unusual reactions of these systems are also reported.

As a background to the work, a brief discussion of the stereochemistry of organic derivatives of tin is presented, together with a survey of the chemistry of compounds containing the tin-nitrogen bond. Simple coordination complexes with nitrogen bases are not surveyed, nor are the pseudohalides, but these are discussed where relevant. Similar aspects of the chemistry of the other Group IVB elements are considered in the appropriate parts of the experimental discussion.

Organotin amines and amides were reviewed in 1965\textsuperscript{1} and 1966\textsuperscript{2}, and were mentioned in wider surveys in 1969\textsuperscript{3} and 1972\textsuperscript{4}. The structural chemistry of tin compounds has been reviewed, from various viewpoints, in 1965\textsuperscript{8}, 1966\textsuperscript{9}, 1967\textsuperscript{10}, 1969\textsuperscript{11} and 1973\textsuperscript{12}. Discussion of these matters in a broader context may also be found in a number of books concerning the chemistry of tin.\textsuperscript{13,14,15,16}

1.2 **Stereochemistry of Organic Derivatives of Tin (Fig.1.1)**

A. **General Considerations**

The electronic configuration of the ground state of the tin atom may be written $[\text{Ne}] 5s^2 5p^2 5d^0$. Thus it can form covalent tin (ii) compounds by use of the two unpaired $p$-electrons to form two covalent bonds, the remaining two $s$-electrons forming the stereochemically important lone pair which would then occupy one position in a trigonal planar arrangement of electron pairs, conveniently described in terms of $sp^2$ hybridisation, as is observed in the gaseous tin (ii) halides.\textsuperscript{17}
Stereochemical configurations of di- and tetravalent tin

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>II Sn</th>
<th>IV Sn</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
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<tr>
<td>3</td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
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<td>4</td>
<td><img src="image5.png" alt="Diagram" /></td>
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<tr>
<td>5</td>
<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
</tr>
<tr>
<td>6</td>
<td><img src="image9.png" alt="Diagram" /></td>
<td><img src="image10.png" alt="Diagram" /></td>
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<td>7</td>
<td><img src="image11.png" alt="Diagram" /></td>
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<tr>
<td>8</td>
<td><img src="image13.png" alt="Diagram" /></td>
<td><img src="image14.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

trigonal bipyramid
tetragonal pyramid
pentagonal bipyramids
dodecahedral
Square antiprism

Figure 1.1
This bonding situation leaves a vacant p-orbital on the tin atom, i.e., tin (II) compounds with a coordination number of two are coordinatively unsaturated, and show a marked tendency to associate via bridging substituents, thereby increasing the coordination number to three. This is generally observed for simple complexes of divalent tin, and three is the commonest coordination number in this oxidation state. Thus the crystal structures of SnCl₂·2H₂O,¹⁸ KSnCl₃,¹⁸ and anhydrous SnCl₂²⁰ all contain 3-coordinate tin.

The lone pair has a marked effect on structures, through lone pair-bond pair repulsions which are reflected in the bond angles. It also allows tin (II) compounds to act as Lewis acids, increasing their coordination numbers by donation of the lone pair to a suitable acceptor molecule, e.g., \((C_5H_5)_2Sn^{\text{II}}\rightarrowBF_3\). A number of transition metal complexes of 'stannylenes' are now known, and have been reviewed.¹⁹

The lowest excited state of the tin atom has the electronic configuration \([Ne] 5s^1 5p^3 5d^0\). Thus it may readily form the four covalent bonds of tetravalent tin. Utilisation of the low-lying empty 5d orbitals enables the coordination number to be readily increased to five (sp³d hybridisation - trigonal bipyramid), six (sp³d² - octahedral) and beyond, compounds with coordination numbers of up to eight being known. Similarly, divalent tin can increase its coordination number beyond three by exploiting the 5d orbitals. Species up to seven-coordinate have been characterised.

It is of interest to note that, whereas all known 5-coordinate tin (IV) compounds have structures based on the trigonal bipyramid (albeit highly distorted in some cases), examples are known for tin (II) based upon both 5-cornered polyhedra, i.e., the trigonal bipyramid and the tetragonal pyramid.

It should at this point be stressed that although the coordination
chemistry of tin has so far been discussed in terms of hybridisation and d-orbital participation, this is not the only approach. Indeed, it is not strictly necessary to invoke d-orbitals at all. A multi-centre bond model in which bond formation involves only the p-orbitals on the central atom can explain most molecular geometries, but does not satisfactorily account for the stereochemical activity of lone pairs, which, for example in the tin (ii) case, would be assigned to the non-directional 5s orbital. (This may be rectified by invoking a degree of hybridisation, so that bond formation involves sp\(^n\) hybrid orbitals on the central atom, to one of which is assigned the lone pair.)

Both approaches, by their extreme assumptions of either full or zero involvement of the outer d-orbitals, are unlikely to be very accurate. Rigorous molecular orbital calculations are extremely complex, however, and in their absence these models provide a qualitatively adequate description.

B. Structural Characteristics of Organic Derivatives of Divalent Tin

Most organotin (ii) compounds so far prepared have unusual structures which stabilise the \(\text{R}_2\text{Sn}^\text{II}\) group, which is otherwise very prone to polymerisation, as shown by the considerable number of dialkyl- and diaryltin (ii) species reported prior to 1960\(^{22}\), which have since been shown to be polymers, oligomers, or ring compounds of tin (iv) containing Sn-Sn bonds.\(^{23}\)

Until 1970, the only monomeric organotin (ii) compounds known were dicyclopentadienyltin (ii)\(^{24a,b}\), bis (methylcyclopentadienyl)tin(ii)\(^{25}\), and 3-stanna-1,2-dicarba-closo-dodecaborane (ii)\(^{26a,b}\), all of which have structures based on pentahapto coordinated organic ligands (Fig.1-2,a,b,c), and bis (2-phenyl-1,2-dicarba-closo-dodecaboran (12)-1-yl)tin(ii)\(^{27}\) (Fig. 1-2d), which does appear to be a truly \(\sigma\)-bonded organotin(ii) compound, presumably stabilised by steric effects.
Figure 1-2: Structures of organotin (ii) compounds.

Since then, however, the compound bis(bis(trimethylsilyl)methyl)tin(ii), \([(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}^{\text{II}}\], has been prepared\(^{28}\), and appears to be monomeric in solution, but the crystal structure\(^{29}\) shows it to be associated in the solid, via a "bent" and weak Sn-Sn double bond, considered to be formed by overlap of each lone pair with the vacant p-orbital on the other tin atom (Fig.1-3).

![Diagram of Sn-Sn double bond](image)

Figure 1-3

Organic tin (ii) derivatives which do not contain a tin-carbon bond tend to be more stable, and generally have simpler structures based on the configurations discussed in the preceding section.

Few compounds are known with the 2-coordinate structure in the solid.
The tin (II) dialkoxides \(^{31-34}\) and tin (II)-oxygen heterocycles \(^{35-36}\) shown in Figure 1-4, are insoluble and non-volatile solids, which has been interpreted in terms of intermolecular association through coordinative tin-oxygen bonding.

The 3-coordinate state, as has been stated, is common. Apart from compounds associated by intermolecular bridging, 3-coordination often appears when one substituent group is able to chelate, as in the tin (II) 1,3-diketonate halides \(^{37}\) (Fig.1-5).

In the 4-coordinate state, based on a 5-cornered polyhedron, two arrangements are possible; that based on a trigonal bipyramid (the lone pair occupying an equatorial site) and that based on a tetragonal pyramid (with the lone pair occupying the apex). Examples of both configurations are known. Thus the trigonal bipyramidal form is adopted by bis-(N,N-diethyldithiocarbamato)tin (II) \(^{38}\), and the unsymmetrical diketonate bis(benzoylacetonato)tin(ii) (Fig.1-6:a-b), and the tetragonal pyramidal form has been demonstrated for phthalocyaninatotin(ii) (Figure 1-6c). Half of the phthalocyanine ring is omitted for clarity) and N,N'-ethylene bis (acetylideneimino)-tin (II) (Figure 1-6d).
Figure 1-6
Higher coordination numbers are considerably rarer. The anion in the ethylenediaminetetraacetic acid complex $\text{Sn}^{II} (\text{Sn}^{II} \text{EDTA.H}_2\text{O})\text{H}_2\text{O}$ has been shown to contain 6-coordinate tin, the structure being based on a very distorted pentagonal bipyramid, the lone pair occupying one apex. The cationic tin atom is linked to seven carboxylate oxygen atoms, the two water molecules being held in the lattice only by hydrogen-bonding.

A material which may be considered to contain 7-coordinate tin (II) (assuming the benzene ring occupies one coordination site) is the unusual compound $(\text{C}_6\text{H}_6)\text{Sn}^{II}(\text{AlCl}_4)_2 \text{C}_6\text{H}_6$, which has a polymeric structure containing hexahapto benzene rings (Fig.1-7). Unusually, the position of the lone pair is not obvious.

The chemistry of organic derivatives of divalent tin, including their structural features, is thoroughly reviewed in reference 41.

![Figure 1-7](image-url)
C. Structural Characteristics of Organic Derivatives of Tetravalent Tin

i) Tetra-coordinate Tin (iv)

Four-coordinate tin with a structure based on the tetrahedron is found in the tetra-alkyl and -aryl tins, the hydrides, the tetrahalides (excepting crystalline SnF₄, which has a structure based on octahedrally-coordinated tin⁴³), the organotin halides in the gas phase⁴⁴, the aminostannanes (section 1.33), and compounds in which bulky organic groups prevent association, for example tricyclohexyltin acetate, which is essentially monomeric in the crystal with a structure based on a flattened tetrahedron⁴⁵, in contrast to most other organotin carboxylates. The four-coordinate state is also considerably more common in solution or the gas phase than in the solid state.

In general, however, because of the acceptor properties of tin (iv) when it is attached to an electron-withdrawing group (the tetra-alkyl and -aryltins have little or no acceptor properties⁴⁶), a large proportion of its compounds with the more electronegative elements are associated to some degree, in the solid if not elsewhere. If the association is weak, structures are adopted which reflect this by the extent to which the trigonal bipyramidal or octahedral arrangement of the strongly associated structure is distorted towards the tetrahedral form of the monomer. This may be seen by comparing the structure of dimethyltin difluoride⁴⁸ and dichloride⁴⁷. The former has a structure containing pure octahedral coordination at tin. It consists of infinite sheets of alternating Me₂Sn groups and fluorine atoms, in a square array (Fig. 1-8a). The chloride structure consists of infinite chains of Me₂Sn groups, bridged by chlorine atoms (Fig.1-8b). The environment of the tin atom is octahedral, but distorted so that the molecular unit is visibly derived from the tetrahedron.

ii) Penta-coordinate Tin (iv)

In general it is found for five-coordinate compounds of tin (iv) that the more electronegative ligands tend to occupy the axial positions of a
trigonal bipyramidal arrangement. This is commonly observed in compounds of the type $\text{R}_3\text{SnX}$ which, if the group $X$ is capable of bridging, adopt a polymeric chain structure, trigonal bipyramidal at tin, with the organic groups in the equatorial positions. Examples are trimethyltin fluoride and the trimethyltin carboxylates (Fig.1-8, c and d). One of the best examples of this type of structure is trimethyltin cyanide, which has a linear chain structure of alternating planar $\text{Me}_3\text{Sn}$ and cyanide groups. Moreover, the C-N bond distance is short for a covalent cyanide, and the carbon and nitrogen atom positions are interchangeable and disordered, as a result of which an ionic structure has been suggested.

In contrast, trimethyl germanium cyanide has a tetrahedral covalent structure, only very slightly distorted by weak C$_2$N...Ge interactions.

Polymeric chain structures have also been observed or inferred for $\text{Me}_3\text{SnOH}$ (explaining its unusual resistance to dehydration), the trialkyltin imidazoles, triazoles, and tetrazoles (section 1.33), trimethyl- and triphenyltin isothiocyanates (bridging through -NCS...Sn), trimethyltin dicyanamide $\text{Me}_3\text{Sn}(\text{CN})_2$ (bridged by Sn-NCNCN-Sn), $\text{Me}_3\text{SnN}_3$ (Mössbauer study), $\text{Me}_3\text{SnClO}_4$, $\text{Me}_3\text{SnBF}_4$, $\text{Me}_3\text{SnAsF}_6$, and the trialkyltin tetrachloroaluminates. Trimethyltin chloride and bromide are also believed to associate in the solid, through less strongly than the fluoride.

Interestingly, in the mixed-crystal complexes $\text{Me}_3\text{SnOH. Me}_3\text{SnXY}$ (XY = NN$^{186}$, CO$^{187}$), the pseudohalide groups bridge through a single nitrogen atom, the other end of the group forming a hydrogen bond to hydroxyl units in the next chain (Fig.1-9a).

Two-dimensional polymers are also known where the bridging group can link to more than two metal atoms. The dialkyltin oxides ($\text{R}_2\text{SnO})_n$, which are insoluble polymeric solids, in marked contrast to the corresponding oligomeric (containing 4-coordinate silicon) silicon compounds, have been shown by Mössbauer studies to contain 5-coordinate tin, and the structure in Figure 1-9b has been postulated.
Figure 1-8
Four-membered cyclostannoxane rings are also observed in the dimeric di- and tristannoxanes. These compounds have an unusual 'ladder' structure, for example tetramethyl-1,3-diisothiocyanatodistannoxane (Fig.1-10).

Apart from such complex materials, there are a great many monomeric 5-coordinate compounds of tin, for example the complex anions \( \text{SnCl}_5 \), \( \text{Me}_2\text{SnCl}_3 \) and \( \text{Me}_3\text{SnCl}_2 \), which have trigonal bipyramidal structures with the methyl groups in equatorial positions. One of the first conclusively proven examples of pentacoordination for tin was the pyridine adduct, \( \text{Me}_3\text{SnCl}.\text{py} \), which here represents the large number of 1:1 complexes of organotin halides with bases (Fig.1-11a).

Two further examples of pentacoordinate monomers will suffice. The recently synthesised stannoxanes, \( \text{RSn(OCH}_2\text{CH}_2)_3\text{N} \), have an unusual cage structure with an internal dative \( \text{N} \rightarrow \text{Sn} \) bond. (Figure 1-11b). The compound \( \text{di-} \mu\text{-acetato-bis-diphenyltin} \) contains a \( \text{Sn-Sn} \) bond, bridged by the two acetate groups (Fig.1-11c).
iii) Hexa-coordinate Tin (iv)

Six coordinate tin (iv) is approximately as common as the five-coordinate state, many examples being known. Association lattices such as that of dimethyltin difluoride, already referred to (Fig.1-8), frequently occur in the solid-state structures of compounds R₂SnX₂, where X is capable of bridging. Thus dimethyltin bis (fluorosulphate), Me₂Sn(FSO₃)₂, has a structure based on a distorted form of the Me₂SnF₂ structure, with fluorosulphate bridges, and the dialkyl- and aryltin carboxylates are presumably similar, steric factors allowing. A number of diorganotin dipseudohalides also adopt this configuration in the solid state, for example both dimethyltin dicyanide¹⁸⁸ (Fig.1-12(a)) and dimethyltin bis-dicyanamide¹⁰⁶ have structures based on a slightly distorted variant of the Me₂SnF₂ structure. Here, unlike the Me₃SnCN structure, the cyanide groups are not disordered. Again, the corresponding silicon and germanium cyanides¹⁸⁸ (Fig.1-12(b))

have a lower coordination number (five), and a structure visibly derived from a tetrahedron, reflecting the decrease in acceptor strength as the group is ascended.
The structure of dimethyltin diisocyanate has been found to be similar to that of Me₂SnCl₂, the isothiocyanate groups bridging through sulphur, Sn-N-C-S...Sn.

Monomeric complexes of the tin tetrahalides and organotin derivatives are very numerous, and hexacoordinate species have been known for some time, the structure of the octahedral hexachlorostannate anion having been first determined in 1933. Structures based on the octahedron are usual for 1:2 complexes of tin (iv) compounds with monodentate bases, or 1:1 complexes with bidentate ligands. This is, of course, on the assumption that such complexes are formed - a lower coordination number may be energetically more favourable, depending upon the substituents on the tin atom. Thus, while Me₃SnCl forms a stable 1:1 trigonal bipyramidal adduct with pyridine, attempts to prepare the 1:2 complex have failed. Also the requirement for a particular coordination number may result in the formation of an ionic compound, such as the terpyridyl complex of dimethyltin dichloride, (Me₂SnCl₂)₂.ter, which has been shown to have an ionic structure containing both 5- and 6-coordinate tin (Fig.1-13).

The question of cis-trans isomerism now arises. For the 1:2 adducts of the tin tetrahalides with monodentate bases, many examples of both geometries are known. The choice of configuration appears to depend upon a number of factors, although it has been suggested that ligands with small steric requirements close to the tin atom, i.e. those where the donor
atom attached to tin holds only a single group, tend to form cis-complexes (e.g. SnCl₄·2CH₃CN⁷⁴), whereas bulkier substituents, i.e. those in which the atom bonded to tin is itself attached to more than one other atom, prefer the trans-position (e.g. SnCl₄·2py⁷⁵). A semi-quantitative stereochemical model has been applied to octahedral tin complexes⁷⁶, and reaches similar conclusions, as does a separate study⁷⁰ which rationalises the commonly observed trans-configuration for the methyl-groups in Me₂Sn⁴⁺ octahedral derivatives. Examples are the 1:2 adduct of Me₂SnCl₂ with pyridine-N-oxide⁷¹ (Fig.1-14(a)) and the complex of 2,2'-bipyridyl with Ph₂SnCl₂⁷³ (Fig.1-14(b)). Octahedral complexes containing a cis-dimethyl arrangement are known, however, such as dimethyltin bis (8-hydroxyquinolate)⁷² (Fig.1-14(c)).

![Figure 1-14](image)

It has been suggested⁷² that, in the latter case, the constraint imposed on the oxygen and nitrogen atoms by the chelate ring structure permits the methyl groups to be far enough apart in the apparently preferred cis-form.

iv) Higher Coordination Numbers

A number of compounds involving tetravalent tin in a coordination number of seven are now known. All appear to have structures derived from a pentagonal bipyramid, with greater or lesser degrees of distortion. This structure has been proposed for the alkyltin tricarboxylates RSn(OOCR')₃¹⁰, and has been established crystallographically for methyltin trinitrate⁷⁸ and for tris (tropolonato) monochloro- and monohydroxytin (iv)⁷⁹, all of which
are compounds of the type $X\text{SnL}_3$ where $L$ is a chelating ligand of relatively small bite (Fig. 1-15(a)).

A pentagonal bipyramidal structure has also been reported for the isothiocyanate complex $\text{Me}_2\text{Sn}(\text{NCS})_2\cdot\text{terpyridyl}^{80}$ (Fig. 1-15(b)). The methyl groups occupy the axial positions, forming a trans-diorgano arrangement which is also seen in the 7-coordinate cation in tris (dimethylsulphonyl)nitrato(diphenyl)tin (iv) nitrate $^{81}$ (Figure 1-15(c)).

![Figure 1-15](image-url)

A distorted pentagonal bipyramidal structure has been found for the ethylenediaminetetraacetic acid complex $\text{Sn}^{IV}\text{EDTA.H}_2O^{83}$.

It appears that only two examples of genuinely 8-coordinate tin (iv) compounds are known at present, which as it happens illustrate two of the most common configurations for 8-coordination. Bis(phthalocyaninatetatin(iv)$^{42}$ has a structure based on a square anti-prism of nitrogen atoms, so that the two phthalocyanine rings form a sandwich with the tin atom in the centre. The ligands are distorted into saucer shapes, so that the nitrogen $sp^2$-hybrid orbitals can point towards the tin atom for more effective orbital overlap.

The tin (iv) nitrate molecule, $\text{Sn}(\text{NO}_3)_4$, has a structure based on a decahedron of oxygen atoms, the four nitrate groups being symmetrically bidentate to the central tin $^{84}$ (Fig. 1-16). The observation that the pairs of chelating oxygens are held closer together than the Van der Waals radii would usually permit has given rise to the suggestion $^{84}$ that the structure
should be considered as based on a tetrahedron, each coordination site
being occupied by two oxygen atoms. Obviously this viewpoint could be
applied to other complexes containing chelating ligands of small bite.

![Figure 1-16]

1.3 Compounds containing the Tin-Nitrogen Bond.

A. Historical Background

Until about fifteen years ago, the chemistry of the tin amines and
related compounds remained to a large extent unexplored. The early
synthesis of N-triethylstannylurea reported in 1860 has never been
repeated. In 1896 the compound N-tributylstannyl-N-phenylformamide was
prepared from the corresponding mercury (ii) derivative and bis(tributylstannyl)
sulphide. A mixture believed to contain tris (trimethylstannyl)amine
was obtained as a side-product from the reaction of trimethylstannylsodium
with iodobenzene in liquid ammonia in 1927, but the stannylamine was not
isolated. The reaction of tin tetrachloride with liquid ammonia, investigated
in 1932, yielded what appears to be the first aminotin compound, ClSn(NH₂)₃.
(This was confirmed and the system further investigated in 1958.) In 1936
a series of tin phthalocyanine derivatives was prepared.

In the early 1950's, reports began to appear of N-organotin-substituted
carbonamides (investigated as potential resin stabilisers) and
sulphonamides. In 1959, further liquid ammonia work yielded the compound
amino-dimethylstannylsodium, Me₂SnNH₂Na, but it was not until 1961, when
the synthesis of aminostannanes was achieved by the reaction of N-lithiumamides
with organotin halides, that systematic exploration of the area began.
Since then, knowledge of tin-nitrogen chemistry has increased dramatically, helped by the high reactivity of the new organotin amines, which makes them ideal starting materials for the synthesis of other tin-nitrogen compounds.

Tin derivatives are now known of hydrazine, triazenes, amides, ureas, guanidines, amidines, cyanamide, phthalocyanines and other tetrapyrroles, imidazoles, triazoles, tetrazoles, phosphorus-nitrogen and sulphur-nitrogen compounds, and more, so that examples of almost any kind of tin-nitrogen compound imaginable are now known.

In contrast to the extensive organonitrogen chemistry of tetravalent tin, similar derivaties of divalent tin are rare, and until quite recently were almost entirely unknown. Until 1969, when some carbamate derivaties of the type Sn(II)\(\text{II} (\text{NR.COO})_2\) were reported, there existed only the 1939 account of phthalocyaninatotin(ii)\(\text{II}^{108}\). Today, however, with the recent synthesis of the highly reactive bis(dialkylamino)tins\(\text{II}^{103,104,105}\), increasing interest is being shown in this area and it seems likely to be an expanding field for some time to come.

The following survey (which is intended more as a representative account of the chemistry involved than as a comprehensive compound index) is divided into sections on divalent and tetravalent tin derivatives; the latter section is further subdivided into compounds containing tin bonded to 3-covalent nitrogen (Sn-N\(<\)), i.e. amines, amides, and related materials, and those containing tin bonded to 2-covalent nitrogen (Sn-N\(=\)), i.e. ketimine derivatives, etc. It will be noted that the organotin pseudohalides (which all contain Sn-N bonds) should fall into the latter category, However, their chemistry differs sufficiently from that of the other tin-nitrogen derivatives that they may be considered a separate
class of compound, and therefore this is not discussed in any detail, although their structural properties, which are of direct relevance, are covered.

B. Organonitrogen Derivatives of Divalent Tin

Phthalocyaninatotin(ii) was first prepared in 1936\textsuperscript{108}, as previously mentioned, by the reaction of phthalonitrile with metallic tin. It is remarkably air-and moisture-stable, reacting with oxygen only on heating, although it is readily oxidised by halogen to the corresponding phthalocyaninato-dihalogenotin(iv)\textsuperscript{108,109}. The crystal structure was reported in 1970\textsuperscript{40}, disproving the earlier conjecture that the molecule was planar\textsuperscript{110}. As stated in Section 1.22, the structure is a tetragonal pyramid, the tin atom lying 1.11 Å above the plane of the four nitrogens. The phthalocyanine ring is significantly distorted towards an inverted saucer shape, presumably so that the nitrogen \(sp^2\) orbitals can interact better with the orbitals of tin.

Tin(ii) dialkoxides react readily with phenyl isocyanate by addition across the carbon-nitrogen double bond. The products have been assigned the tin-nitrogen bonded structures in Fig.1-17(a) and (b) by analogy with the similar tin (iv) reaction (Section 1.33i(a)), although the alternative tin-oxygen bonded forms (Fig.1.17(c)) have not been unequivocally disproven.

Two methods have been used to prepare dialkylaminotin(ii) compounds (Eqn's 1.1 and 1.2).

\[
\text{SnCl}_2 + 2\text{LiNR}_2' \rightarrow 2\text{LiCl} + (\text{R}'\text{R}"\text{N})_2\text{Sn} \quad 1.2
\]

\[
(\text{RC}_3\text{H}_4)_2\text{Sn} + \text{HNR}_2' \rightarrow 2 \text{RC}_3\text{H}_4 + (\text{R}'\text{R}"\text{N})_2\text{Sn} \quad 1.1
\]
The first method exploits the sensitivity of dicyclopentadienyltin (ii) (or its dimethyl derivative) to protic reagents. This may be contrasted with the tin (iv) systems, where the reverse reaction occurs. Compounds prepared in this way include N,N'-ethylenebis(acetylideneimino)tin(ii)\(^6\), the structure of which has already been described (Section 1.22), and the tin (ii) derivatives of imidazole, 1,2,4-triazole, and 3,4,5-trimethyl 1,2-diazole.\(^{11}\) These compounds are of particular interest, since the first two are insoluble in organic solvents (they are decomposed by water, like most compounds containing the Sn\(^{II}\) - N bond) and are stable indefinitely, unlike the diazole, which is soluble and polymerises at room temperature over a few hours. It is concluded that the first two are stabilised by bridging through the nitrogen atom in the 3-position of the ring (Fig.1-18), whereas the 1,2 diazole has adjacent nitrogens and cannot bridge. A similar effect is observed for the parallel triorganotin (iv) derivatives.

**Figure 1-17**

\[
\text{Sn(OR)}_2 + 2\text{PhNCO} \rightarrow \text{Sn(N-C-OR)}_2 \quad \text{(a)}
\]

\[
\begin{array}{c}
\text{Sn(OR)}_2 + 2\text{PhNCO} \\
\text{NPh} \\
\text{Sn(OR)}_2
\end{array}
\]

**Figure 1-18**
The second method of preparation has been used for all the bis-(dialkylamino)tin(ii) compounds yet prepared. The majority of these have contained very bulky alkyl groups to prevent association and possible polymerisation. The compounds $[{(\text{Me}_3\text{Si})_2\text{N}}]_2\text{Sn}^{\text{II}}$ and $[{(\text{BuMe}_3\text{Si})_2\text{N}}]_2\text{Sn}^{\text{II}}$ are stable, volatile, coloured (yellow or red), diamagnetic, soluble in hydrocarbons, and apparently monomeric in solution, although this has been disputed. Certainly the less sterically hindered bis(dimethylamino)tin(ii) is dimeric in solution, a bridged structure being postulated (Fig.1-19).

![Figure 1-19](image_url)

A number of compounds with tin(ii) in a heterocyclic ring have also been prepared (Fig.1-20a, b, c and d). No information seems to be available on the state of association of these materials, but they are sterically crowded and therefore probably monomeric. The THF complex (c) generates the parent heterocycle on removal of THF under vacuum, whereas (d) decomposes.

![Figure 1-20](image_url)
TABLE 1
Reactions of \((R_2N)_2Sn\)^{II}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protolysis:</td>
<td></td>
</tr>
<tr>
<td>(i) ((R_2N)_2Sn + HX \rightarrow 2R_2NH + SnX_2), (X = \text{OEt, OMe, Cl, C}_5\text{H}_5)</td>
<td>103, 104, 105</td>
</tr>
<tr>
<td>(ii) ([\text{Me}_2N]_2Sn_2 + 2(\text{HOCH}_2\text{H}_2)_2\text{NMe})</td>
<td>105</td>
</tr>
<tr>
<td>Metathesis:</td>
<td></td>
</tr>
<tr>
<td>(iii) ((R_2N)_2Sn + Sn^\text{II}Y_2 \rightarrow 2YSnNR_2), (Y = \text{C}_5\text{H}_5)</td>
<td>103, 104</td>
</tr>
<tr>
<td>(iv) ((R_2N)_2Sn + 2\text{LiCHR}_2 \rightarrow \text{Sn}^\text{II}(\text{CHR}^'_2) + 2\text{LiNR}^'_2)</td>
<td>103, 29</td>
</tr>
<tr>
<td>(v) (\text{Me}_2\text{SiSn}^\text{II} + \text{SnCl}_4 \rightarrow \text{Me}_2\text{SiSn}^\text{IVCl}_2 + \text{SnCl}_2)</td>
<td>112</td>
</tr>
<tr>
<td>Complex Formation:</td>
<td></td>
</tr>
<tr>
<td>(vi) ([\text{Me}_2N]_2Sn^\text{II}_2 + 2\text{py} \rightarrow 2(\text{Me}_2N)_2Sn^\text{II} \cdot \text{py})</td>
<td>105</td>
</tr>
<tr>
<td>Addition to Unsaturated species:</td>
<td></td>
</tr>
<tr>
<td>(vii) ((R_2N)_2Sn + 2\text{Ph-N=CO} \rightarrow [\text{Sn(NPh.CO.NR}^'_2)_2]_n)</td>
<td>103</td>
</tr>
<tr>
<td>Structure not confirmed.</td>
<td></td>
</tr>
<tr>
<td>Oxidation:</td>
<td></td>
</tr>
<tr>
<td>(viii) ((R_2N)_2Sn^\text{II} + \text{O}_2 \rightarrow [(R_2N)_2Sn^{IV\text{O}}]_n)</td>
<td>104</td>
</tr>
<tr>
<td>(ix) ((R_2N)_2Sn^\text{II} + \text{C}_5\text{H}_5(\text{CO})_2\text{FeMe} \rightarrow \text{C}_5\text{H}_5(\text{CO})_2\text{Fe-Sn}^{IV}(\text{NR}^'_2)_2\text{-Me})</td>
<td>103</td>
</tr>
<tr>
<td>(x) ((R_2N)_2Sn^\text{II} + R-X \rightarrow (R_2N)_2Sn^{IV\text{X.R}^''})</td>
<td>113</td>
</tr>
<tr>
<td>(R^'' = \text{Alkyl, Aryl})</td>
<td></td>
</tr>
<tr>
<td>(X = \text{Cl, Br, I})</td>
<td></td>
</tr>
</tbody>
</table>
The sterically crowded materials are generally low melting point solids or liquids, unlike the dimeric \([\text{(Me}_2\text{N})_2\text{Sn}]_2\) (M.Pt.92°C). All are extremely reactive and air- and moisture-sensitive. The reactions which have been investigated are summarised in Table 1.

The high reactivity of the \(\text{Sn}^{1\text{V}}\)-N bond has been attributed to weakness combined with high polarity.\(^2\) The same is probably true of the \(\text{Sn}^{1\text{I}}\)-N bond, although no thermodynamic data are yet available. Many of its reactions parallel those of tin (iv) e.g. protolysis (Table 1, (i) and (ii)), metathesis, (iii - v), and addition to unsaturated substrates, (vi). Complex formation with bases, in contrast, is little known for \(\text{Sn}^{1\text{V}}\)-N compounds; the trialkylstannylamines and tetrakis (dialkylamino) tins apparently undergo no reaction with pyridine.\(^{192}\)

The tin (ii) compounds also differ from the tin (iv) in readily undergoing oxidative processes. The insertion of the metal into polar bonds (Table 1, (ix) and (x)) parallels the similar reactions of carbenes\(^{114}\) although reaction (x) may be free radical.\(^{113}\) Conversely, however, rather than adding across double bonds to form a three-membered ring, as the carbenes do,\(^{114}\) the tin (ii) amines undergo insertion of the unsaturated species into the Sn-N bond without change in oxidation state.

Not shown in the Table is the reaction whereby irradiation of a hexane solution of \([\text{(Me}_3\text{Si})_2\text{N}]_2\text{Sn}^{1\text{I}}\) yields the tris(dialkylamino)tin\(^{1\text{I}}\) radical, \([\text{(Me}_3\text{Si})_2\text{N}]_3\text{Sn}^+\), which, owing to the bulky amino-groups, has an exceptionally long half-life (3 months in hexane at 20°C).\(^{115}\)

It might be expected that the tin (ii) lone-pair would show Lewis basicity in these compounds, but attempts to show this have failed.\(^{103}\) However, a helium (l) photoelectron spectroscopy investigation\(^{116}\) showed that, in the tin (ii) amides \((\text{Me}_3\text{Si},\text{RN})_2\text{Sn}^{1\text{I}}\) (R=Me\(_3\text{Si},\text{Bu})\), the \(s^2\) lone pair is more tightly bound than in the dialkyls, which do show basic behaviour. No evidence was discovered for \(\text{N}\equiv\text{Sn}^{1\text{I}}(p\equiv\text{d})\) \(\pi\)-bonding, although \(\text{N}\equiv\text{Si}\) bonding of this type was detected.
The area being so new, little systematic investigation of physical properties apart from melting points, boiling points, etc. has been undertaken. In the infra-red, $\nu_{as} (\text{Sn}^{II}_2\text{N}_2)$ has been identified for a number of compounds $^{104,105}$; it appears to lie in the range 360-440cm$^{-1}$ (cf. 690cm$^{-1}$ for $\nu_{as} (\text{Sn}^{IV}_2\text{N}_2)$Section 1.33 i c). $\nu_{as} (\text{Sn}^{II}_2\text{N}_2)$ has been suggested to lie about 10-22cm$^{-1}$ below $\nu_{as}$.

The oxidation state of most of the Sn$^{II}$-N compounds mentioned here has been confirmed by Mössbauer measurements; the Mössbauer isomer shift is dependent on the s-electron density about the tin nucleus, and hence on the oxidation state. Sn$^{II}$ compounds generally have a much higher electron density in the 5s orbital than Sn$^{IV}$ compounds, due to the lone pair, and therefore have a higher isomer shift. The isomer shifts for Sn$^{II}$ and Sn$^{IV}$ compounds fall into two groups, with the dividing line formed approximately by the value for $\alpha$-Sn (grey tin) (there is in fact a slight overlap of the two groups$^{41}$, for example the IS value for [(Me$_3$Si)$_2$CH]$_2$Sn$^{II}$ is very close to that of $\alpha$-Sn$^{128}$, but in general the isomer shift forms a good guide to oxidation state).
C. Organonitrogen Derivatives of Tetravalent Tin

1) Compounds containing Tin bonded to 3-covalent Nitrogen

This section covers N-stannyamines, amides and related compounds.

a) Preparative Aspects

The non-appearance of the stannyamines until 1961 is probably due to the fact that, unlike silicon and germanium, the tin(iv) halides do not undergo aminolysis because of the high stability of the initially formed complexes (Eqn. 1.3). It has, however, been found that at low temperatures the tin tetrahalides will react with liquid ammonia

$$\text{R}_2\text{NH} + \text{SnX}_4 \rightarrow \text{R}_2\text{NH}_2\text{SnX}_4 \rightarrow \text{R}_2\text{NSnX}_3 + \text{HX}$$  \hspace{1cm} (1.3)

$$\text{SnX}_4 + 2\text{NH}_3 \rightarrow \text{NH}_4\text{X} + [\text{X}_3\text{SnNH}_2] \rightarrow \text{XSn(NH}_2)_3$$  \hspace{1cm} (1.4)

$$X = \text{Cl, Br.}$$

and a range of preparations are now available based on the reaction of organotin halides or phenyls with liquid ammonia in the presence of alkali metal amides (Eqn. 1.5).

$$\text{R}_3\text{SnX} + \text{NH}_3 \rightarrow \text{[R}_3\text{SnNH}_2] + \text{HX}$$

$$\text{X} = \text{Hal, Ph.}$$

(disproportionates)  \hspace{1cm} (1.5)

$$(\text{R}_3\text{Sn})_2\text{NH} \text{ or } (\text{R}_3\text{Sn})_3\text{N}$$

$R = \text{Pr, iPr, Bu, neopentyl, cyclohexyl}; R'' = \text{Me, Et, nPr.}$$

The products depend upon the alkyl substituents on tin; if $R = \text{iBu}$, the primary stannyamine is stable to disproportionation. If starting materials such as tetraphenyltin or hexaphenylditin are used, complete substitution can be effected, giving rise to alkali metal salts of the hexaaminostannate anion $\text{Sn(NH}_2)_6^{2-}$. 
One of the most widely used methods for the preparation of aminotin compounds is transmetallation, usually by the reaction of a tin tetrahalide or organotin halide with a lithium dialkylamide (Eqn. 1.6). A wide range of organotin dialkylamides have been prepared in this fashion \(^9\),\(^8\),\(^9\),\(^12\),\(^6\),\(^13\),\(^0\),\(^13\),\(^11\),\(^3\),\(^0\). Lithium nitride, \(\text{Li}_3\text{N}\), has also been used in the preparation of tris (trialkylstannyl)amines \(^12\).

Sodium dialkylamides have been used, for example in the preparation of silylstannylamines \(^12\) (Eqn. 1.7) and the synthesis of \((\text{Me}_3\text{Sn})_3\text{N}\) from trimethyltin alkoxides \(^12\) (Eqn. 1.8), but in general the lithium reagents are superior.

\[
\text{R}_4\text{SnX}_n + n\text{LiNR}_n^+ \xrightarrow{\text{R}_4\text{SnX}_n + n\text{LiNR}_n^+} \text{nLiX} + \text{R}_4\text{Sn(NR}_n^+)^n_n
\]

\(\text{R} = \text{Me}, \text{Bu}\)

\[
(\text{Me}_3\text{Si})_2\text{NaN} + R_3\text{SnCl} \xrightarrow{\text{Me}_3\text{Si})_2\text{NaN} + R_3\text{SnCl}} \rightarrow (\text{Me}_3\text{Si})_2\text{NSnR}_3 + \text{NaCl}
\]

\(\text{R} = \text{Me}, \text{Bu}\)

\[
\text{Me}_3\text{SnOR} + \text{NaNH}_2 \xrightarrow{\text{Me}_3\text{SnOR} + \text{NaNH}_2} \rightarrow \text{NaOR} + [\text{Me}_3\text{SnNH}_2] \rightarrow (\text{Me}_3\text{Sn})_3\text{N} + \text{NH}_3
\]

Diethylaminomagnesium bromide has been used as an aminating agent \(^13\),\(^2\),\(^4\),\(^0\) as have dialkylaminotrimethylsilanes, although in the latter case the reaction proceeds via a complex which decomposes to the products on heating. In some cases this complex has proved stable to heat (presumably for steric reasons, thereby blocking the reaction \(^12\) (Eqn. 1.9).

\[
\text{Me}_3\text{SnBr} \xrightarrow{\text{Me}_3\text{SnHET}} \text{Me}_3\text{Si-NHet} \xrightarrow{\Delta} \text{MeSiBr} + \text{Me}_3\text{SnHET}
\]

\[
\text{Me}_3\text{SnHET} \xrightarrow{\Delta} \text{MeSiBr} + \text{Me}_3\text{SnHET}
\]

Transmetallations involving sodium sulphonamides \(^9\),\(^1\),\(^2\),\(^9\),\(^3\) (which are easily prepared by the reaction of the parent sulphonamide with sodium hydroxide) have been used to prepare N-organostannyl sulphonamides,
The sodium and potassium derivatives of pyrroles, imidazoles and triazoles have also been used in the synthesis of their trialkyl-tin derivatives.96,140

The reaction of the silver salt of 1,3-diphenyltriazene with phenyltin chlorides has been used to prepare some unusual triazen derivatives of tin134 (Eqn.1.10).

\[
\text{Ph}_n\text{SnCl}_{4-n} + m\text{AgN}_3\text{Ph}_2 \rightarrow m\text{AgCl} + \text{Ph}_n\text{SnCl}_{4-(m+n)}(\text{NPh-N}=\text{NPh})_m
\]

\[n=0,1,3; m = 1,2.\]

\[
\text{PhHgNS}_7 + \text{Me}_3\text{SnCl} \rightarrow \text{PhHgCl} + \text{Me}_3\text{SnNS}_7
\]

The early preparation of N-tributylstannyln-N-phenylformamide from a mercuric compound has already been mentioned (Section 1.3i). A mercury derivative has also been used in the preparation of an N-trimethylstannyl substituted sulphur-nitrogen ring289 (Eqn.1.11).

An advantage of the use of organolithium reagents is that, if protons remain on the nitrogen atom after the first lithiation, the product from the reaction with an organometal halide can be re-lithiated and reacted with a different halide. This process has been used to prepare a number of mixed silyl, germyl, and stannyl amines135,136,137,138,139 and bis-stannylamines138,139 (Eqn.1.12), as well as tin-nitrogen cyclic compounds138,139 (Eqn.1.13)

\[
\text{BuLi} \quad \text{R}_3\text{MNH}_2 \rightarrow \text{R}_3\text{MNHLi} \quad \text{R}_3\text{M}^{'\prime}\text{Cl} \rightarrow \text{R}_3\text{M}^{'\prime}\text{N}-\text{H}
\]

\[\text{M,M,M}^\prime = \text{Si},\text{Ge},\text{Sn}\]

\[
\begin{aligned}
\text{BuLi} & \rightarrow \text{R}_3\text{MNH}_2 \\
& \rightarrow \text{R}_3\text{MNH}^{'\prime}\text{Li} \\
& \rightarrow \text{R}_3\text{MNH}^{'\prime}\text{Cl} \\
& \rightarrow \text{R}_3\text{MNH}^{'\prime}\text{N-Li}
\end{aligned}
\]
Although it is not applicable to preparation of the very hydrolytically-sensitive stannylamines, the reaction between trialkyltin oxides, hydroxides, or alkoxides and the N-H bond, with elimination of water or alcohol, has been used in a number of cases where the N-H proton has acidic character or where the product is less sensitive to hydrolysis due to intermolecular association. Continuous removal of water by azeotropic distillation is often employed. This method has been used to prepare organotin derivatives of sulphonamides, carboxamides, ureas and isocyanurates, imidazoles and triazoles, and alkanolamines. Some amino-derivatives have even been prepared in this way, using alkyltin trialkoxides. Some examples are given in equations 1.14-17. Only derivatives of N,N'-diarylureas have been prepared in this fashion. The reaction with primary ureas (and biurets) goes further to yield isocyanates (Eqn.1.18).

\[
\text{Et}_3\text{SnOH} + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHSnEt}_3 \quad (93) \quad 1.14
\]

\[
\text{EtOH} + 3(\text{Bu}_3\text{Sn})_2\text{O} \underset{\text{reflux}}\rightarrow (\text{Bu}_3\text{SnNCO})_3 \quad (144) \quad 1.15
\]
Another example of the exchange process is transamination. The general process for secondary amines is indicated in Eqn. 1.19.

This reaction appears to be volatility controlled and the displacement series \( \text{Bu}_2\text{N} \rightarrow \text{Et}_2\text{N} \rightarrow \text{Me}_2\text{N} \) has been demonstrated. This method has been used as a route to organotin derivatives of hydrazines, amides, silylaminostannanes, aziridines, sulphamides, and to tin-nitrogen heterocycles.

Examples are given in equations 1.20 - 23.
Interestingly, the attempted preparation of the ethylenediamine derivative in equation 1.24 gave a polymeric product. In contrast the corresponding silicon and germanium compounds exist as monomers, stable when pure, although the germanium compound polymerises reversibly in the presence of impurities. The same polymer product was obtained in a preparation via the lithioamine.

Aminostannanes derived from secondary amines also undergo transamination with primary amines, and therefore it must be assumed that here there is steric control of the reaction (Eqns. 1.25-1.27). In each case the only products obtained were those indicated, even in the presence of excess primary amine. It has been inferred that condensation to form the more highly substituted amine must occur very quickly, when steric factors allow it.

\[
\begin{align*}
\text{Me}_3\text{SnNR}_2' + \text{R''NH}_2 & \rightarrow \text{Me}_3\text{SnNR''} + \text{R_2NH} \\
\text{Me}_3\text{SnNR}_2' + \text{R''NH}_2 & \rightarrow (\text{Me}_3\text{Sn})_2\text{NR''} + 2\text{R_2NH} \\
3\text{Me}_3\text{SnMe}_2 + \text{NH}_3 & \rightarrow (\text{Me}_3\text{Sn})_3\text{N} + 3\text{Me}_2\text{NH}
\end{align*}
\]
The reaction of distannazanes with primary amines has been used to obtain cyclostannazanes\textsuperscript{130,131} (Eqn.1.28), and the condensation reaction has been utilised to provide a synthesis of a 4-membered \( \text{Sn}_2\text{N}_2 \) ring\textsuperscript{158} (Eqn.1.29)

\[
3(\text{Me}_2\text{N})_2\text{SnMe}_2 + 3\text{EtNH}_2 \rightarrow 6\text{Me}_2\text{NH} + \text{EtN} \quad \text{(Eqn.1.28)}
\]

\[
t_{\text{Bu}_2}\text{Sn(NMe)}_2 + 2\text{RNH}_2 \rightarrow t_{\text{Bu}_2}\text{Sn(NHR)}_2 + 2\text{Me}_2\text{NH}
\]

\[
R = \text{Me}, \text{C}_6\text{H}_5\text{CH}_2
\]

\[
R_3\text{Sn} - X + R' - \text{N=Y} \rightarrow R_3\text{Sn}-\text{N-Y-X}
\]

The majority of other preparations involve the addition of an \( \text{Sn-X} \) bond across an unsaturated bond to nitrogen. (Eqn.1.30).

Numerous reactions of this type have been reported, and they are summarised in Table 2. In most cases the \( \text{Sn-N} \) bonded product is capable of further reaction with an excess of unsaturated reactant, to form a wide range of materials\textsuperscript{168,171,173}.

It is of interest that, while the reaction of organotin hydrides with isocyanates yields an \( \text{Sn-N} \) bonded material, isothiocyanates yield compounds containing an \( \text{Sn-S} \) bond\textsuperscript{160,161} (Eqn.1.31)

\[
R_3\text{SnH} + R'\text{NCS} \rightarrow R' - \text{N=CH-S-SnR}_3
\]

However, the stannylamines react with both isocyanates and isothiocyanates to produce \( \text{Sn-N} \) bonded products. This presumably reflects the stabilising effect of the thiourea structure on the \( \text{C=S} \) bond.
### TABLE 2

**Preparation of the Sn-N bond by reaction of organotin compounds with unsaturated species.**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) ( \text{R}_3\text{Sn-H} + \text{R}'-\text{N}=\text{C}=\text{O} )</td>
<td>( \text{R}_3\text{Sn-NR'}-\text{CH}=\text{O} )</td>
<td>160,161</td>
</tr>
<tr>
<td>(ii) ( \text{R}_3\text{Sn-X} + \text{Ph-N=N=N} )</td>
<td>( \text{R}_3\text{SnNXPh} + \text{N}_2 )</td>
<td>162</td>
</tr>
<tr>
<td>( \text{X} = \text{H, Li} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iii) ( \text{Ph}_3\text{Sn-H} + \text{Ph-N=N-Ph} )</td>
<td>( \text{Ph}_3\text{SnNNHNPh}_3 )</td>
<td>163</td>
</tr>
<tr>
<td>(iv) ( \text{R}_3\text{Sn-H} + \text{R}'-\text{CH}=\text{N}-\text{R''} )</td>
<td>( \text{R}'-\text{CH}_2-\text{NR''}-\text{Sn}_3 )</td>
<td>164,165,166</td>
</tr>
<tr>
<td>(v) ( \text{Bu}_3\text{SnBu}_3 + \text{m-ClC}_6\text{H}_4\text{N}=\text{C}=\text{O} )</td>
<td>( \text{m-ClC}_6\text{H}_4-\text{N-CO-SnBu}_3 )</td>
<td>167</td>
</tr>
<tr>
<td>(vi) ( \text{R}_3\text{SnOR'} + \text{R''N}=\text{C}=\text{O} )</td>
<td>( \text{R}_3\text{Sn}-\text{N-C-OR'} )</td>
<td>168-174,253,303</td>
</tr>
<tr>
<td>( \text{R'} = \text{Alkyl, R}_3\text{Sn} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(vii) ( \text{Bu}_3\text{SnOSO}_2\text{R} + \text{R'}\text{N}=\text{C}=\text{O} )</td>
<td>( \text{Bu}_3\text{SnNR'}-\text{C-OR} + \text{SO}_2 )</td>
<td>175</td>
</tr>
<tr>
<td>(viii) ( \text{R}_3\text{SnON}=\text{CR'}R'' + \text{Ph-N}=\text{C}=\text{X} )</td>
<td>( \text{R}_3\text{SnN-C-O-N}=\text{CR'}R'' )</td>
<td>327</td>
</tr>
<tr>
<td>( \text{X} = \text{O, S} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ix) ( \text{(R}_3\text{Sn})_2 + \text{Ar-N}=\text{S}=\text{N}=\text{Ar} )</td>
<td>( \text{R}_3\text{Sn-N-S}-\text{N-SnR}_3 )</td>
<td>175</td>
</tr>
<tr>
<td>(x) ( \text{R}_3\text{SnOR'} + \text{Np-N}=\text{C}=\text{N-Np} )</td>
<td>( \text{R}_3\text{Sn-N-C-OR'} )</td>
<td>253,303</td>
</tr>
<tr>
<td>( \text{R'} = \text{Alkyl}, \text{SnR}_3, \text{Np} = 1\text{-naphthyl} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(xi) ( \text{R}_3\text{SnNR'}_2 + \text{R''N}=\text{C}=\text{X} )</td>
<td>( \text{R}_3\text{Sn-N-C-NR'} )</td>
<td>130,176,177</td>
</tr>
<tr>
<td>( \text{X} = \text{O, S} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(xii) ( \text{Me}_3\text{SnNR'}_2 + \text{R'}\text{N}=\text{C}=\text{N-R'} )</td>
<td>( \text{Me}_3\text{Sn-N-C-NR''} )</td>
<td>176,177,178</td>
</tr>
<tr>
<td>(xiii) ( \text{R}_3\text{SnNMe}_2 + \text{PhN}=\text{S}=\text{O} )</td>
<td>( \text{R}_3\text{Sn-N-S-NMe}_2 )</td>
<td>177,234</td>
</tr>
<tr>
<td>(xiv) ( \text{Me}_3\text{SnX} + \text{p-tos-N}=\text{S}=\text{N-p-tos} )</td>
<td>( \text{Me}_3\text{Sn-N-S-X} )</td>
<td>234,254</td>
</tr>
<tr>
<td>( \text{X} = \text{Me, NMe}_2, \text{OMe} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTES to Table 2:**

a) Addition followed by rearrangement with elimination.

b) Reaction has been observed to go further if isocyanate is in excess, to form compounds of the type \( \text{R}_3\text{Sn-C-N-C-OR''} \), which may eliminate \( \text{CO}_2 \) to give a urea derivative.

c) Catalysts, e.g. \( \text{ZnCl}_2 \), suppress side reactions when \( \text{R'}, \text{R''} \) contain unsaturated groups.

d) When \( \text{R} = \text{tBu} \), addition occurs across the \( \text{S}=\text{O} \) bond, followed by rearrangement:

\[
2\text{tBu-N}=\text{S}-\text{OSnMe}_3 \rightarrow \text{Me}_3\text{SnO-S-NMe}_2 + \text{tBu-N}=\text{S}=\text{N}-\text{tBu}
\]
The reaction of alkyl and aryl halides with bis(dialkylamino)tin(ii) compounds to produce dialkylaminotin(iv) derivatives has already been mentioned (Section 1.32).

Organotin derivatives of nitrogen-containing heterocycles have been prepared by the reaction of trialkyltin azides and bis(trialkylstannyl) diazomethanes with unsaturated species (Eqns. 1.32-35).

\[
\text{PhNCS} + \text{Bu}_3\text{SnN}_3 \rightarrow \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S}
\end{array}
\begin{array}{c}
\text{N} \\
\text{SnBu}_3
\end{array} \tag{179} \label{eqn:1.32}
\]

\[
\text{R-} = \text{N} + \text{R}^1\text{SnN}_3 \rightarrow \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S}
\end{array}
\begin{array}{c}
\text{N} \\
\text{SnR}^1
\end{array} \tag{180} \label{eqn:1.33}
\]

\[
\text{Ph-NCS} + \begin{array}{c}
\text{C} \\
= \text{N}=\text{N}
\end{array} \rightarrow \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S}
\end{array}
\begin{array}{c}
\text{Me}_3\text{Sn} \\
\text{N-SnMe}_3
\end{array} \tag{181} \label{eqn:1.34}
\]

\[
\text{MeOOC-C=COOMe} + \begin{array}{c}
\text{C} \\
= \text{N}=\text{N}
\end{array} \rightarrow \begin{array}{c}
\text{Me}_3\text{Sn} \\
\text{N} \\
\text{SnMe}_3
\end{array} \tag{181} \label{eqn:1.35}
\]

Unlike the corresponding silicon and germanium systems, the reaction of organotin azides with Group IVB hydrides (or organotin hydrides with Group IVB azides) does not produce Sn-N bonded species.182

Organotin derivatives of uracil183 and succinimide184 have been prepared by reactions between the N-chloro imides and tetraalkyltins or alkyltin chlorides (Eqns. 1.36, 37). The reaction between N-chlorosuccinimide and hexaalkylditins appears to be a free-radical process.184

\[
\text{R}_3\text{SnSnR}_3 + \begin{array}{c}
\text{N} \\
\text{Cl}
\end{array} \rightarrow \text{R}_3\text{SnCl} + \begin{array}{c}
\text{N} \\
\text{SnR}_3
\end{array} \tag{184} \label{eqn:1.36}
\]

Phthalocyaninato-derivatives of tin(iv) have been prepared by
transmetallation using the sodium salt of the ligand, and also by direct
reaction of the ligand with tin tetrachloride. However, the usual
method, like most metallophthalocyanine preparations, is by reaction
of the central unit of the product (in this case SnCl₂) with phthalonitriles
(Eqn. 1.38)

\[
\text{SnCl}_2 + 4 \text{PhClCN} \rightarrow \text{Ph}_4\text{SnCN}_4  \quad 1.38
\]

b) Reactions

In general, unless stabilised by other groups in the molecule,
compounds containing the Sn-N bond are hydrolytically unstable,
decomposing to the organotin oxide or hydroxide on exposure to water.
This forms one example of a large class of protolysis reactions, the
general form of which is given in Equation 1.39. This reaction is of
considerable use in organometallic synthesis, and was one of the first

\[
R_3\text{SnNR'}_2 + HA \rightarrow R_3\text{SnA} + HNR'_2'  \quad 1.39
\]

\[
\text{Me}_3\text{SnNET}_2 + \text{MeOH} \xrightarrow{-50^\circ \text{C}} \text{Me}_3\text{SnOMe} + \text{HNMe}_2  \quad 1.40
\]
reactions of stannylamines to be extensively investigated. In a number of instances it provides easy access to compounds which are difficult to obtain by other routes; for example trimethyltin methoxide (Eqn. 1.40). Representative examples are shown in Table 3. (Transaminations, which have already been discussed, are not included). It will be observed that the range of the reaction extends to hydrocarbons with acidic protons. In general the reactions are clean and proceed under mild conditions.

Similar reactions not shown in the table are those with nitroalkanes and \( \alpha \)-hydrogen-containing nitriles.

Stannylamines react with benzonitrile by addition across the \( \text{C}=\text{N} \) bond (see Table 5). However, nitriles possessing an \( \alpha \)-hydrogen react as protic species with elimination of amine (Eqn. 1.41), the nitrile group being insufficiently polar (in the absence of electron-withdrawing groups) for the competing addition reaction to occur to any great extent. A clean reaction is not obtained, apparently due to redistribution of the nitrile-containing products.

\[
R_3\text{SnNR'}_2 + R''R'''\text{CHCN} \rightarrow R_3\text{SnCR''R'''CN} + \text{HNR'}_2 \\
\text{Redistribution}
\]

Mixture of products

A similar observation is made for the reaction with nitromethane, although a clean reaction is obtained if the isopropyl compound, \( \text{Me}_2\text{CHNO}_2 \), is used.

The reaction with acetone has been claimed to proceed via abstraction of \( \alpha \)-hydrogen, but in the light of later work this process is seen to more properly belong to the class of additions to unsaturated species, and will be discussed with these.
### TABLE 3
Protolysis Reactions of Stannylamines

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products *</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) ( R_3\text{SnNR}_2 ) + HCl</td>
<td>( R_3\text{SnCl} + R_2'\text{NH}_2\text{Cl}^- )</td>
<td>132, 176, 192</td>
</tr>
<tr>
<td>(ii) ( R_3\text{SnNR}_2 ) + ('H_2\text{CO}_3' ) ((\text{H}_2\text{O} + \text{CO}_2))</td>
<td>((R_3\text{Sn})_2\text{CO}_3)</td>
<td>120, 132, 192</td>
</tr>
<tr>
<td>(iii) ( R_{4-n}\text{Sn(NR')_2} + R'\text{OH} ) ( n = 1-4 )</td>
<td>( R_{4-n}\text{Sn(OR'')}_n )</td>
<td>99, 192, 193, 194, 195</td>
</tr>
<tr>
<td>(iv) ( R_3\text{SnMe}_2 + \text{Ph}_2\text{MH} )</td>
<td>( R_3\text{SnPh}_2 )</td>
<td>176, 192</td>
</tr>
<tr>
<td>( R = \text{Me, Et}; \text{M} = \text{P, As} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v) ( R_{4-n}\text{Sn(NEt'2)_n} + \text{HCN} ) ( n = 1, 2; \text{R} = \text{Me, Et, Bu, Ph} )</td>
<td>( R_{4-n}\text{Sn(CN)}_n )</td>
<td>196</td>
</tr>
<tr>
<td>(vi) ( R_{4-n}\text{Sn(NR')_2} + \text{HN}_3 ) ( n = 1-4 )</td>
<td>( R_{4-n}\text{Sn(N)}_3'_n )</td>
<td>197</td>
</tr>
<tr>
<td>(vii) ( R_3\text{SnNR'}_2 + \text{H-C}=:\text{CR''} )</td>
<td>( R_3\text{Sn-}\text{C}=\text{C-R''} )</td>
<td>176, 192, 198, 199</td>
</tr>
<tr>
<td>( R'' = \text{Pr, Bu, Ph, C}_6\text{F}_5, -(\text{CH}_2)_2\text{CHMe}_2, -\text{CMe} = \text{CH}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(viii) ( R_3\text{SnNR'}_2 + \text{C}_6\text{H}'_5 )</td>
<td>( R_3\text{SnC}_6\text{H}_5 )</td>
<td>176, 192</td>
</tr>
<tr>
<td>(ix) ( R_3\text{SnMe}<em>2 + \text{C}</em>{6}'\text{F}_5 )</td>
<td>( R_3\text{SnC}_6\text{F}_5 )</td>
<td>199</td>
</tr>
<tr>
<td>(x) ( R_3\text{SnNR'}_2 + R'\text{CHN}_2 )</td>
<td>( R_3\text{SnR'}\text{CN}_2 )</td>
<td>200, 201</td>
</tr>
<tr>
<td>( R'' = \text{H, COOEt, COR''} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(xi) ( R_3\text{SnNET}_2 + \text{HCX}_3 )</td>
<td>( R_3\text{SnCX}_3 )</td>
<td>202</td>
</tr>
<tr>
<td>( X = \text{Cl, Br} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(xii) ( \text{Bu}_3\text{SnNR'}_2 + R'\text{CHC-NR''} )</td>
<td>( \text{Bu}_3\text{SnCR'}\text{CNR''} )</td>
<td>152</td>
</tr>
<tr>
<td>( R'' \neq \text{H} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(xiii) ( \text{Bu}_3\text{SnNET}_2 + \text{CH}_3\text{O.SO.Ph} )</td>
<td>( \text{Bu}_3\text{SnCH}_2\text{O.SO.Ph} )</td>
<td>203</td>
</tr>
</tbody>
</table>

* Amine may be assumed, unless otherwise indicated.

**NOTES:**

a) If \( R'' = \text{H} \), disubstitution will occur, forming \( R_3\text{Sn-C}=\text{C-SnR}_3 \)

b) If \( R''=\text{H} \), disubstitution will occur, forming \((R_3\text{Sn})_2\text{CN}_2\)

c) If \( R''=\text{H} \), transamination will occur, forming \( \text{Bu}_3\text{SnNR''CCR''} \)
A reaction related to protolysis is that with metal hydrides. The general reaction is given in Equation 1.42.

\[ \text{Sn-N} + \text{H-ML}_n \rightarrow \text{Sn-ML}_n + \text{H-N} \]  \hspace{1cm} 1.42

Tin-tin bonds have been prepared by the reaction of organotin hydrides with organotin-substituted amines, \(^{205-210}\) hydrazines, \(^{163}\) and amides. \(^{163,211,212}\) By the use of di- and tri-hydrides and amines, linear and branched polystannanes have been prepared \(^{210,211,212}\) (Equations 1.43, 44). The method is particularly useful for the production of unsymmetrically substituted compounds. Cyclostannanes have also been prepared by this route \(^{207}\) (Eqn. 1.45).

\[ R_3\text{SnNPhCHO} + R_2'SnH_2 \rightarrow R_3\text{Sn-SnR}_2'H + \text{HNPhCHO} \]  \hspace{1cm} (211) 1.43

\[ 3 R_3\text{SnNPhCHO} + \text{PhSnH}_3 \rightarrow (R_3\text{Sn})_3\text{SnPh} + 3\text{HNPhCHO} \]  \hspace{1cm} (212) 1.44

\[ nR_2\text{SnH}_2 + nR_2\text{Sn(NEt}_2)_2 \rightarrow 2n\text{HNEt}_2 + \left[ \text{SnR}_2 \right]_{2n} \]  \hspace{1cm} (207) 1.45

\(2n = 4, 6, 8\) depending upon \(R\) and reaction conditions.

Rate studies on the reaction of trialkyltin hydrides with trialkyltin amines and amides suggest that the mechanism consists of electrophilic attack by hydrogen on nitrogen \(^{213}\) (unlike most tin hydride additions, which appear to have free-radical mechanisms \(^{214}\)). This evidently reflects the polarity of the Sn-N bond. Similar reactions have
been used to prepare bonds between tin and germanium\textsuperscript{215,216,217} (not silicon – silicon hydrides do not react), platinum,\textsuperscript{218} and tungsten.\textsuperscript{218}

In contrast, dialkyldiaminotins react with aluminium and boron hydrides by a metathetical process forming tin hydrides and amino-alanes or boranes.\textsuperscript{219} (Eqn. 1.46, 47). This is presumably the result of the greater acceptor properties of boron and aluminium in these compounds, favouring an intermediate of the type shown in Figure 1-21(a), rather than

\[
R_{4-n}\text{Sn}(\text{NEt}_2)_n + n\text{Bu}_2\text{AlH} \rightarrow R_{4-n}\text{SnH}_n + n\text{Bu}_2\text{AlNET}_2 \quad 1.46
\]

\[
2R_{4-n}\text{Sn}(\text{NEt}_2)_n + n(\text{BH}_3)_2 \rightarrow 2R_{4-n}\text{SnH}_n + 2n\text{H}_2\text{BNET}_2 \quad 1.47
\]

the transition state obtained by abstraction of a proton by nitrogen (Fig. 1-21(b)).

![Diagram](a)

![Diagram](b)

\textbf{Figure 1-21}

The basicity of the nitrogen in stannylamines is shown by the formation of stable complexes such as \(\text{Sn}(\text{NEt}_2)_4\cdot\text{VOCl}_3\)\textsuperscript{220} (see also Section (c)). The tin does not appear to be particularly acidic, however. Although a number of Sn–N compounds contain 5-coordinate tin by association with donor atoms elsewhere in the molecule, no complexes of the simple stannylamines are known. Diethylamino-trimethyl stannane and tetrakis(diethylamino)tin show no reaction with pyridine, for example.\textsuperscript{192}
The generalised metathetical reaction in Equation 1.48 is known for a large number of systems. Representative examples are given in Table 4.

\[ R_3\text{Sn-N} + X-Y \longrightarrow R_3\text{Sn-X} + Y-N \quad 1.48 \]

The reactions commonly proceed smoothly and cleanly under mild conditions, although violent reaction is met with in some cases, particularly where the product is trimethyltin fluoride. The ease of reaction has been ascribed to the high donor strength of the stannylamines, the weak and polar Sn-N bond, and the high heats of formation of many of the organotin products, especially the above-mentioned fluoride. It may be noted that the phthalocyanine structure stabilises the Sn-N bond to such an extent that, for the dihalogenotin(iv) phthalocyanines, halogen exchange occurs rather than Sn-N bond cleavage.

The reaction with anhydrides and esters (Table 4 x & xi) although apparently straight-forward metathesis, on closer examination appears to be an addition across a 1,2-dipole, followed by rearrangement (e.g. Eqn. 1.49).

\[ R_3\text{SnNMe}_2 + (R'\text{CO})_2\text{O} \longrightarrow R_3\text{Sn-O-CNMe}_2 \longrightarrow R_3\text{SnOCOR'} + R'\text{CONMe}_2 \quad 1.49 \]

For the ester rearrangement, two pathways are possible (Eqn. 1.50).

\[ R_3\text{SnNMe}_2 + R'\text{COR}'' \longrightarrow R_3\text{Sn} \quad \text{a} \quad R'' \quad \text{b} \]
### TABLE 4

**Metathetical Reactions of Stannylamines**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $\text{Me}_3\text{SnNMe}_2 + \text{CF}_6$</td>
<td>$\text{Me}_3\text{SnF} + \text{CF}_5\text{NMe}_2$</td>
<td>221,222</td>
</tr>
<tr>
<td>(ii) $\text{Me}_3\text{SnNMe}_2 + \text{CF}_2 = \text{CFCl}$</td>
<td>$\text{Me}_3\text{SnF} + \text{CFCl} = \text{CFNMe}_2$</td>
<td>221,222</td>
</tr>
<tr>
<td>(iii) $\text{Me}_3\text{SnNMe}_2 + \text{HN(CF}_3)_2$</td>
<td>$\text{Me}_3\text{SnF} + \text{CF}_3\text{NHCF}_2\text{NMe}_2$</td>
<td>221,222</td>
</tr>
<tr>
<td>(iv) $\text{Bu}_3\text{SnNEt}_2 + \text{RX}$</td>
<td>$\text{Bu}_3\text{SnX} + \text{RNMe}_2^*$</td>
<td>313</td>
</tr>
</tbody>
</table>

$R = \text{PhCH}_2, \ X = \text{Cl}, \text{Br}; \ R = \text{CH}_2=\text{CHCH}_2, \ X = \text{Cl}, \text{Br}, \text{I}$

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v) $\text{Me}_3\text{SnN}^\downarrow + X-B^\downarrow$</td>
<td>$\text{Me}_3\text{SnX} + \text{N-B}^\uparrow$</td>
<td>221,222</td>
</tr>
</tbody>
</table>

$X = \text{F}, \text{nBu}, \text{Ph}, \text{OMe}$

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(vi) $2\text{Me}_3\text{SnNMe}_2 + (\text{AlEt}_3)_2$</td>
<td>$2\text{Me}_3\text{SnEt} + (\text{Et}_2\text{AlNMe}_2)_2$</td>
<td>221,222</td>
</tr>
<tr>
<td>(vii) $\text{Me}_3\text{Sn-N}^\downarrow + \text{F-M}$</td>
<td>$\text{Me}_3\text{SnF} + \text{N-M}$</td>
<td>221,222</td>
</tr>
</tbody>
</table>

$M = \text{As}, \text{Sb}$

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(viii) $\text{Me}_3\text{Sn-N}^\downarrow + \text{Cl-Si}^\downarrow$</td>
<td>$\text{Me}_3\text{SnCl} + \text{N-Si}^\uparrow$</td>
<td>221,222,226,227</td>
</tr>
<tr>
<td>(ix) $\text{Et}_3\text{SnNMe}_2 + \text{Cl}_2$</td>
<td>$\text{Et}_3\text{SnCl} + \text{ClNMe}_2$</td>
<td>221,222</td>
</tr>
<tr>
<td>(x) $\text{R}_3\text{SnN}^\downarrow + (\text{R'}\text{CO})_2\text{O}$</td>
<td>$\text{R}_3\text{SnOCOR}^\prime + \text{NCOR}^\prime$</td>
<td>221,222,229,230</td>
</tr>
<tr>
<td>(xi) $\text{R}_3\text{SnNMe}_2 + \text{R'}\text{COOR}''$</td>
<td>$\text{R}_3\text{SnOR}'' + \text{R'CONMe}_2$</td>
<td>221,222,229</td>
</tr>
</tbody>
</table>

* : For the n-butyl halides ($R = \text{nBu}, \ X = \text{Cl}, \text{Br}, \text{I}$), a mixture of products is obtained owing to redistribution of the amine alkyl groups:

$$\text{Bu}_3\text{SnNEt}_2 + \text{BuX} \rightarrow \text{Bu}_3\text{SnX} + \text{BuNEt}_2, \text{Bu}_2\text{NEt}, \text{Bu}_3\text{N}, \text{Et}_3\text{N}$$
Bond breaking at (a) (acyl-oxygen fission) leads to the reaction usually observed (1.50a). Bond-breaking at (b) (alkyl-oxygen fission), however, would give the trialkylstannyl carboxylate and an amine (1.50b), and observation of these products where \( R'' = CH_{2}CH- \) has been taken to confirm the addition and rearrangement mechanism. Interestingly, when \( R'' = CH_{2}CMe- \), route (a) has been claimed to be followed,\(^{229}\) although other workers report yet another process\(^{232}\) (Eqn. 1.51)

\[
\text{Et}_{3}\text{SnNMMe}_{2} + \text{CH}_{2}C-CO\text{OMe} \rightarrow \text{Et}_{3}\text{SnCH}_{2}\text{CMe} + \text{MeCNMe}_{2}\text{Me}^{0}\text{0} \quad 1.51
\]

Attempted reaction of trimethyltin dimethylamide with chlorides containing hydrogen may lead to dehydrochlorination and formation of the complex \( \text{Me}_{3}\text{SnCl.HNMe}_{2} \), rather than a simple metathetical exchange. This has been exploited as a useful synthetic process in both organometallic and organic chemistry.\(^{209,231}\) Two examples are given in Equations 1.52 and 53.

\[
\text{Cl}_{2}\text{HlIr}^{III} (\text{PPh}_{3})_{3} + \text{Me}_{3}\text{SnNMMe}_{2} \rightarrow \text{ClIr}^{I} (\text{PPh}_{3})_{3} + \text{Me}_{3}\text{SnCl.HNMe}_{2}\quad 1.52
\]

\[
\text{BuCl}^{n} \text{Me}_{3}\text{SnMe}_{2} \rightarrow \text{cis-MeCH=CHMe} + \text{trans-MeCH=CHMe} + \text{EtCH=CH}_{2}\quad 1.53
\]

The production of new tin-nitrogen compounds by the reaction of organotin amines and amides with unsaturated nitrogen-containing compounds was discussed in the preceding section. This forms one aspect of

\[
\text{Sn-N} \quad + \quad \text{S-} \quad \text{S+} \quad \rightarrow \quad \text{Sn-A-B-N}\quad 1.54
\]

the general reaction with unsaturated 1,2-dipoles (Eqn. 1.54), which in turn forms part of a much larger area of insertion processes of unsaturated groups into bonds M-X, where M is a metal or metalloid.
Many examples are known for both the transition elements and the main groups, and X can be H, Hal, O, S, N, P, C, M, and M'. Further examples for the Sn–N bond are listed in Table 5.

Carbon–carbon unsaturated linkages do not normally react, unless activated by electron-withdrawing substituents (Table 5, (vii)-(xi)). The mechanism in all cases seems to be nucleophilic attack by nitrogen at the most electropositive site. The methyl acrylate reaction (Table 5, (xi)) may be compared with the more usual ester reaction already referred to (Table 4, (xi)). In contrast, methyl methacrylate follows the normal route, yielding the amide and a methoxide.

The bis-, tris-, and tetrakis-dialkylaminotins generally react in a similar manner to the mono-amino derivatives, although steric factors may prevent reaction of all the Sn–N bonds in the more highly substituted compounds. The bis- and tris-stannylamines also react similarly, except in the case of reaction with the C= S double bond, in which insertion does occur, but it is followed by rearrangement with elimination of bis(trialkylstannyl)sulphide (Eqn. 1.55).

\[
\text{Me}_3\text{Sn-N-SnMe}_3 + \text{C=S} \rightarrow \text{Me}_3\text{Sn-SnMe}_3 \rightarrow (\text{Me}_3\text{Sn})_2\text{S} + \text{C=NR} \quad 1.55
\]

Amine groups attached to the thiocarbonyl moiety lower the reactivity; thus while thiobenzophenone, \( \text{Ph}_2\text{C=S} \), reacts at room temperature, \( \text{N,N'-dimethyl thiobenzamide, PhCS.NMe}_2 \), requires forcing conditions and \( \text{N,N,N',N'-tetramethylthiourea, (NMe}_2\text{)}_2\text{C=S} \), does not react at all. This reaction was also investigated for \( \text{OCS, CS}_2 \) and \( \text{PhNCS} \), which reacted as in Equation 1.55. The corresponding C=O derivatives gave only the
### TABLE 5

Reactions of the Sn-N bond with unsaturated systems

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) (\text{Me}_3\text{SnNMe}_2 + CX_2) (X = O, S)</td>
<td>(\text{Me}_3\text{Sn}-X-C-N\text{Me}_2)</td>
<td>130,177</td>
</tr>
<tr>
<td>(ii) (\text{Me}_3\text{SnNMe}_2 + \text{O}=\text{C}=\text{S})</td>
<td>(\text{Me}_3\text{Sn-S-CO-NMe}_2)</td>
<td>235</td>
</tr>
<tr>
<td>(iii) (\text{Me}_3\text{SnNMe}_2 + \text{CH}_2=\text{C}=\text{O})</td>
<td>(\text{Me}_3\text{SnCH}_2-CO-N\text{Me}_2)</td>
<td>177,232</td>
</tr>
<tr>
<td>(iv) (\text{Me}_3\text{SnNMe}_2 + \text{Ph-}C\equiv\text{N})</td>
<td>(\text{Me}_3\text{Sn-N=CPh-NMe}_2) *</td>
<td>176,177</td>
</tr>
<tr>
<td>(v) (\text{Me}_3\text{SnNMe}_2 + \text{Ph-}C-N-C=\text{O})</td>
<td></td>
<td>236</td>
</tr>
</tbody>
</table>

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(vi) (\text{Me}_3\text{SnNMe}_2 + \text{SO}_2)</td>
<td>(\text{Me}_3\text{Sn-O-SO-NMe}_2)</td>
<td>177</td>
</tr>
<tr>
<td>(vii) (\text{Me}_3\text{SnNMe}_2 + \text{EtOOC-C≡C-COOEt})</td>
<td></td>
<td>238,239</td>
</tr>
<tr>
<td>(viii) (\text{Me}_3\text{SnNMe}_2 + \text{PhC≡CCl})</td>
<td></td>
<td>238,239</td>
</tr>
<tr>
<td>(ix) (\text{R}_3\text{SnNMe}_2 + \text{CH}_2=\text{CR'}\text{CN}) (\text{R}=\text{Me, R'}=\text{H}; \text{R}=\text{Et, R'}=\text{Me.})</td>
<td>(\text{Me}_2\text{N-CH}_2-\text{CR'-CN})</td>
<td>238,239</td>
</tr>
<tr>
<td>(x) (\text{Et}_3\text{SnNMe}_2 + \text{R-CH=CH-CH}=\text{O}) (\text{R}=\text{H, Me Ph.})</td>
<td>(\text{Me}_2\text{N-CHR-CH-CH}=\text{O})</td>
<td>238,239</td>
</tr>
<tr>
<td>(xi) (\text{Et}_3\text{SnNMe}_2 + \text{CH}_2=\text{CH-COOMe})</td>
<td>(\text{Me}_2\text{N-CH}_2-\text{CH-COOMe})</td>
<td>238,239</td>
</tr>
<tr>
<td>(xii) (\text{Me}_3\text{SnNMe}_2 + (\text{CF}_3)_2\text{C}=\text{O})</td>
<td>(\text{Me}_3\text{Sn-O-C(\text{CF}_3)_2-NMe}_2)</td>
<td>243</td>
</tr>
</tbody>
</table>

* Reaction does not occur with alkyl cyanides unless they contain electron-withdrawing groups (e.g. \(\text{CCl}_3\text{CN} 237\)). If \(\alpha\)-hydrogen is present, protolysis may occur. \(\text{tBuCN}\) does not react at all.237
usual insertion products. However, other workers have found that if bis(tributylstannyl)amines are used, elimination of the oxide may occur (Eqn. 1.56).

\[
R - CO - R' + (Bu_3Sn)_2NEt \rightarrow RR'C = NEt + (Bu_3Sn)_2O \quad 1.56
\]

\[
R = Me, Et, R' = C_{1-4} alkyl; \quad R = Ph, R' = Me, iPr.
\]

The reaction of mono-trialkylstannylamines with aliphatic ketones and aldehydes has also been shown to be complex. The possible reaction products are shown in Equation 1.57. The distribution of products seems to be very sensitive to substituent effects (both steric and electronic), and is further complicated by interconversion of the products. For example, the insertion product II is readily converted to the enamine I by elimination of trialkyltin hydroxide; in many cases II is too unstable to be isolated. Also, the enoxytin compound III reacts with excess tin amine to form the enamine I and bis(trialkyltin) oxide. The reaction with acetone, however, appears to be to a large
extent dominated by a tendency to dimerise under the basic conditions of the reaction. The distribution of products is again sterically sensitive (to the substituents on the tin amine) (Eqn. 1.58).

\[
\begin{align*}
(R_3\text{Sn})_2\text{O} + & \quad CH_2=CH-C=Me \quad + \quad \text{R'}_2\text{NH} \\
\text{Me}_2C=CH-C=Me \quad + \quad \text{R'}_2\text{NH} + (R_3\text{Sn})_2\text{O} \\
\text{Me}_2C=CH-C=CH_2 \quad + \quad \text{R'}_2\text{NH} + (R_3\text{Sn})_2\text{O} \\
\text{R}_3\text{SnCH}_2\text{CH}_3 \quad + \quad \text{R'}_2\text{NH}
\end{align*}
\]

Insertion reactions also occur with ring-systems containing polar bonds, with opening of the ring as a result (Equations 1.59-61).

\[
\begin{align*}
\text{O} + \quad \text{Me}_3\text{SnR}_2 & \quad \longrightarrow \quad \text{Me}_3\text{SnOCH}_2\text{CH}_2\text{CNR}_2 \\
\text{R} = \text{Me}, \text{Et.}
\end{align*}
\]

\[
\begin{align*}
\text{Me}_3\text{SnNMe}_2 & \quad \longrightarrow \quad \text{Me}_3\text{Sn}(\text{NMe}_2)_2 \\
\text{(249)} \quad 1.60
\end{align*}
\]

\[
\begin{align*}
\text{R}-\text{CH}_2-\text{CH}_2 + \quad \text{R}_3'\text{SnR}''_2 & \quad \longrightarrow \quad \text{R}_3\text{Sn'}-\text{X}-\text{CHR}_2-\text{NR}_2'' \\
\text{X} = \text{S,O}; \quad \text{where X = O, LiNEt}_2 \quad \text{was used as catalyst.}
\end{align*}
\]

\[
\begin{align*}
2(\text{Me}_3\text{Sn})_3\text{N} + \quad \text{S}_4\text{N}_4 & \quad \longrightarrow \quad 3\text{Me}_3\text{Sn-N=S-N-SnMe}_3 + \quad \text{S} \\
4\text{Me}_3\text{SnNMe}_2 + \quad \text{S}_4\text{N}_4 & \quad \longrightarrow \quad 2(\text{Me}_2\text{N})_2\text{S} + \quad 2\text{Me}_3\text{Sn-N=S-N-SnMe}_3
\end{align*}
\]

A basically similar, although rather more complex, reaction is that with the sulphur-nitrogen cage, $S_{4N_4}$ (Eqns 1.62,63).
The photo-cleavage of the Sn-N bond in primary stannylamines has also been studied. The overall reaction (which is a multi-step free-radical process) is given in Equation 1.64.

\[
\text{Me}_3\text{SnNET}_2 \xrightarrow{\text{hv}} \text{Me}_3\text{Sn-SnMe}_3 + \text{Et}_2\text{NH} + \text{MeCH=NET}
\]  \hspace{1cm} \text{1.64}

The N-stannylcarboxamides and sulphonamides also show the reactions typical of the Sn-N bond, but are generally less reactive than the stannylamines. For both substitution and addition (insertion) reactions, the reactivity sequence \( R_3\text{SnNR}_2 \rightarrow R_3\text{SnNR'-COR''} \rightarrow R_3\text{SnNR'-SO}_2\text{R''} \) has been demonstrated, in agreement with the suggestion that the dominant factor in these reactions is the nucleophilicity of the nitrogen atom.

Generally speaking, heterocycles containing the Sn-N bond show much the same types of reaction as the simple amines. Some examples are given in Equations 1.65-68. Ring expansion and ring cleavage are observed, but the basic chemistry is essentially that found for the stannylamines.

\begin{align*}
\text{tBu}_2\text{Sn} \quad &+ 2\text{PhCN} \rightarrow \text{tBu}_2\text{Sn} \quad (139) \quad \text{1.65} \\
\text{tBu}_2\text{Sn} \quad &+ 2\text{CS}_2 \rightarrow \text{tBu}_2\text{Sn} \quad (139) \quad \text{1.66} \\
\text{tBu}_2\text{Sn} \quad &+ \text{Me}_3\text{SiCl} \rightarrow 3\text{tBu}_2\text{Sn} \quad (138, 139) \quad \text{1.67}
\end{align*}
c) Physical and Structural Properties

The organotin amine derivatives are, in the main, liquids or low melting-point solids, readily soluble in non-polar solvents, and thermally stable\(^1,2\) (most can be distilled under vacuum). Colligative measurements\(^13\) indicate the monomeric nature of all compounds in which the only nitrogen atoms in the molecule are bonded to tin (the presence of nitrogen, or other donor, atoms not directly bonded to tin often leads to association). The only exception to this statement is N-trimethyltin aziridine,\(^15\) which is dimeric in solution (cf. the tin(II) amines) (Fig. 1-22(a)), associated in the gas phase, and apparently oligomeric or polymeric (with non-planar Me\(_3\)Sn groups) in the solid (Fig. 1-22(b)). It further differs from all other mono-trialkyl stannylamines in being a solid at room temperature (M.Pt. 28.5°C) and in

![Figure 1-22](attachment:image.png)

Figure 1-22
being only moderately sensitive to atmospheric moisture. A Mössbauer study\textsuperscript{154} on this and its homologues derived from cyclic amines of three to seven members, shows a considerably higher \(^{119}\text{Sn}\) quadrupole splitting (\(\sim 2.3\text{mm.s.}^{-1}\)) for the aziridine than for open-chain stannylamines or cyclic derivatives of ring size greater than four (0.8-1 mm.s.\(^{-1}\)). This is consistent with a structure containing 5-coordinate tin. Substitution with a 2-methyl group or increasing the ring size to four gives an intermediate value for the quadrupole splitting, presumably indicating rather weaker association.

As has been stated, the presence of other donor atoms in the molecule often leads to association. Many of the N-triorganostannyl carboxamides, sulphonamides, ureas, and biurets are liquids at room temperature (although examples with quite high melting points are known)\textsuperscript{1,2} and some, particularly the biurets, are thermally unstable. The initial characterisation of the N-organostannyl formamides was by NMR, UV, and I.R. spectroscopy,\textsuperscript{160} and in the latter the lowering of \(\nu\) (C=O) relative to the parent formamide has been ascribed to strong C=O..Sn interactions\textsuperscript{255} (Fig. 1-23a). Intermolecular coordination of this type has been confirmed by Mössbauer studies,\textsuperscript{255} and similar association was inferred for the N-trialkylstannylcarbamates (Fig 1-23a or b). It has also been demonstrated by Mössbauer measurements for the

\[ \begin{align*}
\text{(a)} & \quad \text{Me} & & \text{R} & & \text{N} & & \text{C}=\text{O} & & \text{Sn} & & \text{Me} & & \text{Me} & & \text{X} \\
\text{Me} & & \text{Me} & & \text{X} \\
\text{Me} & & \text{Sn} & & \text{Me} & & \text{Me} & & \text{X} & & \text{Sn} & & \text{Me} & & \text{Me} & & \text{X} \\
\text{R}_3\text{Sn} & & \text{NR} & & \text{C} & & \text{O} & & \text{SnR}_3 & & \text{O} & & \text{C} & & \text{O} \\
\text{X} = \text{H}, \text{OEt}, \text{OSnMe}_3.
\end{align*} \]

\textbf{Figure 1-23}
N-triorganostannylsulphinamides. A similar polymeric structure has been obtained by X-ray diffraction for N-(trimethylstannyl)-N-nitromethylamine \(^{326}\) (Fig 1-24), although it is considered to be monomeric in solution. It seems likely that this type of association is fairly common where it is sterically possible. It is undoubtedly a contributory factor to the lower reactivity of these systems relative to the stannylamines.

A similar effect accounts for the high melting points, hydrolytic stability (in the solid), and high viscosities of solutions of the N-trialkylstannyl derivatives of heterocycles containing nitrogen atoms in the 1,3-positions of a five-membered conjugated ring. This is the case for the imidazoles, benzimidazoles, 1,2,3- and 1,2,4-triazoles, benztriazoles, \(^{96,140,257}\) and the tetrazoles. \(^{180,256}\) (Fig. 1-25).

![Figure 1-24](image_url)

![Figure 1-25](image_url)
The 5-coordinate structure has been confirmed by Mössbauer work. The degree of association appears to be dependent on the ring substituents.

The 1,3-arrangement of nitrogens is important; pyrole, pyrazole, and 1,2,5-triazole derivatives are monomeric and reactive.

The stabilising effect of the higher coordination number at tin on the Sn-N bond is no doubt also part of the reason for the very high stability to heat and chemical attack of the tin(iv)phthalocyanines and similar compounds, although the effect of delocalisation over the almost planar system must not be discounted.

Systematic studies of physical properties other than those normally associated with synthetic chemistry (i.e. melting points, boiling points, densities, etc.) are comparatively infrequent for tin-nitrogen compounds. The various spectroscopic techniques (I.R., NMR, Mössbauer, etc.) are of importance for the structural information they provide, and particularly for the light they can throw on the nature of the Sn-N bond. In an unassociated compound this may be a simple \( \sigma \)-bond (Fig. 1-26a), or may involve \((p\rightarrow d)\pi\)-bonding (Fig. 1-26b). In the former case a tetrahedral

![Figure 1-26](image)

sp\(^3\) arrangement at nitrogen is expected, while for optimum orbital overlap in the latter case, sp\(^2\) hybridisation with a planar configuration at nitrogen would be predicted (although it has been demonstrated that sufficient overlap can occur in pyramidal systems for substantial \((p\rightarrow d)\pi\)-bonding to be at least possible). Structures planar at
nitrogen have been observed for trisilylamine and several other silyl
amines,\textsuperscript{261,262} and also for the very unstable trigermylamine \textsuperscript{263}
(mostly by electron-diffraction techniques). (p\rightarrow d) \pi-bonding seems
likely to account for the planarity at nitrogen, together with the
observation that the metal-nitrogen bond distance is shorter than
the theoretical value for a single bond.

This shortening is found to be much less for germanium than for
silicon (0.063Å against 0.127Å), and it has been suggested\textsuperscript{262} that this
is because 2p-4d overlap is less favoured than 2p-3d, with a weaker \pi-bond
as a result. On this basis, N-Sn (p\rightarrow d) \pi-bonding, involving 2p-5d
overlap, would be expected to be still weaker, and it is therefore not
surprising to find that vibrational analysis of the I.R. and Raman
spectra of (Me\textsubscript{3}Sn)\textsubscript{3}N\textsuperscript{264} and tBu\textsubscript{3}SnNH\textsubscript{2}\textsuperscript{265} shows these compounds to be
pyramidal at nitrogen. The former study suggests that the Sn-N
bonds are unusually long, while the latter gives a Sn-N bond order of
1.05, with a low force constant; hence their weakness and consequent
reactivity.

This is particularly interesting in view of the result of an
electron-diffraction study on gaseous Sn(NEt\textsubscript{2})\textsubscript{4}, which shows the bonds at
nitrogen to be nearly coplanar.\textsuperscript{266} The shortening of the Sn-N bond
relative to the calculated single-bond distance, is, at 0.063Å,
comparable to that of the Ge-N bond in trigermylamine, and a similar
amount of \pi-bonding may be inferred. This may perhaps be due to there
being four electron-withdrawing groups about tin, so that there is
sufficient drainage of electron-density from the central atom to
induce some back-donation.

Apart from its common use as an analytical tool, infra-red
spectroscopy has been useful in the study of Sn-N compounds for
structural elucidation. For trialkylstannyl derivatives, the coordination at tin may be determined from consideration of the Sn-C stretching modes. For the 4-coordinate, tetrahedral, case, the pyramidal SnC$_3$ arrangement should have both the asymmetric and symmetric stretching modes active in the infra-red (e.g. (Me$_3$Sn)$_3$N$^{264}$), whereas a planar SnC$_3$ group, as found in many 5-coordinate species, should show only one active vibration (observed for the N-trialkylstannylimidazoles$^{259}$).

Identification of the Sn-N absorptions caused some initial confusion; the first assignment for (Me$_3$Sn)$_3$N$^{120}$ gave $\nu_{as}$(NSn$_3$) = 728 cm$^{-1}$ and $\nu_s$(NSn$_3$) < 400 cm$^{-1}$, while slightly later work$^{264}$ suggested 672 cm$^{-1}$ and 514 cm$^{-1}$ respectively. Neither compared well with $\nu$(Sn-N) = 843 cm$^{-1}$ claimed for N-trimethylstannylaniline$^{267}$ although this last assignment may be doubted, since it assigns the suspiciously close values of 899 and 855 cm$^{-1}$ for the corresponding silicon and germanium compounds. Since then, however, full vibrational analyses have been published for the I.R. and Raman spectra of N-ethylhexabutyldistannazane (Bu$_3$Sn)$_2$NEt, several tributylstannylamines Bu$_3$SnNRR', and some bis(dialkylamino) dibutyltins Bu$_2$Sn(NR$_2$)$_2$. Assignments have also been made for a number of hexaalkyldistannazanes (R$_3$Sn)$_2$NH.$^{269}$

Generally, for R$_3$SnNR'R, $\nu$(Sn-N) falls in the region 560-600 cm$^{-1}$. For R$_2$Sn(NR')$_2$, $\nu_{as}$(SnN$_2$) ~ 690 cm$^{-1}$, $\nu_s$(SnN$_2$) ~ 600 cm$^{-1}$, and for (R$_3$Sn)$_2$NER, $\nu_{as}$(NSn$_2$) ~ 700 cm$^{-1}$, $\nu_s$(NSn$_2$) ~ 590 cm$^{-1}$. These values may be compared with $\nu_{as}$(NSi$_2$) 900-1000 cm$^{-1}$ and $\nu_s$(NSi$_2$) 400-600 cm$^{-1}$,$^{270}$ clearly showing the effect of the heavier tin atom.

The valence force field for the system C$_3$SnNMe$_2$ has been calculated, with good agreement with experiment.$^{268}$ The I.R. spectra of a series of tin phthalocyanines have also been assigned.$^{110}$
Nuclear magnetic resonance, particularly proton-NMR, has also been commonly used in the characterisation of new Sn-N compounds. An additional feature of the spectra is due to the fact that the NMR-active tin isotopes $^{117}$Sn and $^{119}$Sn occur naturally to a sufficient extent that coupling with these nuclei is commonly observed. ($^{115}$Sn also has a spin quantum number of $\frac{1}{2}$ and is NMR-active like $^{117}$Sn and $^{119}$Sn, but has a much lower abundance. It has therefore been little studied in this context, but some $^1$H-$^{115}$Sn coupling constants have been reported, including those for Me$_3$SnNMMe$_2$. Indeed, the apparent absence of this feature in the spectra of the N-methylaminostannanes lead to the proposal that this was due to rapid amine exchange, even at low temperatures. A detailed study, using the $^{117}$,$^{119}$Sn-N-C-$^1$H coupling effect, found that exchange appeared to be favoured by greater numbers of amino-groups on tin, or by smaller alkyl groups on both tin and nitrogen. Some doubt was cast on this, however, when later workers detected the missing couplings.

Detailed $^1$H-NMR studies have been carried out on the series

\[ R\text{Sn(NET}_2\text{)}_{4-n} R = \text{Me, Ph, n = 0-3}; \quad \text{Me}_4\text{Sn(NET}_2\text{)}_{n} n = 1-3; \quad \text{Me}_4\text{Sn(NR}_2\text{)}_{n} R = \text{Me, Et, n = 1-4}; \quad \text{and Me}_3\text{Sn(NMe}_2\text{)}_2 N\text{(SiMe}_3\text{)}_2 n = 0-2. \]

$^{119}$Sn-NMR has also been exploited, and the $^{119}$Sn chemical shifts of the methyltin amines, together with the coupling constants $^{117}$,$^{119}$Sn-C-$^1$H and $^{117}$,$^{119}$Sn-N-C-$^1$H, were considered to show little or no evidence of N-Sn ($p\rightarrow d$) $\pi$-bonding. The data was also interpreted in terms of the absence of Sn-N----Sn bridging, although indications were found of association via C-H----N-Sn hydrogen bonding. The N-methyl $^{13}$C-$^1$H coupling constants for the series Me$_3$NNMe$_2$ and M(NMe$_2$)$_4$ ($M = \text{Si, Ge, Sn}$),
together with basicity measurements on the Si and Ge compounds, were interpreted as indicative of a decrease in (p-d) π-overlap from Si to Sn, with the major change occurring between Si and Ge. 328

The other comparatively widely used spectroscopic technique for these systems is 119m Sn-Mössbauer spectroscopy. Some mention has already been made of its uses as a structural probe; coordination numbers are generally readily discriminated, as are oxidation states. Systematic studies have been undertaken on the N-organostannylazoles, N-organostannyl cyclic amines,154 tin(iv) phthalocyanines and porphins stannylamines, aminostannanes, and stannazanes,255,274 and stannyl imines, amides, and carbamates.255 For the substituted amines the variation and magnitude of the quadrupole splitting parameters have been related to small differences in the group electronegativities of the amino moieties.274 A compilation of all Mössbauer parameters of organotin compounds reported up to 1970 has appeared.307

The electronic absorption spectra of aminostannanes and related compounds seem to have received little or no attention, although UV spectroscopy has been used in the study of aminosilanes as a guide to the extent of (p→d) π-bonding,278,279 deduced from its effect on transitions involving the nitrogen lone-pair.

The Helium (1) photoelectron spectrum of Sn(NMe2)2 4 has been measured, together with its carbon, silicon, and germanium analogues; 281 the conclusion is drawn that free rotation about the M–N bond increases down the group.

The relative basicities of the Group IVB amines are of particular interest since they may be expected to reflect the availability of the nitrogen lone pair, and hence the extent of (p→d) π-bonding. It is
possible to make quantitative comparisons between isostructural materials or compounds with similar steric environments for nitrogen, by utilising the hydrogen-bonding interaction with chloroform. This has been followed by the shift in the C-D stretching frequency for solutions of deuterochloroform in the organometallic bases, or the change in $^1$H-chemical shift for similar solutions of chloroform. The amine series $\text{Me}_2\text{N}(\text{NET}_2)_2$, $\text{Me}_3\text{M}(\text{NET}_2)_2$, and $(\text{Me}_3\text{M})_3\text{N}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) have been compared in this way, and it is generally found that basicity increases $\text{Si} < \text{Ge} < \text{Sn}$. Indeed, $(\text{Me}_3\text{Si})_3\text{N}$ was found to have no basic properties at all, whereas $(\text{Me}_3\text{Sn})_3\text{N}$ was the strongest base examined (it even reacted with $\text{Me}_3\text{SnBr}$ to form an ammonium salt, $(\text{Me}_3\text{Sn})_4\text{N}^+\text{Br}^-$). This would seem to argue for a marked decrease in $\pi$-bonding down the group.

Reports of other physical properties are rather rarer. Dipole moments for a series of amino-stannanes have been measured. The partial moment of $\text{Sn-NEt}_2$ was calculated as 1.7D. The molecular refraction of the Sn-N bond in $N$-tributylstannylsuccinimide has been calculated as 4.02.

Thermochemical data are also sparse. The Sn-N bond energy has been derived from the heat of hydrolysis of liquid $\text{Me}_3\text{SnNMe}_2$ and found to be $\sim 40 \text{ kcal.mole}^{-1}$; a separate determination (from the heats of combustion and formation) for $\text{EtSnNET}_2$ gave the value $62 \text{ kcal.mole}^{-1}$. These may be compared with the values for $\text{EtSiNET}_2$ ($90 \text{ kcal.mole}^{-1}$) and $\text{EtGeNET}_2$ ($80 \text{ kcal.mole}^{-1}$), showing the comparative weakness of the Sn-N bond.

ii) Compounds containing Tin bonded to 2-covalent Nitrogen.

The $N$-organostannylmethyleneamines (or ketimines) $R_4\text{Sn}(N=CR'_2)_n$ are quite similar in their preparative chemistry and most of their properties to the stannylamines. Most compounds of this type that
have been studied were synthesised by transmetallation, reacting ketimino-lithiums with organotin chlorides (Eqn. 1.69). In this way, have been prepared $\text{Ph}_2\text{CNSnR}_3$; $R = \text{Me, Ph},_{290}\text{Bu}^{298}$; $\text{Bu}_2\text{CNSnMe}_3^{291}$; $(\text{p-MeC}_6\text{H}_4)_2\text{CNSnMe}_3^{291}$; $\text{Me}_4\text{nSn}(\text{N=C(CF}_3)_2)_{2n}^{n=1-4};_{291,292}$ and $(\text{Ph}_2\text{CN})_4\text{Sn}^{293}$ (see also this work). The di-p-tolylketimine derivative has also been prepared by transamination $^{291}$ (Eqn. 1.70).

$$R_{4-n}\text{SnCl}_n + n\text{LiN} = \text{CR'}_2  \rightarrow R_{4-n}\text{Sn(N=CR'}_2)_n + n\text{LiCl}$$ \hspace{1cm} 1.69

$$\text{Me}_3\text{SnNMe}_2 + \text{HN=C (C}_6\text{H}_4\text{p-Me})_2 \rightarrow (\text{p-MeC}_6\text{H}_4)_2\text{CNSnMe}_3 + \text{HNMe}_2$$ \hspace{1cm} 1.70

These materials are generally liquids or crystalline solids, monomeric, and very moisture-sensitive. Like the tin amines, they are very reactive. They react readily with protic reagents (Eqn. 1.71).

$$\text{Me}_{4-n}\text{Sn(NCR}_2)_n + n\text{HA} \rightarrow \text{Me}_{4-n}\text{SnA}_n + n\text{HNCR}_2$$ \hspace{1cm} 1.71

$n = 1, \ A = \text{OH, } -\text{C}==\text{CPh}, \text{ C}_6\text{F}_5^{291}$

$n = 2, \ A = \text{Cl}^{294}$

The reaction of HCl with $\text{Me}_2\text{M}(\text{N=C(CF}_3)_2)_2, \ M = \text{Si, Sn},^{294}$ is interesting in that it reflects the relative reactivities of the Si-N and Sn-N bonds. While the Sn-N bond undergoes protolysis, as above, the Si-N bond is unaffected; instead, addition of HCl across the C=N bond is observed.

Transamination with dibutylamine does not occur.$^{169}$ Reaction with metal hydrides yields $\text{M-Sn}$ bonded species $^{291}$ (Eqns. 1.72, 1.73).
The presence of halogens in the system may lead to competing reactions involving elimination of trialkyltin halide (Eqn. 1.74). Product I is the same as that obtained by reaction with the zero-valent platinum complex in Equation 1.75, where insertion of the transition metal into the Sn-N bond occurs.

Metathetical reactions with metal halides have been used to prepare a number of imino-derivatives of the transition metals (Eqns. 1.76, 77).

\[
\text{Me}_3\text{SnN}=\text{C}(\text{CF}_3)_2 + \pi-\text{C}_5\text{H}_5\text{Mo}(	ext{CO})_3 \rightarrow \text{C}_5\text{H}_5\text{Mo}(	ext{CO})_3\text{SnMe}_3 + \text{HNC}(	ext{CF}_3)_2 \quad 1.72
\]

\[
\text{Me}_3\text{SnN}=\text{C}^\text{tBu}_2 + \text{trans}-\left(\text{PPh}_3\right)_2\text{PtCl} \rightarrow \text{trans}-\left(\text{PPh}_3\right)_2\text{PtClSnMe}_3 + \text{HNC}^\text{tBu}_2 \quad 1.73
\]

\[
\text{Me}_3\text{SnN}=\text{C}(\text{CF}_3)_2 + \text{trans}-\left(\text{PPh}_3\right)_2\text{PtCl} \rightarrow \text{trans}-\left(\text{PPh}_3\right)_2\text{PtSnMe}_3.\text{N}=\text{C}(\text{CF}_3)_2 + \left(\text{PPh}_3\right)_2\text{Pt}.\text{HN}=\text{C}(\text{CF}_3)_2 + \text{Me}_3\text{SnCl} \quad 1.74
\]

\[
\left(\text{Ph}_3\text{P}\right)_3\text{Pt} + \text{Me}_3\text{SnN}=\text{C}(\text{CF}_3)_2 \rightarrow \text{Me}_3\text{Sn-Pt}\left(\text{PPh}_3\right)_2.\text{N}=\text{C}(\text{CF}_3)_2 + \text{PPh}_3 \quad 1.75
\]

\[
\text{Me}_3\text{SnN}=\text{CR}_2 + \text{LM-Cl} \rightarrow \text{Me}_3\text{SnCl} + \text{LM-N}=\text{CR}_2 \quad 1.76
\]

\[
\text{R}=\text{CF}_3, \text{LM}=\left(\pi-\text{C}_5\text{H}_5\right)_2\text{TiCl}^{291}, \text{cis-}\left(\text{PPh}_3\right)_2\text{PtCl}, \quad 291,296
\]

\[
\text{R}=\text{Ph}, \text{LM}=\text{cis-}\left(\text{PPh}_3\right)_2\text{PtCl}^{291}
\]

\[
\text{R}_3\text{SnN}=\text{C}(\text{CF}_3)_2 + \text{Mn}(	ext{CO})_5\text{Br} \rightarrow \left(\text{OC}\right)_3\text{Mn}^3\text{N}=\text{C}(\text{CF}_3)_2 + \text{R}_3\text{SnBr} \quad 1.77
\]

\[
\text{R} = \text{Me, Et}
\]

\[
\text{Me}_3\text{Sn-N}=\text{C}(\text{CF}_3)_2 + \text{Br}_2 \rightarrow \text{Me}_3\text{SnBr} + \text{BrN}=\text{C}(\text{CF}_3)_2 \quad 1.78
\]
The Sn-N bond is also cleaved by bromine \(^{291}\) (Eqn. 1.78).

Ketiminotin compounds also react with unsaturated 1,2-dipoles, in the same manner as other Sn-N compounds, although they are less reactive than the aminostannanes. \(^{291}\) Reactivity has been found to decrease in the sequence \(\text{Me}_3\text{SnNR}_2 > \text{Me}_3\text{SnN}=\text{CPh}_2 > \text{Me}_3\text{SnN}=\text{C}(\text{CF}_3)_2\). The reactions are summarised in Table 6.

The reactions with isocyanates were initially reported \(^{298}\) to proceed rapidly under mild conditions, but this has been disputed \(^{291}\) and the suggestion made that the reactions are catalysed by the free imine, produced by a trace of water. It was suggested that this may apply to all reactions of iminotins with unsaturated species (Eqn. 1.79).

\[
\begin{align*}
\text{R}_3\text{SnN}=\text{CR'}_2 + \text{X}=\text{Y} & \quad \text{slow} \quad \Rightarrow \quad \text{R}_3\text{Sn-X-Y-N}=\text{CR'}_2 \\
\text{H}_2\text{O} + \text{H-N}=\text{CR'}_2 & \quad \text{fast} \quad \Rightarrow \quad \text{H-X-Y-N}=\text{CR'}_2
\end{align*}
\]

N-metallated ketimines are of particular interest since their structures should reflect the extent of \(N\rightarrow M\) dative \(\pi\)-bonding in the \(M-N=C\) bond angle. This has been followed by a number of spectroscopic techniques, and the results are discussed in Chapter 2. The crystal structure of \((\text{Ph}_2\text{CN})_4\text{Sn}\) has been reported \(^{301,302}\) (see also this work).

Several other imino-derivatives have been prepared by the insertion of nitriles into tin-oxygen and tin-nitrogen bonds (Eqns. 1.80, 81).

\[
\begin{align*}
\text{RBu}_2\text{SnOR'} + \text{CCl}_3\text{C}=\text{N} & \quad \Rightarrow \quad \text{RBu}_2\text{Sn-N}=\text{C} \quad \text{(253,303)} \quad 1.80 \\
\text{Me}_3\text{SnNMe}_2 + \text{PhC}=\text{N} & \quad \Rightarrow \quad \text{Me}_3\text{Sn-N}=\text{C} \quad \text{(176,177)} \quad 1.81
\end{align*}
\]
TABLE 6

Reactions of N-Stannylketimines with Unsaturated Species

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $\text{Me}_3\text{Sn}=\text{CR}_2' + \text{R''NCO}$</td>
<td>$\text{Me}_3\text{Sn-NR''-CO-N=CR}_2'$ *</td>
<td>291, 299</td>
</tr>
<tr>
<td></td>
<td>$\text{R} = \text{Me}, \text{R}' = \text{Ph},\text{CF}_3, \text{R''} = \text{Ph},\text{Me}$</td>
<td>291, 299</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
</tr>
<tr>
<td>(ii) $\text{Me}_3\text{Sn}=\text{CPh}_2 + \text{R'NCS}$</td>
<td>$\text{Me}_3\text{Sn-S-C-N=CPh}_2$</td>
<td>298, 299</td>
</tr>
<tr>
<td></td>
<td>$\text{R} = \text{Me, Bu}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{R'} = \text{Me, Ph}$</td>
<td></td>
</tr>
<tr>
<td>(iii) $\text{Me}_3\text{Sn}=\text{CPh}_2 + \text{CH}_2=\text{CH-CN}$</td>
<td>$\text{Me}_3\text{Sn-SH-CH}_2\text{-N=CPh}_2$</td>
<td>291, 298</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iv) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \alpha\text{-Np-N=CH=CH}_2$</td>
<td>$\text{Bu}_3\text{Sn-N-C-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \text{PhN}=\text{SO}_2$</td>
<td>$\text{Bu}_3\text{Sn-NPhSO-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td>(vi) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \text{CCl}_3$</td>
<td>$\text{Bu}_3\text{Sn-NCCl}_3\text{-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td>(vii) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \text{X=SO}_2$</td>
<td>$\text{Bu}_3\text{Sn-X-C-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td>(viii) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \text{X=OS}_2$</td>
<td>$\text{Bu}_3\text{Sn-O-CRR'-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td>(ix) $\text{Bu}_3\text{Sn}=\text{CPh}_2 + \text{RR'C}=\text{O}$</td>
<td>$\text{Bu}_3\text{Sn-O-CRR'-N=CPh}_2$</td>
<td>298</td>
</tr>
<tr>
<td>(x) $\text{Me}_3\text{Sn}=\text{CPh}_2 + \text{CH}_2=\text{CH-CN}$</td>
<td>$\text{Me}_3\text{Sn-N-C-N=CPh}_2$</td>
<td>300</td>
</tr>
</tbody>
</table>

*: Further reaction with another mol. of RNCO gives $(4\pi + 2\pi)$ cycloaddition to form a cyclic product.

The isothiocyanate system gives only the normal insertion product.
The latter is an example of an unsymmetrically substituted amidine; it appears to be monomeric\textsuperscript{177} and has also been prepared from the N-lithioamidine and Me\textsubscript{3}SnCl.\textsuperscript{304} Although the symmetrically substituted amidino-tins seem to have a 5-coordinate, probably delocalised, structure\textsuperscript{304} (see also this work) (e.g. Fig 1-27), which may be shared by similarly substituted guanidines, it seems unlikely that there is any intramolecular association in the unsymmetrically substituted material; organo-tin(iv) amines do not appear to be very good acceptors unless there is some additional factor involved to drive the process, such as the delocalisation of the amidine group here. Amidine derivatives are discussed in greater detail in Chapter 4.

Related to the imino-compounds are the diimines, \(-\text{N} = \text{N}\)-, and the nitroso-derivatives, \(-\text{N} = \text{O}\). Although they are known for silicon and germanium, all attempts to prepare the bis(trialkylstannyl)diimines have failed. The corresponding germanium compounds are extremely sensitive to oxidation, and the tin compounds would be expected to be even more so, which probably accounts for their preparative failure.\textsuperscript{305}

Nitroso-trimethyl- and triphenylstannanes have been prepared as blue and dark green solutions in THF by the reaction of triorganostannyl-lithiums with nitrosyl chloride at low temperatures. The solutions

\[
\begin{align*}
\begin{array}{c}
\text{R}_1 - \text{N}^+ - \text{Sn}^+ - \text{N}^\text{R}_2 \\
\text{Sn} \\
\text{R}^\prime_3
\end{array}
\end{align*}
\]

\textit{Figure 1-27}
decompose at 

\[ \text{Their UV and IR spectra were recorded together} \]

with those of the corresponding silicon, germanium, and lead compounds. 306

Other examples of the Sn-N=X system are the phosphinimines,

\[ R_3\text{Sn-N}=PR'_3 \]. These have been prepared via the phosphinimino-lithiums, 308

and from the parent phosphinimines by transamination, 197 but the usual

synthetic route is by the reaction of a substituted phosphine with an

organotin azide. (Eqn. 1.82). Earlier reports 311,312 suggested that

triphenyltin azide does not react, but this has been disproved.

\[ R_3\text{SnN}_3 + R'_3P \xrightarrow{\Delta} R_3\text{Sn-N}=PR'_3 + N_2 \uparrow \quad 1.82 \]

\[ R = \text{Ph, R' = Ph, } \text{n-octyl, } \text{n-Bu.} \quad 309 \]

\[ R = \text{Et, n-Bu, R' = Ph, n-Bu, NMe}_2. \quad 197 \]

\[ R_3\text{SnN}_3 + (\text{MeO})_3P \rightarrow N_2\uparrow + R_3\text{Sn-N-P(OMe)}_2 \quad 1.83 \]

\[ \text{MeO} \]

\[ 2\text{Me}_3\text{SnN}_3 + R_3P \rightarrow \text{Me}_4\text{Sn} + \text{Me}_2\text{Sn(N}_3\text{)-N}=PR'_3 + N_2\uparrow \quad 1.84 \]

\[ R = \text{Me, Et, Ph.} \]

If trimethoxyphosphine is used, the product is not a phosphinimine

but an N-stannylphosphoramide 197 (Eqn. 1.83).

Under the reaction conditions (which involve heating mixtures of
the reactants until gas evolution ceases) trimethyltin azide

disproportionates, and the ultimate product is derived from dimethyltin

diazide 310 (Eqn. 1.84). Only one azide group appears to react.
The products are colourless liquids or crystalline solids, hydrolytically sensitive (both the $P=N$ and $Sn-N$ bonds are attacked) and thermally stable. Their reactions, in so far as they have been investigated, resemble those of the stannylamines (Eqns. 1.85-87).

\[
\begin{align*}
R_3Sn-N&=PR_3 + 2HCl \rightarrow R_3SnCl + R_3'P=NH_2^+Cl^- & 1.85 \\
R_3Sn-N&=PR_3 + 2R''I \rightarrow R_3SnI + R_3'P=NR''^+I^- & 1.86 \\
R_3Sn-N&=PR_3 + R''OH \rightarrow R_3SnOR'' + R_3'P=NH & 1.87
\end{align*}
\]

Some $^1H$-NMR and IR data have been reported, and a comparison with the corresponding silicon and germanium compounds has indicated less metal-nitrogen π-bonding for the germanium and tin derivatives than for silicon.

No $N$-stannyl sulphinimines, $R_3Sn-N=SR'$ appear to have been reported, although the $N,N'$-bis(trialkylstannyl)sulphur diimides, $R_3Sn-N=S=N-SnR_3$, are well known.

The latter compounds are an example of $Sn-N$ derivatives containing cumulated double bonds, although in this instance the system is bent at sulphur, due to the sulphur lone pair. Linear heterocumulenes include the $N$-stannylketenimines, and the carbo-diimides.

Most of the pseudohalides also contain linear systems of cumulated double bonds, which undoubtedly contributes to the stability of the pseudohalide groups, and thus to their significant differences from other $Sn-N$ compounds. It is therefore no surprise to find that the carbodiimides and the related cyanamides show some pseudohalide-like properties, although it may be more appropriate to consider the $NCN$ group as a pseudo-chalogen. For example, just as the trialkyltin hydroxides readily lose water to form the bis(trialkyltin)oxide, the triorganotin...
cyanamides readily eliminate cyanamide to yield the carbodiimide (Eqn. 1.88).

\[
2R_3\text{SnNHCN} \xrightarrow{\Delta} R_3\text{Sn-N=CN-SnR}_3 + \left[H_2\text{N-CN}\right] \\
\text{dimerises} \quad 1.88
\]

\[
\text{H}_2\text{N-C-NH-CN} \\
\text{NH}
\]

\[
\text{Bu}_3\text{SnNCSnBu}_3 + \text{PhNCO} \rightarrow \text{Ph-N=CN=CN-SnBu}_3 \text{SnBu}_3
\]

The cyanamides and carbodiimides are considerably more stable to hydrolysis than most Sn-N compounds (apart from the pseudohalides), and generally their chemistry seems to be dominated by the effect of the linear cumulated \( \pi \)-system, although they do show some reactions similar to those of the more typical Sn-N systems, for example that with phenyl isocyanate (Eqn. 1.89).

The crystal structure of bis(trimethylstannyl)carbodiimide contains 5-coordinate tin, with each carbodiimide group bound to four trimethyltin groups. It has been considered to be intermediate between the carbodiimide, cyanamide, and ionic extremes (Fig. 1-28), further emphasising the 'pseudochalcoogen' character of the carbodiimide group.

All the N-stannylketenimines known contain cyano-substituents at the 2-position, since they are synthesised from 1,1-dicyanoethylenes (Eqns. 1.90-93). The preparation of the N-stannyl ketenimine in Equations 1.92 and 1.93 has also been effected by the reaction oftrialkylstannyl methoxides or acetates with the trimethylsilyl analogue.
Figure 1-28

\[
\text{Me}_3\text{SnX} + \text{CF}_3\cdot\text{R}\cdot\text{C}=\text{C}(-\text{CN})_2 \rightarrow \text{Me}_3\text{Sn-N}=\text{C}=\text{C}-\text{X}. \quad \text{(322)} \quad 1.90
\]

\[ R = \text{CF}_3, \quad \text{X} = \text{SMe}, \text{AsMe}_2', \text{C}_3\text{H}_5', \text{C}_4\text{H}_7; \quad R = \text{CF}_2\text{Cl}, \quad \text{X} = \text{SMe} \]

\[
\text{R}_3\text{Sn}-\text{H} + \text{R}'\text{R}''\text{=C}(-\text{CN})_2 \rightarrow \text{R}_3\text{Sn-N}=\text{C}=\text{C}-\text{H} \quad \text{(320)} \quad 1.91
\]

\[ R = \text{Et},\text{Bu}; \quad \text{R}' = \text{H},\text{R}'' = \text{Me}, \text{Ph},\text{OEt}, \text{Furyl}, \text{p-}\text{XC}_6\text{H}_4(\text{X} = \text{Me}_2\text{N}, \text{MeO},\text{Cl},\text{NO}_2); \]

\[ \text{R}' = \text{R}'' = \text{Me},\text{Ph}. \]

\[
\text{tBuHgSnR}_3 + \text{XC}_6\text{H}_4\text{CH}=\text{C}(-\text{CN})_2 \rightarrow \text{R}_3\text{Sn-N}=\text{C}=\text{C}-\text{C}_6\text{H}_4\text{X} + \text{Hg} \quad \text{(323)} \quad 1.92
\]

\[ \text{XC}_6\text{H}_4\text{CH}^{\text{tBu}}-\text{C}(-\text{CN})_2\text{Hg}^{\text{tBu}} + \text{Et}_3\text{SnH} \rightarrow \text{tBuH} + \text{Hg} + \text{Et}_3\text{Sn-NCC-CH}^{\text{tBu}}\text{C}_6\text{H}_4\text{X} \quad \text{(323)} \quad 1.93 \]
The products are involatile viscous oils or white solids. The fluorinated materials are stable to air and moisture, although the others are moisture sensitive. They decompose above 50°C. The cryoscopic molecular weights (in benzene) increase with concentration, suggesting 5-coordinate tin with association through the cyanide group, perhaps with a delocalised \( \pi \)-system (Fig. 1-29).

\[
\begin{array}{c}
\text{Me} \\
\text{Sn} \\
\text{Me} \\
\text{Me} \\
\text{N} & \text{C} & \text{C} & \text{C} & \text{C} & \text{N} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me}
\end{array}
\]

Figure 1-29

The non-fluorinated compounds are hydrolysed by alcohols, and react with alkyl and acyl halides and bromine (Eqn. 1.94).

\[
\begin{align*}
R'CH_2C(CN)=C=NSnR_3 & + R''X \longrightarrow R'CH_2C(CN)=C=N-R'' & + & R_3SnX \\
R''X = CH_2CH_2Br; & CH_3CH=CHCH_2Cl; & Ph-CH_2Cl; & PhCOCl; & CH_3COCl; & Br_2
\end{align*}
\]

Some similarities to the related pseudohalogen tricyanomethanides might have been expected, but the only example appears to be the tendency to associate.

The sulphur diimide derivatives have been briefly mentioned. These compounds show no pseudohalide (or chalcogenide) character. The only method of preparation appears to be the reaction of \( S_4N_4 \) with triorganostannylamines (Eqn. 1.95).
The products are yellow crystalline solids, hydrolytically sensitive and soluble in organic solvents. They undergo exchange with chlorosilanes,\textsuperscript{227,254} eliminating trimethyltin chloride, and on heating with sulphur give an unusual dimeric tin-nitrogen heterocycle\textsuperscript{251} (Eqn. 1.96).

\[
2\text{Me}_3\text{SnN=S=NSnMe}_3 + 2\text{S} \rightarrow \text{Me}_3\text{SnN=S=NSnMe}_3 + 2\text{Me}_4\text{Sn} \quad 1.96
\]

A number of N-stannyl iminosulphuranes are also known.\textsuperscript{324} Preparative routes include transamination, transmetallation, and dehydrochlorination of the imine-tin chloride complex by base. (Eqn. 1.97).

\[
\begin{align*}
2\text{R}_3\text{SnNMe}_2 + \text{Me}_2\text{S(=NH)}_2 & \quad 2\text{R}_3\text{SnX} + \text{Me}_2\text{S(=NM)}_2 \\
2\text{R}_3\text{SnM} + \text{Me}_2\text{S(=NX)}_2 & \\
\text{Me}_2\text{S(=NH)}_2\cdot\text{SnR}_3\text{Cl} + \text{Et}_3\text{N} \text{ or NaOMe}
\end{align*}
\]

\( R = \text{Me, Ph}; \ X = \text{Cl, Br}; \ M = \text{Li, Na, K}. \)
Similar reactions with diorganotin derivatives or tin tetrahalides produce two- and three-dimensional polymers. The mono-stannylated iminosulphuranes are not preparable due to rapid disproportionation.

The di-substituted compounds are monomeric, colourless, crystalline solids. If \( R = \text{Ph} \), the material is only slowly hydrolysed, and is generally unreactive. If \( R = \text{Me} \), the material is very moisture sensitive, and reacts readily with alkyl halides and unsaturated species, towards which it is monofunctional only (Eqn. 1.98).

\[
2 \text{MeI} \rightarrow \text{Me}_2\text{S(=NSnMe}_3\text{)}_2
\]

\[
\text{Me}_2\text{S(=NSnMe}_3\text{)}_2 + \text{Me}_3\text{SnI} \rightarrow \text{Me}_2\text{S(=NSnMe}_3\text{)}_2 + \text{Me}_3\text{SnI}
\]

\[\text{XY}_2 = \text{CO}_2, \text{CS}_2, \text{SO}_2.\]

The latter reaction is believed to produce only the 1:1 adduct because the product is stabilised by association, either intramolecular (\( \text{XY}_2 = \text{CS}_2 \), Fig. 1-30(a)) or intermolecular (\( \text{XY}_2 = \text{CO}_2, \text{SO}_2 \), Fig. 1-30(b)).

Figure 1-30
No derivatives of sulphur triimide, $S(=\text{NH})_3$, appear to have been reported. However a number of methyl sulphur diimide amides are known.

The usual preparative routes for Sn-N compounds are followed (Eqns. 1.99-102).

$$\text{Me}_n\text{Sn(NR}_2\text{)}_{4-n} + (4-n)\text{MeN=S=NMe} \rightarrow \text{Me}_n\text{Sn(MeS(NMe)}_2\text{NMe)}_{4-n} + (4-n)\text{Me}_2\text{NH}\text{NHMe}$$

$R = \text{Me, Et}; \quad n = 0-3$

$$\text{Me}_n\text{SnCl}_{4-n} + (4-n)\text{MeS(NMe)}_2\text{NMeNa} \rightarrow \text{Me}_n\text{Sn(MeS(NMe)}_2\text{NMe)}_{4-n} + (4-n)\text{NaCl}$$

1.99

1.100

$$\text{Ph}_3\text{SnCl} + \text{MeS(NMe)}_2\text{NMeNa} \rightarrow \text{Ph}_3\text{Sn(MeS(NMe)}_2\text{NMe)} + \text{NaCl}$$

1.101

but:

$$\text{Ph}_n\text{SnCl}_{4-n} + (4-n)\text{MeS(NMe)}_2\text{NMeNa} \rightarrow \text{Ph}_n\text{SnCl(MeS(NMe)}_2\text{NMe)}_{3-n} + (3-n)\text{NaCl}$$

$n = 1,2$

1.102

Except for $\text{Me}_3\text{Sn(MeS(NMe)}_2\text{NMe)}$, which is a distillable liquid, the products are thermally stable crystalline solids. Like the dimethylsulphur diimide derivatives, the methyl tin compounds are hydrolytically sensitive, while the phenyl substituted materials are much less so. They are monomeric in solution, and the $^1\text{H}-\text{NMR}$ spectra are interpreted in terms of a fluxional system (Fig. 1-31(a)), rather than the symmetrical delocalised form (Fig. 1-31(b)).
iii) The Tin-Nitrogen Bond in the Organotin Pseudohalides

The chemistry of the pseudohalides is not discussed here, but details may be found in a number of reviews. Organometallic azides were covered in 1966, and a review of the Group IIIIB and IVB pseudohalides appeared at about the same time. A more general survey of organometallic pseudohalides was published in 1967.

Certain aspects of their structural properties, particularly the extent of $N \rightarrow Sn$ ($p \rightarrow d$) $\pi$-bonding, are however directly relevant to much of this thesis, so further discussion seems appropriate.

Adopting a similar argument to that applied to imino-derivatives (see Chapter 2), it might be expected that a covalent metal pseudohalide containing the $M-N=C$ unit would adopt a structure bent at nitrogen in the absence of $N \rightarrow M$ dative $\pi$-bonding (Fig. 1-32(a)), and would progressively approach linearity as the extent of $N-M \pi$-interaction increased (Fig. 1-32(b)),

![Diagram](image-url)
due to modification of the hybridisation at nitrogen from sp\(^2\) to sp.

Although this hypothesis has often been used to explain MNC bond angles in the pseudohalides, it ignores the possibility that other canonical forms which involve linearity at nitrogen without N-M \(\pi\) -bonding, such as Fig. 1-32(c), may make a significant contribution to the structure. This argument does not apply to the azides, since the most important contributions to the structures of both the N-M \(\pi\) -bonded and non-\(\pi\) -bonded forms will be made by bent species (Fig. 1-32(d) and (e)).

A number of structural studies on the pseudohalides of silicon and germanium illustrate these points. Relevant bond lengths and angles are listed in Table 7. It may be seen that there is considerable variation in the MNC bond angle, and little correlation with the shortening of the M-N bond relative to the calculated value for a single bond; such a correlation would be expected if the bond angle accurately reflects the extent of (p-d)\(\pi\) -bonding. All that can be said is that the silicon compounds generally show a somewhat greater degree of M-N bond shortening, together with a wider bond angle, than the germanium compounds, consistent with the expected greater importance of d-orbital participation for silicon.

Less quantitative studies on the vibrational spectra of several other compounds indicate that \(\text{H}_3\text{GeNCS}\) has a bent skeleton,\(^{365}\) while \(\text{Cl}_3\text{SiNCO}\) and \(\text{Cl}_3\text{SiNCS}\) were considered to be linear at nitrogen.\(^{367}\) In contrast to the electron diffraction study, the vibrational spectrum of \(\text{Si(NCO)}_4\)\(^{368}\) was interpreted in terms of a highly symmetric molecule with linear Si-N-C units (a similar result was obtained for Si(NCS)\(^4\)\(^{369}\)), while Ge(NCO)\(^4\)\(^{368}\) was considered to be less symmetric, probably due to a bent Ge-N-C skeleton. Like the corresponding germanium compound, \(\text{H}_3\text{SiN}_3\) was found to be bent.\(^{366}\)
Bonding possibilities for some metal pseudohalides.

\[ M = \text{N} = \text{C} = X \]
\[ M^- = \text{N}^+ = \text{C} = X \]
\[ M - \text{N} = \text{C} = X^- \]
\[ M - \text{N} = \text{N}^+ = \text{N}^- \]
\[ M^- = \text{N} = \text{N}^+ = \text{N} \]

Figure 1-32
### TABLE 7

**Structural Data for Some Silicon & Germanium Pseudohalides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-N°</th>
<th>Δ(M-N) Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{SiNCS}^a$</td>
<td>linear 1.71 0.16</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>$\text{Me}_3\text{SiNCS}^b$</td>
<td>154 1.78 0.09</td>
<td>362</td>
<td></td>
</tr>
<tr>
<td>$\text{Me}_3\text{SiNCO}^b$</td>
<td>150 1.76 0.11</td>
<td>362</td>
<td></td>
</tr>
<tr>
<td>$\text{Si(NCO)}_4^b$</td>
<td>146.8 1.69 0.18</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{GeNCO}$</td>
<td>141.3 1.83 0.09</td>
<td>363$^b$,364$^a$</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{GeNCNGeH}_3^b$</td>
<td>138 1.81 0.11</td>
<td>363</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{GeN}_3^b$</td>
<td>119 1.85 0.07</td>
<td>363</td>
<td></td>
</tr>
</tbody>
</table>

*a: Microwave spectrum;  b: Electron diffraction.*

$\Delta (\text{M-N}) = (\text{M-N})_{\text{calculated}} - (\text{M-N})_{\text{experimental}}$

Calculated (M-N) single bond lengths: $^{372}$ Si-N: 1.87Å; Ge-N: 1.92Å.
In contrast to the silicon and germanium compounds, which appear to be essentially monomeric, the organotin (and lead) pseudohalides are generally associated (this effect decreases with increasing size of the organic substituents, probably for steric reasons). As a result, crystal structures give little information about the isolated molecule, and no gas-phase studies appear to have been carried out, possibly because of relatively low volatilities.

X-ray diffraction studies have been undertaken on $\text{Me}_3\text{SnNCS}$, $\text{Ph}_3\text{SnNCS}$, $\text{Me}_2\text{Sn(NCS)}_2$, $\text{Me}_3\text{SnN}≡\text{NSnMe}_3$, $\text{Me}_3\text{SnN(CN)}_2$, and $\text{Me}_2\text{Sn(N(CN))}_2$. In each case the Sn-N-C unit is close to linear, but the Sn-N bond length shows no significant shortening compared to the calculated single bond distance. It has been suggested that this is due to the importance of valence bond extremes involving linearity at nitrogen (Fig. 1-33(a) and (b)), rather than $(p\rightarrow d)\pi$-bonding. $N\rightarrow\text{Sn}\pi$-donation would in any case be less likely here, since the electron demand of the tin is being satisfied by donation from another pseudohalide group, i.e. increase in coordination number to five.

![Figure 1-33](image)

The decrease in stability of the triphenyl monoazides down the group has been ascribed to a decrease in $(p\rightarrow d)\pi$-bonding. Infra-red spectroscopic studies on the trimethyl mono-isocyanates, -isothiocyanates, and -azides of the Group IVB elements led to anomalously high energy
pseudohalide group absorptions for the silicon and germanium compounds, which were explained in terms of $N\rightarrow M \ (p\rightarrow d)^\pi$-donation. This was considered to decrease down the group, but no account was taken of the possible effects of association in the solid state for tin and lead (many spectra were run on mulls). However, an ultra-violet spectroscopic study on the azides $\text{Me}_3\text{MN}_3$ ($M=\text{Si,Ge,Sn,Pb}$), carried out in solution where the effect of association should be reduced, suggested that, whereas $(p-d)^\pi$-bonding could be inferred for Si and Ge, there was little evidence for it for Sn and Pb.
CHAPTER TWO

METHYLENEAMINO-DERIVATIVES OF THE GROUP IVB ELEMENTS IN THE TETRAVALENT STATE
2.1 Introduction.

This chapter describes the preparation and properties of some new methyleneamino derivatives of the Group IVB elements (principally tin) in oxidation state (IV). Their spectroscopic and structural features are discussed in the light of earlier results on related compounds. As a background, the structural and spectroscopic properties of the methyleneamino group are briefly described.

2.2 Bonding and Structure in Methyleneamino derivatives

The preparative chemistry and reactions of the N-organostannylmethyleneamines $R_3SnN=CR_2$ were discussed in Chapter 1. As was stated there, these compounds are of particular interest because of the possibility of following $N\rightarrow M$ dative $\pi$-bonding through its effect on the shape of the $C=N-M$ linkage. This has been studied for a number of systems, both in the transition elements and the main groups (for a review see reference 329).

A number of structural possibilities exist for $N$-metallated methyleneamines, since the methyleneamino group may act as a one- or three-electron donor (Fig. 2-1). In the former case the structure will involve $sp^2$ hybridisation at nitrogen with a corresponding $CNM$ angle of $\sim 120^\circ$ (Fig. 2-la). Bent structures of this type have been observed or inferred for di-$t$-butylmethyleneamine$^{330}$ (hence presumably other methyleneamines as well) and a number of $N$-organomethyleneamines.$^{331-4}$ They would be expected for any derivatives in which there is no bonding interaction between the nitrogen lone-pair and the $N$-attached substituent, for example in compounds $R_2C=NMX_n$ where the metal $M$ is coordinatively saturated (e.g. $(\text{Ph}_2\text{CN})_3P^{351}$).

If it is coordinatively unsaturated, however, donation of the nitrogen lone-pair may occur, either through bridging to a second metal atom (Fig. 2-lb) with the formation of a dimeric or oligomeric species, or through $N\rightarrow M$ dative $\pi$-bonding (Fig. 2-lc). In the latter case,
Bonding Possibilities for the Methyleneamino-group

(a)

(b)

(c)

(d)

(e)

Figure 2-1.
for maximum overlap of the nitrogen and metal orbitals, a linear arrangement at nitrogen is required, with modification of the hybridisation to sp (Fig. 2-1d shows the case of (p→d) π-interaction).

It has been demonstrated, from overlap integral calculations on silicon systems, that quite substantial (p→d) π-bonding is at least possible in the bent form (Fig. 2-le), but it is expected to be maximised by a linear arrangement, and a number of workers have used the angle at nitrogen as an indication of the extent of dative π-bonding (ref. 329 and references therein).

Examples for which crystallographic data are available are bis(di-t-butylmethyleneamino)beryllium dimer, diphenylmethyleneamino-
dimesitylborane, tris(di-t-butylmethyleneamino)borane, lithium tetrakis(di-t-butylmethyleneamino)alane, and tris(diphenylmethyleneamino)-phosphine. Their structures are shown in Fig. 2-2a–e. The beryllium compound contains two types of imino-group, bridging and terminal. The terminal substituents have almost linear C-N-Be units, the bond lengths being consistent with considerable N→Be (p→p) π-bonding. Similarly, the C-N-B angles in the boron compounds are close to 180° (173° for the mono-imino derivative, 165° for the tris-imino compound).

The aluminium compound also contains both terminal and bridging imino groups (bridging to lithium in this case). The terminal ketimino groups are essentially linear and the Al-N bond lengths are shorter than the calculated values for an Al-N single bond, consistent with N→Al dative π-bonding, which in this case must be by (p-d) π-interaction, since the aluminium p-orbitals are all involved in the four Al-N σ-bonds. (The tris(methyleneamino)alanes, which spectroscopic studies suggest are planar at aluminium and close to linear at nitrogen (Fig.2-3), would contain (p→p) π-bonding like the boron analogues). An
Structures of some methyleneamino derivatives

(a)

(b)

(c)

(d)

(e)

Figure 2-2
additional point of interest in the structure of the lithium compound

[Chemical structure]

is the unusual Li-H-C interaction (Fig. 2-2d).

The tris-iminophosphine \((\text{Ph}_2\text{CN})_3\text{P}\) has a pyramidal structure with all the imino groups bent at nitrogen, showing little evidence of \(N\rightarrow P\ \pi\)-bonding, consistent with the relatively poor acceptor properties expected for phosphorus (III). (Fig. 2-2e)

Crystal structures for some Group IVB methyleneamine derivatives are discussed in the experimental part of this chapter.

The methyleneamines chosen for study must fulfill the following criteria. Dialkylmethyleneamines containing \(\alpha\)-hydrogen atoms need to be avoided, because of the possibility of ketimine-enamine tautomerism\(^{290,335}\) (e.g. Fig. 2-4). Bulky substituents such as

[Chemical structures]

\(t\)-butyl are commonly used to discourage association via imine bridges.

The imines used in the course of this work were di-\(t\)-butylmethylenamine (which possesses no \(\alpha\)-hydrogen), and diphenylmethylenamine together with some of its \(p, p'\)-disubstituted derivatives (di-\(p\)-tolyl and di-\(p\)-chloro). Other workers have made use of bis(trifluoromethyl)methyleneamine.\(^{291,292}\)
The diphenyl compound has some spectroscopic disadvantages (the complexity of the phenyl $^1$H-NMR signals prevents their use for determination of whether the molecule is bent at nitrogen), but it is convenient for the development of preparative routes, and frequently provides crystalline derivatives. The di-t-butyl, -p-tolyl, and -trifluoromethyl methyleneamines are more useful spectroscopically.

2.3 Spectroscopic Studies on methyleneamino-derivatives

A. Nuclear Magnetic Resonance Spectroscopy

For NMR spectroscopic study, the substituent groups $R$ in the methyleneamine group $R_2CN$ are chosen so as to give a single signal (e.g. $R = ^t$Bu, CF$_3$, or CH$_3$ in p-CH$_3$C$_6$H$_4$). If both $R$ groups are in magnetically equivalent environments, as would be expected for a linear skeleton (Fig. 2-5a), then only one absorption should be observed, whereas if the structure is bent at nitrogen (Fig. 2-5b), the groups $R$ will be in magnetically inequivalent environments and two signals would be expected.

![Figure 2-5](image_url)
Unfortunately, owing to the relatively low energy barrier to inversion at nitrogen in the bent system (Fig. 2-5c), resolution of the signals from R and R' is rarely observed at normal temperatures (the N-aminomethyleneamine \( t^2Bu_2C=N-NMe_2 \) has been found to exhibit two \( t^2Bu \) resonances in its \( ^1H \)-NMR spectrum at temperatures as high as 136°C, but this is an isolated example).

On cooling, however, the rate of inversion may be slowed sufficiently relative to the NMR time-scale to allow resolution. For example, the spectrum of \( t^2Bu_2CNH \) shows only a single \( t^2Bu \) absorption at room temperature, but on cooling to -30°C this splits into two signals of equal intensity.

Syn-anti isomerism in methyleneamines and the associated inversion process at nitrogen has attracted considerable interest, and has been reviewed. The mechanism has been studied, and the magnitude of the inversion barrier has been determined for several N-alkylated and -arylated compounds. The activation energy for the process is generally found to be 15-20 kcal.mole\(^{-1}\). Similar, though somewhat lower, values were obtained for a series of N-cyanomethyleneamines, \( R_2C=N-C\equiv N \) (R = Me, SMe, OMe, NMe\(_2\)).

Interestingly, N-metallated methyleneamines seem to have much lower barriers to inversion than their N-organo counterparts. Thus in the proton-NMR spectrum of the unsymmetric germanium derivative \( p-CF_3C_6H_4(Ph)C=NGeMe_3 \) the methyl groups show a single sharp absorption at temperatures \( \geq 70^\circ C \). At \( -110^\circ C \), their spectrum consists of two overlapping singlets corresponding to the syn- and anti-forms. The inversion barrier is calculated as 9.2 kcal.mole\(^{-1}\).

Theoretical calculations have established a correlation between the electronegativity of the substituent on nitrogen and the magnitude of the inversion barrier, which may account for the low rate of inversion.
of $^{t}$Bu$_2$CNNMe$_2$, but for N-metallated species, because most metals have accessible vacant orbitals, inversion may be facilitated by bimolecular exchange (Fig. 2-6), or stabilisation of a linear intermediate by N-M $\pi$-interaction, $R_2C=N\equiv M$.

![Figure 2-6](image)

**B. Infra-red Spectroscopy**

The azomethine stretching frequencies, $\nu(C=N)$, for the methyleneamines used in this work are listed in Table 8. The change in this value on substitution at nitrogen by an organometallic group has been used as an indication of whether the CNM unit is bent or linear and hence of the extent of N$\rightarrow$M dative $\pi$-bonding.

**TABLE 8**

$\nu(C=N)$ for some methyleneamines, $R_2C=NH$

<table>
<thead>
<tr>
<th>R</th>
<th>$\nu(C=N)$ cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>1603</td>
<td>335</td>
</tr>
<tr>
<td>p-CH$_3$C$_6$H$_4$</td>
<td>1597</td>
<td>345</td>
</tr>
<tr>
<td>p-ClC$_6$H$_4$</td>
<td>1590</td>
<td>344</td>
</tr>
<tr>
<td>$^{t}$Bu</td>
<td>1604</td>
<td>a</td>
</tr>
</tbody>
</table>

a: This work. Previously reported as 1610 cm$^{-1}$ 344
For N-metallated methyleneamines, \( R_2C\equiv N-MX \), linearity in the CNM skeleton has been found to lead to an increase in \( \nu(C=\equiv N) \) relative to the parent imine. For derivatives of the lighter metals and metalloids, this increase may be as much as 100-140 cm\(^{-1}\). The effect has been rationalised in terms of coupling between the C=N and N=\( M \) vibrations (maximised by the linearity of the cumulated \( \pi \)-system), the observed high energy absorption corresponding to the asymmetric stretching vibration of the C=N=\( M \) unit. \(^{346}\) It may also be compared to the shift in \( \nu(C=\equiv N) \) to higher energy observed when the parent imines complex with strong Lewis acids. \(^{344}\) This parallels the similar effect for nitriles, \(^{347}\) which is believed to arise in part from the mechanical constraint applied to the nitrogen upon coordination, \(^{384-6}\) although there is crystallographic evidence \(^{348,349}\) that coordination is accompanied by a slight shortening of the C=\( N \) bond, i.e. by an increase in bond order and bond strength. The increase in \( \nu(C=\equiv N) \) for coordinated methyleneamines or linear C=N=\( M \) systems may also be rationalised in terms of bond order changes.

The azomethine stretching frequencies of those compounds whose crystal structures are known are given in Table 9. It may be seen that compounds containing more than one type of imino-group give more than one absorption in the azomethine stretching region. The lower values are attributed to bridging imino-groups, and the higher to those terminally bonded, it being argued that the absence of a cumulative C=N=\( M \) \( \pi \)-system for the bridged form gives rise to a weaker C=N bond and hence a lower energy stretching vibration. The effect of an additional massive metal atom bonded to the nitrogen will also tend to lower the energy of the C=N vibration, as a result of which bent terminal methylamino groups absorb at frequencies between those of linear and bridging groups attached to a given element. The
tris-imino boron compound has slightly bent CNB units (bond angle 165°) and therefore a lower C=N stretching frequency than the essentially linear diphenylmethyleneaminoboron derivative, consistent with a lower C-N bond order (the expected C-N bond order would be 1.33, since the boron atom has only one vacant orbital, and can therefore accept only one third of an electron pair from each nitrogen in (tBu₂CN)₃B). The phosphorus derivative, which appears to contain little or no (p-d) π-bonding, the CNP angles being 120°, shows little variation in \( \nu(C=N) \) from the parent imine.

Although the azomethine stretching frequency forms a reasonably good guide to the skeletal geometry, particularly for derivatives of the lighter elements, other factors may also affect \( \nu(C=N) \). These may be considered under two headings: the nature of the central metal, and other substituent effects.
The nature of the central metal.

The more electronegative the group attached to nitrogen, the lower should be the electron density in the $\geq C=N -$ link, and therefore the C=N stretching frequency should also be lower. However, this is often dominated by other effects; for example the electronegativities of the Group IVB elements follow the series C$\rangle$Pb$\rangle$Ge$\rangle$Sn$\approx$Si,$^{352}$ and it may be observed that the $\nu(C=N)$ frequencies for their methyleneamino derivatives do not follow this trend (Table 10).

Another property of the metal atom that will have an effect will be its size. Orbital overlap is more effective between orbitals of like size, i.e. 2p-2p $\pi$-overlap will be most effective, 2p-3p or d less so, and so on. Hence the lighter the element, the more likely will be dative $\pi$-bonding with nitrogen, with its associated linear or partially bent CNM skeleton in the case of a methyleneamine derivative. This effect is well shown for Group IVB in Table 10, the azomethine frequencies decreasing Si$\rangle$Ge$\rangle$Sn, the inference being that $N\rightarrow M$ (p$\rightarrow$d) $\pi$-interactions decrease down the group.

The mass of the metal is also important, since more massive substituents on nitrogen will lower the azomethine stretching frequency. Increased mass also appears to have the effect of reducing the separation of the $\nu(C=N)$ absorptions for imino-groups with different structural geometries. This effect can be seen to a certain extent in Table 10, where the difference between the trimethyl- and triphenyl-derivatives decreases from silicon to germanium, and disappears at tin. It is also visible in the variation of terminal and bridging $\nu(C=N)$ frequencies for analogous beryllium and magnesium compounds (Table 11).
**TABLE 10**

\[ \gamma(C=N) \text{ frequencies for some diphenylmethyleneamino derivatives of the Group IVB elements.} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>( \gamma(C=N) \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ph}_2\text{CNMMMe}_3 )</td>
<td>Si</td>
<td>1642</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1630</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>1613</td>
</tr>
<tr>
<td>( \text{Ph}_2\text{CNMPH}_3 )</td>
<td>Si</td>
<td>1662</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1633</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>1613</td>
</tr>
</tbody>
</table>

(cf. \( \text{Ph}_2\text{CNH} \); \( \gamma(C=N) = 1603 \text{cm}^{-1} \))

**TABLE 11**

\[ \gamma(C=N) \text{ frequencies for some related imino-beryllium and magnesium derivatives.} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \gamma(C=N) \text{cm}^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \left[\left(\text{Ph}_2\text{CN}\right)_2\text{Be}\right]_n )</td>
<td>Terminal 1732 Bridging 1627</td>
<td>353</td>
</tr>
<tr>
<td>( \left[\left(\text{Ph}_2\text{CN}\right)_2\text{Mg}\right]_n )</td>
<td>Terminal 1650 Bridging 1612</td>
<td>329</td>
</tr>
<tr>
<td>( \left[\left(\text{tBu}_2\text{CN}\right)_2\text{Be}\right]_2 )</td>
<td>Terminal 1721 Bridging 1631</td>
<td>380</td>
</tr>
<tr>
<td>( \left[\left(\text{tBu}_2\text{CN}\right)_2\text{Mg}\right]_2 )</td>
<td>Terminal 1665 Bridging 1604</td>
<td>329</td>
</tr>
</tbody>
</table>
Substituent effects

In the generalised methyleneamine derivative \( R_2C\equiv N-M^X \) the substituents \( X \) on the metal \( M \) may influence the metal-nitrogen bond (and hence the \( \nu(C\equiv N) \) frequency) by both \( \sigma \) and \( \pi \) effects. Electron-releasing groups will tend to weaken the metal-nitrogen \( \sigma \)-bond by reducing its polarity, while electron-withdrawing groups tend to strengthen it. The resulting increase in polarity may also encourage \( N\rightarrow M \) dative \( \pi \)-bonding.

The \( \pi \)-bonding ability of \( X \) may also be important; apart from competing with the nitrogen lone pair for the metal orbitals, \( X\rightarrow M \) \( \pi \)-back-donation would also reduce the ability of the metal to accept further electron-density from nitrogen.

The electronic effects of the groups \( R \) may also influence \( \nu(C\equiv N) \); although Table 8 shows comparatively little difference between the parent imines (an exception is \((CF_3)_2C\equiv NH\), with \( \nu(C\equiv N) = 1702\text{cm}^{-1}\)), there is often considerable variation between derivatives of different imines with similar structures, pointing to differing \( N\rightarrow M \) \( \pi \)-bonding abilities.

C. Ultra-Violet Spectroscopy.

The presence of the potential chromophore \( C\equiv N \) in the methyleneamine system has led to comparatively little study in the field of \( N\)-metallated methyleneamines, the only reported investigation having concerned a series of diarylmethyleneamino derivatives of the Group IVB elements. \(^{290}\) Each spectrum showed two absorptions in the range 200-400\(\text{m} \mu\), corresponding to the \( n\rightarrow \pi^* \) transition of a nitrogen non-bonding electron and the \( \pi\rightarrow \pi^* \) transition of the \( C\equiv N\rightarrow M \) \( \pi \)-system. (Fig. 2-7).
If the nitrogen lone pair is involved in (p→d) π-bonding, a shift in the n→π* transition would be expected if π-electron donating groups (e.g. Ph, vinyl, -OR, -NR₂) on the metal are in competition with it. No such shift was observed for silicon, leading to the conclusion (probably erroneous in the light of crystallographic data quoted later) that the C=N-Si unit is fully bent, involving little or no N≡Si π-bonding. However, it has been suggested³²⁹ that, if the energies of both the π* and n levels were lowered to about the same extent by substitution at nitrogen, the n→π* transition will not significantly alter on further substitution, in which case the results could accommodate both linear and bent C=N-Si units.
Energy levels and transitions for the C=N-Si group

Figure 2-7

2.4 **Experimental**

The majority of products, and many of the reactants, were air and moisture sensitive. All procedures were therefore carried out under an atmosphere of dry nitrogen (see Appendix for details).

**A. Diphenylmethyleneamine derivatives**

i) **Reaction of diphenylmethyleneaminolithium with tin tetrachloride**

(Mole ratio 4:1)

A solution of 30 mmol. diphenylmethyleneaminolithium in approximately 55ml. dry diethyl ether/hexane was cooled to -196° and 0.88ml. tin tetrachloride (7.5 mmol.) was added. The mixture was allowed to warm to room temperature with stirring and occasional vigorous shaking to break up the solid masses which tended to form. The characteristic red colour of the imino-lithium faded, and at room temperature the reaction mixture consisted of a yellow solution over a bright yellow precipitate. The mixture was stirred at room temperature for ~3 hours, then filtered and the yellow solid was pumped dry. 40ml. dry toluene were added and the mixture was heated to ~90° with stirring and filtered while hot, giving a white filter cake (LiCl) and a yellow solution, which on cooling deposited bright yellow bipyramidal crystals of tetrakis-(diphenylmethyleneamino)tin(iv), \((\text{Ph}_2\text{CN})_4\text{Sn}^\text{IV}\), M.Pt. 170-180° (sealed tube).

(Found: C 75.5, H 5.2, N 7.0, Cl 0%)

C\(_{52}\)H\(_{40}\)N\(_4\)Sn requires: C 74.4, H 4.8, N 6.7, Cl 0%.

\(\nu_{\text{max}}\) (Nujol mull): 3081w, 3059mw, 3026 mw, 1964vw, 1953 vw, 1893 vw, 1816vw, 1600 sh, 1590 vs, 1568 vs, 1560 sh, 1496 sh, 1489 mw, 1445s, 1442 s, 1310 mw, 1261 s, 1194 vw, 1184 sh, 1176 m, 1161 mw, 1153 sh, 1075 mw,
Reaction of diphenylmethyleneaminolithium with tin tetrachloride (Mole ratio 3:1)

A solution of $30\text{mmol.} \text{Ph}_2CN\text{Li}$ in $50\text{ml.}$ dry diethyl ether/hexane was cooled to $-196^\circ$ and $1.17\text{ ml.}$ tin tetrachloride ($10\text{mmol.}$) was added. The mixture was allowed to warm to room temperature with stirring, and was then stirred at room temperature for $\sim 5$ hours, by which time it consisted of a yellow solution over a yellow solid. The latter was filtered off, dried, and mixed with $50\text{ ml.}$ dry toluene. The mixture was heated to $\sim 90^\circ$ and filtered while hot, giving a white solid (LiCl) and a dark yellow solution. The latter on standing at $-10^\circ$, deposited a yellow crystalline mass, which on isolation and drying formed a yellow powder identified as tris(diphenylmethyleneamino)tin(iv) chloride $[(\text{Ph}_2\text{CN})_3\text{SnIVCl}]_n$, M.P. $140-5^\circ$ (sealed tube).

(Found: C 68.6, H 4.9, N 6.2, Cl 5.3%)

$\text{C}_{39}\text{H}_{30}\text{N}_3\text{SnCl}$ requires: C 67.4, H 4.3, N 6.1, Cl 5.1 %

$\nu_{\text{max}}$(Nujol mull): 3080sh, 3057mw, 3022mw, 1950vw, 1880vw, 1810vw, 1612vs, 1597sh, 1574s, 1535s, 1525sh, 1489m, 1444s, 1309mw, 1285sh, 1267ms, 1194vw, 1180w, 1158w, 1147vw, 1076w, 1030mw, 1003w, 969vw, 948w, 938mw, 908mw, 890sh, 844vw, 789m, 773s, 731mw, 706sh, 697vs, 680sh, 667mw, 660mw, 650mw, 625mw, 608sh, 523mw, 505sh, 469sh, 455w, 432mw cm$^{-1}$.

Reaction of diphenylmethyleneaminolithium with tin tetrachloride (Mole ratio 2:1)

A solution of $30\text{ mmol.}$ diphenylmethyleneaminolithium in approximately $50\text{ ml.}$ dry ether/hexane was cooled to $-196^\circ$ and $1.76\text{ ml.}$ tin tetrachloride ($15\text{ mmol.}$) was added. The mixture was allowed to
warm to room temperature with stirring, then stirred for \( \sim 3 \frac{1}{2} \) hours. The resulting cream-coloured precipitate was filtered from the yellow solution and pumped dry. It was then mixed with 75 ml. dry toluene, heated to \( \sim 90^\circ \), and filtered while hot, leaving a white filter cake of lithium chloride. On cooling, the resulting deep yellow solution deposited colourless needle crystals of \( \text{bis(diphenylmethyleneamino)tin(iv) dichloride, } [(\text{Ph}_2\text{CN})_2\text{Sn}^{IV}\text{Cl}_2]_n, \text{ M.Pt. } 185-190^\circ \text{ (sealed tube).} \)

(Found: C 60.6, H 3.4, N 5.2, Cl 11.4% 
\( \text{C}_{26}\text{H}_{20}\text{N}_2\text{SnCl}_2 \text{ requires: } \text{C } 56.1, \text{H } 3.6, \text{N } 5.0, \text{Cl } 12.7\% \))

\( \gamma_{\text{max}} \text{(Nujol mull): } 3080\text{sh}, 3055\text{mw}, 3020\text{mmw}, 1960\text{vw}, 1900\text{vw}, 1817\text{vw}, 1607\text{s}, 1590\text{s}, 1567\text{sh}, 1553\text{vs}, 1489\text{m}, 1446\text{s}, 1402\text{w}, 1319\text{w}, 1310\text{w}, 1291\text{mw}, 1272\text{m}, 1181\text{mw}, 1161\text{w}, 1146\text{vw}, 1075\text{mmw}, 1029\text{mmw}, 1001\text{mw}, 972\text{vw}, 951\text{mw}, 938\text{mw}, 914\text{vw}, 892\text{sh}, 850\text{w}, 788\text{m}, 780\text{ms}, 773\text{m}, 729\text{ms}, 712\text{s}, 702\text{sh}, 696\text{vs}, 670\text{m}, 661\text{m}, 624\text{vw}, 617\text{vw}, 532\text{mw}, 468\text{w}, 456\text{w}, 435\text{w}, 367\text{vw}, 348\text{vw} \text{ cm}^{-1} \).

iv) **Reaction of diphenylmethyleneaminolithium with tin tetrachloride**

**(Mole ratio 1:1)**

This reaction gave rise to an ortho-metallated product rather than the desired diphenylmethyleneaminotin(iv)trichloride, \( \text{Ph}_2\text{CNSnCl}_3 \). It is therefore described and discussed with other ortho-metallation reactions of tin in Chapter 5.

v) **Reaction of diphenylmethyleneaminolithium with germanium tetrachloride**

**(Mole ratio 1:1)**

A solution of 15 mmol. diphenylmethyleneaminolithium in \( \sim 50 \text{ml.} \) dry ether/hexane was cooled to \(-196^\circ\) and 1.74 ml. germanium tetrachloride (15 mmol.) was added. The mixture was allowed to warm to room temperature with stirring, then stirred overnight. Removal of solvent
from the resulting yellow solution over a white precipitate left an 
opaque, viscous, yellowish oil. Extraction of this with hot toluene 
yielded a white solid (LiCl) and a yellow solution, removal of solvent 
from which produced a brownish-yellow, viscous, cloudy oil, believed 
to be diphenylmethyleneaminobermanium trichloride \( \text{Ph}_2\text{CNGeCl}_3 \).

\[ \gamma \max (\text{Thin film}): 3108\text{sh}, 3091\text{w}, 3069\text{mw}, 3038\text{w}, 2968\text{w}, 2938\text{w}, 2870\text{vw}, 1973\text{vw}, 1910\text{vw}, 1818\text{vw}, 1730\text{vw}, 1624\text{sh}, 1609\text{vs}, 1593\text{vs}, 1571\text{vs}, 1565\text{sh}, 1495\text{mw}, 1451\text{s}, 1318\text{s}, 1284\text{vs}, 1257\text{sh}, 1186\text{m}, 1164\text{mw}, 1079\text{mw}, 1033\text{m}, 1006\text{sw}, 978\text{vw}, 947\text{s}, 916\text{m}, 850\text{w}, 788\text{vs}, 752\text{w}, 706\text{vs}, 695\text{s}, 631\text{mw}, 621\text{vw}, 546\text{mw}, 434\text{vs}, 405\text{vs. cm}^{-1}. \]

The attempted distillation of this oil at 210°/0.1mm Hg failed, and 
on cooling the material set to a clear glass. Recrystallisation of 
this from a 1:1 toluene/hexane mixture gave a small quantity of 
colourless crystals, identified as bis(diphenylmethyleneamino)germanium 
dichloride (\( \text{Ph}_2\text{CN} \))\(_2\text{GeCl}_2 \), M.Pt. 110-125°.

(Found: C 60.1, H 3.7, N 5.5, Cl 15.0 % M = 540
\[ \text{C}_{26}\text{H}_{20}\text{N}_2\text{GeCl}_2 \text{ requires: C 62.0, H 4.0, N 5.6, Cl 14.1% ; M = 504} \]

\[ \gamma \max (\text{Nujol mull}): 3090\text{w}, 3072\text{sh}, 3060\text{mw}, 3031\text{mw}, 1989\text{vw}, 1971\text{w}, 1968\text{vw}, 1929\text{vw}, 1910\text{vw}, 1888\text{vw}, 1820\text{vw}, 1780\text{vw}, 1728\text{vw}, 1697\text{vw}, 1626\text{sh}, 1610\text{vs}, 1596\text{vs}, 1577\text{vs}, 1496\text{s}, 1452\text{vs}, 1337\text{vw}, 1317\text{vs}, 1300\text{s}, 1281\text{sh}, 1275\text{vs}, 1254\text{sh}, 1188\text{s}, 1185\text{s}, 1172\text{sh}, 1165\text{m}, 1160\text{sh}, 1081\text{m}, 1032\text{m}, 1007\text{m}, 994\text{vw}, 986\text{sh}, 980\text{w}, 975\text{w}, 948\text{s}, 939\text{m}, 918\text{s}, 893\text{mw}, 851\text{w}, 793\text{vs}, 785\text{s}, 753\text{mw}, 734\text{mw}, 708\text{vs}, 699\text{vs}, 691\text{s}, 682\text{s}, 633\text{sh}, 629\text{m}, 622\text{w}, 577\text{vw}, 548\text{m}, 542\text{sh}, 478\text{w}, 448\text{vs}, 425\text{s}, 419\text{s}, 409\text{vs}, 320\text{w. cm}^{-1}. \)
vi) Reaction of diphenylmethyleneamine with silicon tetrachloride in the presence of triethylamine (Mole ratio 1:1:1)

3.65 ml. diphenylmethyleneamine (21.84 mmol.) was added to a solution of 2.5 ml. silicon tetrachloride (21.84 mmol.) in 60 ml. dry toluene with stirring. The solution became yellow and a pale yellow precipitate formed. The mixture was heated to boiling and 3.22 ml. dry triethylamine (21.84 mmol.) was added. An immediate voluminous white precipitate formed under a bright yellow solution. A further 20 ml. toluene was added to facilitate stirring, and the mixture was refluxed for ~2 hours. Filtration of the mixture yielded a white solid (identified as triethylamine hydrochloride by comparison of its infra-red spectrum with that of a genuine sample) and a yellow solution. The solvent was removed under vacuum and replaced by 20 ml. dry hexane. Concentration and cooling of the resulting yellow solution yielded a pale yellow semi-crystalline solid, identified as bis(diphenylmethyleneamino)dichlorosilane, \((\text{Ph}_2\text{CN})_2\text{SiCl}_2\), by comparison of its infra-red spectrum with the published data.\(^{355}\)

(Found: C 68.5, H 5.2, N 5.4, Cl 16.5%; C\(_{26}H_{20}N_2\text{SiCl}_2\) requires: C 67.1, H 4.4, N 6.1, Cl 15.5%).

vii) Reaction of bis(diphenylmethyleneamino)dichlorosilane with silicon tetrachloride

To 4.5 g. bis(diphenylmethyleneamino)dichlorosilane (~10 mmol.) were added 10 ml. silicon tetrachloride (large excess). On heating to boiling point the yellow iminosilane slowly dissolved. The mixture was refluxed overnight, then filtered to remove small quantities of decomposition products, yielding a pale yellow solution which on cooling to ~10\(^{\circ}\) slowly deposited colourless crystals. These redissolved very
readily on warming, and only sufficient product could be obtained for one infra-red spectrum and preliminary analysis. This was tentatively identified as diphenylmethyleneaminotrichlorosilane, \( \text{Ph}_2\text{CNSiCl}_3 \).

(Found: C 52.4%; \( \text{C}_{13}\text{H}_{10}\text{NSiCl}_3 \) requires C 51.3%)

\( \gamma_{\text{max}} \) (Nujol mull): 3085sh, 3063w, 3031w, 1954vw, 1920vw, 1819vw, 1650vs, 1599s, 1582m, 1452s, 1404vw, 1326mw, 1279s, 1198sh, 1184mw, 1168m, 1078m, 1004vw, 976w, 941mw, 916m, 875s, 847vw, 800mw, 761vw, 730w, 706vs, 637s, 618m, 598vs, 589vs, 556mw, 472mw, 456vw. cm\(^{-1}\).

B. Di-t-butylmethyleneamine derivatives

i) Reaction of di-t-butylmethyleneaminolithium with tin tetrachloride (Mole ratio 4:1)

1.76ml. tin tetrachloride (15 mmol.) was added to a solution of 60 mmol. di-t-butylmethyleneaminolithium in 85ml. dry pentane at -196°. On warming to room temperature, with stirring, the characteristic lemon-yellow colour of the imino-lithium darkened to yellow-orange, and a pale yellow precipitate formed. The mixture was stirred overnight at room temperature, then the solvent was removed under vacuum and replaced by 40ml. dry toluene. The mixture was then heated to boiling point and filtered while hot, yielding a white solid (LiCl) and a golden-yellow solution. The latter was evaporated to dryness and the resulting crystalline residue was recrystallised from 40ml. dry hexane, giving colourless bipyramidal crystals of tetrakis(di-t-butylmethyleneamino)tin(iv), \( (\text{tBu}_2\text{CN})_4\text{Sn}^{\text{IV}} \), M.Pt. 110-120° dec. (sealed tube).

(Found: C 63.6, H 10.6, N 8.2, Cl 0%; \( \text{M} = 653 \). \( \text{C}_{36}\text{H}_{72}\text{N}_4\text{Sn} \) requires: C 63.5, H 12.3, N 8.7, Cl 0%; \( \text{M} = 679 \)).
\( \gamma_{\text{max}} \) (Nujol mull): 1738w, 1627vs, 1460vs, 1383s, 1360vs, 1320vw, 1258vw, 1217s, 1204sh, 1174vw, 1037m, 948s, 928sh, 876vw, 838w, 810vw, 793w, 723vw, 693m, 577mw, 534mw, 471mw, 374vw. cm\(^{-1}\).

ii) Reaction of di-t-butylmethyleneaminolithium with tin tetrachloride

(Mole ratio 3:1)

1.76ml. tin tetrachloride (15 mmol.) was added to a solution of 45 mmol. di-t-butylmethyleneaminolithium in 65 ml. dry pentane at \(-196^\circ\). The mixture was allowed to warm to room temperature with stirring, at which point it consisted of a yellow solution over a yellow solid. On stirring overnight the colour of the solid faded to white. The mixture was then filtered, giving a white solid (LiCl) and a yellow solution, which on removal of solvent yielded a viscous yellow oil, tris(di-t-butylmethyleneamino)tin(iv) chloride, \((^{t}\text{Bu}_2\text{CN})_3\text{Sn}^{IV}\text{Cl}\), B.Pt. 95-125\(^\circ\)/0.5mm Hg. w. extensive decomposition.

(Found: C 54.7, H 8.2, N 7.8, Cl 6.9 %; \( M = 360 \) dec.
\( C_{27}H_{56}N_3\text{SnCl} \) requires: C 56.4, H 9.4, N 7.3, Cl 6.2 %; \( M = 574.2 \))

\( \gamma_{\text{max}} \) (Thin film): 2980sh, 2950vs, 2915vs, 2867s, 1736vw, 1627vs, 1480s, 1456sh, 1388s, 1364vs, 1323vw, 1260vw, 1218m, 1204sh, 1168w, 1038m, 953s, 930mw, 876vw, 839vw, 807sh, 792w, 698mw, 576w, 546mw, 472mw, 381vw. cm\(^{-1}\).

(The infra-red spectrum of the pale yellow distillate revealed it to be a mixture of t-butyl cyanide, \(^t\text{BuCN}, \) and di-t-butylmethyleneamine, \(^t\text{Bu}_2\text{CNH}, \) together with a little imino-tin).

iii) Reaction of di-t-butylmethyleneaminolithium with tin tetrachloride

(Mole ratio 2:1)

A solution of 60 mmol. di-t-butylmethyleneaminolithium in 85ml. dry
pentane was cooled to -196° and 3.5ml. tin tetrachloride (30 mmol.) were added. The mixture was allowed to warm to room temperature with stirring, and then stirred overnight. The resulting white precipitate of lithium chloride was filtered off and the yellow solution was evaporated to dryness, yielding a mobile yellow oil, identified as bis(di-t-butylmethyleneamino)tin(IV)dichloride, (tBu₂CN)₂SnIVCl₂, which decomposed rapidly at ~60° or over ~14 days at room temperature.

(Found: C 48.5, H 6.7, N 5.9, Cl 14.5 %.

C₁₈H₃₆N₂SnCl₂ requires: C 45.9, H 7.7, N 6.0, Cl 15.1 %).

νmax (Thin film): 2952vs, 2921s, 2868s, 1720vw, 1627vw, 1478s, 1467s, 1457sh, 1387m, 1363s, 1322vw, 1257w, 1216m, 1204sh, 1162m, 1038mw, 1016w, 953m, 929mw, 877vw, 838vw, 816sh, 806w, 792w, 697mw, 570w, 545mw, 466w, 380 vw. cm⁻¹.

iv) Attempted reaction of di-t-butylmethyleneaminolithium with tin tetrachloride (Mole ratio 1:1)

A solution of 30 mml. di-t-butylmethyleneaminolithium in 70ml. dry pentane was cooled to -196° and 3.5ml. tin tetrachloride (30 mmol.) were added. The mixture was allowed to warm to room temperature with stirring, at which point it consisted of a yellow solution over a voluminous yellow precipitate. On stirring overnight, the colour of the solid faded to white. The mixture was filtered, and the solid was washed with a little pentane and pumped dry. The infra-red spectrum showed nothing but a few very weak bands attributable to traces of t-butyl cyanide. Analytical data indicated that the solid consisted of a 1:1 mixture of lithium chloride and tin(ii) dichloride.

(Found: Li 2.7, Cl 42.0 %, leading to Li:Cl = 1:3.06.

LiSnCl₃ requires Li 3.0, Cl 45.8%).
Removal of solvent from the filtrate gave a sticky pale yellow semi-crystalline solid in very low yield. The infra-red spectrum showed some similarities to those of the decomposition products of \((\text{Bu}_2\text{CN})_2\text{SnCl}_2\).

(v) Reaction between tris(di-t-butylmethylenearmino)tin(iv)chloride and lithium tris(di-t-butylmethylenearmino)tin(ii)

A solution of 0.973g. tris(di-t-butylmethylenearmino)tin(iv)chloride (1.69 mmol.) in 10ml. dry pentane was added to a solution of 0.920g lithium tris(di-t-butylmethylenearmino)tin(ii) (1.68 mmol.) in 20ml. dry pentane at 0\(^\circ\). On warming to room temperature a white precipitate began to form and the colour of the solution changed from greenish-yellow to a bright yellow-orange. The mixture was stirred overnight and filtered to remove lithium chloride. On standing, more precipitate formed, so all solvent was removed under vacuum, replaced by 30ml. dry toluene, and the mixture was refluxed for one hour. The resulting orange-brown, slightly hazy solution was evaporated to dryness, and the residue was heated with 30ml. dry hexane and filtered, giving a yellow solution and a small amount of brown solid, identified from its infra-red spectrum as a decomposition product, the result of exposure to slight traces of air or moisture. The extremely air-sensitive solution was concentrated to ~5ml. and left at ~-10\(^\circ\) for several weeks, over which time it deposited large colourless cubic crystals of hexakis(di-t-butylmethylenearmino)ditin(iv), \((\text{Bu}_2\text{CN})_6\text{SnIV}_2\), m.pt. 110-20\(^\circ\) (sealed tube).
(Found: C 62.6, H 9.8, N 7.2%; M = 538 dec.

C_{54}H_{108}N_{6}Sn_{2} requires: C 60.1, H 10.0, N 7.8%; M = 1078)

\nu_{\text{max}} (Nujol Mull): 1740vw, 1631vs, 1464s, 1383s, 1360vs, 1260vw, 1217m,
1202sh, 1038m, 947s, 928mw, 838vw, 810sh, 791w, 723vw, 692m, 578w, 545w,
472mw. \text{cm}^{-1}.

vi) Thermal decomposition of bis(di-t-butylmethyleneamino)tin(iv)dichloride

On standing at room temperature for \(\sim 10\) days (or on heating to \(\sim 60^\circ\))
a sample of bis(di-t-butylmethyleneamino)tin(iv)dichloride deposited a
yellow crystalline solid. This was filtered off, washed with a little
pentane, pumped dry, and identified as bis(di-t-butylmethylenaminotin(ii)-
chloride)hydrochloride, \((^{t}\text{Bu}_{2}\text{CNSn}^\text{II} \text{Cl})_{2}\cdot \text{HCl}\) or \((^{t}\text{Bu}_{2}\text{CN})_{2}\text{HSn}_{2}^\text{Cl}_{3}\),
M.Pt.: 100-130\(^{\circ}\), loss of \(^{t}\text{Bu}_{2}\text{CNH}, \text{mats} 149-153\(^{\circ}\) dec. (sealed tube).

(Found: C 35.3, H 4.9, N 4.3, Cl 15.5 %

C_{18}H_{37}N_{2}Sn_{2}Cl_{3} requires: C 34.6, H 5.9, N 4.5, Cl 17.0 %)

\nu_{\text{max}} (Nujol mull): 3280mw, 1596sh, 1586s, 1552vs, 1481vs, 1398s, 1387s,
1366vs, 1319w, 1258vw, 1224m, 1203s, 1040mw, 966m, 941mw, 930mw, 866m,
843w, 834w, 791vw, 736vw, 728w, 722sh, 658mw, 600m, 565vw, 544vw, 487mw. \text{cm}^{-1}.

The supernatant liquor exhibited a band in the infra-red spectrum
at 2218 cm\(^{-1}\), corresponding to \(\nu(C=N)\) in t-butyl cyanide.

The filtrate was extracted with 30ml. hot pentane, yielding an
intractable yellow-brown solid residue and a pale greenish-yellow solution,
which on cooling to \(-10^\circ\) deposited a small amount of pale leafy crystals,
apparently tris(di-t-butylmethylenaminotin(ii)chloride)dihydrochloride,
\((^{t}\text{Bu}_{2}\text{CNSn}^\text{II} \text{Cl})_{3}\cdot 2\text{HCl}\) or \((^{t}\text{Bu}_{2}\text{CN})_{3}\text{H}_{2}\text{Sn}_{3}^\text{Cl}_{5}\), M.Pt. 70-71\(^{\circ}\) (sealed tube).
(Found: C 34.1, H 5.9, N 5.2, Cl 21.0%)

C_{27}H_{56}N_{33}SnCl_{35} requires: C 33.9, H 5.9, N 4.4, Cl 18.6%)

\gamma_{\text{max}}^\nu (Nujol mull): 3245\text{sh}, 3156\text{br.vs}, 1671\text{vs}, 1653\text{sh}, 1632\text{m}, 1604\text{vw},
1587\text{w}, 1578\text{w}, 1534\text{m}, 1400\text{mv}, 1365\text{s}, 1308\text{vw}, 1332\text{w}, 1311\text{w}, 1172\text{m}, 1152\text{s},
970\text{vw}, 937\text{sh}, 903\text{s}, 842\text{mv}, 755\text{vw}, 738\text{mw}, 723\text{w}, 663\text{sh}, 645\text{mw}, 570\text{s}, 540\text{sh},
494\text{mv}, 478\text{mv}, 460 \text{ w. cm}^{-1}.

vii) Reaction of di-t-butylmethyleneamine with tin tetrachloride (Mole ratio 1:1).

1.17ml. tin tetrachloride (10 mmol.) were dissolved in 20ml. dry pentane and 1.8ml. di-t-butylmethyleneamine (10 mmol.) were added dropwise with stirring at room temperature. A white precipitate formed immediately under a pale greenish-yellow solution. The precipitate was filtered off, washed with a little pentane, and pumped dry. The resulting white powder was identified as di-t-butylmethyleneamine tin tetrachloride, \( \text{tBu}_2\text{CNH.SnCl}_4 \), m.pt. 210-12\degree dec., sublimation (sealed tube).

(Found: C 28.3, H 4.7, N 4.9, Cl 37.0%)

C_{9}H_{19}NSnCl_{4} requires: C 26.9, H 4.7, N 3.5, Cl 35.4%)

\gamma_{\text{max}}^\nu (Nujol mull): 3376\text{s}, 3310\text{sh}, 3276\text{s}, 3233\text{sh}, 1712\text{m}, 1653\text{sh}, 1641\text{vs},
1576\text{sh}, 1568\text{s}, 1559\text{sh}, 1523\text{m}, 1479\text{vs}, 1400\text{s}, 1311\text{w}, 1222\text{mw}, 1212\text{mw},
1196\text{w}, 1159\text{s}, 1048\text{w}, 1033\text{w,972\text{mw}, 942\text{w}, 935\text{w}, 903\text{vw}, 842\text{vs}, 795\text{vw}, 768\text{vw},
727\text{s}, 661\text{vw}, 643\text{w}, 588\text{vw}, 550\text{vw}, 534\text{vw},457\text{vw}, 358 \text{ m. cm}^{-1}.

The material was sufficiently volatile to sublime slowly at atmospheric pressure in direct sunlight, forming colourless cubic crystals on the walls of the storage vessel. Sublimation under reduced pressure resulted in a micro-crystalline form.
Reactive di-t-butylmethyleneamine with tin tetrachloride
(Mole ratio 2:1)

3.6ml. di-t-butylmethyleneamine (20 mmol.) were dissolved in 30ml.
dry pentane and 1.17ml. tin tetrachloride (10 mmol.) were added
dropwise with stirring. Transient yellow colours appeared, then a
thick cream-coloured precipitate formed under a pale yellow solution.
The mixture was stirred for 1½ hours, then filtered and the precipitate
was washed with a little pentane and pumped dry. The resulting off-
white powder was identified as bis(di-t-butylmethyleneamine) tin
tetrachloride, (Bu₂CNH)₂SnCl₄, m.pt. 137-9° dec. (sealed tube).

(Found: C 39.4, H 7.4, N 5.2, Cl 27.8%)

C₁₈H₃₈N₂SnCl₄ requires: C 40.5, H 7.0, N 5.2, Cl 26.2%.

υ max (Nujol mull): 3365m, 3287vs, 3190sh, 1725sh, 1662s, 1608sh,
1583s, 1538m, 1488vs, 1406sh, 1399s, 1324w, 1263w, 1228s, 1206mw, 1166m,
1054m, 1038w, 1023w, 977s, 936mw, 909vw, 879mw, 857vs, 850sh, 800mw, 731m,
667w, 650w, 596w, 557w, 542w, 442w, 336mw. cm⁻¹
2.5 Discussion

A. Preparation and Stability of Methyleneamino derivatives of Group IVB

The new compounds prepared are listed in Table 12. The decomposition products of ($^{t}$Bu$_2$CN)$_2$SnCl$_2$ are not listed here, since their spectroscopic and structural properties will be discussed in Chapter 3.

<table>
<thead>
<tr>
<th>New Methyleneamino derivatives of Group IVB elements in oxidation state (IV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph$_2$CN)$_4$Sn$^{IV}$</td>
<td>yellow crystals</td>
</tr>
<tr>
<td>[(Ph$_2$CN)$_3$Sn$^{IV}$Cl]$_n$</td>
<td>yellow powder</td>
</tr>
<tr>
<td>[(Ph$_2$CN)$_2$Sn$^{IV}$Cl$_2$]$_n$</td>
<td>colourless crystals</td>
</tr>
<tr>
<td>(Ph$_2$CN)$_2$GeCl$_2$</td>
<td>colourless crystals</td>
</tr>
<tr>
<td>Ph$_2$CNGeCl$_3$</td>
<td>yellow oil</td>
</tr>
<tr>
<td>Ph$_2$CNSiCl$_3$</td>
<td>colourless crystals</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CN)$_4$Sn$^{IV}$</td>
<td>colourless crystals</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CN)$_3$Sn$^{IV}$Cl</td>
<td>yellow oil</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CN)$_2$Sn$^{IV}$Cl$_2$</td>
<td>yellow oil</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CN)$_6$Sn$_2$</td>
<td>colourless crystals</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CNH).SnCl$_4$</td>
<td>white powder</td>
</tr>
<tr>
<td>($^{t}$Bu$_2$CNH)$_2$.SnCl$_4$</td>
<td>white powder</td>
</tr>
</tbody>
</table>

*: Tentative identification

All the new compounds are very air- and moisture-sensitive (the Sn-Sn bonded species particularly so), decomposing rapidly on slight
exposure with formation of the parent imine by hydrolysis of the metal-nitrogen bond. This hydrolytic instability parallels that of other methyleneamine derivatives of the Group IVB elements. Their relative stabilities to hydrolysis are of interest; a comparative study of the compounds \( \text{Me}_n \text{M(NC(CF}_3}_2 \text{n} \) (\( \text{M} = \text{Si, Ge, Sn; } n = 1\) to \( 4 \)) found that hydrolytic sensitivity increased \( \text{Si} < \text{Ge} < \text{Sn} \) and \( n = 1 \) to \( 4 \). The latter result was also found for the series \( (\text{Ph}_2 \text{CN})_n \text{SiR}_4\text{n} \) but the new compounds described here showed no such effect, possibly owing to the complicating presence of \( \text{M-Cl} \) bonds.

Also, while \( (\text{Ph}_2 \text{CN})_4 \text{Sn} \) resembles the corresponding silicon compound in its high sensitivity to atmospheric moisture, the germanium analogue is stable to air exposure for several hours. Other imino-germanium derivatives are very moisture sensitive, so that this is probably a kinetic effect associated with the crystal packing (the three \( (\text{Ph}_2 \text{CN})_4 \text{M} \) compounds have quite different arrangements in the crystal).

The new compounds are probably monomeric, with the exception of the diphenylmethyleneaminotin chlorides, \( (\text{Ph}_2 \text{CN})_n \text{SnCl}_4\text{n} \), \( n = 2, 3 \), for which the infra-red data, together with the results of a preliminary Mössbauer study, may be interpreted in terms of association. Mass spectra provided no firm evidence for dimeric or polymeric structures, and where the compounds were sufficiently soluble in cold benzene, cryoscopic molecular weights corresponding to the monomeric value were found (low values are due to partial sample decomposition in handling). All previously reported methyleneamino derivatives of the Group IVB elements (in oxidation state \( \text{iv} \)) are monomeric, the associated nature of the diphenylmethyleneaminotin chlorides being attributable to the greater Lewis acidity of tin(iv) halides. The di-t-butylmethyleneaminochlorotin chlorides are, however, almost certainly monomeric, which
may be due to the greater bulk of the t-butyl groups.

The observed molecular weight for \((tBu_2CN)_3Sn\) is very close, at 538, to half the formula weight of 1078, and it is tempting to suggest dissociation in solution to tris-imino-tin radicals (Eqn. 2.1), promoted by crowding of the bulky \(tBu\) groups. However, even quite crowded hexaorganoditins (e.g. hexa-o-tolyl ditin) show no evidence of dissociation in solution, so that the molecular weight must be low due to sample decomposition (the compound is extremely sensitive to traces of air), the observed value being fortuitous.

The preparative route to this compound parallels the standard synthetic route to hexaorganoditins (Eqns. 2.2 and 3), and is related to the procedure used for the majority of preparations in this chapter, i.e. the well-established metathetical reaction between a methyleneaminolithium and a metal chloride (Eqn. 2.4).

It proved possible to prepare the tetrakis(di-t-butylmethyleneamino) tin, \((tBu_2CN)_4Sn\), in contrast to the germanium and silicon systems, for which the most highly substituted derivatives preparable were \((tBu_2CN)_3GeCl\) and \(tBu_2CNSiCl_3\) respectively. This may be explained in terms of the bulk of the \(tBu\) groups and the increasing size of the metal from silicon to germanium to tin(iv) (covalent radii 1.17, 1.22,
and 1.40 Å respectively, but the marked change in behaviour between silicon and germanium, corresponding to a difference in size of only 0.05 Å, appears somewhat anomalous.

The reaction between methyleneamines and metal halides in the presence of base has been little used as a preparative route to metallated imines, and apparently not at all for derivatives of Group IVB, with the isolated exception of the preparation of Ph₂CNSiPh₃ from Ph₂CNH and Ph₃SiCl. Here it provides an alternative route to the known compound, (Ph₂CN)₂SiCl₂ (Eqn. 2.5).

$$\text{Ph}_2\text{CNH} + \text{SiCl}_4 + \text{Et}_3\text{N} \xrightarrow{\Delta} \text{Et}_3\text{NH}^+\text{Cl}^- + \left[\text{Ph}_2\text{CNSiCl}_3\right]$$

$$\downarrow \times 2 \quad 2.5$$

$$(\text{Ph}_2\text{CN})_2\text{SiCl}_2 + \text{SiCl}_4$$

Interestingly, as in the earlier preparation via the imino-lithium, reaction of equimolar quantities leads to the bis-imino substituted product, presumably via disproportionation of the initially formed mono-substituted compound. This type of reaction appears to be general for unsymmetrically substituted monodiarylmethyleneaminosilanes (Eqn. 2.6), although in the case of Ph₂CNSiMe₂Cl the process is sufficiently slow to enable the monosubstituted compound to be isolated and characterised before significant disproportionation occurs. The corresponding di-t-butyl compounds, in contrast, are quite stable, indeed the disubstituted materials cannot be prepared.
It is therefore of particular interest to find that reaction of 
\((\text{Ph}_2\text{CN})_2\text{SiCl}_2\) with a large excess of silicon tetrachloride yields a 
crystalline material, the properties of which (insofar as they could 
be ascertained) are consistent with the formulation \(\text{Ph}_2\text{CNSiCl}_3\). The 
possibility of this material being an adduct (Fig. 2-8) is eliminated 
by consideration of the azomethine stretching frequency, which at \(1650\text{cm}^{-1}\) 
is too high for a bridged imino-group. Other possible explanations, such 

![Diagram](image)

**Figure 2-8**

as incorporation of non-bonded \(\text{SiCl}_4\) into the \((\text{Ph}_2\text{CN})_2\text{SiCl}_2\) lattice, do 
exist, however, and further work is necessary to elucidate this matter.

For germanium systems there is less evidence of disproportionation. 
Again the di-t-butylmethylenamine derivatives show no tendency to 
disproportionate, but attempts to prepare the di-p-tolylmethylen-
aminogermanium halides were abandoned after preliminary experiments led 
to products of variable composition. The present work suggests that 
disproportionation also occurs here, but less readily than for the 
silicon derivatives. Thus heating is necessary to decompose \(\text{Ph}_2\text{CNGeCl}_3\) 
(Eqn. 2.7).

\[2\text{Ph}_2\text{CNGeCl}_3 \xrightarrow{\triangle} (\text{Ph}_2\text{CN})_2\text{GeCl}_2 + \text{GeCl}_4\uparrow\] 

2.7
If the trend continues down the group, it might be expected that the corresponding tin derivatives would show even less tendency to disproportionate. However, this cannot be determined, because an alternative rearrangement is observed. The diarylmethyleneaminotin(iv) trichlorides cannot be isolated because they rapidly rearrange by ortho-metallation (Eqn. 2.8). Similar processes appear to occur on heating the other diarylmethyleneaminotin chlorides,

\[
[(\text{RC}_{6\,\text{H}_{4}}\text{H})_{2}\text{CNSnCl}_{3}] \rightarrow \text{C}_{6\,\text{H}_{4}}\text{C} \equiv \text{N-H} \quad \text{2.8}
\]

\[(\text{RC}_{6\,\text{H}_{4}}\text{H})_{2}\text{CNSnCl}_{3} \quad \text{n = 2,3}, \quad \text{see Chapter 5}.
\]

No trace of any such reaction could be found in the silicon and germanium systems, even under forcing conditions. The reaction appears to involve electrophilic attack on the aromatic ring, and therefore reflects the greater Lewis acidity of the -SnCl\text{3} group.

The di-t-butylmethyleneaminotin(iv) chlorides are also unstable to rearrangement, quite unlike their silicon and germanium analogues. Here an additional driving force may be the stability of the lower oxidation state for tin, since the overall reaction appears to involve oxidation of one ketimino group to t-butyl cyanide. A postulated mechanism involves elimination of isobutene and HCl in a cyclic rearrangement (Eqn. 2.9). \( \text{tBuCN and tBu}_{2}\text{CNH (from protolysis of imino-tin species by HCl)} \) could be
identified in the reaction products. The reaction becomes slower with increasing \( n \); \( tBu_2CNSnCl_3 \) (\( n = 0 \)) is not preparable, and \( (tBu_2CN)_2SnCl_2 \) (\( n = 1 \)) and \( (tBu_2CN)_3SnCl \) (\( n = 2 \)) decompose at room temperature over periods of several days and several months respectively. The order of stability is therefore:

\[
(\text{tBu}_2\text{CN})_4\text{Sn} \gg (\text{tBu}_2\text{CN})_3\text{SnCl} \gg (\text{tBu}_2\text{CN})_2\text{SnCl}_2 \gg \text{tBu}_2\text{CNSnCl}_3
\]

i.e. the stability decreases as the number of chlorines (and therefore the electrophilicity of the tin atom) increases.

It might be expected that reaction of the HCl produced with the iminotin(ii) product would yield an imine adduct of the type \( (\text{tBu}_2\text{CN})_n\text{HSn}^\text{II}\text{Cl}_3-n \) (\( n = 1,2 \)). However, from \( (\text{tBu}_2\text{CN})_2\text{SnCl}_2 \), rather than the expected product \( \text{tBu}_2\text{CNSnCl}_2 \), a series of compounds of general formula \( (\text{tBu}_2\text{CNSnCl})_n.(n-1)\text{HCl} \) (\( n = 2,3 \)) was obtained. The structures of these compounds are discussed in the next chapter, but it appears that their preferential formation is due to the stability of the Sn—N—Sn bridge.

The formation of 1:1 and 2:1 adducts between \( \text{tBu}_2\text{CNH} \) and tin tetrachloride is in line with the complex-forming abilities of tin(iv) halides. The 1:1 adduct is more volatile than the 2:1, possibly indicating a different type of structure. An ionic form, \( \text{tBu}_2\text{CNH}^+\cdot\text{tBu}_2\text{CNSnCl}_4^- \),
might be possible for the latter, but the spectroscopic evidence is not consistent with such a structure. It is probable that $^{t}{\text{Bu}}_{2}\text{CNH}.\text{SnCl}_{4}$ and $(^{t}{\text{Bu}}_{2}\text{CNH})_{2}\text{SnCl}_{4}$ are both monomeric, involving 5- and 6-coordinate tin respectively. It is probable that in the latter case a trans-octahedral arrangement would be adopted for steric reasons. Both adducts appear to be stable to heat (melting points $\sim$120°), showing the comparative stability of tin(iv) halides to aminolysis.\(^{118}\)

B. Spectroscopic and Structural Data

i) Mass Spectra

The new tetrakis(methyleneamino)tins showed nothing but peaks due to the parent imines and their breakdown products in their mass spectra. Of the iminotin chlorides, only $(^{t}{\text{Bu}}_{2}\text{CN})_{3}\text{SnCl}$ showed any tin-containing fragments; a single peak, m/e 155, corresponding to SnCl\(^+\) (intensity 2 relative to $^{t}{\text{Bu}}_{2}\text{CN}^{+}$ 100). The sample of $(^{t}{\text{Bu}}_{2}\text{CN})_{2}\text{SnCl}_{2}$ had undergone extensive decomposition before a spectrum could be run. The metal-containing fragments for those new compounds for which spectra could be obtained are listed in Table 13(a-d).

The two di-t-butylmethyleneamine adducts exhibit peaks corresponding to the stepwise loss of chlorine from SnCl\(_4\), together with some methylated fragments due to recombination processes; dissociation of the complexes is evidently fairly facile (Table 13 c & d).

The absence of any ditin-containing fragments in the spectrum of $(^{t}{\text{Bu}}_{2}\text{CN})_{6}\text{Sn}_{2}$ (Table 13a) or of any fragments of mass charge ratio greater than that of $(^{t}{\text{Bu}}_{2}\text{CN})_{3}\text{Sn}^{+}$, suggests that the Sn-Sn bond may be comparatively weak in this compound, probably due to crowding of the bulky imino groups.
**TABLE 13**

Major metal-containing and other significant fragments in the mass spectra of some new methyleneamino derivatives of Group IVB.

### a) \((\text{tBu}_2\text{CN})_6\text{Sn}_2\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Rel.Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Rel.Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>4</td>
<td>((\text{tBu}_2\text{CN})_3\text{Sn}^+)</td>
<td>649</td>
<td>0.1</td>
<td>((\text{Ph}_2\text{CN})_3\text{GeCl}^+)</td>
</tr>
<tr>
<td>457</td>
<td>26</td>
<td>((\text{tBu}_2\text{CN})_2\text{Sn}^+\text{Bu}^+)</td>
<td>614</td>
<td>0.7</td>
<td>((\text{Ph}_2\text{CN})_3\text{Ge}^+)</td>
</tr>
<tr>
<td>400</td>
<td>13</td>
<td>((\text{tBu}_2\text{CN})_2\text{Sn}^+)</td>
<td>504</td>
<td>1.3</td>
<td>((\text{Ph}_2\text{CN})_2\text{GeCl}_2^+)</td>
</tr>
<tr>
<td>343</td>
<td>100</td>
<td>\text{tBu}_2\text{CN}(\text{BuCN})\text{Sn}^+</td>
<td>469</td>
<td>1.3</td>
<td>((\text{Ph}_2\text{CN})_2\text{GeCl}^+)</td>
</tr>
<tr>
<td>260</td>
<td>100</td>
<td>\text{tBu}_2\text{CNSn}^+</td>
<td>433</td>
<td>0.4</td>
<td>\text{Ph}_2\text{CNGe}_2\text{Cl}_3^+</td>
</tr>
<tr>
<td>203</td>
<td>36</td>
<td>\text{tBuCNSn}^+</td>
<td>427</td>
<td>0.5</td>
<td>\text{Ph}_2\text{CN(PhCN)}_2\text{GeCl}_2^+</td>
</tr>
<tr>
<td>140</td>
<td>2</td>
<td>\text{tBu}_2\text{CN}^+</td>
<td>401</td>
<td>0.6</td>
<td>\text{Ph}_2\text{CN.PhGeCl}_2^+</td>
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<tr>
<td>120</td>
<td>8</td>
<td>\text{Sn}^+</td>
<td>398</td>
<td>*</td>
<td>\text{Ph}_2\text{CNGe}_2\text{Cl}_2^+</td>
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</tbody>
</table>

### b) \((\text{Ph}_2\text{CN})_2\text{GeCl}_2\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Rel.Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>614</td>
<td>0.7</td>
<td>((\text{Ph}_2\text{CN})_3\text{Ge}^+)</td>
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<tr>
<td>504</td>
<td>1.3</td>
<td>((\text{Ph}_2\text{CN})_2\text{GeCl}_2^+)</td>
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<tr>
<td>469</td>
<td>1.3</td>
<td>((\text{Ph}_2\text{CN})_2\text{GeCl}^+)</td>
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<td>433</td>
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<td>\text{Ph}_2\text{CNGe}_2\text{Cl}_3^+</td>
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<tr>
<td>427</td>
<td>0.5</td>
<td>\text{Ph}_2\text{CN(PhCN)}_2\text{GeCl}_2^+</td>
</tr>
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<td>398</td>
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<td>359</td>
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<tr>
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<tr>
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<td>55</td>
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</tr>
<tr>
<td>221</td>
<td>9</td>
<td>\text{PhGeCl}_2^+</td>
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<tr>
<td>180</td>
<td>100</td>
<td>\text{Ph}_2\text{CN}^+</td>
</tr>
<tr>
<td>179</td>
<td>*</td>
<td>\text{GeCl}_3^+</td>
</tr>
<tr>
<td>144</td>
<td>5</td>
<td>\text{GeCl}_2^+</td>
</tr>
<tr>
<td>109</td>
<td>25</td>
<td>\text{GeCl}^+</td>
</tr>
</tbody>
</table>

m/e values refer to most intense peak of group, i.e. that containing the most abundant isotopes.

* overlapping neighbouring peak envelope.

off-scale.
<table>
<thead>
<tr>
<th>m/e</th>
<th>Rel. Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Rel. Intensity</th>
<th>Assignment</th>
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<td>SnCl$_4^+$</td>
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<td>MeSnCl$_3^+$</td>
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</tr>
<tr>
<td>225</td>
<td>85</td>
<td>SnCl$_3^+$</td>
<td>190</td>
<td>44</td>
<td>SnCl$_2^+$</td>
</tr>
<tr>
<td>205</td>
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<td>MeSnCl$_2^+$</td>
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<tr>
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<tr>
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<td>t$_{Bu_2CNH_2}^+$</td>
<td>120</td>
<td>32</td>
<td>Sn$^+$</td>
</tr>
<tr>
<td>141</td>
<td>59</td>
<td>t$_{Bu_2CNH}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>38</td>
<td>Sn$^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>Rel. Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Rel. Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>4</td>
<td>SnCl$_4^+$</td>
<td>260</td>
<td>4</td>
<td>SnCl$_4^+$</td>
</tr>
<tr>
<td>225</td>
<td>44</td>
<td>SnCl$_3^+$</td>
<td>190</td>
<td>44</td>
<td>SnCl$_2^+$</td>
</tr>
<tr>
<td>190</td>
<td>39</td>
<td>t$_{Bu_2CNH_2}^+$</td>
<td>120</td>
<td>32</td>
<td>Sn$^+$</td>
</tr>
<tr>
<td>155</td>
<td>100</td>
<td>t$_{Bu_2CNH}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>142</td>
<td>45</td>
<td>t$_{Bu_2CNH}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>141</td>
<td>59</td>
<td>t$_{Bu_2CNH}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>38</td>
<td>Sn$^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**c)** $t_{Bu_2CNH}.SnCl_4$

**d)** $(t_{Bu_2CNH})_2.SnCl_4$
The \((R_2CN)_3M^+\) ion, where M is a Group IVB element, is expected to be relatively stable, since it is isoelectronic with the corresponding tris-imino derivatives of Group IIIB, which are planar, involving \(N\rightarrow M (p\rightarrow p) \pi\)-donation. It also appears, as a result of recombination, in the spectrum of \((Ph_2CN)_2GeCl_2\) (Table 13b), which, apart from a very complete breakdown pattern for the parent compound, also exhibits the results of a redistribution process (Eqn. 2.10). An interesting feature is the presence of two peaks (presumably due to recombinations) tentatively assigned to fragments containing two germanium atoms, probably held together by a bridging imino-group. Fragments of similar formulation observed in the mass spectra of \(Ph_2CN\)-derivatives of divalent tin seem to be comparatively stable (see following chapter). Unfortunately, in this germanium case they are overlapped by adjoining peak envelopes, so no confirmation for the assignment can be obtained from isotopic ratios.

ii) Proton nuclear magnetic resonance spectra

No spectra were recorded for the derivatives of diphenylmethyleneamine, because past experience has shown that the signals obtained from the phenyl groups are too complex to provide a reliable guide to the molecular geometry.\(^{329,346,355}\) Variable-temperature techniques were employed for all the di-t-butylmethylenamine derivatives, in the temperature range \(-100^\circ\) to \(+45^\circ\)C, and the results are summarised in Table 14. Spectra were run on solutions in \(d^8\)-toluene or chloroform.
TABLE 14

$^1$H-NMR spectroscopic data for some di-t-butylmethyleneamine derivatives of Sn$^IV$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma$ values p.p.m.$^a$</th>
<th>Effect of cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(tBu_2CN)_6Sn_2$</td>
<td>8.76s</td>
<td>-100°C: No effect</td>
</tr>
<tr>
<td>$(tBu_2CN)_4Sn$</td>
<td>8.83s</td>
<td>&quot;</td>
</tr>
<tr>
<td>$(tBu_2CN)_3SnCl$</td>
<td>8.72s</td>
<td>&quot;</td>
</tr>
<tr>
<td>$(tBu_2CN)_2SnCl_2$</td>
<td>8.75br.s (8.80sh, 8.78sm, 8.77sh)</td>
<td>&quot;</td>
</tr>
<tr>
<td>$tBu_2CNH.SnCl_4^b$</td>
<td>C-H: 8.00s (18) N-H: 1.26s (1)</td>
<td>-70°C: Partially resolved doublet, separation 0.11 p.p.m</td>
</tr>
<tr>
<td>$(tBu_2CNH)_2.SnCl_4^c$</td>
<td>C-H: 8.00s (18) N-H: -0.32s (1)</td>
<td>-49°C: Partially resolved doublet, separation 0.09 p.p.m</td>
</tr>
</tbody>
</table>

$a$: Relative to $\gamma$(TMS) = 10 p.p.m. (External reference)

All spectra run on solutions in $^8$-toluene at 43°C except:

$b$: CHCl$_3$, 43°C

$c$: CDCl$_3$, 10°C

$s$: singlet; $br$: broad; $sh$: shoulder; $sm$: subsidiary maximum

Relative intensities in parentheses.
All the spectra contained a single sharp absorption, corresponding to the \textsuperscript{t}Bu resonance, at ambient temperatures except for that of \((\textsuperscript{t}Bu_2CN)_2SnCl_2\), which exhibited a comparatively broad singlet, slightly split at the apex. This splitting may be due to association of methyl groups with nearby chlorine atoms via weak hydrogen-bond-type interactions, as postulated in section (a) to account for the decomposition process (Fig. 2-9). The complexity of the \textsuperscript{t}Bu signals in the \textsuperscript{1}H-NMR spectrum of \(Li(\textsuperscript{t}Bu_2CN)_4Al\) may be partially due to a similar effect, though involving C-H·······metal interactions, since two of the \textsuperscript{t}Bu groups have been shown to be interacting with the lithium atom in the solid, and this may persist in solution.

None of the iminotins show any splitting of the signal on cooling. Because of the low barrier to inversion at nitrogen in N-metallated methyleneamines, it is not possible to interpret this definitely in terms of a linear \(\text{C}_2\text{N} \equiv \text{Sn}\) unit, and since, in the light of infra-red and crystallographic evidence, it appears probable that there is little or no \(\text{Sn-N} \pi\)-bonding in these compounds, it seems most likely that the CNSn unit is bent, but with a low barrier to inversion at nitrogen.

The two adducts also exhibit sharp singlets for the \textsuperscript{t}Bu absorptions at room temperature. However, on cooling it is possible to resolve them
as ill-defined doublets, corresponding to the different environments in Figure 2-10. The rapid interchange of tBu and tBu' at higher temperatures may be due to intermolecular proton or imine exchange, since the barrier to rotation about the C=N double bond would be expected to be quite high.

![Figure 2-10](image)

The marked difference in chemical shift of the N-H proton between the 1:1 and 2:1 adducts is of interest. This is unlikely to be a solvent effect, and the temperature difference should not cause such a large change. It may reflect the different shielding characteristics of the trigonal bipyramidal (5-coordinate) and octahedral (6-coordinate) structures. Sn-H coupling was not observed.

The chemical shifts of the t-butyl groups show little variation from compound to compound (the marked difference between the adducts and the methyleneaminotins is most probably a solvent effect). This may be due to the distance of five bonds between the t-butyl protons and the central metal, although any direct C-H····Cl-Sn interaction might be expected to have a more pronounced effect than that observed if this is the case.

iii) Infra-red spectra

a) Azomethine stretching frequencies

The infra-red spectra of all the compounds prepared were recorded on
nujol mulls or neat liquids, and their azomethine stretching frequencies, \(\nu(C=N)\), are listed in Tables 15 and 16, together with those of some related compounds.

Assignment of \(\nu(C=N)\) for diphenylmethyleneamino-derivatives (Table 15) is complicated by the presence of two additional absorptions in this region, generally at 1590-1600 cm\(^{-1}\) and 1570-1580 cm\(^{-1}\), which are most probably due to skeletal vibrations of the phenyl rings. These absorptions frequently overlie those due to the C=N bond and make identification of \(\nu(C=N)\) difficult. This is illustrated in Figure 2-11, which shows the absorptions in the region 1500-1700 cm\(^{-1}\) for the compounds \((\text{Ph}_2\text{CN})_2\text{MCl}_2\) (M = Si, Ge, Sn) (Figure 2-11 a-c), and also for \((\text{Ph}_2\text{CN})_3\text{SnCl}(d)\). The shift of \(\nu(C=N)\) to lower energy down the group can clearly be seen, as is also found in the series \((\text{Ph}_2\text{CN})_4\text{M}\) and \(\text{Ph}_2\text{C}N\text{MC}l_3\).

The large difference between silicon and germanium is probably indicative of a sharp change in properties; a significant amount of (p-d) \(\pi\)-bonding for silicon, compared to little for germanium and tin, might produce such an effect. Earlier reports\(^{290,293,355}\) on the diarylmethyleneamino-derivatives of the Group IVB elements concluded that all had M-N=C skeletons which were bent to some extent (the shift to higher energy for \(\nu(C=N)\) in the case of the silicon derivatives was considered to be too small to allow for complete linearity), with N\(\rightarrow\)M dative \(\pi\)-bonding decreasing sharply down the group, little being apparent for tin and lead. A similar conclusion seems appropriate here.

For the compounds \((\text{Ph}_2\text{CN})_2\text{SnCl}_2\) and \((\text{Ph}_2\text{CN})_3\text{SnCl}\), there are at least two bands assignable to C=N stretching vibrations (in the latter case the pronounced shoulder on the low energy side of the lower
TABLE 15
Azomethine stretching frequencies, ν(C=N)cm⁻¹, for some diphenylmethylenamino derivatives of Group IVB

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>ν(C=N)cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph₂CN)₄Si</td>
<td>Mull</td>
<td>1646</td>
<td>356</td>
</tr>
<tr>
<td>(Ph₂CN)₄Ge</td>
<td>&quot;</td>
<td>1601</td>
<td>293</td>
</tr>
<tr>
<td>(Ph₂CN)₄SnIV</td>
<td>&quot;</td>
<td>1590</td>
<td>a</td>
</tr>
<tr>
<td>[(Ph₂CN)₃Sn⁴Cl]₄IV</td>
<td>&quot;</td>
<td>1612, b 1535c</td>
<td>a</td>
</tr>
<tr>
<td>(Ph₂CN)₂SiCl₂</td>
<td>&quot;</td>
<td>1656</td>
<td>355</td>
</tr>
<tr>
<td>(Ph₂CN)₂GeCl₂</td>
<td>&quot;</td>
<td>1610</td>
<td>a</td>
</tr>
<tr>
<td>[(Ph₂CN)₂Sn⁴Cl₂]₄IV</td>
<td>&quot;</td>
<td>1607, b 1553c</td>
<td>a</td>
</tr>
<tr>
<td>Ph₂CNSiCl₃</td>
<td>&quot;</td>
<td>1650</td>
<td>a</td>
</tr>
<tr>
<td>Ph₂CNGeCl₃</td>
<td>liquid film</td>
<td>1609</td>
<td>a</td>
</tr>
<tr>
<td>cf. Ph₂CNH</td>
<td>&quot;</td>
<td>1603</td>
<td>335</td>
</tr>
</tbody>
</table>

a: This work
b: ν(C=N) terminal
c: ν(C=N) bridging
Infra-red spectra in the 1500-1700 cm$^{-1}$ region for some
diphenylmethyleneamino derivatives of Group IVB

Figure 2-11
absorption may indicate further splitting). Two explanations are possible. Although organotin(IV) amines and imines are rarely associated by bridging through a single atom (Chapter 1), the presence of chlorine bonded to tin may increase its acceptor properties sufficiently to allow this, giving rise to structures such as those in Figure 2-12, which involve 5- and 6-coordinate tin. In this case the higher energy absorption corresponds to the stretching vibration of

\[
\begin{align*}
  \text{(a) } & \quad X = \text{Cl, NCPh}_2 \\
  \text{(b) } & \quad \text{Sn-NCPH}_2
\end{align*}
\]

Figure 2-12.

the terminally-bonded imino-groups, the lower energy absorption to the bridging groups (on this basis a 6-coordinate polymeric structure (Figure 2.12b) seems unlikely for \((\text{Ph}_2\text{CN})_2\text{SnCl}_2\), since it would preclude the appearance of \(\nu(\text{C=N})_{\text{terminal}}\). \((\text{Ph}_2\text{CN})_4\text{Sn}\), which has been proven by X-ray crystallography to be monomeric,\(^{301,302}\) gives a single fairly sharp \(\nu(\text{C=N})\) absorption overlying one of the ring vibrations.

An alternative explanation, which assumes the compounds to be monomeric, invokes coupling between the vibrations of the azomethine groups to account for the observed splitting of the \(\nu(\text{C=N})\) absorption. Since the CNSn linkages are most probably bent at nitrogen, it is difficult to predict the number of infra-red active stretching modes
to be expected, but it is reasonable to assign the higher energy absorption to anti-symmetric combinations, and the lower energy absorption to symmetric. However, no such coupling has been reported for other N-metallated methyleneamines, and none is observed for the corresponding di-t-butylmethylenediamino derivatives. Additionally, associated structures are supported by preliminary Mössbauer data, which are inconsistent with a tetrahedral environment for tin in these two compounds.

The di-t-butylmethylenediamine systems have much simpler spectra (Table 16). All showed a single very strong absorption in the azomethine stretching region, apart from the two adducts, which exhibit multiple bands. The major peaks are listed in the table. The shift to higher frequency relative to the parent imine for the 1:1 adduct is as expected for coordination of a methyleneamine to a strong Lewis acid such as SnCl$_4$.344

The two absorptions for the 2:1 adduct could be explained either as the result of coupling of the vibrations of the two C=N units, or in terms of an ionic structure, $^t$Bu$_2$C$\equiv$NH$_2$$. However, the compound lacks a strong peak in its mass spectrum corresponding to the postulated cation, and in the $^1$H-NMR spectrum only a single $^t$Bu resonance is observed at ambient temperatures, whereas two would be expected if an ionic structure persisted in solution. It is probable that a trans-configuration is adopted by the imine groups (for steric reasons) in an essentially octahedral complex. The related compound, bis(benzalhydrazono)tin(iv) tetrachloride, was also considered to have a trans-configuration (Fig. 2-13), and similarly appeared to exhibit two C=N stretching absorptions (at 1615 and 1560 cm$^{-1}$).387
TABLE 16
Azomethine stretching frequencies, $\nu$(C=N) cm$^{-1}$, for some di-t-butyl-methyleneamine derivatives of the Group IVB elements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>$\nu$(C=N) cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(t^6Bu_2CN)<em>{6}Sn</em>{2}^IV$</td>
<td>Nujol mull</td>
<td>1631</td>
<td>a</td>
</tr>
<tr>
<td>$(t^4Bu_2CN)_{4}Sn^IV$</td>
<td>&quot;</td>
<td>1627</td>
<td>a</td>
</tr>
<tr>
<td>$(t^3Bu_2CN)_{3}GeCl$</td>
<td>liquid film</td>
<td>1652</td>
<td>293</td>
</tr>
<tr>
<td>$(t^3Bu_2CN)_{3}Sn^IVCl$</td>
<td>&quot;</td>
<td>1627</td>
<td>a</td>
</tr>
<tr>
<td>$(t^2Bu_2CN)_{2}GeCl_2$</td>
<td>&quot;</td>
<td>1645</td>
<td>293</td>
</tr>
<tr>
<td>$(t^2Bu_2CN)_{2}Sn^IVCl_2$</td>
<td>&quot;</td>
<td>1627</td>
<td>a</td>
</tr>
<tr>
<td>$tBu_2CNSiCl_3$</td>
<td>&quot;</td>
<td>1729</td>
<td>355</td>
</tr>
<tr>
<td>$tBu_2CNH.SnCl_4$</td>
<td>Nujol mull</td>
<td>1641</td>
<td>a</td>
</tr>
<tr>
<td>$(t^2Bu_2CNH)_{2}SnCl_4$</td>
<td>&quot;</td>
<td>1662, 1583</td>
<td>a</td>
</tr>
<tr>
<td>cf. $tBu_2CNH$</td>
<td>liquid film</td>
<td>1604</td>
<td>a</td>
</tr>
</tbody>
</table>

a: This work
The new di-t-butylmethyleneamino derivatives of tin (IV) have very similar spectra in the region studied (4000-250 cm\(^{-1}\)), and variation in number and type of substituent on tin has little effect on the position of \(\nu(C=N)\). Comparison with parallel silicon and germanium systems once again provides the order Si\(\geq\)Ge\(\geq\)Sn, but compared to the corresponding diarylmethyleneamino-derivatives, the shifts of \(\nu(C=N)\) to higher energy relative to the parent imine are considerably larger, and have been interpreted in terms of appreciable N\(\rightarrow\)M \(\pi\)-bonding for the silicon derivatives, with associated linearity of the C=N=Si unit.\(^{355}\) A lesser extent of \((p\rightarrow d)\ \pi\)-bonding, with a bent skeleton, has been suggested for the germanium compounds.\(^{293}\)

It is therefore probable that the new tin compounds have skeletons bent at nitrogen and a smaller amount of N-M \(\pi\)-bonding than the germanium derivatives, although there is still a shift of \(\nu(C=N)\) to higher frequency relative to the parent imine (albeit only 23 cm\(^{-1}\)).

The di-t-butylmethyleneaminitin chlorides show a single \(\nu(C=N)\) absorption, consistent with their formulation as monomers, in contrast to the diphenyl analogues, which are probably dimeric or polymeric, containing imino bridges. This is probably a result of the greater steric requirements of the t-butyl groups, although the \(^{t}\text{Bu}_2\text{CN}\)-derivatives of tin (II) appear to be associated, possibly as a result of the larger covalent radius of Sn\(^{II}\) (1.63 \(\text{\AA}\) compared to 1.40 \(\text{\AA}\) for Sn\(^{IV}\)\(^{372}\)).
It is of interest to compare these results with those of a study on a series of Group IVB derivatives of bis(trifluoromethyl)methyleneamine, \([\text{CF}_3]_2\text{CN} \) \(\text{MMe}_4\) \(\text{n} = 1-4, \text{M} = \text{Si,Ge,Sn}\) (Table 17). A similar picture emerges with respect to \(\text{V}(\text{C=N})\), i.e. \(\text{Si} > \text{Ge} > \text{Sn}\), with a similar interpretation in terms of \((p\rightarrow d)\pi\)-bonding. If, however, the \(\text{V}(\text{C=N})\) values for the Group IVB derivatives of the three imines are compared (Table 18) an additional feature emerges.

It might be expected that an electron-withdrawing group attached to the methyleneamine residue would diminish the electron-donating ability of the imine nitrogen. Conversely, an electron-donating group would be expected to enhance it. On this basis, the \(\text{N} \rightarrow \text{M} \pi\)-bonding ability of the imino-groups \(\text{R}_2\text{CN}^-\) might be expected to decrease \(\text{R} = \text{tBu} > \text{Ph} > \text{CF}_3\). The observed order, in so far as this can be derived from \(\text{V}(\text{C=N})\) values for the Group IVB elements, is \(\text{tBu} > \text{CF}_3 > \text{Ph}\).

The reason for this is not immediately apparent, since \(\text{tBu}_2\text{CNH}\) and \(\text{Ph}_2\text{CNH}\) appear to have similar basicities (see section iv), and a similar effect is by no means universally observed in other areas of the periodic table. Methylenediamino-derivatives of the lighter metals in particular show comparatively little difference in \(\text{V}(\text{C=N})\) frequency between \(\text{tBu}_2\text{CN}^-\) and \(\text{Ph}_2\text{CN}^-\) derivatives, apart from those attributable to steric effects (consider, for example, the bis-imino derivatives of Be and Mg in Table 11). Since \(\text{N} \rightarrow \text{M} \pi\)-bonding generally involves \((p-p)\pi\)-interaction for the lighter metals, this will give rise to a stronger bond, less sensitive to other influences than the weaker \((p-d)\) interaction found in Group IVB.

b) Metal-Nitrogen stretching frequencies

Assignment of \(\text{M-N}\) stretching frequencies presents a problem, due
**TABLE 17**

Azomethine stretching frequencies, $\nu$(C=N) cm$^{-1}$, for some Group IVB derivatives of (CF$_3$)$_2$C=N.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(C=N) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M = Si</td>
</tr>
<tr>
<td>$[(CF_3)_2CN]_4^M$</td>
<td>1786</td>
</tr>
<tr>
<td>$[(CF_3)_2CN]_3^{MMe}$</td>
<td>1774</td>
</tr>
<tr>
<td>$[(CF_3)_2CN]_2^{MMe_2}$</td>
<td>1770</td>
</tr>
<tr>
<td>$(CF_3)_2CNMMMe_3$</td>
<td>1765$^a$</td>
</tr>
<tr>
<td>cf. $(CF_3)_2CNH$</td>
<td></td>
</tr>
</tbody>
</table>

$a$: Other workers found 1780 cm$^{-1}$.  

**TABLE 18**

Frequency shifts, $\Delta\nu$(C=N) cm$^{-1}$, for Group IVB derivatives $(R_2C=N)_4^M$ relative to the parent imine.  

<table>
<thead>
<tr>
<th>R</th>
<th>$\Delta\nu$(C=N) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M = Si</td>
</tr>
<tr>
<td>$^{t}$Bu</td>
<td>(125)$^a$</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>84</td>
</tr>
<tr>
<td>Ph</td>
<td>43</td>
</tr>
</tbody>
</table>

$\Delta\nu$(C=N) = $\nu$(C=N) - $\nu$(C=N)$_{parent}$ imine  

$a$: $^{t}$Bu$_2$CNSiCl$_3$; $b$: $(^{t}$Bu$_2$CN)$_3$GeCl. Higher derivatives not preparable.
to the complexity of the spectra in the 500-950 cm\(^{-1}\) region, where these absorptions would be expected. Earlier workers in the Group IVB methyleneamine area have followed the example of Lappert and Palmer, who, in their study of \((\text{CF}_3)_2\text{CN}^-\) derivatives of Si, Ge, and Sn, assigned \(\nu(M-N)\) in the range 950-960 cm\(^{-1}\), regardless of M. This is outside the generally observed ranges for Ge-N and Sn-N stretching vibrations, and seems unlikely in view of the substantial change in properties from silicon to tin.

Comparison of the spectra of related compounds of Si, Ge, and Sn allows more realistic assignments to be made from the bands which move on changing the central atom (Table 19). These assignments are to some extent tentative, and in some cases alternatives are given. The bis- and tris-imino derivatives would be expected to show two infra-red active M-N stretching vibrations, and the quoted values most probably refer to the more energetic of these, the asymmetric stretching vibration. It might have been expected that the associated compounds \((\text{Ph}_2\text{CN})_2\text{SnCl}_2\) and \((\text{Ph}_2\text{CN})_3\text{SnCl}\) would show \(\nu(M-N)\) bands due to both terminal and bridged imino- groups. However, their spectra showed no significant differences from that of \((\text{Ph}_2\text{CN})_4\text{Sn}\) in the region 300-600 cm\(^{-1}\), and no even tentative assignments could be made for \(\nu(M-N)\), the quoted values probably referring to terminally bonded groups.

The values show the expected shift to lower energy from silicon to germanium to tin, again with a wider gap between silicon and germanium, reflecting the greater ability of silicon to increase the M-N bond order by (p-d) \(\pi\)-bonding.

It is interesting to note the generally higher \(\nu(M-N)\) frequencies for di-t-butylmethyleneamine derivatives, implying a stronger M-N bond than in the diphenyl analogues. This difference corresponds to the parallel effect on \(\nu(C=\text{N})\), and may indicate a greater extent of N-M \(\pi\)-bonding for the di-t-butylmethyleneamine derivatives.
TABLE 19
Possible assignments for $\gamma(M-N)$ for some methyleneamino derivatives
of the Group IVB elements

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma(M-N) \text{ cm}^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Ph}_2\text{CN})_4\text{Si}$</td>
<td>866 (913)</td>
<td>a, (374)</td>
</tr>
<tr>
<td>$(\text{Ph}_2\text{CN})_4\text{Ge}$</td>
<td>700$^b$ (892)</td>
<td>a, 293, (346)</td>
</tr>
<tr>
<td>$(\text{Ph}_2\text{CN})_4\text{Sn}^\text{IV}$</td>
<td>654</td>
<td>a, 293</td>
</tr>
<tr>
<td>$[(\text{Ph}_2\text{CN})_3\text{Sn}^\text{IV}\text{Cl}_2]^n$</td>
<td>667, 660, 650</td>
<td>a</td>
</tr>
<tr>
<td>$(\text{Ph}_2\text{CN})_2\text{SiCl}_2$</td>
<td>894 (913)</td>
<td>a, (355)</td>
</tr>
<tr>
<td>$(\text{Ph}_2\text{CN})_2\text{GeCl}_2$</td>
<td>700$^b$</td>
<td>a</td>
</tr>
<tr>
<td>$[(\text{Ph}_2\text{CN})_2\text{Sn}^\text{IV}\text{Cl}_2]^n$</td>
<td>670, 661</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{CNSiCl}_3$</td>
<td>875</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{CNGeCl}_3$</td>
<td>700$^b$</td>
<td>a</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_6^\text{IV}\text{Sn}_2$</td>
<td>692</td>
<td>a</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_4^\text{IV}\text{Sn}$</td>
<td>693</td>
<td>a</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_3^\text{IV}\text{GeCl}$</td>
<td>731 (958)</td>
<td>a, (346)</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_3^\text{IV}\text{SnCl}$</td>
<td>698</td>
<td>a</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_2^\text{IV}\text{GeCl}_2$</td>
<td>741 (959)</td>
<td>a, (346)</td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_2^\text{IV}\text{SnCl}_2$</td>
<td>697</td>
<td>a</td>
</tr>
</tbody>
</table>

Previous assignments in parentheses.

a : This work
b : Obscured by phenyl absorption
iv) **Basicity measurements on \((\text{Bu}_2\text{CN})_n\text{SnCl}_{4-n}, n = 2,3\)**

The base strengths of a wide range of organic bases have been measured by making use of the hydrogen-bonding effect;\(^{375}\) alcohols and phenols are the most widely used reference acids. Organometallic bases, however, tend to react with such materials, and therefore, for their study, Abel and co-workers have made use of the hydrogen-bonding effects with chloroform.\(^ {282-5}\) (Although stannylamines have been shown to react with haloforms,\(^ {202}\) the reaction is sufficiently slow when the haloform is in high dilution to allow basicity studies;\(^ {285}\) the solutions used in this work slowly darkened and deposited crystalline solids over a period of several weeks).

This effect has been followed in two ways. In the infra-red spectrum, the shift in the X-H stretching frequency, \(\Delta \nu(X-H)\), upon formation of a hydrogen bond, X-H···B, is directly observable, and appears to be virtually unaffected by changes in concentration\(^ {376}\) (although the intensity of \(\nu(X-H···B)\) is concentration-dependant). It has proven convenient in practice to use deuterochloroform for infra-red studies, since \(\nu(C-D)\) lies clear of interfering absorptions of the bases under examination.

In the proton NMR spectrum it is not possible to directly observe the signal due to the hydrogen-bonded species, because of the rapidly exchanging equilibrium between free and hydrogen-bonded base (Eqn. 2.11).

\[
\text{Cl}_3\text{C-H} + \text{Base} \rightleftharpoons \text{Cl}_3\text{C-H···Base} \quad 2.11
\]

The observed frequency, \(\nu_0\), is intermediate between that of the hydrogen-bonded species, \(\nu_H\), and free chloroform, \(\nu_F\). \(\nu_0\) is concentration-
dependant, but the extrapolated shift at infinite dilution (of chloroform in solution) relative to free chloroform, $\nu_\infty$, has been used as a measure of the basicity of the solvent.\textsuperscript{285}

When both methods were applied to iso-structural series of bases, good agreement was found, parallel variations in $\Delta \nu(C-D)$ and $\nu_\infty$ being observed. However, when compounds of differing structures were compared, the two methods no longer gave parallel results. This was considered to be due to the longer NMR relaxation time, because of which $\nu_0$ is strongly affected by the equilibrium constant of Equation 2.11, which in turn is sensitive to steric effects.\textsuperscript{285}

Both methods require liquid bases, since low concentrations of chloroform must be used. As a result, only the di-t-butylmethyleneaminotin chlorides could be examined. Infra-red studies were carried out on solutions of CDC\textsubscript{3} \textit{(c.} 1 mole) in base (c. 5 moles). Comparison measurements were also made on $^t$Bu$_2$CNH and Ph$_2$CNH. Spectra were recorded on a Perkin-Elmer Model 477 spectrometer (scale expansion x10) using internal calibration with the water-vapour absorption at 3852 cm$^{-1}$ as reference. Frequency shifts are to low energy relative to gaseous CDC\textsubscript{3} ($\nu(C-D) = 2264$ cm$^{-1}$). Results are listed in Table 20. $\nu(C-D-B)$ absorptions appeared as subsidiary peaks partially superimposed on the free CDC\textsubscript{3} band. This may have been due to the comparatively high concentrations of CDC\textsubscript{3} necessitated by the limited availability of the organometallics, but similar effects have been observed for other stericly crowded organometallic bases.\textsuperscript{283} Only a single absorption was observed for the methyleneamines.

$^1$H-NMR studies were carried out over a range of concentrations, using neat CHCl\textsubscript{3} as external reference, but it was not possible to work at sufficiently low concentrations to obtain realistic extrapolations to infinite dilution. The curves of $\nu_0$ against concentration may,
however, be used for qualitative comparisons, and data were also obtained for $\text{Bu}_2\text{CNH}$ and cyclohexane, the latter providing a base-line corresponding to zero basicity. Results are listed in Table 21, and illustrated graphically in Figure 2-14. Chemical shifts are uncorrected for bulk susceptibility errors due to the use of an external reference.

The two sets of data are not in complete agreement. The infra-red results suggest hydrogen-bonding abilities for the iminotin chlorides about mid-way between those of liquid CDCl$_3$ and the parent imine, whereas the NMR data suggest similar base strengths to that of chloroform itself. This is probably due to the effects of the bulky t-butyl groups, which, by blocking the approach of chloroform molecules, would tend to shift the position of the equilibrium in Equation 2.11 to the left, and hence $\nu_0$ closer to $\nu_F$. Competing Sn-Cl···H-C hydrogen bonding may also contribute to this behaviour.

It is clear, however, that the iminotin chlorides are less basic than the parent imine, and substantially less so than those organotin amines which have been studied (less, even, than some organosilylamines, in which substantial (p-d)$\pi$-bonding might be expected). This may point to involvement of the nitrogen lone pairs in a certain amount of $\text{N}\rightarrow\text{Sn}$ dative $\pi$-bonding, or alternatively may be due to their inaccessibility for steric reasons.

It is interesting to note that, although the N-metallated derivatives of $\text{Bu}_2\text{CNH}$ and $\text{Ph}_2\text{CNH}$ have differing properties in many cases, the parent imines have very similar basicities. They are, however, less basic than dialkylamines such as $\text{tBuNH}_{\text{Et}}$. 
### TABLE 20

$\Delta \nu(C-D)$ for solutions of CDCl$_3$ in some organic and organometallic bases

<table>
<thead>
<tr>
<th>Base</th>
<th>$\Delta \nu(C-D)$ cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(^t\text{Bu}_2\text{CN})_3\text{SnCl}$</td>
<td>25</td>
<td>a</td>
</tr>
<tr>
<td>$(^t\text{Bu}_2\text{CN})_2\text{SnCl}_2$</td>
<td>24</td>
<td>a</td>
</tr>
<tr>
<td>$^t\text{Bu}_2\text{CNH}$</td>
<td>42</td>
<td>a</td>
</tr>
<tr>
<td>Ph$_2\text{CNH}$</td>
<td>43</td>
<td>a</td>
</tr>
<tr>
<td>Me$_3\text{CNHEt}$</td>
<td>89</td>
<td>283</td>
</tr>
<tr>
<td>Me$_3\text{SiNET}_2$</td>
<td>64</td>
<td>284</td>
</tr>
<tr>
<td>Me$_3\text{SnNET}_2$</td>
<td>90</td>
<td>284</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Sn})_3\text{N}$</td>
<td>106</td>
<td>284</td>
</tr>
<tr>
<td>liquid CDCl$_3$</td>
<td>12</td>
<td>283</td>
</tr>
</tbody>
</table>

$\Delta \nu(C-D) = \nu(C-D)_{\text{gaseous CDCl}_3} - \nu(C-D)_{\text{soln.}}$

a: This work. b: freshly prepared.

### TABLE 21

$^1$H Chemical shifts* for solutions of CHCl$_3$ in some organic and organometallic bases

<table>
<thead>
<tr>
<th>Base</th>
<th>Mole Fraction CHCl$_3$</th>
<th>$\nu_0$ cps</th>
<th>Base</th>
<th>Mole Fraction CHCl$_3$</th>
<th>$\nu_0$ cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(^t\text{Bu}_2\text{CN})_3\text{SnCl}$</td>
<td>0.534</td>
<td>0.90</td>
<td>$(^t\text{Bu}_2\text{CN})_2\text{SnCl}_2$</td>
<td>0.495</td>
<td>-2.97</td>
</tr>
<tr>
<td></td>
<td>0.696</td>
<td>1.34</td>
<td></td>
<td>0.658</td>
<td>-1.57</td>
</tr>
<tr>
<td></td>
<td>0.821</td>
<td>1.78</td>
<td></td>
<td>0.746</td>
<td>-0.40</td>
</tr>
<tr>
<td></td>
<td>0.873</td>
<td>1.73</td>
<td></td>
<td>0.797</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>0.902</td>
<td>1.72</td>
<td></td>
<td>0.854</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.883</td>
<td>0.65</td>
</tr>
<tr>
<td>$^t\text{Bu}_2\text{CNH}$</td>
<td>0.286</td>
<td>-30.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.445</td>
<td>-27.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.546</td>
<td>-24.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.667</td>
<td>-18.5</td>
<td>Cyclohexane</td>
<td>0.286</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>0.737</td>
<td>-12.2</td>
<td></td>
<td>0.546</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.667</td>
<td>11.7</td>
</tr>
</tbody>
</table>

*: Upfield relative to neat CHCl$_3$
Uncorrected dilution curves for solutions of chloroform in $\text{Bu}_2\text{CNH}_4\cdot\frac{\text{Bu}_2\text{CN}}{\text{SnCl}_4}$, $n = 2, 3$, and cyclohexane.

Figure 2-14
(v) **Crystallographic studies.**

N.W. Alcock and co-workers have determined the crystal and molecular structures of the tetrakis(diphenylmethyleneamino) derivatives, \((\text{Ph}_2\text{CN})_4M, M = \text{Si, Ge, Sn}\). The molecular structures are illustrated in Figure 2-15, and relevant bond lengths and angles are listed in Table 22. The three compounds are by no means isomorphous, the crystal systems being respectively triclinic, monoclinic, and tetragonal. They are all monomeric, and there are two crystallographically independent molecules (A and B) in the unit cell of the silicon compound.

The three compounds have similar general conformations, each containing an approximately tetrahedral \(\text{N}_4\text{M}\) unit. The lack of isomorphism is accounted for by the variation in the \(\text{M}-\text{N} = \text{C}\) bond angle (from 139.1° and 134.5° (averages) for silicon to 121.3° for tin). The most likely explanation for this variation in bond angle is that the hybridisation at nitrogen is changing from \(sp^2\) for tin towards \(sp\) for silicon, in order to increase the p character of the orbital containing the lone pair and so maximise its overlap with a metal d-orbital for formation of a \((p\rightarrow d)\) dative \(\pi\)-bond.

The electron demand of the central metal will not be such as to require full or equal involvement of all four nitrogen lone pairs in the formation of \(\text{N}\rightarrow\text{M}\ \pi\)-bonding. As a result, the bond angles at nitrogen are all less than 180°, and can vary somewhat in order to accommodate external influences such as the packing requirements of the phenyl groups.

The MNC angles show a marked reduction from silicon to germanium to tin, suggesting considerably reduced \(\text{M}-\text{N}\ \pi\)-bonding for germanium, and very little, if any, for tin. This interpretation is supported by the \(\text{M}-\text{N}\)
### TABLE 22

Bond lengths and angles for the compounds \((\text{Ph}_{2}\text{CN})_4\text{M}, \text{M} = \text{Si,Ge,Sn}\). \(^{302}\)

<table>
<thead>
<tr>
<th>M</th>
<th>M-N</th>
<th>M=N=\text{C}^\text{O}</th>
<th>C=\text{N}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Calc.</td>
<td>(\Delta)</td>
</tr>
<tr>
<td>Si</td>
<td>1.719(16)</td>
<td>1.879</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>1.716(16)</td>
<td>1.879</td>
<td>0.163</td>
</tr>
<tr>
<td>Ge</td>
<td>1.872(5)</td>
<td>1.928</td>
<td>0.056</td>
</tr>
<tr>
<td>Sn</td>
<td>2.06(4)</td>
<td>2.108</td>
<td>0.048</td>
</tr>
</tbody>
</table>

\(\Delta\) = Calc. - Obs.

\(\text{Av.}\) : Mean values

\(\text{Av.}\) : Derived by combining M-C, C-C (1.544 \(\text{\AA}\)), and C-N= (1.475 \(\text{\AA}\)) \(^{389}\)

Standard deviations in parentheses.
Molecular structures of the compounds \((\text{Ph}_2\text{CN})_4\text{M}^{\text{IV}}\)

\[ \text{M} = \text{Si, Ge, Sn}. \]

Figure 2-15
bond distances; silicon shows a substantial shortening relative to the calculated Si-N single bond distance, germanium much less so, and for tin the apparent reduction is of the same order as the experimental error in the bond length, although it would appear to be less than for germanium.

The C=N bond distances for the silicon and germanium compounds do not differ significantly from the calculated value for a C=N double bond, 1.265 Å. The value for the tin compound (1.33 Å) is considerably longer, however, possibly implying interactions between the C=N π-orbitals and the Sn d-orbitals. Any accompanying shortening of the Sn-N bond would be hidden by the experimental error. The only other structural determination on a compound containing a tetrahedral SnN₄ unit, the tetrakis(dimethylamino) derivative, (Me₂N)₄Sn, gave an Sn-N bond distance of 2.045 Å (i.e. close to the value observed here) with accompanying planarity at nitrogen, implying some (p-d) σ-bonding (electron diffraction study).

A preliminary crystallographic study has been carried out on (tBu₂CN)₄Sn. Decomposition of the crystal prevented determination of bond lengths and angles to any degree of accuracy, but the compound appeared to be essentially similar to its diphenyl analogue.

C. Summary

It is probable that all the new compounds described in this chapter are monomeric, with the exception of the diphenylmethyleneaminotin(iv) chlorides, (Ph₂CN)₂SnCl₂ and (Ph₂CN)₃SnCl, which appear to be associated. The 1:1 and 2:1 adducts formed by tBu₂C=NH with SnCl₄ probably contain discrete molecules rather than ions. Diphenylmethyleneamino groups, terminally bonded to Sn IV, are bent at nitrogen with little evidence of (p-d) π-bonding. In the absence of conclusive structural data, the
evidence for di-t-butylmethylenamine derivatives leaves room for a small amount of \(N \rightarrow Sn\) \(\pi\)-donation.

It is clear that, for organonitrogen derivatives of the Group IVB elements in the tetravalent state, \(N \rightarrow M\) (\(p \rightarrow d\)) dative \(\pi\)-bonding decreases sharply from silicon to germanium, and is of little importance for tin (and presumably lead). Although tin(IV) halide groups are better acceptors than their silicon and germanium analogues, it would appear that they prefer to increase their coordination number rather than the bond order to nitrogen (\(\sigma\)-bond formation will be less sensitive than \(\pi\)-bond formation to d-orbital size). If such stabilisation by increase in coordination at tin is blocked by steric effects, the stability of tin(II) species may lead to decomposition via a redox process.
CHAPTER THREE

METHYLENEAMINE DERIVATIVES OF TIN(II)
3.1 Introduction

This chapter describes the preparation and properties of some new methyleneamino-derivatives of tin(II). Their spectroscopic and structural features are discussed and compared to related compounds. The discussion section (Section 3.3) commences on p. 145.

3.2 Experimental

Compounds containing the SnII-N bond are, in general, extremely sensitive to atmospheric moisture and oxygen, particularly in solution. Greater care than usual was therefore necessary in experimental manipulations. Cryoscopic molecular weights tend to be low due to partial sample decomposition.

A. Diphenylmethyleneamine derivatives.

i) Reaction of diphenylmethyleneamine with tin dichloride (Mole ratio 1:1)

2.51 cm$^3$ diphenylmethyleneamine (15 mmol.) were added by syringe to a suspension of 2.865 g. anhydrous tin dichloride (15 mmol.) in 30 cm$^3$ dry toluene, with stirring. The mixture was heated to reflux temperature, by which time all solid had dissolved, giving a slightly cloudy yellow solution. The mixture was refluxed for 18 hours, then allowed to cool and filtered. The filtrate was concentrated by vacuum evaporation until solid appeared, then cooled to $\sim$-20°C. Over a period of 3 days the solution deposited a mass of white solid, identified as the adduct diphenylmethyleneamine tin(II) dichloride, Ph$_2$CNH.SnCl$_2$, M.Pt. 132-3°C (sealed tube).

(Found: C 42.8; H 3.7; N 3.6; Cl 20.0%.

C$_{13}$H$_{11}$NSnCl$_2$ requires: C 42.1; H 3.0; N 3.8; Cl 19.2%).
\( \nu_{\text{max}} \) (Nujol mull): 3247m, 3070w, 3025w, 1988vw, 1968vw, 1923vw, 1832vw, 1787vw, 1601sh, 1594vs, 1567vs, 1563sh, 1554sh, 1491m, 1450vs, 1386vs, 1331mw, 1307w, 1300sh, 1265vw, 1232s, 1200sh, 1192w, 1182mw, 1164m, 1108vw, 1088sh, 1080mw, 1034mw, 1003mw, 978vw, 941s, 916mw, 883vs, 860w, 853w, 840sh, 794vs, 768s, 732m, 708vs, 703vs, 679w, 643s, 624vw, 619vw, 612vw, 583vw, 572vw, 471m, 452vw, 430vw, 420vw, 408vw cm\(^{-1}\).

ii) Attempted reaction of diphenylmethyleneamine with tin dichloride in the presence of triethylamine (Mole ratio 1:1:1).

To a suspension of 2.87g. anhydrous tin dichloride (15 mmol.) in 40 cm\(^3\) dry toluene were added 2.51 cm\(^3\) diphenylmethyleneamine (15 mmol.), and the mixture was heated to reflux temperature. When all the solid had dissolved, 2.1 cm\(^3\) dry triethylamine (15 mmol.) were added. The yellow solution immediately turned orange, but no precipitate of triethylammonium chloride formed, even on refluxing overnight. On cooling to about -20°C, the solution deposited a mass of yellow solid, which did not give conclusive analyses, although a \(^1\)H-N.M.R. spectrum in d\(^8\)-toluene solution indicated the presence of triethylamine and toluene of crystallisation. Attempted recrystallisation from toluene resulted in a product whose infra-red spectrum was identical with that of \( \text{Ph}_2\text{CNH.SnCl}_2 \). (Confirmed by analysis: Found, N 3.7; Cl 19.0%).

iii) Reaction of diphenylmethyleneaminolithium with tin dichloride (Mole ratio 1:1)

A suspension of 3.044g. anhydrous tin dichloride (16 mmol.) in 20 cm\(^3\) dry ether was cooled to -196°C and a solution of 16 mmol. diphenylmethyleneaminolithium in 20 cm\(^3\) ether/pentane was added. The mixture was allowed to warm with stirring, then stirred at room temperature
overnight. Solvent was then removed under vacuum, and replaced with 40 cm$^3$ dry toluene. The mixture was refluxed for about 6 hours, then filtered while hot, yielding a mixture of a white solid with a mass of orange crystals, and an extremely air-sensitive yellow solution. This, on cooling to $\sim -20^\circ$C, deposited a bright yellow crystalline solid, identified as diphenylmethylenamine bis(diphenylmethyleneamino) ditin(II)-dichloride mono-toluene, Ph$_2$CNH. (Ph$_2$CNSn$^{II}$Cl)$_2$. C$_7$H$_8$, M.Pt. (sealed tube): Toluene lost at 121°C, turns orange and partially melts 175-185°C, completely melts $\sim 245^\circ$C.

(Found: C 58.2; H 3.5; N 4.5; Cl 7.8%; M = 246
C$_{46}$H$_{39}$N$_2$Sn$_2$Cl$_2$ requires: C 58.6; H 4.1; N 4.5; Cl 7.5%; M = 941).

$\gamma_{\text{max}}$ (Nujol mull): 3204mw, 3063mw, 3057mw, 1970vw, 1915vw, 1827vw, 1781vw, 1600vs, 1593vs, 1573vs, 1564sh, 1496mw, 1493mw, 1454s, 1447s, 1412vw, 1319mw, 1293mw, 1274m, 1233m, 1187w, 1183sh, 1170w, 1162mw, 1159mw, 1080mw, 1032mw, 1004w, 997vw, 983w, 954w, 950sh, 946sh, 937w, 924mw, 860w, 799mw, 792m, 780s, 737m, 732s, 714vs, 705vs, 700sh, 688w, 670s, 639mw, 628vw, 620vw, 588vw, 529m, 476w, 464mw, 459w, 448vw, 415vw cm$^{-1}$.

The orange-white filter cake was briefly refluxed with 60 cm$^3$ dry toluene and filtered while hot, giving a white solid (LiCl) and an orange solution which, on cooling to room temperature, deposited large orange crystals of diphenylmethylenaminotin(II) chloride dimer, (Ph$_2$CNSn$^{II}$Cl)$_2$, M.Pt. 245-255°C (sealed tube).

(Found: C 46.4; H 3.3; N 4.2; Cl 11.1%; M = 546 slight dec.
C$_{26}$H$_{20}$N$_2$Sn$_2$Cl$_2$ requires: C 46.7; H 3.0; N 4.2; Cl 10.6%; M = 668).
iv) Reaction of diphenylmethyleneaminolithium with tin dichloride  
(Mole ratio 2:1)

A solution of 30 mmol. diphenylmethyleneaminolithium in \( \sim 35 \text{ cm}^3 \) ether/hexane was added to a suspension of 2.84g. anhydrous tin dichloride (15 mmol.) in 5 cm\(^3\) dry ether at \(-196^\circ\text{C}\). The mixture was allowed to warm to room temperature with stirring, then stirred overnight, giving a voluminous orange precipitate under a red solution.

The solvent was then removed under vacuum and replaced by 55 cm\(^3\) dry toluene. The mixture was then heated to \( \sim 95^\circ\text{C} \) with stirring and filtered while hot, yielding a small quantity of orange solid (mainly LiCl) and a very dark red solution. The latter was concentrated to about 30 cm\(^3\) and cooled to \(-20^\circ\text{C} \), when it deposited a bright red microcrystalline solid, bis(diphenylmethyleneaminotin(II)dimer, \([\text{Ph}_2\text{CN}]_2\text{Sn}^{\text{II}}]_2 \) M.Pt. 133-4°C (Sealed Tube).

(Found: C 61.5; H 6.3; N 5.2; Cl 0%; \( M = 733 \) slight dec. \( \text{C}_{52}\text{H}_{20}\text{N}_{10}\text{Sn}_{2} \) requires: C 65.2; H 4.2; N 5.8; Cl 0%; \( M = 958 \)).

\( \gamma_{\text{max}} \) (Nujol Mull): 3073vw, 3054w, 3028mw, 1978w, 1900vw, 1833vw, 1780vw, 1599sh, 1588vs, 1564vs, 1546sh, 1493mw, 1448vs, 1406w, 1319s, 1294m, 1280s, 1268m, 1193sh, 1184mw, 1170mw, 1166mw, 1081m, 1031m, 1007mw, 1004sh, 988w, 979mw, 956s, 941w, 928mw, 893vw, 862w, 853w, 797sh, 792vs, 783vs, 736m, 712vs, 687sh, 671vs, 656sh, 646vw, 630vw, 623vw, 529s, 512mw, 467mw, 458s, 415 vw cm\(^{-1}\).
v) **Attempted reaction of diphenylmethyleneaminolithium with tin dichloride (Mole ratio 3:1).** (Performed by Mr B. Hall)

A solution of 45 mmol. diphenylmethyleneaminolithium in about 50 cm$^3$ ether/hexane was added to a suspension of 2.84g. anhydrous tin dichloride (15 mmol.) in 10 cm$^3$ ether at -196°C. The mixture was allowed to warm to room temperature with stirring, and then stirred overnight. Solvent was removed under vacuum, and the resulting red solid was extracted with 60 cm$^3$ hot toluene, yielding a red solution from which no characterisable product could be obtained.

vi) **Attempted reaction of diphenylmethyleneaminotin(II) chloride dimer with sodium cyclopentadienide**

A solution of 2.99 mmol. sodium cyclopentadienide in 10 cm$^3$ dry THF was added dropwise to a stirred solution of lg. (Ph$_2$CNSnCl)$_2$ (1.495 mmol.) in 30 cm$^3$ dry THF at 0°C. The initially bright yellow solution darkened to orange-red. The mixture was stirred at room temperature for about 12 hours, then all solvent was removed under vacuum and replaced by 20 cm$^3$ dry toluene. The mixture was warmed to complete solution, then filtered to remove the fine suspension of NaCl. The resulting orange-red solution was concentrated to about 10 cm$^3$ and cooled to -20°C, when a very small quantity of deep yellow crystalline solid separated out. Attempts to increase the yield by addition of non-solvent hexane resulted in partial decomposition of the extremely air-sensitive product, and all that could be obtained was an opaque red-brown oil, the infra-red spectrum of which showed $\tilde{\nu}(C=N)$ at 1604 cm$^{-1}$ and a broad strong absorption at 766 cm$^{-1}$ (typical of a $\pi$-complexed C$_5$H$_5$ group), consistent with the presence of C$_5$H$_5$Sn$^{II}$N=CPh$_2$. 
vii) Attempted preparation of a diphenylmethyleneaminotin(II) chloride dimer - THF adduct.

0.6g. \((\text{Ph}_2\text{CNSnCl})_2\) were dissolved in 20 cm\(^3\) dry THF with warming, and the resulting yellow solution was allowed to cool. 15 cm\(^3\) dry hexane (non-solvent) were added, and the mixture was concentrated under vacuum until crystals appeared. The solution was then cooled to -20°C, and over a period of several days it deposited an orange crystalline solid, whose analytical and infrared spectral properties were identical to those of the starting material, \((\text{Ph}_2\text{CNSnCl})_2\).

(found: C 46.6%; \(\text{C}_{26}\text{H}_{20}\text{N}_2\text{Sn}_2\text{Cl}_2\) requires C 46.7%).

It was concluded that no complex is formed with THF.

B. Di-t-butyldimethyleneamine derivatives

i) Reaction of di-t-butyldimethyleneaminolithium with tin dichloride
(Mole ratio 2:1)

A solution of 60 mmol. di-t-butyldimethyleneaminolithium in approximately 50 cm\(^3\) dry pentane was added to a suspension of 6.0g. anhydrous tin dichloride (31.7 mmol. - slight excess) in 100 cm\(^3\) dry ether at -196°C. The mixture was allowed to warm to room temperature with stirring. As it warmed up, the lemon-yellow colour of the iminolithium deepened almost to orange, and a yellow precipitate began to form. The mixture was stirred overnight, and then all solvent was removed under vacuum. The residue was extracted with 50 cm\(^3\) dry hexane, yielding a pale yellow solid (LiCl) and a yellow-brown solution, which on concentration under vacuum and cooling deposited a brownish-yellow semi-crystalline solid, identified as \(\text{bis(di-t-butyldimethyleneamino)tin(II)}\), \([\text{(tBu}_2\text{CN)}_2\text{Sn}^{\text{II}}]_n\), M.Pt. 121-3°C dec. (sealed tube).

(found: C 47.4; H 8.7; N 7.0; Cl 0; Li 0%; M = 237 dec.
\(\text{C}_{18}\text{H}_{36}\text{N}_2\text{Sn} \) requires: C 54.2; H 9.0; N 7.0; Cl 0; Li 0%; M = 399).
\( \nu_{\text{max}} \) (Nujol mull): 1628s, 1604sh, 1477s, 1390m, 1362s, 1321w, 1205m, 1038mw, 961m, 947m, 927mw, 876w, 838w, 785vw, 729vw, 673w, 657mw, 594m, 564mw, 546sh, 479m, 388vw, 354vw cm\(^{-1}\)

Several other attempts at the preparation of this compound, which followed essentially the same experimental procedure but made use of stoichiometric quantities of the reactants, gave crystalline products of variable composition and appearance, ranging from yellow needles to yellow-brown elongated hexagonal prisms. All these compounds contained lithium in varying quantities, and their composition appeared to lie between the extremes of \((^{t}\text{Bu}_2\text{CN})_2\text{Sn}\) and \(\text{Li}(^{t}\text{Bu}_2\text{CN})_3\text{Sn}\), tending towards the latter.

ii) Reaction of di-t-butylmethylenediaminolithium with tin dichloride 
(Mole ratio 3:1)

A solution of 45 mmol. di-t-butylmethylenediaminolithium in about 65 cm\(^3\) dry pentane was added to a suspension of 2.845g. anhydrous tin dichloride (15 mmol.) in 20 cm\(^3\) dry ether at -196\(^\circ\)C, and the mixture was allowed to warm to room temperature with stirring, then stirred overnight. The resulting yellow solution over a brownish-yellow precipitate was evaporated to dryness under vacuum, and the residue was refluxed for 30 mins. in 40 cm\(^3\) dry hexane. The mixture was filtered while hot, yielding lithium chloride as the filter cake and a dark yellow solution, which, on concentration to about half volume, heating to redissolve precipitated solid, and cooling to room temperature, deposited large golden-yellow hexagonal prisms of lithium tris(di-t-butylmethylenediamino)tin (II), \(\text{Li}(^{t}\text{Bu}_2\text{CN})_3\text{Sn}^{\text{II}}\), M.Pt. 170-180\(^\circ\)C dec. without melting (sealed tube).
(Found: C 58.9; H 9.6; N 7.7; Li 1.6%; M = 347 dec.

C_{27}H_{54}N_{3}SnLi requires: C 59.4; H 9.9; N 7.7; Li 1.3%; M = 545).

\nu_{\text{max}} (Nujol mull): 1619vs, 1592sh, 1480s, 1386m, 1361vs, 1350sh, 1323w, 1209m, 1039mw, 1024w, 957m, 930w, 877w, 838w, 796vw, 723vw, 663mw, 588mw, 559w, 492mw, 406m, 365vw cm\textsuperscript{-1}
3.3 Discussion

A. Preparation and stability of methyleneamine derivatives of tin(II)

The new compounds are listed in Table 23. They are divided into four groups for the discussion of their structural and spectroscopic properties.

<table>
<thead>
<tr>
<th>TABLE 23</th>
</tr>
</thead>
<tbody>
<tr>
<td>New tin(II) derivatives of methyleneamines</td>
</tr>
</tbody>
</table>

Group A:

- $(\text{Ph}_2\text{CNSnCl})_2$: orange crystals
- $[(\text{Ph}_2\text{CN})_2\text{Sn}]_2$: red microcrystalline solid
- $[\left(\text{tBu}_2\text{CN}\right)_2\text{Sn}]_n^a$: yellow crystalline solid

Group B:

- $\text{Ph}_2\text{CNH.SnCl}_2$: white solid
- $\text{Ph}_2\text{CNH.}(\text{Ph}_2\text{CNSnCl})_2\cdot\text{C}_7\text{H}_8$: yellow crystals
- $\left(\text{tBu}_2\text{CN}\right)_2\text{HSn}_2\text{Cl}_3^b$: yellow crystalline solid

Group C:

- $\left(\text{tBu}_2\text{CN}\right)_3\text{H}_2\text{Sn}_2\text{Cl}_5^b$: colourless crystals

Group D:

- $\text{Li}(\text{tBu}_2\text{CN})_3\text{Sn}$: yellow crystals

$a$: n probably = 2

$b$: preparation and infra-red spectrum described in Chapter 1.

All the new compounds are air- and moisture-sensitive, with the exception of $(\text{Ph}_2\text{CNSnCl})_2$, which is stable in the solid state to several hours' exposure to air. This is presumably a kinetic effect associated
with the structure of the crystal, since solutions of this compound are extremely sensitive to traces of moisture, which accounts for the formation of the methyleneamine adduct $\text{Ph}_2\text{C}NH.\left(\text{Ph}_2\text{CNSnCl}\right)_2\cdot\text{C}_7\text{H}_8$ from traces of the free imine produced by hydrolysis of the imino-tin(II) during the course of preparation.

On exposure to air, the compounds become wet with the parent methyleneamine, the di-t-butyl derivatives turning white and the diphenyl derivatives first yellow, then white on longer exposure. The latter yellowing is accompanied by the appearance in the infra-red spectrum of a broad band at about 530-560 cm$^{-1}$, attributable to a tin-oxygen stretching vibration. It is probable that direct oxidation by atmospheric oxygen occurs additionally to hydrolysis of the Sn$^{II}$-N bond (cf. the action of oxygen on dialkylaminotins, Chapter 1, Table 1).

Most of the new compounds are highly coloured, particularly the bis-imino derivatives, in contrast to the methyleneamino derivatives of tin(IV), which are generally colourless or pale yellow. It might be expected that the nature of the M-N bond will affect the electronic spectrum of the imino-group due to its interaction with the C=N chromophore. It therefore appears likely that the investigation of the UV spectra of iminosilanes undertaken by Chan and Rochow could be profitably extended to other N-metallated methyleneamines, particularly in view of the considerable variation in colour of such materials.

The synthetic route to the new compounds in most cases involved the reaction of tin dichloride with the appropriate imino-lithium, with elimination of lithium chloride (Eqn. 3.1). An alternative route, involving abstraction of HCl from the imine-tin dichloride complex by triethylamine (Eqn. 3.2), failed.
\[ \text{SnCl}_2 + n\text{LiN=CR}_2 \rightarrow (\text{R}_2\text{CN})_n\text{SnCl}_{2-n} + n\text{LiCl} \quad 3.1 \]
\[ \text{Et}_3\text{N} + \text{Ph}_2\text{CNH.SnCl}_2 \rightarrow \text{Ph}_2\text{CNSnCl} + \text{Et}_3\text{NH}^+\text{Cl}^- \quad 3.2 \]

N-lithiated reagents have also been used in the preparation of bis(dimethylamino)tin(II) and other bis(dialkylamino)tins; like the former, the new methyleneamino derivatives attain coordination numbers at tin greater than two by the use of nitrogen bridges. Coordination numbers of three and four are also achieved using the parent methyleneamine as a ligand.

The existence of the monomeric dialkyllaminotin(II) cyclopentadienyls, \( \text{R}_2\text{NSn}^{\text{II}}\text{C}_5\text{H}_5 \), prompted an attempt to prepare the corresponding diphenylmethyleneamino derivative, \( \text{Ph}_2\text{C}=\text{NSn}^{\text{II}}\text{C}_5\text{H}_5 \), which would be expected to contain a \( \tau \)-bonded \( \text{C}_5\text{H}_5 \) ring and a terminally bonded imino group. The spectrum of the product suggested that the reaction between \( \text{(Ph}_2\text{CNSnCl)}_2 \) and \( \text{NaC}_5\text{H}_5 \) (Eqn. 3.3) had produced the required compound,
\[ \text{(Ph}_2\text{CNSn}^{\text{II}}\text{Cl})_2 + 2\text{NaC}_5\text{H}_5 \rightarrow 2\text{Ph}_2\text{C}=\text{NSn}^{\text{II}}\text{C}_5\text{H}_5 + 2\text{NaCl} \quad 3.3 \]
but the reaction was performed on too small a scale to tolerate the inevitable minor atmospheric contamination, and a pure product could not be isolated. The structure of such a compound would be of interest, and it is hoped that repetition on a larger scale will lead to a successful preparation.
B. Spectroscopic and Structural Properties.

For the purpose of discussion the new tin(II) derivatives have been divided into four groups of related compounds. Some more general points are covered in an additional section. Spectroscopic data are tabulated at the end of this chapter, commencing on p.176.

Mass spectra are listed in Table 27a-e for all the new compounds, excepting Ph$_2$CNH.SnCl$_2$, [(Ph$_2$CN)$_2$Sn$^{II}$]$_2$, and (Bu$_2$CN)$_3$H.Sn_Cl$_5$, which generated no metal-containing fragments.

The $^1$H-NMR spectra of the di-t-butylmethyleneamine derivatives (Table 28) were recorded as solutions in $d^8$-toluene or C$_6$D$_6$ at about 45°C and temperatures down to -100°C. The diphenylmethyleneamine derivatives, with the exception of the complex (Ph$_2$CN)$_3$H.Sn.Cl$_2$.C$_7$H$_8$, were not investigated, since their spectra were considered to be unlikely to provide additional structural information.

The infra-red spectra of the new compounds were recorded as nujol mulls. Their azomethine stretching frequencies are listed in Table 29. As in the case of the tin(IV) compounds, some difficulty was encountered in assigning $\nu$(C=N) for the diphenylmethyleneamino derivatives because of the obscuring aromatic absorptions, and some assignments are necessarily tentative.

S. Wallwork and M.M. Mahmoud have determined the crystal and molecular structures of (Ph$_2$CN$\cdot$SnCl)$_2$ and its diphenylmethyleneamine adduct, Ph$_2$CNH.(Ph$_2$CN$\cdot$SnCl)$_2$.C$_7$H$_8$, by X-ray diffraction. Their results are discussed in detail in the sections dealing with those compounds.

1) **Group A. Compounds of the type** (R$_2$CN$\cdot$SnX)$_n$, **X = R$_2$CN,Cl.**

For the methyleneaminotin(II) compounds in general, cryoscopic molecular weights, determined using benzene as solvent, tended to be
low due to partial sample decomposition. The results obtained, however, indicate that the diphenylmethyleneamino derivatives (Ph-CN)_2Sn and Ph_2CNSnCl are associated and probably dimeric in solution, with structures of the type shown in Figure 3-1. A trans configuration for the groups X

\[ \text{Figure 3-1} \]

would be expected to minimise repulsion between the metal lone pairs. A crystallographic study has confirmed this structure for (Ph_2CNSnCl)_2, described in full at the end of this section.

A similar dimeric structure might be expected for the di-t-butyl methyleneamino compound (tBu-CN)_2Sn, but its cryoscopic molecular weight, although very low due to sample decomposition (it is lower than the monomer weight), would be consistent with a monomeric state in solution, a conclusion supported by its \(^1H\)-NMR spectrum. This shows a single tBu resonance at ambient temperatures (Table 28; p.178) in contrast to the results obtained for the compounds [(tBu-CN)_2M]_2 (M = Be, Zn, Mg), whose spectra all clearly differentiate between bridging and terminal methyleneamino groups even at room temperature (for the beryllium and zinc compounds, the slightly bent terminal C=N=M skeleton is also indicated by further splitting, a total of three signals being observed). The spectrum of the tin compound is, however, partially resolved into two signals at very low temperatures (-100°C), probably corresponding to bridging and terminal methyleneamino groups.
A similar effect is observed for the dimeric tin(II) amine, 
\[\text{[(Me}_2\text{N)}_2\text{Sn} \text{]}_2\], which gives a single methyl signal at room temperature, but at \(-40^\circ\text{C}\) this is resolved as a doublet (with some additional resonances due probably to the presence of the cis-isomer as well as the sterically-favoured trans-form), corresponding to the terminal and bridging Me\(_2\)N-groups. Cryoscopic studies indicated that 
\[\text{[(Me}_2\text{N)}_2\text{Sn} \text{]}_2\] was dimeric in solution, and the \(^1\text{H-NMR}\) results were interpreted in terms of rapid intramolecular exchange of amino-groups. A similar explanation seems likely here, although, owing to the bulk of the \(\text{tBu}\)-groups, there may be an equilibrium in solution between dimer and monomer.

The infra-red spectrum, however, shows two \(\nu(C=N)\) absorptions (Table 29), corresponding to terminal and bridging imino groups, which indicates association in the solid. It would not be unreasonable to ascribe a tendency to dissociate in solution to the steric requirements of the bulky \(\text{tBu}\)-butyl groups, but the corresponding beryllium compound, 
\[\text{[(tBu}_2\text{CN)}_2\text{Be} \text{]}_2\], which would be expected to be more crowded because of the smaller metal atom, is a stable dimer.\(^{380}\) The tin compound may similarly be dimeric in the solid, but a polymeric structure (Fig. 3-2) is also possible.

\[\text{Figure 3-2}\]
Such a structure might also explain the difficulty experienced in preparing \([\left(\text{tBu}_2\text{CN}\right)_2\text{Sn}]_n^{\text{II}}\), free of lithium, in contrast to \([\left(\text{Ph}_2\text{CN}\right)_2\text{Sn}]_2^{\text{II}}\), where no problem was encountered. In a polymeric structure, it would be possible for chains of varying lengths to be terminated by iminolithium groups (Fig. 3-3).

\[ \begin{array}{c}
\text{Li} \\
\text{C} \quad \text{Bu}_2 \\
\text{N} \\
\text{C} \quad \text{Bu}_2 \\
\text{Sn} \\
\text{C} \quad \text{Bu}_2 \\
\text{N} \\
\text{C} \quad \text{Bu}_2 \\
\text{Li} \\
\end{array} \]

Figure 3-3

It is of interest that both \((\text{tBu}_2\text{CN})_2\text{Be}\) \(^{380}\) and \((\text{tBu}_2\text{CN})_3\text{Al}\) \(^{329}\) were similarly found to be difficult to prepare from the metal chloride and the iminolithium, due to formation of \(\text{Li}(\text{tBu}_2\text{CN})_3\text{Be}\) and \(\text{Li}(\text{tBu}_2\text{CN})_4\text{Al}\) respectively, whereas the related diphenylmethylenediamino derivatives \((\text{Ph}_2\text{CN})_2\text{Be}\) and \((\text{Ph}_2\text{CN})_3\text{Al}\) were readily preparable by this route. \(^{330,353}\)

The azomethine stretching frequencies for the new tin(II) compounds are listed in Table 29 (p. 179). The compounds \([\left(\text{Ph}_2\text{CN}\right)_2\text{Sn}]_2\) and \([\left(\text{tBu}_2\text{CN}\right)_2\text{Sn}]_n\) both appear to show two bands corresponding to \(\nu(C=N)\) due to terminal and bridging imino-groups, consistent with the postulated associated structures, whereas only one is found for \((\text{Ph}_2\text{CNSnCl})_2\).

The \(\nu(C=N)\) values for terminally bonded methylenediamino groups are quite similar for corresponding derivatives of tin(II) and tin(IV) (see Chapter 2, Tables 15 and 16, for the latter). This may indicate that there is little or no tin-nitrogen \(\pi\)-interaction in these compounds, since otherwise the differing electronegativities of tin(II) and tin(IV) (1.78 and 1.93 respectively, derived from thermochemical data \(^{352}\)), and their difference in size (1.63 \(^{397}\) and 1.40 \(^{372}\) A), might be expected to
have a greater effect on $\nu(\text{C=N})$ than is observed.

There is comparatively little variation in bridging azomethine stretching frequencies among the tin(II) derivatives (with the exception of the probably ionic species $(t\text{Bu}_2\text{CN})_3\text{H}_2\text{Sn}_3\text{Cl}_5$). Generally, the absorptions vary little in position from that of the bridging imino-groups in $
abla (\text{Ph}_2\text{CN})_2\text{Sn}^{\text{IV}}\text{Cl}_2$ (1553 cm$^{-1}$; see Chapter 2).

The mass spectra of $(t\text{Bu}_2\text{CN})_2\text{Sn}$ and (Ph$_2$CNSnCl)$_2$ are listed in Table 27 (p. 176). The former (Table 27d) does not generate any fragments containing more than one metal atom, and the presence of peaks corresponding to $(t\text{Bu}_2\text{CN})_3\text{Sn}^+$ (m/e 540) and its break-down products, which could be taken as proof of association in the gas-phase, could also arise as a result of recombination (from $(t\text{Bu}_2\text{CN})_2\text{Sn}^+$ and $t\text{Bu}_2\text{CN}^+$), so that no firm support for an associated structure is provided. However, the spectrum of (Ph$_2$CNSnCl)$_2$ (Table 27a) clearly reveals its dimeric nature. It is of interest that one of the most intense peaks attributable to a tin-containing fragment corresponds to the fragment Ph$_2$CNSn$_2$Cl$_2^+$ (m/e 490). In view of the structure from which it is derived, this is probably an imino-bridged species (Fig. 3-4), and its 

![Figure 3-4](attachment:image.png)

relatively high stability serves to confirm the stability of the Sn-N-Sn bridge when tin is bonded to electron-withdrawing groups.
The crystal structure of (Ph$_2$CNSn$^{II}$Cl)$_2$.

The crystal and molecular structures of diphenylmethyleneaminotin(II) chloride dimer, (Ph$_2$CNSn$^{II}$Cl)$_2$, have been determined by X-ray diffraction. The molecular structure is illustrated in Figure 3-6, and relevant bond lengths and angles are listed in Table 24.

The structure is based upon an Sn$_2$N$_2$ ring. The cross-ring Sn-Sn distance, 3.507 Å, is considerably greater than the Sn-Sn bond distances reported for (Ph$_2$Sn)$_6$ (average 2.78 Å) or crystalline [(Me$_3$Si)$_2$CH]$_2$Sn$_2$ (2.764 Å), implying the absence of a metal-metal bond.

For (Ph$_2$CNSnCl)$_2$, there is no evidence for an asymmetric ring of the type shown in Fig. 3-5; the nitrogens bridge symmetrically between the metal atoms, although N(2) is slightly further away from the tins than N(1).

![Figure 3-5](image)

This distortion is accompanied by a slight tilt of both Sn-Cl bonds towards N(1). The environment of nitrogen is approximately planar, but the Sn$_2$N$_2$ ring is slightly puckered, the dihedral angle between the planes defined by Sn(1)N(1)Sn(2) and by Sn(1)N(2)Sn(2) being 168.1°.

The most important feature of this structure is the 3-coordinate pyramidal environment of the tin atoms. The chlorine atoms lie trans to one another above and below the Sn$_2$N$_2$ mean plane, the Sn-Cl bonds being approximately perpendicular to it. The bond angles at tin are much
### TABLE 24

**Bond lengths and angles from the X-ray crystal structure**

of (Ph₂CNSnCl₂)²⁺

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>( \bar{\AA} )</th>
<th>Bond angles</th>
<th>°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-N(1)</td>
<td>1.286 (7)</td>
<td>Sn(1)N(1)Sn(2)</td>
<td>105.6 (2)</td>
</tr>
<tr>
<td>C(2)-N(2)</td>
<td>1.276 (8)</td>
<td>Sn(1)N(2)Sn(2)</td>
<td>103.7 (2)</td>
</tr>
<tr>
<td>Sn(1)-N(1)</td>
<td>2.208 (5)</td>
<td>N(1)Sn(1)N(2)</td>
<td>75.0 (2)</td>
</tr>
<tr>
<td>Sn(1)-N(2)</td>
<td>2.230 (6)</td>
<td>N(1)Sn(2)N(2)</td>
<td>74.7 (2)</td>
</tr>
<tr>
<td>Sn(2)-N(1)</td>
<td>2.193 (5)</td>
<td>Cl(1)Sn(1)N(1)</td>
<td>84.6 (2)</td>
</tr>
<tr>
<td>Sn(2)-N(2)</td>
<td>2.228 (5)</td>
<td>Cl(1)Sn(1)N(2)</td>
<td>90.5 (2)</td>
</tr>
<tr>
<td>Sn(1)-Cl(1)</td>
<td>2.452 (2)</td>
<td>Cl(2)Sn(2)N(1)</td>
<td>84.8 (2)</td>
</tr>
<tr>
<td>Sn(2)-Cl(2)</td>
<td>2.472 (2)</td>
<td>Cl(2)Sn(2)N(2)</td>
<td>90.6 (2)</td>
</tr>
</tbody>
</table>

**Non-bonded distances \( \bar{\AA} \)**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2)</td>
<td>2.692 (7)</td>
</tr>
<tr>
<td>Sn(1)-Sn(2)</td>
<td>3.507 (1)</td>
</tr>
</tbody>
</table>

**Calculated bond lengths \( \bar{\AA} \)**

\[
\begin{align*}
\text{Sn}^{II} &- \text{Cl} & 2.62 & \text{(from covalent radii)} \\
\text{Sn}^{II} &- \text{N} & 2.33 \\
\text{C} &- \text{N} & 1.265 & \text{(389)}
\end{align*}
\]

Estimated standard deviations in parentheses
Molecular structure of \( \text{Ph}_2\text{CNSn}^{\text{II}}\text{Cl}_2 \).
smaller than the tetrahedral angle, implying a large amount of p-character in the bonds, and the NSnN angles of 75.0° and 74.7° are unusually small, probably a result of the stereochemical activity of the tin(II) lone pair, since in other methyleneamino derivatives containing an M₂N₂ ring a considerably smaller angle at nitrogen is tolerated in order to permit a wider angle at the metal (Table 25). The ClSnN angles are similar to the bond angles found in other pyramidal tin(II) species, such as the SnCl₃⁻ ion. 395,396

Table 25 lists the ring bond angles for those methyleneamino derivatives containing M₂N₂ rings whose structures are known. The majority of these are derivatives of the lighter elements of Groups II and III, i.e. Be, Mg, B and Al. The M-N bond distances (not listed) were generally close to the calculated values for single bonds, with the exception of the beryllium and tin compounds, where they were found to be shorter. For the beryllium compound this may be due to a small amount of π-delocalisation around the ring, 336 but although such delocalisation might be possible for tin(II) by the use of d-orbitals, it is perhaps more likely that an inaccurate value for its covalent radius (concerning which there is some controversy) has given rise to a calculated value for the Sn²⁺-N single bond length (2.33Å) which is too large. The covalent radius derived by Rundle and Olsen 397 has been used here (1.63Å), but values in the range 1.35-1.86 Å have been assigned. 12 The observed ring Sn²⁺-N bond lengths of 2.215 and 2.207 Å (average values) in fact compare well with 2.25 Å found for phthalocyaninato tin(II), 40 and if they are assumed to be single bonds, then the nitrogen single-bond covalent radius of 0.70 Å 372 would give a covalent radius for tin(II) of about 1.52 Å. 
### TABLE 25

Selected bond angles from the structures of some methyleneamino derivatives containing the \( \text{M}_2\text{N}_2 \) ring system

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \angle \text{MNM} ) (°)</th>
<th>( \angle \text{NNM} ) (°)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([t\text{Bu}_2\text{CN}]_2\text{Be}]_2</td>
<td>83.1 (7)</td>
<td>96.9 (7)</td>
<td>336</td>
</tr>
<tr>
<td>(Ph\text{CNMgBr.} \text{THF})_2 \text{THF}</td>
<td>88.0 (2)</td>
<td>89.0 (2)</td>
<td>382</td>
</tr>
<tr>
<td>(MeCH=\text{NBe}_2) \text{2}</td>
<td>93.6 (3)</td>
<td>86.4 (3)</td>
<td>399</td>
</tr>
<tr>
<td>(t\text{BuMeC=NAlMe}_2) \text{2}</td>
<td>94.6 (5)</td>
<td>85.4 (5)</td>
<td>399</td>
</tr>
<tr>
<td>(p-\text{BrC}_6\text{H}_4 \text{PhC=NAlPh}_2) \text{2C}_6\text{H}_6</td>
<td>97.1</td>
<td>82.9</td>
<td>400</td>
</tr>
<tr>
<td>(Ph\text{_2CNSnCl})_2</td>
<td>104.7 (2)(^a)</td>
<td>74.9 (2)(^a)</td>
<td>378</td>
</tr>
<tr>
<td>Ph\text{2CNH.(Ph}_2\text{CNSnCl})_2 \text{C}_7\text{H}_8</td>
<td>101.5 (3)(^a)</td>
<td>77.1 (3)(^a)</td>
<td>378</td>
</tr>
</tbody>
</table>

\(\(^a\)\) Average

Estimated standard deviations in parentheses.
Comparison of the bond angles within the $M_2N_2$ rings for those compounds which may be considered to involve approximately $sp^3$ hybridisation at the metal (i.e. the B, Al, and Sn compounds) shows that the angle at tin is about 9° smaller than for the lighter elements, allowing the angle at nitrogen to expand considerably. The bridging $\widehat{NMN}$ angle for the beryllium compound is about 12° greater than for the boron and aluminium compounds, which has been explained in terms of the low atomic number of beryllium, which causes it to be less tolerant of deformation of the bond angles away from the 120° expected for $sp^2$ hybridisation. For tin the reverse will be true, so that a greater degree of departure from the angle expected for $sp^3$ hybridisation is allowed. Alternatively, the small angles at tin may be seen as an example of the tendency for the heavier elements to bond using unhybridised $p$-orbitals.

The magnesium compound also has a relatively large angle at the metal, but this is probably due to the bridging THF molecule, which makes the magnesium 5-coordinate. The imino-bridges occupy two equatorial positions of a distorted trigonal bipyramid, so that the optimum $\widehat{NMgN}$ bond angle would be 120°.

The average Sn-Cl bond length for $(\text{Ph}_2\text{CNSnCl})_2$, 2.462 Å, is considerably shorter than the calculated single bond distance of 2.62 Å (although better agreement is obtained if the modified covalent radius for Sn$^{II}$, derived earlier, is used), and is shorter than most other Sn$^{II}$-Cl bond lengths in the literature. Other terminal Sn$^{II}$-Cl bond lengths are 2.67 Å (crystalline SnCl$_2^{20}$), 2.59 Å (SnCl$_2.2\text{H}_2\text{O}^{18}$), 2.63 and 2.54 Å (KSnCl$_3^{395}$) and 2.679 Å (C$_5$H$_5$SnCl$_3^{379}$). However, there is quite good agreement with the values found for gaseous SnCl$_2^{17}$ (2.42 Å, by electron diffraction) and the green form of chloro-bis 1,2-bis(diphenyl-
In the latter two compounds, there are no weak, long distance, M···Cl-Sn interactions such as those observed for the other examples quoted, so that the short Sn-Cl bond lengths found here may merely reflect the lack of such weak interactions in crystalline \((\text{Ph}_2 \text{CNSnCl})_2\). Unassociated \(\text{Sn}^{IV}\)-Cl bonds are considerably shorter, e.g. 2.32 Å in \(\text{Ph}_3\text{Sn}^{IV}\text{Cl}\).

ii) **Group B.** The methyleneamine adducts, \(\text{R}_2\text{CNH.(R}_2\text{CN})_2\text{SnCl}_{2-n}(2m-n)\).

The compounds discussed in this section are the related adducts \(\text{Ph}_2\text{CNH.SnCl}_2\), \(\text{Ph}_2\text{CNH.(Ph}_2\text{CNSnCl})_2\text{C}_7\text{H}_8\), and \(\text{tBu}_2\text{CNH.tBu}_2\text{CNSnCl}_2\).

The diphenylmethyleneamine-tin dichloride adduct, \(\text{Ph}_2\text{CNH.SnCl}_2\), is likely to be a monomeric, 3-coordinate species, although no evidence for its state of association could be obtained.

The other diphenylmethyleneamine adduct, \(\text{Ph}_2\text{CNH.(Ph}_2\text{CNSnCl})_2\text{C}_7\text{H}_8\), is derived from the dimer \((\text{Ph}_2\text{CNSnCl})_2\), and a crystallographic study has shown that the \(\text{Sn}_2\text{N}_2\) ring is retained on complex formation, so that the resulting compound contains both 3- and 4-coordinate tin(II) (Fig. 3-7). The coordinated methyleneamine group is comparatively weakly bonded; it is readily lost on
heating and the cryoscopic molecular weight (246) is sufficiently close to one third of the formula weight for \((\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\cdot\text{C}_7\text{H}_8\) (313.8) to suggest complete dissociation in solution (Eqn. 3.4). Weaker bases, such as THF, do not form stable complexes.

\[
(\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\cdot\text{C}_7\text{H}_8 \rightarrow \text{Ph}_2\text{CNH} + (\text{Ph}_2\text{CNSnCl})_2 + \text{C}_7\text{H}_8 \quad 3.4
\]

Of the unusual complexes obtained from the thermal decomposition of the tin(IV) derivative \((^\dagger\text{Bu}_2\text{CN})_2\text{Sn}^{\text{IV}}\text{Cl}_2\) (Chapter 2), \((^\dagger\text{Bu}_2\text{CN})_2\text{HSn}_2\text{Cl}_3\) is probably related to the diphenylmethyleneamine derivative \((\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\) and the spectroscopic evidence is consistent with a related structure (Fig. 3-8).

![Figure 3-8](image)

The presence of a bridging chlorine atom is uncertain; such bridges are well known for tin(II) chloro-compounds, but it might be expected that the complex would be stable with both tin atoms 3-coordinate. However, the coordinated imine molecule is not very strongly held; it is lost on heating, unlike that in \(\text{Ph}_2\text{CNH},\text{SnCl}_2\), but like the methyleneamine attached to four-coordinate tin(II) in \(\text{Ph}_2\text{CNH},(\text{Ph}_2\text{CNSnCl})_2,\text{C}_7\text{H}_8\).

The dinuclear structure of \((^\dagger\text{Bu}_2\text{CN})_2\text{HSn}_2\text{Cl}_3\) is demonstrated by the appearance of several di-tin-containing fragments in its mass spectrum (Table 27e), although no parent peak is seen. The coordinated
methyleneamine molecule will probably be readily lost; the additional imino-group in the fragment \((^t\text{Bu}_2\text{CN})_2\text{Sn}_2\text{Cl}^+\) (m/e 555) is probably a result of recombination (from \(^t\text{Bu}_2\text{CNSnCl} + ^t\text{Bu}_2\text{CNSn}\). The only detectable metal-containing fragment in the spectrum of \(\text{Ph}_2\text{CNH}\cdot\left(\text{Ph}_2\text{CNSnCl}\right)_2\cdot\text{C}_7\text{H}_8\) corresponds to the ion \(\text{Ph}_2\text{CNSnCl}_2^+\). (Table 27b).

Further evidence for the proposed structure of \((^t\text{Bu}_2\text{CN})_2\text{HSnCl}_3\) is provided by its \(^1\text{H}-\text{NMR}\) spectrum (Table 28) which exhibits three singlet absorptions in the \(^t\text{Bu}\) region, of which the upfield pair may be assigned to a \(^t\text{Bu}_2\text{CN}\) ligand whose \(^t\text{Bu}\) groups are in differing chemical environments. Because of the generally facile inversion process at nitrogen for N-metallated methyleneamines, this group must be strongly restrained from inversion, for example by bridging between dissimilar tin-containing groups. On this basis, the remaining singlet may be assigned to an N-protonated imino-group, to account for the other spectroscopic properties.\((^t\text{Bu}_2\text{CN})_2\text{HSnCl}_3\), from its infra-red spectrum, contains a coordinated methyleneamine group, and the structure shown in Fig. 3-9 accounts for the observed \(^1\text{H}-\text{NMR}\) spectrum. Surprisingly, the signal due to the coordinated imine group could not be resolved as a doublet on cooling, unlike the \(^t\text{Bu}_2\text{CNH}\cdot\text{tin tetrachloride adducts}\) (Chapter 2).
The spectrum of \((\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\cdot\text{C}_7\text{H}_8\)

as expected, gives little information about the molecular geometry, due to the complexity of the phenyl absorptions. The presence of two groups of peaks is not unusual for the phenyl protons in N-metallated diphenylmethyleneamines (examples may be found in studies on magnesium\(^{329}\) and boron\(^{383}\)). The integration for this spectrum gives a ratio of 20:3 for the aromatic and aliphatic protons, suggesting that the formula should be \((\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\cdot\text{C}_7\text{H}_8\)

in contrast to both the analytical data and the crystal structure, which confirm that there is one molecule of toluene per molecule of complex.

The azomethine stretching frequencies for these compounds are listed in Table 29. \(\text{Ph}_2\text{CN}.\text{SnCl}_2\) has one band assignable to \(\nu(\text{C}=\text{N})\), while \((\text{Ph}_2\text{CN})_3\text{HSn}_2\text{Cl}_2\cdot\text{C}_7\text{H}_8\) and \((\text{Bu}_2\text{CN})_2\text{HSn}_2\text{Cl}_3\) have two, corresponding to the coordinated methyleneamine molecule and the bridging methyleneamino groups; the \(\nu(\text{C}=\text{N})\) frequencies for the latter differ little from those found for similarly bridging ligands in the compounds \([\text{Ph}_2\text{CN}]_2\text{Sn}\), \([((\text{Bu}_2\text{CN})_2\text{Sn})_n\), and \((\text{Ph}_2\text{CNSnCl})_2\), discussed as Group A.

It may be seen that \(\nu(\text{C}=\text{N})\)is shifted to lower energy relative to the parent imine for coordinated methyleneamine molecules, in contrast to the situation observed with tin tetrachloride and other strong Lewis acids,\(^{344}\) where the complexes show a pronounced shift to higher energies. This seems to be due to the relatively low acidity of derivatives of tin(II), similar effects being observed for the methyleneamine adducts of the comparatively weakly acidic boron,\(^{390}\) aluminium,\(^{391}\) and gallium\(^{392}\) alkyls.

The crystal structure of \(\text{Ph}_2\text{CN}.(\text{Ph}_2\text{CNSn}^{\text{II}}\text{Cl})_2\cdot\text{C}_7\text{H}_8\)

The crystal and molecular structures of the imine adduct

\(\text{Ph}_2\text{CN}.(\text{Ph}_2\text{CNSn}^{\text{II}}\text{Cl})_2\cdot\text{C}_7\text{H}_8\) have been determined by X-ray diffraction.\(^{378}\)

Relevant bond lengths and angles for the imine adduct,
The molecule is illustrated in Figure 3-10. The structure is essentially based upon that of (Ph₂CNSnCl)₂, with an additional molecule of diphenylmethylenamine coordinated to one tin atom, so that the complex contains both 3- and 4-coordinate tin(II). The toluene incorporated in the crystal is clearly not bonded to the complex, the molecules being more than 4 Å apart. The structure of the toluene molecule is in no way unexpected.

The dimensions of the Sn₂N₂ ring do not vary significantly from those of the parent compound (Ph₂CNSnCl)₂, in spite of the differing coordination numbers of the tin atoms. The ring is in fact slightly more symmetric; the four Sn-N distances are equal within experimental error. The two bridging imino-groups are no longer quite planar at nitrogen, being bent slightly away from the bulky coordinating imine molecule. Surprisingly, however, steric crowding between this and the adjacent chlorine, Cl(2) (i.e. that attached to the 3-coordinate tin atom), does not lead to any significant widening of the angle between the Sn(2)-Cl(2) bond and the Sn₂N₂ ring. Presumably any such effect is cancelled out by the opposing repulsion of the Sn(2) lone pair.

The Sn(2)-Cl(2) distance, 2.550 Å, is significantly greater than that found in (Ph₂CNSnCl)₂ (average 2.462 Å). This may be due to the inductive effect on Sn(2) of the extra electron density available to Sn(1) through coordination by Ph₂CNH; the resulting reduction in the polarity of the Sn(2)-Cl(2) bond would weaken and hence lengthen it.

The geometry about Sn(1), the 4-coordinate tin atom, is considered to derive from a distorted trigonal bipyramid, the equatorial positions being occupied by the bridging imino-groups and the lone pair. The distortion may be ascribed to the repulsive effects of the lone pair.
TABLE 26
Bond Lengths and Angles from the X-ray crystal structure
of Ph₂CNH₂Ph₂SnCl₂·C₂H₅

<table>
<thead>
<tr>
<th>Bond lengths, Å</th>
<th>Bond angles, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-N(1)</td>
<td>1.273 (13) Sn(1)N(1)Sn(2) 101.6 (3)</td>
</tr>
<tr>
<td>C(2)-N(2)</td>
<td>1.284 (12) Sn(1)N(2)Sn(2) 101.3 (3)</td>
</tr>
<tr>
<td>C(3)-N(3)</td>
<td>1.274 (12) N(1)Sn(1)N(2) 77.3 (3) N(1)Sn(2)N(2) 76.9 (3)</td>
</tr>
<tr>
<td>Sn(1)-N(1)</td>
<td>2.198 (8)</td>
</tr>
<tr>
<td>Sn(1)-N(2)</td>
<td>2.206 (8) Cl(1)Sn(1)N(1) 72.8 (2)</td>
</tr>
<tr>
<td>Sn(1)-N(3)</td>
<td>2.474 (8) Cl(1)Sn(1)N(2) 75.7 (2)</td>
</tr>
<tr>
<td>Sn(2)-N(1)</td>
<td>2.211 (8) Cl(1)Sn(1)N(3) 143.8 (2)</td>
</tr>
<tr>
<td>Sn(2)-N(2)</td>
<td>2.211 (8)</td>
</tr>
<tr>
<td>Sn(1)-Cl(1)</td>
<td>2.753 (8) Cl(2)Sn(2)N(1) 83.5 (2)</td>
</tr>
<tr>
<td>Sn(2)-Cl(2)</td>
<td>2.550 (3) Cl(2)Sn(2)N(2) 93.5 (2) N(3)Sn(1)N(1) 81.3 (3) N(3)Sn(1)N(2) 74.3 (3) N(3)Sn(1)C(3) 132.3 (6)</td>
</tr>
</tbody>
</table>

Non-bonded distances Å

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2)</td>
<td>2.750 (11)</td>
</tr>
<tr>
<td>Sn(1)-Sn(2)</td>
<td>3.416 (1)</td>
</tr>
</tbody>
</table>

Estimated standard deviations in parentheses.
Molecular structure of \( \text{Ph}_2\text{CNH} \cdot (\text{Ph}_2\text{CNSn}^{II} \text{Cl})_2 \cdot \text{C}_8\text{H}_8 \).

(Toluene of crystallisation and all protons are omitted for clarity).

Figure 3-10
(the axial species are bent away from it; the N(3)Sn(l)Cl(l) axial angle is only 143.8°) together with the constraint imposed by formation of the Sn₂N₂ ring. The latter accounts for the small angle between equatorial bonds (77.3°) when compared to the other two Sn° compounds known to have structures based on the trigonal bipyramid, bis(benzylacetonato)tin(II)³⁹ and bis(N,N'-diethylthiocarbamato)tin(II),³⁸ which have equatorial angles of 94.7° and 96.2° respectively.

The angle between the axial bonds, 143.8° compares well with the figures for bis(benzylacetonato)tin(II) (150.4°)³⁹ and bis(N,N'-diethylthiocarbamato)tin(II) (139.6°).³⁸

The axial Sn(l)-Cl(l) bond length (2.753 Å) is considerably longer than the majority of known Sn°-Cl bonds. This is probably due to the higher coordination number of Sn(l), although it is also generally observed that the axial bonds of a trigonal bipyramidal complex tend to be longer than equatorial bonds to the same ligand. The bond length is similar to the axial Sn°-Cl bond distance of 2.766 Å found in the pentagonal bipyramidal complex π-C₆H₆Sn°(AlCl₄)₂·C₆H₆, 77a although here the chlorine atom is bridging between tin and aluminium.

The axially coordinating methyleneamine group has a C=N bond distance of 1.274 Å, little different from those of the bridging methyleneamino groups, and not significantly longer than the calculated carbon-nitrogen double-bond distance of 1.265 Å.³⁸⁹ The Sn(l)N(3)C(3) bond angle of 132.3° is greater than the sp² hybrid angle of 120°, probably as a result of repulsion between the methyleneamine molecule and the Sn(l) lone pair. The Sn(l)-N(3) bond length, 2.474 Å, is significantly greater than the ring Sn-N distances (average 2.207 Å), or the average values
for phthalocyaninatotin(II) (2.25 Å). It is, however, similar to the coordinate N→Sn bonds found in the EDTA complexes Sn\textsuperscript{II} \[ \text{Sn}^{\text{II}}\text{EDTA} \cdot H_2O \] (2.45 and 2.46 Å)\textsuperscript{21} and Sn\textsuperscript{II}H_2EDTA (2.39 and 2.44 Å)\textsuperscript{402}, both of which contain 6-coordinate tin(II). The longer axial Sn-N bond compared to those in the equatorial positions is as expected for a trigonal bipyramidal complex. All the Sn\textsuperscript{II}—N bond distances may be compared to 2.06 Å found for (Ph\textsubscript{2}CN)\textsubscript{4}Sn\textsuperscript{IV}.\textsuperscript{301,302} They are longer, as expected, consistent with the greater size of tin(II).

### iii) Group C: \((\text{tBu-CN})_2\text{H}_2\text{Sn}_3\text{Cl}_5\)

The other material isolated from the decomposition products of \((\text{tBu-CN})_2\text{Sn}^{\text{IV}}\text{Cl}_2\) is more complex. Several structures could be postulated for its formula, \((\text{tBu-CN})_3\text{H}_2\text{Sn}_2\text{Cl}_5\), but the infra-red spectrum, which shows a high frequency for \(\gamma(\text{C=\text{N}})\) and a broad, intense \(\gamma(\text{N-H})\) absorption, is consistent with the presence of di-t-butylmethyleneaminium ions, \(\text{tBu}_2\text{C=\text{NH}}_2^+\).

The \(^1\text{H-NMR}\) spectrum (Table 28 p. 178) consists of three singlet absorptions in the tBu region, integral ratios (in order of increasing field) 1:1:1. To account for this it is necessary to postulate an anion containing bridging imino-groups of the type shown in Fig. 3-11 (the structure of the anion is probably stabilised by chlorine bridges, but these are not shown since several arrangements are possible). The singlet at lower field is thus assigned to the \(\text{tBu}_2\text{CNH}_2^+\) ion; it lies rather lower than the resonances of most di-t-butylmethyleneamine derivatives, consistent with a positively charged species. The remaining two higher field absorptions correspond to \(\text{tBu}_1\) and \(\text{tBu}_2\) in the diagram.
The infra-red spectrum of $^{t\text{Bu}_2\text{CN}}\text{H}_3\text{Sn}_3\text{Cl}_5$ contains two bands assignable to $\nu(C=N)$ (Table 29; p. 179) the higher energy absorption corresponds quite closely to the value found for $^{t\text{Bu}_2\text{CNH}}^+\text{Cl}^-$ (1670 cm$^{-1}$). The lower energy absorption may be assigned to bridging $^{t\text{Bu}_2\text{CN}}$ groups, but is lower than the observed values for other bridging methyleneamino groups in the compounds described in this chapter, or for the tin(IV) derivative $[(\text{Ph}_2\text{CN})_2\text{Sn}^{\text{IV}}\text{Cl}_2]_n$ (1553 cm$^{-1}$; see Chapter 2). It is, however, closer to that of $[(\text{Ph}_2\text{CN})_3\text{Sn}^{\text{IV}}\text{Cl}]_n$ (1535 cm$^{-1}$). It is probable that variations in $\nu(C=N)$ bridging will arise from changes in the SnNSn bond angle, in accordance with which those compounds which probably contain 4-membered Sn$_2$N$_2$ rings all absorb at 1550-1560 cm$^{-1}$. This may support the suggestion of an Sn$_2$NCl ring for the compound $^{t\text{Bu}_2\text{CN}}\text{H}_3\text{Sn}_3\text{Cl}_3$, since this would similarly constrain the angle at nitrogen. The low frequencies for $^{t\text{Bu}_2\text{CN}}\text{H}_3\text{Sn}^{\text{II}}\text{Cl}_3$ and $[(\text{Ph}_2\text{CN})_3\text{Sn}^{\text{IV}}\text{Cl}]_n$ may therefore indicate a significant difference in structure, the absence of Sn$_2$N$_2$ rings suggesting a more open skeleton with a wider angle at nitrogen. For the tin(IV) compound, a trimeric structure would be possible (Fig. 3-12a), or a three-dimensional polymer (involving 6-coordinate tin).

For the anion $^{t\text{Bu}_2\text{CN}}\text{Sn}_3\text{Cl}_5^-$, this serves to confirm a structure in which all three tin atoms are linked by bridging amino-groups, rather than one containing a 4-membered Sn$_2$N$_2$ ring (e.g. Fig 3-12b).
iv) Group D: Li(tBu-CN)₃SnⅡ.

Lithium tris(di-t-butylmethyleneamino)tin(II), Li(tBu-CN)₃SnⅡ, may be prepared without difficulty, in contrast to its diphenylmethyleneamino analogue, which could not be obtained. Its formulation as a tin(II) compound, rather than as a derivative of tin(IV) containing an Sn-Li bond, has been confirmed by preliminary Mössbauer studies. The lithium triorganotins, R₃SnLi, are considered to be largely ionic, but if the known structure of Li(tBu-CN)₄Al (Fig. 2-2d) is paralleled here, a structure involving an LiN₂Sn ring (Fig 3-13a) might be expected. This is, however, inconsistent with the spectroscopic evidence, which implies that all the C=N groups are equivalent (there is only one ν(C=N) absorption in the infra-red spectrum) and that all the t-butyl groups are in similar
chemical environments (only one resonance is observed in the $^1$H-NMR spectrum). The only structure which could accommodate these requirements is an ionic one in which there is rapid inversion at nitrogen to equilibrate the $t$-butyl groups (Fig. 3-13b). However the very high solubility in hydrocarbon solvents reduces the likelihood of such a structure.

The $^1$H-NMR spectrum consists of a single sharp signal (Table 28), which is unaffected by cooling. This is in contrast to the beryllium analogue, Li($t$Bu$_2$CN)$_3$Be, which shows two $t$Bu resonances (split further on cooling), and for which no structure wholly consistent with its spectra has been postulated; the presence of the tin(II) lone pair would, however, be expected to cause major structural differences.

A structure for Li($t$Bu$_2$CN)$_3$Sn$^{II}$ in which all the C=N bonds are equivalent (e.g. Fig. 3-14) would require two $t$Bu resonances in the proton NMR spectrum. It is possible, however, that rapid equilibration in solution of the type shown in Fig. 3-15 would provide opportunity for imine inversion and coalescence of the signals. This is, however, inconsistent with the infra-red data, unless a change of structure upon dissolution is assumed, and solution of the problem must await a crystal structure determination.
v) **General considerations**

The structural evidence for these compounds shows the apparent stability of the Sn\(^{II}\)←N→Sn\(^{II}\) bridge, notably when electronegative groups such as chlorine (which enhance the acceptor properties of the metal) are attached to tin. It appears to be weaker under other conditions (for example, the mass spectrum of \((t^3\text{BuCN})_2\text{Sn}^{II}\)_\(_n\) contains no di- or poly-tin-containing fragments, and the compound is probably at least partially dissociated in solution). Similar bridged species are known for methyleneamino-derivatives of other metals in oxidation state II, and a brief comparison may be appropriate.

Methyleneamino-derivatives of beryllium, magnesium, and zinc have been prepared. The major stereochemical difference between these elements and tin(II) is the presence of the lone pair of electrons in the latter; also four-coordinate complexes are more stable for the Group II elements, although the three-coordinate state is known, particularly for beryllium and zinc.

Dimeric structures analogous to \([\text{(Ph}_2\text{CN})_2\text{Sn}^{II}]_2\) and \((\text{Ph}_2\text{CN}\text{Sn}^{II}\text{Cl})_2\) are well-known; the di-t-butylmethylenearie-derivatives all appear to be dimeric,\(^{329,336,353,380}\) though planar at the metal due to the lack of a stereochemically active lone pair. This planarity at the metal also provides the optimum geometry for N→M (p→p) dative \(\pi\)-bonding in the
Some Methyleneamino-derivatives of the Group II elements

M = Be, Zn, Mg.

(a) $t_{Bu_2}C\equiv N\equiv M^t_{Bu_2}$

(b) $[\begin{array}{c} CPh_2 \\ N \\  \vdots \\ CPh_2 \end{array}] n M = Be, Zn.$

(c) $p\text{-}tolyl_2 C\equiv N\equiv Be$ $Be\equiv N\equiv Cp\text{-}tolyl_2$

M = Be$^{353,380}$; $X = Cl, Bu; R = Ph, p\text{-}tolyl, t_{Bu}$.

M = Zn; $X = Cl, Me, Bu; R = t_{Bu}^{380}$.

M = Mg; $X = Br, R = t_{Bu}^{329}$.

(d)

(e) $Mg$ $Br$ $THF$

(f) $Mg$ $Li$

Figure 3-16
case of the bis-imino derivatives (Fig. 3-16a and d). The bis-diaryl-
methyleneamino-derivatives, however, are generally oligomers or
polymers (Fig. 3-16b and c). 329,380

The propensity of magnesium in particular for a coordination
number of at least four leads many of its imino-derivatives to be
isolated as etherates (Fig. 3-16e and f). 329 A crystal structure on
the complex (Ph₂CNMgBr)₂·3THF is particularly interesting in that it
reveals the presence of a unique weakly-bonded THF molecule bridging
between the two magnesium atoms, which are thus five-coordinate. 382
Although the imino-magnesium etherates generally have structures which
can be related to those of the tin(II) derivatives by replacement of
a terminal ether molecule by the tin lone pair, attempts to form a
similarly THF-bridged tin(II) compound (Fig. 3-17) failed. Although

![Figure 3-17](image)

the Sn^II atom is larger than Mg^II (covalent radii 1.63 Å 397 and
1.36 Å 372 respectively), the cross-ring metal-metal distance is 3.507 Å
in (Ph₂CNNSn^IICl)₂ 378 (compared to 2.886 Å for the THF-bridged magnesium
compound 382) which is probably too great for effective orbital overlap
between a single THF molecule and both tin atoms simultaneously.

An additional matter of some interest concerns metal-nitrogen
stretching frequencies. Comparison of the spectra of the di-t-butyl-
methyleneamino derivatives of tin(II) and tin(IV) allows the tentative
assignment of $\nu$(Sn$^{II}$-N) for Li($t$Bu$_2$CN)$_3$Sn and [(tBu$_2$CN)$_2$Sn]$_n$ as 663 and 657 cm$^{-1}$ respectively, showing the expected shift to lower energy relative to the derivatives of the more electronegative oxidation state ( $\nu$(Sn$^{IV}$-N) ≈ 690-700 cm$^{-1}$). Assignments are few in the literature for Sn$^{II}$-N stretching frequencies; it has been suggested that for {
\begin{align*}
[(\text{Me}_{3}\text{Si})_{2}\text{N}]_{2}\text{Sn}^{II}\n\end{align*}} and some related compounds, $\nu_{\text{as}}$(Sn-N) lies in the region 350-400 cm$^{-1}$, the symmetric vibration lying 10-22 cm$^{-1}$ to lower energy, consistent with the data for the cadmium analogues 
\begin{align*}
\nu_{\text{as}}(\text{Cd-N}) = 410 \text{ cm}^{-1}, \nu_{\text{s}}(\text{Cd-N}) = 385 \text{ cm}^{-1}.
\end{align*}
Similarly $\nu_{\text{as}}$(Sn$^{II}$-N) for [{(\text{Me}_{2}\text{N})}_{2}\text{Sn}^{II}]_2 was assigned at 440 cm$^{-1}$. The spectra of Li($t$Bu$_2$CN)$_3$Sn$^{II}$ and [(tBu$_2$CN)$_2$Sn$^{II}$]$_n$ do in fact show well-defined absorptions (which are not seen for $t$Bu$_2$CNH or $t$Bu$_2$CN-derivatives of Sn$^{IV}$) in this region at 406 and 356 cm$^{-1}$, and 388 and 354 cm$^{-1}$ respectively. However, no such bands were found in the spectrum of [{(\text{Ph}_{2}\text{CN})}_{2}\text{Sn}^{II}]_2, or the spectra of any of the other imino-tin(II) derivatives, and attempts to assign $\nu$(Sn$^{II}$-N) for [{(\text{Ph}_{2}\text{CN})}_{2}\text{Sn}^{II}]_2 by comparison of spectra with diphenylmethyleneaminotin(IV) derivatives did not give realistic results.

In absence of definite guide-lines to the appropriate region of the spectrum, it is therefore not possible to draw any firm conclusions about the position of $\nu$(Sn$^{II}$-N) in these compounds.

C. Summary.

The new methyleneamino derivatives of tin(II) all contain tin with a coordination number of three or more, as a result of which many are associated, generally as dimers containing an Sn$_2$N$_2$ ring.

For the di-$t$-butylmethyleneamine derivative [(tBu$_2$CN)$_2$Sn$^{II}$]$_n$ the
imino-bridges are relatively labile, rapid exchange between bridging and terminal imino-groups occurring in solution, in which it may be largely dissociated into monomers at ambient temperatures. In contrast, the diphenyl analogue \([(\text{Ph}_2\text{CN})_2\text{Sn}^{\text{II}}]_2\) is dimeric in solution as well as the solid, although the imino-bridge appears to be relatively easily broken.

If electron-withdrawing groups are also attached to the tin, however, the methyleneamino bridge is considerably strengthened, to the extent that it persists in the gas phase, and additional ligands may be accommodated without cleavage of the Sn\(_2\text{N}_2\) ring.

Where the compounds contain terminally-bonded imino-groups, there is little evidence for \((p\rightarrow d) \text{N}\rightarrow\text{Sn}^{\text{II}}\) dative \(\pi\)-bonding with associated linearity of the C=N=Sn skeleton. This behaviour is similar to that of Sn\(_{\text{IV}}\), probably for similar reasons, one of the most important of which may be that the \(\pi\)-overlap between the N2p and Sn5d orbitals is too small for significant bond formation.
### TABLE 27

**Major metal-containing fragments in the mass spectra of some methylene-amino derivatives of tin(II)**

#### a) \((\text{Ph}_2\text{CN})\text{SnCl}_2\)_2

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>1.5</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>635</td>
<td>1.0</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>534</td>
<td>0.4</td>
<td>(\text{?})</td>
</tr>
<tr>
<td>525</td>
<td>0.4</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>490</td>
<td>18</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>335</td>
<td>2</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>300</td>
<td>7</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>258</td>
<td>2</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>197</td>
<td>22</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>190</td>
<td>4</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>180</td>
<td>100*</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>155</td>
<td>25</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>120</td>
<td>5</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
</tbody>
</table>

**m/e values refer to the peaks containing the most abundant isotopes \((^{120}\text{Sn}, ^{35}\text{Cl})\).**

#### b) \((\text{Ph}_2\text{CN})\text{HSnCl}_2\cdot\text{C}_7\text{H}_8\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>490</td>
<td>0.01</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>181</td>
<td>57</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>180</td>
<td>100</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
<tr>
<td>91</td>
<td>100*</td>
<td>((\text{Ph}_2\text{CN})\text{SnCl}_2^+)</td>
</tr>
</tbody>
</table>

#### c) \((\text{tBu}_2\text{CN})\text{Sn}\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>407</td>
<td>7</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>260</td>
<td>1</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>204</td>
<td>0.4</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>203</td>
<td>0.8</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>165</td>
<td>5</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>141</td>
<td>100</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>140</td>
<td>13</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
<tr>
<td>135</td>
<td>4</td>
<td>((\text{tBu}_2\text{CN})\text{Sn}^+)</td>
</tr>
</tbody>
</table>

*: Off-scale
### d) $\left(\text{^tBu}_2\text{CN}\right)_2\text{Sn}_n$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>1.5</td>
<td>$\left(\text{^tBu}_2\text{CN}\right)_3\text{Sn}^+$</td>
</tr>
<tr>
<td>483</td>
<td>0.2</td>
<td>$\left(\text{^tBu}_2\text{CN}\right)_2\text{^tBuCNSn}^+$</td>
</tr>
<tr>
<td>457</td>
<td>4</td>
<td>$\left(\text{^tBu}_2\text{CN}\right)_2\text{^tBuSn}^+$</td>
</tr>
<tr>
<td>400</td>
<td>2</td>
<td>$\left(\text{^tBu}_2\text{CN}\right)_2\text{Sn}^+$</td>
</tr>
<tr>
<td>374</td>
<td>3</td>
<td>$\text{^tBu}_2\text{CN}^+. \text{^tBu}_2\text{Sn}^+$</td>
</tr>
<tr>
<td>352</td>
<td>7</td>
<td>?</td>
</tr>
<tr>
<td>343</td>
<td>14</td>
<td>$\text{^tBu}_2\text{CN}^+. \text{^tBuCNSn}^+$</td>
</tr>
<tr>
<td>260</td>
<td>28</td>
<td>$\text{^tBu}_2\text{CNSn}^+$</td>
</tr>
<tr>
<td>204</td>
<td>13</td>
<td>$\text{^tBuCHNSn}^+$</td>
</tr>
<tr>
<td>203</td>
<td>14</td>
<td>$\text{^tBuCNSn}^+$</td>
</tr>
<tr>
<td>141</td>
<td>100</td>
<td>$\text{^tBu}_2\text{CNH}^+$</td>
</tr>
<tr>
<td>140</td>
<td>14</td>
<td>$\text{^tBu}_2\text{CN}^+$</td>
</tr>
</tbody>
</table>

### e) $\left(\text{^tBu}_2\text{CN}\right)_2\text{HSn}_2\text{Cl}_3$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>555</td>
<td>0.2</td>
<td>$\left(\text{^tBu}_2\text{CN}\right)_2\text{Sn}_2\text{Cl}^+$</td>
</tr>
<tr>
<td>450</td>
<td>0.4</td>
<td>$\text{^tBu}_2\text{CNSn}_2\text{Cl}^+$</td>
</tr>
<tr>
<td>381</td>
<td>0.3</td>
<td>?</td>
</tr>
<tr>
<td>295</td>
<td>0.6</td>
<td>$\text{^tBu}_2\text{CNSnCl}^+$</td>
</tr>
<tr>
<td>260</td>
<td>2</td>
<td>$\text{^tBu CNSn}^+$</td>
</tr>
<tr>
<td>238</td>
<td>6</td>
<td>$\text{^tBuCNSnCl}^+$</td>
</tr>
<tr>
<td>190</td>
<td>87</td>
<td>$\text{SnCl}_2^+$</td>
</tr>
<tr>
<td>155</td>
<td>100</td>
<td>$\text{SnCl}^+$</td>
</tr>
<tr>
<td>141</td>
<td>44</td>
<td>$\text{^tBu}_2\text{CNH}^+$</td>
</tr>
<tr>
<td>140</td>
<td>14</td>
<td>$\text{^tBu}_2\text{CN}^+$</td>
</tr>
<tr>
<td>120</td>
<td>42</td>
<td>$\text{Sn}^+$</td>
</tr>
</tbody>
</table>

*: Off-scale
**TABLE 28**

$^1$H-NMR Spectroscopic data for some methyleneamino derivatives of tin(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma^a$ values. ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{t Bu}_2\text{CN}]_2\text{Sn}]_n$</td>
<td>8.77s$^b$</td>
</tr>
<tr>
<td>Li($\text{t Bu}_2\text{CN}$)$_3\text{Sn}$</td>
<td>8.88s.</td>
</tr>
<tr>
<td>($\text{t Bu}_2\text{CN}$)$_2\text{HSn}2\text{Cl}_3$</td>
<td>C-H: 8.79s(2), 9.06s(1), 9.19s(1) &lt;br&gt;N-H: not detected.</td>
</tr>
<tr>
<td>($\text{t Bu}_2\text{CN}$)$_3\text{H}_2\text{SnCl}_5$</td>
<td>C-H: 8.35s(1), 9.04s(1), 9.18s(1) &lt;br&gt;N-H: not detected.</td>
</tr>
<tr>
<td>(Ph$_2\text{CN}$)$_3\text{HSnCl}_2\text{C}_7\text{H}_8$</td>
<td>Ar-H: 2.54br.m, 3.40s.(total 20) &lt;br&gt;CH$_3$: 8.13s(3). &lt;br&gt;N-H$^d$: 0.16br.s.</td>
</tr>
</tbody>
</table>

Relative intensities in parentheses

a: Relative to $\gamma$(TMS) = 10 ppm. (external reference)  
b: Partially resolved at $-100^\circ$C as a doublet, separation 0.10ppm.  
c: C$_6$D$_6$ solution. All others in d$_8$-toluene.  
d: Integration prevented by high noise to signal ratio.  
s: singlet; br: broad; m: unresolved multiplet.
TABLE 29
Azomethine stretching frequencies, $\nu(C=\text{N}) \text{cm}^{-1}$, for some new methyleneamino derivatives of tin(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu(C=\text{N}) \text{cm}^{-1}$</th>
<th>Terminal</th>
<th>Bridging</th>
<th>Coordinated $R_2\text{C}=\text{NH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ph}_2\text{CNH},\text{SnCl}_2$</td>
<td>1603</td>
<td>1560</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>$[(\text{Ph}_2\text{CN}),\text{Sn}]_2$</td>
<td>1564</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{Ph}_2\text{CNSnCl})_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{PhC}_3\text{H}_2\text{CN})_2\text{SnCl}_2\cdot\text{C}_7\text{H}_8$</td>
<td>1564</td>
<td>?</td>
<td>1600</td>
<td></td>
</tr>
<tr>
<td>$[(\text{tBu}_2\text{CN}),\text{Sn}]_n$</td>
<td>1628</td>
<td>1560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Li}(\text{tBu}_2\text{CN})_3\text{Sn}$</td>
<td></td>
<td></td>
<td>1619</td>
<td></td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_2\text{HSn}_2\text{Cl}_3$</td>
<td>1552</td>
<td></td>
<td>1586</td>
<td></td>
</tr>
<tr>
<td>$(\text{tBu}_2\text{CN})_3\text{H}_2\text{Sn}_3\text{Cl}_5$</td>
<td>1534</td>
<td></td>
<td>1671 *</td>
<td></td>
</tr>
</tbody>
</table>

All spectra were recorded on nujol mulls.

cf. $\nu(C=\text{N})$ for the parent imines:
- $\text{Ph}_2\text{CNH}$: $1603 \text{ cm}^{-1}$
- $\text{tBu}_2\text{CNH}$: $1604 \text{ cm}^{-1}$

*: $\text{tBu}_2\text{CNH}_2^+$
CHAPTER FOUR

SOME AMIDINO-DERIVATIVES OF THE GROUP IVB ELEMENTS
4.1 Introduction

This chapter describes some N,N'-diphenylacetamidino-derivatives of the Group IVB chlorides. This study was originally undertaken, as part of a series of investigations of ortho-metallation reactions in this Group, as a result of the preparation of the ortho-metallated amidino-palladium derivatives illustrated in Fig. 4-1; arylmethylenamines were known to undergo ortho-metallation with both palladium(II) and tin(IV) chlorides (see Chapter 5).

No such ortho-metallation reactions were in fact observed for amidino-tin(IV) chlorides (N,N'-diphenylacetamidinotin(IV)trichloride is stable to 200°C), but some related amidino compounds of silicon, germanium, and tin(II) were prepared for comparison.

Derivatives of the symmetrically N,N'-disubstituted amidino ligand are of interest because this group is isoelectronic with the π-allyl and carboxylato groups, but, when acting as a bidentate ligand, bonds like the latter, so that the metal lies in the same plane as the \( \text{C}_2 \text{X}_2 \) unit (\( \text{X} = \text{O}, \text{NR} \)) (Fig. 4-2 c or d), rather than above the plane in the pseudo-π-allyl arrangement (Fig. 4-2b).

Several other bonding possibilities are available for the amidino group, illustrated in Figure 4-2. It may act as a one- or three-electron...
Bonding possibilities for N,N'-disubstituted amidino ligands

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4-2
ligand to a single metal atom (Fig. 4-2 a-d), or may bridge between two metals (Fig. 4-2 e or f). Both localised and delocalised forms are known.

Until comparatively recently, few symmetrically substituted N-metallated amidines had been prepared. In the main groups, only a single study appears to have been reported, concerning some benzamidino derivatives of the Group IVB elements and arsenic, although it is probable that amidino-magnesium compounds have been made as intermediates (which were not isolated) in the early work on the reaction of Grignard reagents with carbodiimides (Eqn. 4.1).

\[
RMgX + R'-N=C=N-R' \rightarrow [R'-N=C-NR'MgX]
\]

\[
X = Br, I
\]

A similar reaction, involving insertion of a carbodiimide into a metal-carbon bond, forms a standard synthesis of N-metallated amidines.

A considerable amount of work, in contrast, has been reported on amidino-derivatives of the transition elements. Examples are known for platinum and palladium, manganese, iron and cobalt, nickel, molybdenum, tungsten, chromium, rhenium, tantalum and niobium, and copper and silver. The majority of these compounds appear to contain amidino groups which are bidentate to a single metal atom, although the nickel derivative appears to be polymeric, probably via bridging amidino groups, and the copper(I) derivative of N,N'-di(2-anthraquinonyl)formamidine was considered.
to be similarly bridged. Molybdenum and rhenium derivatives are also known in which a metal-metal bond is bridged by two or more amidino groups.

The known Group IVB derivatives of N,N'-disubstituted amidines comprise the series \((\text{MeN=CPh.NMe})_{3} M\text{Me}_3 (M = \text{Si,Sn})\), and \((\text{Me}_3\text{SiN=CPh.NMe})_{3} M\text{Me}_3 (M = \text{Si,Ge,Sn,Pb})\). The compounds were generally considered to contain the delocalised bidentate skeleton illustrated in Figure 4-3,

![Figure 4-3](image)

although for the latter series of compounds an equilibrium appeared to exist, giving rise to mixtures of isomers (Eqn. 4.2). The localised
forms A and C appear to be preferred for $M = \text{Si}$, and the delocalised form B for Ge, Sn, and Pb.

Other compounds of the Group IVB elements containing similar potentially delocalised bidentate ligands, generally $R-N=X-NR-M$, include the triazenes ($X = N, M = \text{Sn}$), \cite{134} the aminophosphinimines ($X = \text{PPh}_2, M = \text{Sn}$)\cite{415} and -arsinimines ($X = \text{AsPh}_2, M = \text{Sn}$)\cite{416} and the aminotroponeimines ($X = \text{tropone}, M = \text{Si, Ge, Sn}$).\cite{280} The triazentonins, which are monomeric, probably contain bidentate ligands (e.g. Fig. 4-4a).\cite{134}

![Figure 4-4](image)

No conclusion was reached for the compounds $\text{Ph}_3\text{SnNPh-MPh}_3\equiv\text{NPh (M = P,As)}$,\cite{415,416} but the aminotroponeimates, on the basis of NMR evidence, were considered to contain five-coordinate metal atoms (Fig. 4-4b),\cite{280} in agreement with the observed decrease in stability of the compounds in the order $M = \text{Sn} > \text{Ge} > \text{Si}$, reflecting the relative stabilities of these elements in the five-coordinate state.

4.2 Experimental

All reactions were carried out under an atmosphere of dry nitrogen (see Appendix for details).
1) **Reaction of N,N'-diphenylacetamidinolithium with silicon tetrachloride (Mole ratio 1:1)**

A solution of 2.103 g, N,N'-diphenylacetamide (10 mmol.) in 60 cm$^3$ dry ether was cooled to $-196^\circ$C and 6.58 cm$^3$ of a 1.52M solution of n-butyl lithium in hexane (10 mmol. $n$-BuLi) were added. The mixture was allowed to warm to room temperature, and stirred for about 15 minutes to complete the lithiation.

The resulting fine white suspension of the amidinolithium was cooled to $-196^\circ$C and 1.146 cm$^3$ (10 mmol.) silicon tetrachloride were added. The mixture was allowed to warm to room temperature and stirred for several hours. All solvent was then removed under vacuum from the resulting white precipitate under a very pale green solution, and 40 cm$^3$ dry toluene were added to the residue. The mixture was refluxed for 30 minutes and filtered while hot, yielding a white solid (LiCl) and a very pale greenish solution, which, on addition of 20 cm$^3$ dry hexane and standing at $-20^\circ$C for 2 days, deposited a white, microcrystalline solid, identified as **bis(N,N'-diphenylacetamidino)dichlorosilane, $[\text{CH}_3\text{C(NPh)}_2]_2\text{SiCl}_2$.**

(Found: C 66.8, H 3.9, N 10.1, Cl 13.3%; $C_{28}H_{26}N_4\text{SiCl}_2$ requires: C 65.0, H 5.0, N 10.8, Cl 13.7%).

$\nu_{\text{max}}$ (Nujol mull): 3061w, 3038w, 1964vw, 1947vw, 1894vw, 1882sh, 1817vw, 1758vw, 1601s, 1587s, 1566vs, 1503vs, 1452s, 1418vs, 1373s, 1332m, 1314mw, 1291w, 1227m, 1179w, 1161vw, 1079m, 1032m, 1004w, 924m, 868m, 841vw, 775s, 757vs, 745s, 700vs, 676w, 634w, 629mw, 608m, 601s, 566s, 517vs, 492s, 478m, 436s, 412m, cm$^{-1}$. 
An attempt to prepare an additional sample of this material for further study followed essentially the same procedure as that outlined above, but made use of a 2:1 mole ratio of amidinolithium to silicon tetrachloride. It was similarly performed on a 10 mmol scale. However, the white, microcrystalline solid obtained was identified as a solvate,

$$\left( [\text{CH}_3\text{C(NPh)}]_2\text{SiCl}_2 \right)_2 \cdot \text{C}_7\text{H}_8$$

M. Pt. (sealed tube) 94-6°C.

(Found: C 68.4, H 8.3, N 9.4, Cl 10.0%; M = 462.

C_{63}H_{60}N_{8}Si_{2}Cl_{4} requires: C 67.2, H 5.3, N 10.0, Cl 12.6%; M = 563^a, 375^b)

a: Assuming formation of dimeric (Am₂SiCl₂)₂ in solution.

b: Assuming formation of monomeric Am₂SiCl₂ in solution.

c: Favoured by ¹H-NMR data.

\(\gamma\) (Nujol mull): 3063w, 3040w, 1959vw, 1948sh, 1896vw, 1825vw, 1804vw, 1760vw, 1602s, 1588s, 1566vs, 1503vs, 1456s, 1422vs, 1381s, 1375s, 1336m, 1317mw, 1294w, 1231m, 1180w, 1163w, 1130m, 1112m, 1082m, 1037m, 1005w, 990w, 972vw, 927m, 870m, 846w, 776mw, 765s, 758s, 740mw, 706vs, 677w, 637w, 631w, 613w, 604m, 565m, 531mw, 519s, 496s, 473mw, 436m, 410sh, 400w cm⁻¹

*: Bands assignable to toluene. Other toluene absorptions obscured.

Toluene of crystallisation could be removed by melting the compound under vacuum. The resulting pale greenish glass, however, appeared to have undergone some further decomposition, and was not suitable as a source of pure (Am₂SiCl₂)₂.
ii) Reaction of N,N'-diphenylacetamidinolithium with germanium tetrachloride (Mole ratio 1:1)

A suspension of 10 mmol. N,N'-diphenylacetamidinolithium in about 65 cm³ ether/hexane (prepared as in the previous reaction) was cooled to -196°C and 1.165 cm³ germanium tetrachloride (10 mmol.) were added. The mixture was allowed to warm to room temperature with stirring, and the resulting white precipitate under a pale greenish solution was stirred overnight. The solvent was then removed under vacuum and replaced by 40 cm³ dry toluene. The mixture was then heated to 100°C and filtered while hot, yielding a white precipitate (LiCl) and a pale greenish-yellow solution. The latter was concentrated under vacuum to 20 cm³ and 10 cm³ dry hexane were added. On cooling to -20°C for several days, the resulting solution deposited a white microcrystalline solid, identified as bis(N,N'-diphenylacetamidino)germanium dichloride, \( \{[\text{CH}_3\text{C(NP}^\prime_2\text{]}_2\text{GeCl}_2\}_n \)

M.Pt. (sealed tube): 166°C, phase transition-sample falls to powder.

Melts, 184-6°C.

(Found: C 60.5, H 5.1, N 9.1, Cl 12.8%; M = 673 dec. C/H/N/GeCl₂ requires: C 59.8, H 4.6, N 10.0, Cl 12.7%; M(monomer) = 561.5).

\( \gamma \) (Nujol mull): 3072w, 3041w, 1954vw, 1886vw, 1806vw, 1752vw, 1650w, 1601m, 1587m, 1566sh, 1554vs, 1503vs, 1453s, 1423vs, 1324w, 1311mw, 1289w, 1277vw, 1221mw, 1179vw, 1161vw, 1076mw, 1035mw, 1004vw, 928w, 917mw, 854m, 825w, 774mw, 759vs, 734mw, 702vs, 677vw, 628vw, 590m, 528mw, 473vw, 441w, 360w, 340w, 324w cm\(^{-1}\)
iii) Reaction between N,N'-diphenylacetamidinolithium and tin tetrachloride (Mole ratio 1:1)

A suspension of 15 mmol. N,N'-diphenylacetamidinolithium in 70 cm$^3$ ether/hexane (prepared according to the procedure in preparation (i)) was cooled to -196°C and 1.76 cm$^3$ tin tetrachloride (15 mmol.) were added. The mixture was allowed to warm to room temperature with stirring. Transient yellow colours developed, but at room temperature the mixture consisted of a pale yellow-green solution over a white precipitate. This was stirred for several hours, then filtered, and the resulting white solid was pumped dry.

Concentration of the filtrate yielded a small quantity of colourless crystals, which did not, however, survive attempts to isolate them. Several attempts to extract further crops from part of the solid filter cake by stirring with cold ether led to uncharacterisable white or yellowish semi-crystalline solids, assumed to be unstable etherates of the amidino-tin trichloride.

The remainder of the filter cake was mixed with 60 cm$^3$ dry toluene and refluxed for 20 minutes. As the temperature rose, the colour of the solution deepened to an intense golden yellow. The mixture was filtered while hot, yielding a white solid (LiCl) and a yellow solution, which on concentration and cooling deposited lustrous bright yellow needle crystals of N,N'-diphenylacetamidinotin(IV)trichloride, $\text{CH}_3\text{C(NPh)}_2\text{Sn}^{\text{IV}}\text{Cl}_3$, M.Pt.: 166-8°C (sealed tube).

(Found: C 35.5, H 3.0, 6.2, Cl 24.6%; $M = 456$.

$\text{C}_{14}\text{H}_{13}\text{N}_2\text{SnCl}_3$ requires: C 38.7, H 3.0, N 6.4, Cl 24.5%; $M = 448$.)
\[ \nu_{\text{max}} \text{ (Nujol mull): } 3078\text{w}, 3039\text{w}, 1956\text{vw}, 1881\text{vw}, 1810\text{vw}, 1750\text{vw}, 1645\text{w}, 1600\text{m}, 1590\text{m}, 1514\text{sh}, 1498\text{vs}, 1455\text{vs}, 1422\text{vs}, 1326\text{mw}, 1310\text{m}, 1291\text{mw}, 1214\text{w}, 1180\text{vw}, 1163\text{vw}, 1080\text{m}, 1034\text{m}, 1008\text{mw}, 978\text{vw}, 925\text{mw}, 917\text{w}, 852\text{m}, 770\text{m}, 759\text{vs}, 753\text{s}, 698\text{vs}, 678\text{w}, 628\text{vw}, 623\text{vw}, 590\text{mw}, 523\text{m}, 470\text{vw}, 446\text{w}, 425\text{vw}, 385\text{vw}, 363\text{sh}, 353 \text{ m cm}^{-1}\]

iv) Reaction between \(N,N'-\text{diphenylacetamidine and tin tetrachloride}
(Mole ratio 1:1)

1.17 cm\(^3\) tin tetrachloride (10 mmol.) were added dropwise to a stirred solution of 2.103g. \(N,N'-\text{diphenylacetamidine (10 mmol.) in 60 cm}^3\) dry toluene. The colourless solution became greenish-yellow, and a sticky pale cream precipitate formed. The mixture was refluxed for 24 hours, then filtered while hot, yielding a dirty white semi-crystalline solid and a bright yellow solution. Analytical data on the former suggested a mixture of the amidine hydrochloride, \(\text{CH}_3\text{C(NHPh)}_2^+\text{Cl}^-\), with the 1:1 amidine-tin tetrachloride adduct, \(\text{CH}_3\text{C(=NPh)NHPh.SnC}_4\text{Cl}_4\), in the approximate mole ratio 2:3.

(Found: C 42.6, H 3.0, N 7.3, Cl 28.8%.
\[\text{C}_{14}\text{H}_{15}\text{N}_2\text{Cl} \text{ requires: C 68.1, H 6.1, N 11.4, Cl 14.4%} \]
\[\text{C}_{14}\text{H}_{14}\text{N}_2\text{SnC}_4\text{Cl}_4 \text{ requires: C 35.6, H 3.0, N 5.9, Cl 30.2%} \]

The yellow solution, on standing for several hours at -20\(^\circ\)C, deposited a mass of bright yellow crystals, identified from their infra-red spectrum as \(N,N'-\text{diphenylacetamidinotin(IV)trichloride, CH}_3\text{C(NPh)}_2\text{Sn}^{IV}\text{Cl}_3\).

v) Reaction of \(N,N'-\text{diphenylacetamidinolithium with tin dichloride}
(Mole ratio 1:1)

A suspension of 16.8 mmol. \(N,N'-\text{diphenylacetamidinolithium}\) in about
50 cm$^3$ ether/hexane (prepared as previously described) was added by syringe to a suspension of 3.193g anhydrous tin dichloride in 20 cm$^3$ dry ether at -196°C. The mixture was allowed to warm to room temperature with stirring, then stirred for 24 hours, at the end of which it consisted of a cream precipitate under a very pale yellow solution. All solvent was then removed under vacuum, and replaced by 40 cm$^3$ dry toluene. The mixture was heated to boiling point, and filtered while hot, yielding a white solid (LiCl) and a very air sensitive yellow solution. The latter was concentrated to about 20 cm$^3$, and 10 cm$^3$ dry hexane were added. On cooling to -20°C for 2 days it deposited a white, microcrystalline solid, identified as N,N'-diphenylacetamidinotin(II)chloride dimer, 

\[
[CH_3C(NPh)_2Sn^{II}Cl_2]_2, \text{M.Pt. 92-4°C (sealed tube)}.
\]

(Found: C 46.9, H 2.7, N 7.7, Cl 9.9%; M = 551 dec. 

C$_{14}$H$_{13}$N$_2$SnCl requires: C 46.3, H 3.5, N 7.7, Cl 9.8%; M (monomer) = 363.5).

\[\nu_{\text{max}} \text{ (Nujol mull): 3063w, 3023w, 1944vw, 1880vw, 1807vw, 1739vw, 1650vw, 1597s, 1580m, 1523vs, 1495vs, 1450s, 1416vs, 1382s, 1320vw, 1301m, 1290mw, 1276s, 1222s, 1184mw, 1178mw, 1160m, 1079mw, 1035m, 1021mw, 1019w, 986w, 971vw, 916mw, 908mw, 842m, 832m, 820w, 775sh, 761s, 750sh, 735w, 700vs, 677w, 668vw, 622vw, 577w, 526m, 509vw, 423vw, 325 vw cm$^{-1}$}

4.3 Discussion

Note: Throughout this chapter the abbreviation Am will be used to represent the N,N'-diphenylacetamidino group. Thus AmH$^+$ represents the parent amidine, AmH$_2^+$ the amidinium ion, etc.
A. Preparative and structural aspects

The new compounds are listed in Table 30. They are all air- and moisture-sensitive, their sensitivities varying approximately in the order Sn$^{II} \succ$ Si$\succ$ Ge$\succ$ Sn$^{IV}$. Decomposition was indicated by the appearance in the infra-red spectrum of a band at $\sim 1640$ cm$^{-1}$, corresponding to $\nu$(C-N) for the free imine, accompanied by a $\nu$(N-H) absorption in the 3200-3400 cm$^{-1}$ region. The high hydrolytic sensitivity of the tin(II) derivative is normal for a compound containing a Sn$^{II}$-N bond, but the observed order for the remaining compounds is the same as that for the M-N bond strengths, i.e. Si$\succ$ Ge$\succ$ Sn, the reverse of the effect which might be expected from other studies. 292 It may, however, reflect the stabilising effect of higher coordination numbers, which would be expected to increase down the group.

The most convenient preparative route to these compounds was the reaction of N,N'-diphenylacetamidinolithium with the metal halide (Eqn. 4.3). This method has been previously used in the preparation of the compounds PhC(NMe)$\cdot$MPh$_3$ ($M = \text{Si,Sn}$), 304 and also extensively in the study of

### TABLE 30

New N,N'-diphenylacetamidino derivatives of the Group IVB elements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{CH}_3\text{C(NPh)}_2\right]\text{SiCl}_2\cdot\text{nC}_7\text{H}_8$</td>
<td>white solids</td>
</tr>
<tr>
<td>$\left[\text{CH}_3\text{C(NPh)}_2\right]\text{GeCl}_2\cdot\text{m}$</td>
<td>white solid</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(NPh)}_2\text{Sn}^{IV}\text{Cl}_3$</td>
<td>yellow crystals</td>
</tr>
<tr>
<td>$\left[\text{CH}_3\text{C(NPh)}_2\text{Sn}^{II}\text{Cl}\right]_2$</td>
<td>white crystalline solid</td>
</tr>
</tbody>
</table>
transition element systems. An alternative route, involving the direct aminolysis of the metal chloride by the unsubstituted amidine, was used in an attempted preparation of the tin(IV) compound AmSn\textsuperscript{IV}Cl\textsubscript{3} (Eqn. 4.4), but the reaction did not go to completion.

\[
\text{AmH} + \text{SnCl}_4 \rightarrow \text{AmH}_2\text{SnCl}_4
\]

Interestingly, owing to the use of diethyl ether as solvent in the first stage of the reaction, the initial product of the reaction between the amidinolithium and tin(IV) tetrachloride (mole ratio 1:1) appeared to be an ether adduct which could not be characterised owing to the facile loss of ether. This may have been a six-coordinate species, e.g. Fig. 4-5 a or b (the diagrams here and elsewhere have been simplified by use of the symbol $\text{N} \equiv \text{N}$ to represent an amidino group). Even mild heating of this white intermediate led to yellowing and formation of AmSn\textsuperscript{IV}Cl\textsubscript{3}.

![Figure 4-5](image-url)
It is interesting that the 1:1 reactions between the amidinolithium and silicon and germanium tetrachlorides lead to the bis-amidino metal dichloride, presumably from disproportionation of the initially-formed mono-amidino metal trichloride (Eqn. 4.5) in a similar manner to the

\[
2\text{AmMCl}_3 \rightarrow \text{Am}_2\text{MCl}_2 + \text{MCl}_4
\]

\[\text{M} = \text{Si, Ge}.
\]
diaryl methyleneamino derivatives (Chapter 2).

Cryoscopic molecular weight determinations suggest that the tin(II) and germanium compounds are associated in solution, while the tin(IV) compound is monomeric. The latter has been confirmed by a crystal structure determination, which shows AmSnIVCl3 to contain five-coordinate tin with a bidentate amidino group (Fig. 4-6).

![Figure 4-6](image)

Interpretation of the observed molecular weight (462) of the silicon compound Am2SiCl2.nC7H8 is complicated by the presence of non-bonded toluene of crystallisation. The 1H-NMR spectrum favours \( n = \frac{1}{2} \), and can be interpreted in terms of a dimeric structure, so that the formula may be better written \( (\text{Am}_2\text{SiCl}_2)_2\cdot\text{C}_7\text{H}_8 \). This gives rise to an expected cryoscopic molecular weight of 563, which is in acceptable agreement with the observed value, allowing for some sample decomposition.
In contrast, the simplicity of the $^1$H-NMR spectrum of the germanium compound $\text{Am}_2\text{GeCl}_2$ suggests that there may be an equilibrium in solution between monomer and dimer, with associated rapid exchange of amidino groups (Eqn. 4.6). This would also account for the observed molecular weight of 673, which, although significantly greater than the monomer weight of 561.5, is considerably smaller than the dimer weight, even allowing for some sample decomposition.

The infra-red spectra of the compounds $\text{Am}_2\text{MCl}_2$ ($\text{M} = \text{Si, Ge}$) show considerable similarity apart from expected frequency shifts due to the differing masses of the metals; it may be inferred that they have similar structures in the solid state. Both compounds show two absorptions assignable to $\nu$(M-Cl), corresponding to the symmetric and asymmetric vibrations. This would rule out a structure involving a linear Cl-M-Cl arrangement, since this would result in an infra-red-inactive symmetric vibration. However, a distorted six-coordinate structure (Fig. 4-7), analogous to that found for $\text{Me}_2\text{M(CN)}_2$ ($\text{M} = \text{Si, Ge, Sn}$) would remain possible for the solid materials. Both show an absorption in the $\nu$(C=N)

![Figure 4-7](image-url)
amidino groups.

The observed molecular weight of 551 for the tin(II) compound, (AmSnCl)_2, is somewhat lower than the dimer weight of 727, but in this case the discrepancy is probably due to some decomposition of the extremely air-sensitive test solution, since the ^1H-NMR spectrum shows no sign of the amidino-group exchange process which would be associated with a monomer-dimer equilibrium; it is considerably more complex than that of the germanium compound, suggesting that the chemical environments of the phenyl protons are less fluid. Thus the compound is probably dimeric, although a monomeric formulation could still accommodate the preferred coordination number of three for tin(II) (Fig. 4-8a). It is probable, however, that the small bite of the amidino group would require too narrow an angle at tin for the monomeric three-coordinate structure (NSnN is 61.1° in AmSn IV Cl_3 compared to 74.9° in the Sn₂N₂ ring in (Ph₂CNSnCl)₂), with the result that a dimeric structure is adopted. The resulting eight-membered ring would be expected to be highly puckered to minimise bond angle strain and steric interactions with the tin(II) lone pairs of electrons. The C=N= systems are therefore probably localised, since maintenance of a planar SnNCNSn skeleton, necessary for delocalisation
over the NCN group, would result in severe angle strain because of the proximity of the two tin atoms (the only known examples of such delocalised amidino bridges are in molybdenum\textsuperscript{415} and rhenium\textsuperscript{416} systems which contain metal-metal bonds).

B. Spectroscopic and structural data.

i) Mass spectra.

All four new compounds gave good spectra, all of which showed parent peaks corresponding to the monomeric units. None displayed any identifiable fragments containing more than one metal atom, although peaks with m/e values greater than those of the monomers were common, even for the monomeric compound AmSn\textsuperscript{IV}Cl\textsubscript{3}, probably as a result of recombination processes. The most important fragments for the four compounds are listed in Table 31 a-d.

The fragmentation patterns are more complex than those of the methyleneamino derivatives, due to the variety of breakdown pathways for the amidino groups. The major primary processes appear to be: progressive loss of amidino groups and/or chlorine atoms; cleavage of the amidino group at nitrogen, with loss of Ph\textsuperscript{'} or PhN\textsuperscript{'}; loss of the methyl group; elimination of the stable molecule acetonitrile, CH\textsubscript{3}C\textequivN, leaving the fragment Ph\textsubscript{2}N-. Further breakdown and recombination processes increase the complexity of the spectrum; in some cases identification of the fragments proved difficult.

The lack of any fragments containing more than one tin atom in the spectrum of (AmSn\textsuperscript{II}Cl)\textsubscript{2} is in contrast to the situation for the methyleneamino-bridged tin(II) derivatives, such as (Ph\textsubscript{2}CNSn\textsuperscript{II}Cl)\textsubscript{2}, where
**TABLE 31**

Important fragments in the mass spectra of some N,N'-diphenyl-acetamidino derivatives of the Group IVB elements

a) \( \text{Am}_2\text{SiCl}_2 \)

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<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
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<tr>
<td>602</td>
<td>7</td>
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<td>271</td>
<td>3</td>
<td>( \text{AmSiCl}^+ - \text{H} )</td>
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<tr>
<td>567</td>
<td>14</td>
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<td>258</td>
<td>2</td>
<td>( \text{Am}<em>2\text{SiCl}</em>{2}^{2+} )</td>
</tr>
<tr>
<td>516</td>
<td>72</td>
<td>( \text{Am}_2\text{SiCl}_2^+ )</td>
<td>240.5</td>
<td>1</td>
<td>( \text{Am}<em>2\text{SiCl}</em>{2}^{2+} )</td>
</tr>
<tr>
<td>500</td>
<td>5</td>
<td>( \text{Am}_2\text{SiCl}_2^{+}-\text{CH}^+_3-\text{H} )</td>
<td>236</td>
<td>7</td>
<td>( \text{AmSi}^+-\text{H} )</td>
</tr>
<tr>
<td>499</td>
<td>7</td>
<td>( \text{Am}_2\text{SiCl}_2^{+}-\text{CH}^+_3-2\text{H} )</td>
<td>230</td>
<td>7</td>
<td>( \text{CH}_3\text{CN}_2\text{PhSiCl}_2^+ )</td>
</tr>
<tr>
<td>481</td>
<td>100*</td>
<td>( \text{Am}_2\text{SiCl}_2^+ )</td>
<td>210</td>
<td>100</td>
<td>( \text{AmH}^+ )</td>
</tr>
<tr>
<td>475</td>
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<td>( \text{PhNCNPh}^+ )</td>
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<td>2</td>
<td>( \text{PhNCPh}^+ )</td>
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<tr>
<td>400</td>
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<td>169</td>
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<td>( \text{Ph}_2\text{NH}^+ )</td>
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<tr>
<td>393</td>
<td>100*</td>
<td>( \text{AmSiCl}_2\text{Ph}^+ - \text{H} )</td>
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<td>8</td>
<td>( \text{Ph}_2\text{N}^+-\text{H} )</td>
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<td>61</td>
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<td>( \text{PhNH}^+ )</td>
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<td>( \text{PhN}^+ )</td>
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<td>( \text{Ph}^+ )</td>
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* : Off-scale.

All m/e values refer to the most intense peak of the group, i.e. that containing the most common isotopes.
### b) $\text{Am}_2\text{GeCl}_2$

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<thead>
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<th>m/e</th>
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<th>Relative Intensity</th>
<th>Assignment</th>
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<td>$\text{Am}^+$</td>
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<tr>
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<td>100*</td>
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<td>$\text{CH}<em>3\text{CN}</em>{2}\text{PhGeCl}_2^{+}\text{H}^-$</td>
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</table>
c) $\text{AmSn}^{IV}\text{Cl}_3$

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<th>m/e Relative Intensity</th>
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<th>m/e Relative Intensity</th>
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<td>180 32</td>
<td>$\text{PhNCPh}^+$</td>
</tr>
<tr>
<td>364 37</td>
<td>$\text{AmSnCl}^+$</td>
<td>168 36</td>
<td>$\text{Ph}_2\text{N}^+$</td>
</tr>
<tr>
<td>352 1</td>
<td>-</td>
<td>155 74</td>
<td>$\text{SnCl}^+$</td>
</tr>
<tr>
<td>342 1</td>
<td>-</td>
<td>118 100*</td>
<td>$\text{PhNCCH}_3^+$</td>
</tr>
<tr>
<td>329 7</td>
<td>$\text{AmSn}^+$</td>
<td>104 21</td>
<td>$\text{PhNCCH}_3^+$</td>
</tr>
<tr>
<td>323 8</td>
<td>$\text{Ph}_2\text{NSnCl}^+$</td>
<td>91 57</td>
<td>$\text{PhN}^+$</td>
</tr>
<tr>
<td>304 1</td>
<td>-</td>
<td>77 100</td>
<td>$\text{Ph}^+$</td>
</tr>
</tbody>
</table>
### d) (AmSn^{II}Cl)_2

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>608</td>
<td>0.1</td>
<td>Am(_2)SnCl(_2)^+</td>
<td>231</td>
<td>8</td>
<td>PhSnCl(^+)-H(^-)</td>
</tr>
<tr>
<td>573</td>
<td>0.1</td>
<td>Am(_2)SnCl(^+)</td>
<td>224</td>
<td>6</td>
<td>PhNCSn(^+)+H(^-)</td>
</tr>
<tr>
<td>538</td>
<td>1</td>
<td>Am(_2)Sn(^+)</td>
<td>209</td>
<td>100(^*)</td>
<td>Am(^+)</td>
</tr>
<tr>
<td>537</td>
<td>1</td>
<td>Am(_2)Sn(^+)-H(^-)</td>
<td>194</td>
<td>67</td>
<td>PhNCNPh(^+)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>4</td>
<td>SnCl(_2)^+</td>
</tr>
<tr>
<td>456</td>
<td>2</td>
<td>(Ph(_2)N)(_2)Sn(^+)</td>
<td>185</td>
<td>8</td>
<td>C(_3)H(_5)Sn(^+)</td>
</tr>
<tr>
<td>441</td>
<td>7</td>
<td>AmSnCl(_2)Ph(^+)</td>
<td>180</td>
<td>7</td>
<td>PhNCPh(^+)</td>
</tr>
<tr>
<td>408</td>
<td>21</td>
<td>-</td>
<td>168</td>
<td>100(^*)</td>
<td>Ph(_2)N(^+)</td>
</tr>
<tr>
<td>364</td>
<td>100(^*)</td>
<td>AmSnCl(^+)</td>
<td>164.5</td>
<td>7</td>
<td>AmSn(^+)2(^+)</td>
</tr>
<tr>
<td>349</td>
<td>4</td>
<td>C(NPh)(_2)SnCl(_2)^+</td>
<td>155</td>
<td>100(^*)</td>
<td>SnCl(^+)</td>
</tr>
<tr>
<td>347</td>
<td>6</td>
<td>C(NPh)(_2)SnCl(_2)^+ -2H(^-)</td>
<td>118</td>
<td>100(^*)</td>
<td>PhNCCH(_3)(^+)</td>
</tr>
<tr>
<td>329</td>
<td>100(^*)</td>
<td>AmSn(^+)</td>
<td>105</td>
<td>100</td>
<td>PhN(_2)^+ , PhNCH(_2)(^+)</td>
</tr>
<tr>
<td>309</td>
<td>3</td>
<td>Ph(_2)SnCl(^+)</td>
<td>91</td>
<td>100(^*)</td>
<td>PhN(^+)</td>
</tr>
<tr>
<td>287</td>
<td>30</td>
<td>CH(_3)CN(_2)PhSnCl(_2)^+</td>
<td>77</td>
<td>100(^*)</td>
<td>Ph(^+)</td>
</tr>
<tr>
<td>272</td>
<td>3</td>
<td>PhNCNSnCl(^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>247</td>
<td>15</td>
<td>PhNSnCl(_2)^+H(^-)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the Sn-N-Sn bridge persists in some of the most stable fragments. Presumably this reflects the relative stabilities of the bridged and monomeric species.

ii) Proton nuclear magnetic resonance spectra.

The proton nuclear magnetic resonance spectra of the new compounds are listed in Table 32, together with that of the parent amidine for comparison. Spectra were recorded on C₆D₆ solutions at approximately 42°C, and on d₈-toluene solutions of (Am₂SiCl₂)₂.C₇H₈ and (AmSnCl₂)_2 for reduced temperature studies.

All the spectra show a single sharp absorption for the amidino methyl group at ambient temperature, with the exception of the silicon compound (Am₂SiCl₂)₂.C₇H₈, which shows two peaks, relative intensities 1:1, probably corresponding to bridging and non-bridging amidino groups. There is a small downfield shift of the signal from the germanium compound to Sn(II) and then to Sn(IV) (although the silicon compound does not fit in this order, which may be due to a number of factors: the electronegativity of the metal, the NCN bond angle, and the extent of π-delocalisation in the system will all have an effect. The methyl group in the parent amidine is slightly more deshielded than those of the metallated compounds.

It is usually difficult to derive structural information from the resonances due to the aromatic protons of monosubstituted benzenes, because the splitting patterns due to spin coupling tend to be complex and vary considerably with the substituent. Here, however, the variation in the substituent group is restricted to changes in the mode of bonding of the amidino group to the metal, and the variation in splitting pattern can be rationalised to some extent.
TABLE 32

$^1$H-NMR spectra for some N,N'-diphenylacetamidino derivatives of the Group IVB elements

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shifts $^\gamma$ ppm. $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar-H</td>
</tr>
<tr>
<td>(Am$_2$SiCl$_2$)$_2$.C$_7$H$_8$</td>
<td>2.92s (~40)</td>
</tr>
<tr>
<td></td>
<td>2.99s$^b$(~5)</td>
</tr>
<tr>
<td>(Am$_2$GeCl$_2$)$_n$</td>
<td>3.10s (10)</td>
</tr>
<tr>
<td>AmSn IV Cl$_3$</td>
<td>3.08,3.12d(10)</td>
</tr>
<tr>
<td>(AmSn IV Cl)$_2$</td>
<td>3.08s (~2.5)</td>
</tr>
<tr>
<td></td>
<td>3.17,3.23d(~6)</td>
</tr>
<tr>
<td></td>
<td>3.30,3.36m(~1.5)</td>
</tr>
<tr>
<td>AmH</td>
<td>2.82s(~2)</td>
</tr>
<tr>
<td></td>
<td>2.88s (~5)</td>
</tr>
<tr>
<td></td>
<td>3.03,3.11,3.18s(~3)</td>
</tr>
</tbody>
</table>

$a$: Relative to TMS = 10 ppm (external reference).

$b$: Toluene resonances.

c: In d$_8$-toluene solution at -40°C, resolved as a doublet, separation 0.13 ppm.

e: Variable temperature study on d$_8$-toluene solution shows no change in the range -90°C - +40°C.

s: singlet
d: doublet
m: multiplet

All spectra run on C$_6$D$_6$ solutions at ~42°C. Integral ratios in parentheses.
The complexity of the spectrum of a group PhX will depend upon the electronic and steric effects of the group X; electron withdrawal, for example, will increase the difference in chemical environment of the aromatic protons, as will a bulky substituent X (its major steric interactions will be with the protons ortho to it). Thus for the N,N'-diphenylacetamidino derivatives, factors of major importance will be the hybridisation of the nitrogen atom attached to the phenyl group under consideration, and whether or not it is coordinated to the metal.

If the two phenyl groups are in different chemical environments, two superimposed patterns will be observed. Thus for the parent amidine, the localised \( \pi \)-system (Fig. 4-9) allows assignment of the strong singlet at 2.88\( \tau \) to the imino-bonded phenyl group (PhN=\( \equiv \)C=O also gives a single Ar-H signal\(^{417} \)) and the remaining multiple absorption to the amino-bonded phenyl (PhNH\(_2\) similarly shows several aromatic resonances\(^{417} \)).

On this basis, the complexity of the spectrum of (AmSn\(^{11}\)Cl\(_2\)) suggests a similarly localised system, further splitting of the imino-bonded phenyl group absorption being perhaps due to coordination of the nitrogen to tin. The dimeric structure is shown by the cryoscopic molecular weight to persist in benzene solution, and such localisation of the \( \pi \)-system would be enforced by the formation of the eight-membered ring, which would have to be severely puckered to minimise angle strain.
The spectrum of the monomeric compound $\text{AmSn}^{\text{IV}}\text{Cl}_3$, which contains a bidentate, probably only partially delocalised amidino group, is considerably simplified in comparison, being reduced to a doublet. This may be due to the acute SnNC angle ($\sim 94^\circ$ compared to $120^\circ$ for sp$^2$ hybridised nitrogen) which would reduce the interactions between the ring protons and the other substituents on the nitrogen atom.

The amidino derivatives of the smaller elements silicon and germanium, $\text{Am}_2\text{MCl}_2$ ($\text{M} = \text{Si, Ge}$), give fairly sharp singlet absorptions for the phenyl protons. The cryoscopic molecular weight of the germanium compound suggests some association in solution, and an equilibrium between monomer and dimer would allow rapid equilibration of the phenyl groups through an amidino group exchange process (Eqn. 4.7), with a single phenyl resonance as the result of time averaging of the environments of the phenyl protons. However, this explanation appears less likely for $\text{Am}_2\text{SiCl}_2$, since its spectrum contains two methyl resonances due to the amidino groups which implies a dimeric structure in which exchange between bridging and terminal amidino groups is slow.
relative to the NMR time-scale. No variation in the spectrum was observed on heating a d$_8$-toluene solution of Am$_2$SiCl$_2$ to 100°C.

On cooling to -40°C, however, the lower of the two methyl resonances could be resolved as a doublet. Since cooling was found to have no effect on the spectrum of (AmSnII)Cl$_2$, which contains only bridging amidino groups, it seems likely that for (Am$_2$SiCl$_2$)$_2$ the resolvable methyl absorption corresponds to terminal amidino groups. To account for this resolution at low temperature, a monodentate terminal amidino group may be postulated (Fig. 4-10), for which cooling would freeze out the inversion process at the imine nitrogen, with associated resolution of the syn and anti isomers and the appearance of two methyl signals. Such a structure would contain five-coordinate silicon; steric crowding about the comparatively small silicon atoms may prevent increase of the coordination number to six.

iii) Infra-red spectra

The stretching vibrations of the NCN unit in N-metallated amidines have been variously assigned. The symmetric and asymmetric modes were considered to lie in the region 1300-1500 cm$^{-1}$ for a number of transition metal carbonyl systems. For several tantalum or niobium chloride derivatives of a number of bidentate N,N'-disubstituted acetamidines, $\nu$(NCN) was assigned to a weak band at $\sim$1640 cm$^{-1}$, often with two or
three other bands in the region 1500-1600 cm$^{-1}$. In this work a weak band was sometimes observed at $\approx 1640$ cm$^{-1}$, but it varied considerably in intensity with the purity of the sample, so that it may have been due to an impurity of the free amidine or its hydrochloride, both of which absorb strongly in this region.

Those bands in the 1300-1600 cm$^{-1}$ region which show variation from compound to compound are assumed to be associated with the NCN stretching vibrations and are listed in Table 33.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(NCN) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Am}_2\text{SiCl}_2)_2$</td>
<td>1566vs, 1332m</td>
</tr>
<tr>
<td>$(\text{Am}_2\text{SiCl}_2)_2\cdot\text{C}_7\text{H}_8$</td>
<td>1566vs, 1336m</td>
</tr>
<tr>
<td>$(\text{Am}_2\text{GeCl}_2)_n$</td>
<td>1554vs, 1324w</td>
</tr>
<tr>
<td>$(\text{AmSn}^{\text{II}}\text{Cl})_2$</td>
<td>1523vs, 1382s</td>
</tr>
<tr>
<td>AmSn$^{\text{IV}}\text{Cl}_3$</td>
<td>?</td>
</tr>
<tr>
<td>AmH</td>
<td>1633vs, 1535vs, 1338s</td>
</tr>
</tbody>
</table>

If the higher energy absorption (1520-1570 cm$^{-1}$) is assigned to $\nu_{\text{as}}$(NCN), then a decrease is observed Si$>_{\text{Ge}}\text{Sn}^{\text{II}}$, consistent with predominance of the mass effect, although a similar effect is not observed for the lower energy absorption (1320-1385 cm$^{-1}$), which may be assigned to the symmetric vibration. This may reflect variations in the
degree of delocalisation of the NCN $\pi$-system.

For the compounds $\text{Am}_2\text{MCl}_2$ ($\text{M} = \text{Si,Ge}$), a dimeric formulation would imply the presence of bridging as well as terminally-bonded amidino groups, of which the latter might act as bidentate chelating ligands (Fig. 4-ll(a)). In this case separate $\nu$(NCN) absorptions would be expected for the two types of ligand. However, $\text{AmSn}^{IV}_2\text{Cl}_3$, which contains only bidentate chelating amidino groups, shows no absorptions in this region apart from the aromatic ring bands at $\sim$1600 cm$^{-1}$ and the very strong band at 1498 cm$^{-1}$ which shows no significant movement from compound to compound. On this basis it seems reasonable to assign the absorptions at 1520-1570 cm$^{-1}$ and 1320-1385 cm$^{-1}$ to vibrations of bridging amidino groups. The $^1$H-NMR evidence for the silicon derivative $\text{Am}_2\text{SiCl}_2$, however, indicates that the non-bridging amidino groups are monodentate in this compound. The apparent absence of a band in the infra-red spectrum corresponding to $\nu$(C=N) for such a localised amidino group may indicate that in the solid state a polymeric structure is adopted in which all the amidino ligands are bridging (Fig. 4-ll(b)). The similarity of the spectrum of the corresponding germanium compound may indicate a similar structure in the solid.

Some N,N'-diphenylacetamidino derivatives of molybdenum and tungsten have been found to show a medium absorption at $\sim$1630 cm$^{-1}$, attributed to $\nu$ (NCN) as This was considered to be consistent with a
bidentate chelating amidino group, so that the weak absorption at 1645 cm\(^{-1}\) in the spectrum of AmSn\(^{\text{IV}}\)Cl\(_3\) cannot be disregarded as a possible candidate for \(\nu_{\text{as}} (\text{NCN})\), in spite of reservations mentioned earlier.

No firm assignment for metal-nitrogen stretching frequencies for the new compounds could be made, with the exception of the silicon compound \((\text{Am}_2\text{SiCl}_2)_2\) where a band at 566 cm\(^{-1}\) does not appear in the spectra of the other compounds. This is in the appropriate region for \(\nu_s (\text{NSiN})\), and it is possible that the asymmetric vibration overlies an absorption of the amidino group, such as that at 868 cm\(^{-1}\).

Metal-chlorine stretching vibrations may be assigned as listed in Table 34. Some alternatives are given. Three bands, corresponding to

| TABLE 34 |
|---|---|
| \(\nu(M-\text{Cl})\) for some N,N'-diphenylacetamidino derivatives of the Group IVB elements |

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(M-\text{Cl})) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Am}_2\text{SiCl}_2)_2)</td>
<td>492</td>
</tr>
<tr>
<td>((\text{Am}_2\text{SiCl}_2)_2\cdot\text{C}_7\text{H}_8)</td>
<td>496</td>
</tr>
<tr>
<td>((\text{Am}_2\text{GeCl}_2)_2\cdot n)</td>
<td>360</td>
</tr>
<tr>
<td>((\text{AmSnCl}_2)_2)</td>
<td>?</td>
</tr>
<tr>
<td>AmSn(^{\text{IV}})Cl(_3)</td>
<td>353</td>
</tr>
</tbody>
</table>
the two asymmetric and one symmetric stretching vibrations of the SnCl$_3$ group, would be expected for AmSn$^\text{IV}$Cl$_3$. The observed band is probably one of the former; $\gamma_s$ is probably outside the range studied.

The presence of absorptions corresponding to $\gamma_s$ (Cl-M-Cl) for the silicon and germanium compounds indicates a non-linear Cl-M-Cl skeleton, as has previously been mentioned. The frequencies are rather low for these metals in a four-coordinate state; this may be indicative of a higher coordination number in these compounds. Generally the expected trend in frequencies is followed, i.e. $\text{Si} > \text{Ge} > \text{Sn}^\text{IV} > \text{Sn}^\text{II}$.

iv) Crystallographic studies.

The crystal and molecular structure of AmSn$^\text{IV}$Cl$_3$ has been determined by X-ray diffraction. The molecular structure is illustrated in Figure 4-12, and relevant structural information is listed in Table 35. The amidino group is bidentate to the five-coordinate tin atom, and appears to be asymmetrically bonded. The CN$_2$Sn ring is planar, and the skeleton is also planar at carbon and both nitrogens, suggesting the possibility of a delocalised $\pi$-system.

The phenyl rings are disordered, so that the estimated standard deviations are comparatively high, and the apparent difference in C-N bond distances has been dismissed as due to experimental error. However, the shorter C-N bond, C(1)-N(1), corresponds to the longer Sn-N bond, Sn-N(1), consistent with a significant contribution from the localised structure shown in Figure 4-6. The C-N bond distances (1.37(4) and 1.29(4) Å) may be compared with the calculated single- and double-bond distances of 1.472 and 1.287 Å respectively, suggesting that partial
TABLE 35

Bond lengths and angles from the crystal structure of CH$_3$C(NPh)$_2$Sn$^{IV}$Cl$_3$

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>( \text{Å} )</th>
<th>Bond angles</th>
<th>°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-N(1)</td>
<td>2.180(20)</td>
<td>N(1)C(1)N(2)</td>
<td>109.5(9)</td>
</tr>
<tr>
<td>Sn-N(2)</td>
<td>2.087(23)</td>
<td>C(1)N(1)Sn</td>
<td>93.7(1.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(1)N(2)Sn</td>
<td>95.6(1.7)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.29 (4)</td>
<td>N(1)SnN(2)</td>
<td>61.1(3)</td>
</tr>
<tr>
<td>C(1)-N(2)</td>
<td>1.37 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-Cl(1)</td>
<td>2.315(3)</td>
<td>C(1)SnCl(2)</td>
<td>106.9(5)</td>
</tr>
<tr>
<td>Sn-Cl(2)</td>
<td>2.335(10)</td>
<td>C(1)SnCl(3)</td>
<td>95.6(1)</td>
</tr>
<tr>
<td>Sn-Cl(3)</td>
<td>2.317(9)</td>
<td>C(1)SnCl(1)</td>
<td>100.7(5)</td>
</tr>
</tbody>
</table>

Non-bonded interactions, \( \text{Å} \)

- Sn-C(1) 2.60(1)

Estimated standard deviations in parentheses.
Molecular structure of $\text{CH}_3\text{C(NPh)}_2\text{Sn}^{IV}\text{Cl}_3$. 

Figure 4-12
delocalisation occurs. In bis(N,N'-di-p-tolylacetamidino)palladium(II), where the bidentate amidino groups are fully delocalised, the C-N bond distance is 1.322(4) Å, and for the tantalum derivative \((\text{PrNCCH}_3\text{N}^1\text{Pr})_2\text{TaCl}_3\) it is 1.35(3) Å. The latter contains two symmetric amidino groups, but the related compound \((\text{C}_6\text{H}_{11}\text{NCCH}_3\text{N}_6\text{H}_{11})_2\text{TaMeCl}_2\) contains one symmetric and one asymmetric ligand; the former has a C-N bond distance of 1.38(3) Å, while the latter has distances of 1.40(3) and 1.27(3) Å.

The expected geometry at tin would be based on a trigonal bipyramid, but due to the very small NSnN angle (61.1°) this is severely distorted.

It has often been found that in a trigonal bipyramidal structure axial bonds to a given ligand are longer than equatorial bonds. Here the longer Sn-N bond, to N(1), lies approximately opposite to the longer Sn-Cl bond, to Cl(2). N(1) and Cl(2) may therefore be considered to occupy the axial positions of the trigonal bipyramid (Fig. 4-13). The asymmetric bonding of the amidino group may thus be a result of its occupying one axial and one equatorial position. Such an arrangement is probably more tolerant of the small NSnN angle than the symmetric form with the ligand occupying two equatorial positions. A similar effect is seen in the structure of \((\text{C}_6\text{H}_{11}\text{NCCH}_3\text{N}_6\text{H}_{11})_2\text{TaMeCl}_2\) which is based on a severely distorted pentagonal bipyramid; the symmetrically bonded amidino group occupies two equatorial sites, and the asymmetrically
bonded group occupies one axial and one equatorial position. The five-coordinate tin(IV) derivative (1,3-diphenylpropane-1,3-dionato) triphenyltin(IV) shows a similar distortion in the bond lengths of the chelating ligand, which also bridges between axial and equatorial positions.446

An alternative picture considers the bidentate amidino-group to occupy one vertex of a tetrahedron, slightly distorted by repulsions between the chlorines and the 'extended ligand' formed by the amidino group. This idea, of regarding a bidentate ligand of small bite as occupying a single ligand site, has been previously suggested in connection with the structures of the titanium(IV)421 and tin(IV)84 tetranitratos, $\text{MIV(NO}_3\text{)}_4$ ($\text{M} = \text{Ti, Sn}$). The asymmetry of the amidino group may then be considered to arise from the symmetry of the entire molecule; two extreme conformations are possible, illustrated in Figure 4-14 (viewing along the Sn-C(1) axis). In the staggered form

(Fig. 4-14a) the symmetry of the molecule requires that the two C-N bonds should be equivalent; in contrast the eclipsed form (Fig. 4-14b) requires them to be inequivalent. A similar argument accounts for the differing Sn-Cl bond lengths. In this case the actual molecule lies between the two extremes, but is much closer to the staggered form; the observed relatively small amount of asymmetry in the molecule reflects this.
The shorter Sn-N bond length, 2.087(23) Å, is slightly longer than those observed in the four-coordinate compounds Sn\(^{IV}\)(NC\(_2\)H\(_5\))\(_2\)\(^{301,302}\) and Sn\(^{IV}\)(NMe\(_2\))\(_2\)\(^{266}\) (2.068(27) and 2.045 Å respectively). The longer, 2.180(20) Å, compares quite well with 2.15(6) Å for the five-coordinate Me\(_3\)SnNCS,\(^{191}\) but is generally shorter than most N-Sn\(^{IV}\) dative bonds,\(^{12}\) e.g. 2.260(5) Å in the ortho-metallated compound 2-SnCl\(_3\)-4-MeC\(_6\)H\(_3\)C(p-tolyl)=NH\(^{436}\) (Chapter 5).

The equatorial Sn-Cl bond lengths (average 2.316(6) Å) compare well with other trigonal bipyramidal tin derivatives (e.g. 2.32 Å for Me\(_2\)SnCl\(_3\)\(_{61}\), 2.316(2) Å average for 2-SnCl\(_3\)-4-MeC\(_6\)H\(_3\)C(p-tolyl)=NH\(^{436}\)), but the axial Sn-Cl bond (2.335(10) Å) is considerably shorter than most others in the literature (e.g. 2.54 Å for Me\(_2\)SnCl\(_3\)\(_{61}\), 2.416(2) Å for 2-SnCl\(_3\)-4-MeC\(_6\)H\(_3\)C(p-tolyl)=NH\(^{436}\)). This is presumably due to the degree of distortion of the trigonal bipyramidal structure. The Sn-Cl bond lengths may also be compared to those in the essentially four-coordinate phenyl tin(IV) chlorides, Ph\(_3\)SnCl (2.318(15) Å)\(^{422}\) and Ph\(_2\)SnCl\(_2\) (2.336(2) Å and 2.355(2) Å).\(^{423}\)

C. Summary

Several new N,N'-diphenylacetamidino derivatives of silicon, germanium, and tin have been prepared. The mono-amidino tin(IV) trichloride is stable, but the silicon and germanium analogues are unstable to disproportionation to the bis-amidino metal dichlorides and cannot be isolated. The mono-amidino tin(II) chloride may also be obtained, as a dimeric species probably containing an eight-membered Sn\(_2\)N\(_4\)C\(_2\) ring involving three-coordinate tin(II). AmSn\(^{IV}\)Cl\(_3\) is monomeric, containing five-coordinate tin(IV) and a bidentate chelating amidino group, which
occupies one axial and one equatorial position in a severely distorted trigonal bipyramidal structure. The germanium compound $\text{Am}_2\text{GeCl}_2$ is partially associated in solution and possibly polymeric in the solid. It appears likely that there is similar association in the solid for the corresponding silicon compound (obtained both with and without toluene of crystallisation), although it appears to be dimeric in solution, with a structure involving five-coordinate silicon; the non-bridging amidino group is apparently only monodentate to the metal, perhaps as a result of crowding around the small silicon atom.
CHAPTER FIVE

ORTHO-METALLATION REACTIONS OF DIARYLMETHYLENEAMINO-
TIN(IV) TRICHLORIDES
5.1 Introduction

The generalised intramolecular aromatic metallative rearrangement of metal complexes may be written as in Equation 5.1. An aryl

\[
\begin{array}{c}
\text{PhRX} \\
\text{ML}_n
\end{array}
\rightarrow
\begin{array}{c}
\text{PhRX} \\
\text{ML}_{n-1} + HL
\end{array}
\]

or

The \( \text{C-H} \) bond of the ligand, \( \text{PhRX} \) (\( \text{X} \) is an electronegative element, e.g. \( \text{O,N,P} \),) reacts with the central metal \( \text{M} \) to form a metal-carbon bond. The hydrogen atom so displaced may be eliminated from the molecule or may be transferred to the group \( \text{X} \). Owing to the steric restrictions, such reactions occur in the position adjacent to the ligand chain, and are termed 'ortho-metallations'. These are well known for transition metal systems, and have been reviewed.\(^{424,425}\) A few examples are given in Equations 5.2-5.

\[
\begin{array}{c}
\text{Ph} = \text{N=N=Ph} \\
+ \quad \text{Mn}_2(\text{CO})_{10}
\end{array}
\rightarrow
\begin{array}{c}
\text{Ph} = \text{N=N=Ph}
\end{array}
\]

\( (426) \)

\[
\begin{array}{c}
\text{PhCH}_2\text{NR}_2
\end{array}
+ \quad \text{PdCl}_2
\rightarrow
\begin{array}{c}
\text{PhCH}_2\text{NR}_2
\end{array}
\]

\( (427) \)

\[
\begin{array}{c}
\text{Ph}_{2}\text{PPh}_3\text{Rh}(\text{PPh}_3)_2
\end{array}
\rightarrow
\begin{array}{c}
\text{Ph}_{2}\text{PPh}_3\text{Rh}(\text{PPh}_3)_2
\end{array}
\]

\( \text{CH}_4 \)

\( (428) \)

\( 5.2. \)

\( 5.3. \)

\( 5.4. \)
Such reactions in the main result in the formation of 5-membered heterocycles, although phosphine ligands in particular often rearrange to give 4-membered rings (Eqn. 5.4). Few reports exist to date of the formation of 6-membered metallocycles by such a process (e.g. Eqn. 5.5).

The mechanism has been variously interpreted. Many writers consider it to involve classical electrophilic substitution, and in some cases, such as the reaction of palladium chlorides with azobenzenes, arylmethylenamines, and related systems (which has been compared to mercuration reactions), this would appear to be a valid interpretation. However, it seems less likely when applied to low oxidation state, electron-rich metal derivatives, where it has been suggested that the mechanism is essentially a nucleophilic insertion of the metal into the sterically-favoured ortho C-H bond. The resulting unstable metal hydride eliminates the proton as hydrogen, or, if an organic group is also bonded to the metal, as a hydrocarbon. The two proposed mechanisms are shown in Equation 5.7.

In the main groups, comparatively few examples of ortho-metallation are known, the majority of which are confined to the lighter elements. Metallation of aromatic rings by lithium alkyls is a well-known and synthetically useful reaction; the presence of a substituent on the aromatic nucleus which can coordinate to the lithium atom leads to directed metallation in the ortho position, with the formation of a lithium-containing ring (e.g. Eqn. 5.6).
It might be expected that similar direction of metatlation could occur in mercuration and thallation reactions, but this does not appear to have been reported.

Alkyl or aryl derivatives of the Group IIA and IIIB elements similarly undergo directed metatlations with elimination of the displaced proton as a hydrocarbon; some examples are given in Equations 5.8-10.
219.

\[ \text{CH}_2 \_n \overset{N-Me}{\text{BH}}_2 \quad \overset{200-230^\circ C}{\text{N-Me} + H_2} \quad (432) \quad 5.9 \]

\[ \text{Me}_3 \text{Si-N-MPh}_3 \quad \overset{230^\circ C}{\text{M = Al, Ga}} \quad \overset{\text{Ph}_2}{\text{N-SiMe}_3} + \text{C}_6\text{H}_6 \quad (433) \quad 5.10 \]

The beryllium system is particularly interesting in that the ortho-
metallated products are dimeric, containing a ten-membered heterocycle.
If the system is sterically hindered, e.g. for the t-butyl beryllium derivative,
an equilibrium exists in solution between the dimer and the monomeric
5-membered ring.

For beryllium and gallium the examples of ortho-metallation given in
Equations 5.8 and 5.10 appear to be unique, but more examples are known
for boron and aluminium.

Like the lithium system, the beryllium reaction goes under mild
conditions, but the Group III derivatives require much higher temperatures.
It may be seen that all these reactions involve elimination of hydrocarbon,
but the reaction mechanism is probably not identical to the nucleophilic
process suggested for transition metal alkyls, which involves formation
of a M-H bonded intermediate; the lack of additional accessible electrons
for the main group metals would either require a multi-centre bond in the
intermediate or (perhaps more likely) a four-centre concerted process (e.g.
Eqn. 5.11).
This chapter describes a novel ortho-metallation process for a main group element, tin, which has not previously been known to take part in such reactions. Moreover, the mechanism apparently involves electrophilic attack on the aromatic ring by a trichlorostannyl group, -SnCl₃, under mild conditions; the only known examples of ortho-metallation involving attack by a halide of a main group element appear to be some reactions of boron chlorides (e.g. Eqns. 5.12 and 13) which involve the use of acid catalysts, or base to remove the HCl formed.

\[
\begin{align*}
\text{CH}_3\text{NH}_2\cdot\text{BCl}_3 & \xrightarrow{\text{Et}_3\text{N}} \text{CH}_3\text{H} & \text{N} & \text{B} & \text{Cl} & \text{Cl} \\
\end{align*}
\]

(434) 5.12

\[
\begin{align*}
\text{C}_6\text{H}_6\text{NH}_2 & + \text{BCl}_3 \xrightarrow{\Delta} \text{NH-BCl}_2 & + & \text{HCl} \\
\end{align*}
\]

(435) 5.13

The experimental section of this chapter follows; the discussion (Section 5.3) commences on p. 232.
5.2 Experimental

All manipulations were carried out under vacuum or an atmosphere of dry nitrogen.

A. Metallations involving diarylmethyleneamine derivatives.

i) Reaction of diphenylmethyleneaminolithium and tin tetrachloride
   (Mole ratio 1:1)

A solution of 16.8 mmol. diphenylmethyleneaminolithium in 50 cm$^3$ dry ether/hexane was cooled to $-196^\circ$C and 1.965 cm$^3$ tin tetrachloride (16.8 mmol.) were added. The mixture was allowed to warm to room temperature with stirring, and was then stirred overnight. The resulting yellow solution over a white precipitate was then evaporated to dryness. The infra-red spectrum of the residue showed no significant absorption in the $\nu$(N-H) region (3100-3400 cm$^{-1}$) and a band corresponding to $\nu$(C=N) at 1555 cm$^{-1}$. A band assignable to coordinated diethyl ether was also visible at 1062 cm$^{-1}$ ($\nu_{as}$(C-O-C)).

40 cm$^3$ dry toluene were then added to the residue, and the mixture was heated to about 100$^\circ$C and then filtered while hot, yielding a white solid (LiCl) and a golden-yellow solution, which, on cooling and standing at room temperature for several hours, deposited a colourless microcrystalline solid, identified as o-trichlorostannyldiphenylmethyleneamine mono-toluene, $\text{o-Cl}_3\text{SnC}_6\text{H}_4\text{C(Ph) = NH.C}_7\text{H}_8$, M.Pt.: 270-310$^\circ$C (sealed tube).

(Found: C 45.9, H 3.5, N 2.8, Cl 21.0%;

C$_{20}$H$_{18}$NSnCl$_3$ requires: C 48.3, H 3.6, N 2.8, Cl 21.4%)

$\nu_{max}$ (Nujol mull): 3332vs, 3102vw, 3080sh, 3057w, 3024w, 1990vw, 1967vw, 1953vw, 1914vw, 1888vw, 1848vw, 1821vw, 1598vs, 1587s, * 1572s, 1548vs, 1523sh,
A sample of the product was heated under vacuum to 150\degree C for 30 mins., and the volatile material evolved was collected in a trap at -196\degree C. On warming to room temperature, the latter melted to a clear liquid, identified as toluene from its infra-red spectrum (identical with that of a genuine sample) and its melting point (the temperature of a toluene slush-bath).

The infra-red spectrum of the white solid residue was essentially similar to that of crude o-SnCl_3\cdot C_6H_4C(Ph)=NH prepared from Ph_2CNSiMe_3 (q.v.). The product obtained in this experiment was therefore considered to be a solvate, containing one molecule of toluene per molecule of complex. In the listing of the infra-red spectrum, bands marked with an asterisk are assigned to toluene absorptions. They show little variation from the spectrum of liquid toluene.

ii) Reaction of diphenylmethyleneaminotrimethylsilane with tin tetrachloride
(Mole ratio 1:1)

4.872g. diphenylmethyleneaminotrimethylsilane (18.97 mmol.) were weighed into a flask which was then fitted with still-head and condensor. 2.22 cm\(^3\) tin tetrachloride (18.97 mmol.) were then added. The liquid mixture became warm to the touch and set to a cloudy yellow semi-solid, which was then heated. At \sim 70\degree C the mixture melted, and
darkened on further heating. At ~140°C a colourless liquid began to slowly distil out. The temperature was raised to 190°C and maintained there for one hour, when the slow distillation began to slacken off. The colourless liquid was identified as trimethylchlorosilane, Me₃SiCl, by comparison of its infra-red spectrum with that of an authentic sample.

The remaining volatile materials were removed from the reaction mixture under vacuum, and the resulting dark brown liquid was allowed to cool. It rapidly set to a crystalline mass, considered to be crude o-trichlorostannyldiphenylmethyleneamine, o-SnCl₃C₆H₄C(Ph)=NH.

\[ \nu_{\text{max}} \text{ (Nujol mull)}: 3312s, 3065w, 3041w, 1995vw, 1974vw, 1937vw, 1917vw, 1869vw, 1832vw, 1605vs, 1578s, 1557vs, 1546sh, 1498mw, 1458s, 1450s, 1406m, 1363vs, 1329mw, 1306m, 1291w, 1272mw, 1268sh, 1217vs, 1193mw, 1168sh, 1161vs, 1124s, 1087mw, 1048vw, 1037mw, 1026sh, 1006mw, 987vw, 978w, 944m, 920s, 906m, 859m, 842vs, 774s, 743vs, 729vs, 703vs, 678mw, 664m, 651s, 622vw, 613vw, 588mw, 574vw, 508w, 484vw, 450w, 434w, 411w, 362s \text{ cm}^{-1} \]

Recrystallisation of the crude product from 20 cm³ dry THF yielded a white microcrystalline solid, identified as o-trichlorostannyldiphenylmethyleneamine mono-THF, o-SnCl₃C₆H₄C(Ph)=NH·THF, M.Pt.: 177-9°C (sealed tube).

(Found: C 40.4, H 3.6, N 3.0, Cl 22.2%)

\[ \text{C}_{17} \text{H}_{18} \text{NO}\text{SnCl}_3 \text{ requires: C 42.8, H 3.8, N 2.9, Cl 22.3%}. \]

\[ \nu_{\text{max}} \text{ (Nujol mull)}: 3303s, 3069w, 3030w, 1996vw, 1973vw, 1948vw, 1888vw, 1844vw, 1810vw, 1599vs, 1579s, 1551vs, 1532sh, 1495mw, 1457s, 1443s, 1406mw, 1370s, 1360vs, 1355m, 1328vw, 1317w, 1305mw, 1269w, 1250vw, 1208vs, 1192w, \]
iii) Reaction of di(p-chlorophenyl)methyleneaminolithium with tin tetrachloride (Mole ratio 1:1).

A solution of 12.35 mmol. di(p-chlorophenyl)methyleneaminolithium in 50 cm$^3$ ether/hexane was cooled to -196°C and 1.443 cm$^3$ tin tetrachloride (12.35 mmol.) was added. The mixture was allowed to warm to room temperature with stirring. The deep orange-red colour of the imino-lithium faded to yellow, and a white precipitate formed. The mixture was stirred for 2 hrs., and then all solvent was removed under vacuum. An infra-red spectrum of the solid residue showed no significant absorption in the N-H stretching region, and a band corresponding to $\nu$(C=N) at 1589 cm$^{-1}$. A band assignable to coordinated diethyl ether was also visible at 1068 cm$^{-1}$.

The solid was heated to $\approx$100°C with 30 cm$^3$ dry toluene and filtered while hot, yielding a white solid (LiCl) and a yellow solution. The latter was refluxed for 24 hours and then filtered while hot, yielding a dark brown solution and a pale brown microcrystalline solid, identified as 2-trichlorostannyl-4-chlorophenyl(p-chlorophenyl)methyleneamine,

$\text{2-Cl}_3\text{Sn-4-CIC}_6\text{H}_4\text{C(p-CIC}_6\text{H}_4)\text{NH}_2$

M.Pt.: 252-7°C dec. (sealed tube).

(Found: C 30.2, H 2.1, N 2.5, Cl 37.9%;
C$_{13}^8\text{H}_8\text{NSnCl}_5$ requires: C 32.9, H 1.7, N 3.0, Cl 37.4%).

$\nu_{\max}$(Nujol mull): 3324s, 3080mw, 1953vw, 1927vw, 1911vw, 1808vw, 1784vw, 1707vw, 1678vw, 1600vs, 1569s, 1545m, 1496s, 1410s, 1387vs, 1364vs, 1311w, 1294sh, 1284mw, 1268vw, 1235vw, 1218s, 1191w, 1166mw, 1145s, 1097vs, 1050vw, 1021m, 969vw, 957w, 921s, 911m, 858s, 850s, 832m, 816vs, 789mw,
iv) Reaction of di-p-tolylmethyleneaminolithium with tin tetrachloride (Mole ratio 1:1)

A solution of 20 mmol. di-p-tolylmethyleneaminolithium in 50 cm³ ether/hexane was cooled to -196°C and 2.34 cm³ tin tetrachloride (20 mmol.) were added. The mixture was allowed to warm to room temperature with stirring. The deep red colour of the imino-lithium faded to yellow, and a yellow precipitate formed, which rapidly became sticky and coagulated. The mixture was stirred overnight, then all solvent was removed under vacuum. The infra-red spectrum of the solid residue showed no significant absorption in the N-H stretching region, and a band at 1570 cm⁻¹ corresponding to ν(C=N). An absorption at 1065 cm⁻¹ corresponded to coordinated diethyl ether.

The solid was heated with 40 cm³ dry toluene to ~100°C, and filtered while hot to remove lithium chloride. On cooling and standing at room temperature for two days, the yellow-brown filtrate deposited pale yellow crystals of 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine, 
\[ \text{2-Cl}_3\text{Sn-4-MeC}_6\text{H}_3(p-\text{MeC}_6\text{H}_4)=\text{NH} \], M.Pt.: 230-240°C (sealed tube).

(Found: C 41.4, H 4.3, N 3.3, Cl 24.3%; C₁₅H₁₄NSnCl₃ requires: C 41.6, H 3.2, N 3.2, Cl 24.8%).

ν max (Nujol mull): 3280vs, 3253sh, 3052sh, 3034w, 1932vw, 1921vw, 1814vw, 1695vw, 1662vw, 1610vs, 1599vs, 1582vs, 1568s, 1562sh, 1546s, 1510m, 1412m, 1395m, 1366vs, 1314mw, 1304mw, 1288mw, 1266w, 1223s, 1211s, 1188s, 1165s, 1146s, 1120vw, 1042mw, 1022mvw, 1002vw, 970vw, 958mw, 925s, 856s, 844sh, 837vs, 820vs, 793m, 757vs, 723w, 700vw, 682w, 673sh, 665m, 638w, 611m,
The experiment was repeated on a 19 mmol. scale. After removal of the ether/hexane solvent under vacuum, a small sample of the residue was mixed with d8-toluene, heated briefly, and sealed in an NMR tube. Its 1H-NMR spectrum was then recorded, listed as follows: (All values γppm, integrations in parentheses).

\[
\begin{align*}
\text{Ar-H:} & \quad 2.48 \quad \text{CH}_3-\text{CH}_2-\text{O:} & \quad 6.47 \\
& \quad 2.60 \quad \text{CH}_3-\text{CH}_2-\text{O:} & \quad 6.57 \\
& \quad 3.02 \quad \text{CH}_3-\text{CH}_2-\text{O:} & \quad 6.69 \quad \text{Quartet (4)} \\
& \quad 3.13 \quad \text{CH}_3-\text{CH}_2-\text{O:} & \quad 6.82 \\
\text{Ar-CH}_3: & \quad 7.97 \quad \text{singlet (6)} \quad \text{CH}_3-\text{CH}_2-\text{O:} & \quad 8.86 \\
& & \quad 8.97 \quad \text{Triplet (6)} \\
& & \quad 9.09
\end{align*}
\]

The aromatic proton resonances consist of a multiplet of four main peaks, which would be consistent with the AA'BB' pattern expected for para-disubstituted benzene derivatives. The spectrum as a whole is consistent with a compound containing one diethyl ether molecule per methyleneamino group. Over the course of one month at room temperature, two additional peaks appeared at 2.89 and 7.86 γ, probably corresponding to the aryl and methyl protons of the ortho-metallated material.

The remaining solid was extracted with hot toluene as in the previous reaction, and the filtrate was divided into two equal portions. To the first portion was added 1.42 cm³ dry N,N,N',N'-tetramethylethylene-diamine (TMED) (9.5 mmol.). A pale precipitate formed immediately, and
the solution darkened. The mixture was filtered, yielding a white powder identified as the adduct TMED\(_2\)SnCl\(_4\) on the basis of its infra-red spectrum and analysis.

(Found: C 20.7, H 4.2, N 6.9, Cl 35.8%.

\(\text{C}_{6}\text{H}_{16}\text{N}\text{SnCl}_{4}\) requires: C 19.1, H 4.3, N 7.4, Cl 37.7%).

Removal of solvent from the filtrate yielded an intractable red-brown gum, the infra-red spectrum of which showed no indication of ortho-metallation.

To the second portion was added 5 cm\(^3\) dry THF (large excess).

The resulting orange-brown solution, on storage at -20\(^\circ\)C for several hours, deposited a colourless, semi-crystalline solid, analysing as an approximately 1:1 mixture of the complex bis-THF tin tetrachloride, \((\text{C}_{4}\text{H}_{8}\text{O})_{2}\text{SnCl}_{4}\), with the mono-THF adduct of di-p-tolylmethyleneaminotin trichloride, 2-SnCl\(_3\)·4-MeC\(_6\)H\(_3\)C(p-tolyl)=NH·THF. The infra-red spectrum indicated that the latter was partially ortho-metallated.

(Found: C 38.9, N 1.4, Cl 28.5%;

\(\text{C}_{15}\text{H}_{14}\text{NSnCl}_{3}\text{C}_{4}\text{H}_{8}\) requires: C 45.1, H 4.4, N 2.8, Cl 21.1%;

\((\text{C}_{4}\text{H}_{8}\text{O})_{2}\text{SnCl}_{4}\) requires: C 23.7, H 4.0, N 0, Cl 35.1%)

v) Reaction of 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine with THF.

0.7g. 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine was dissolved in 10 cm\(^3\) dry THF with warming, and the solution was allowed
to cool. 10 cm$^3$ dry hexane were then added, with no effect. The mixture was concentrated under vacuum until a substantial quantity of solid appeared, and was then heated to redissolve the precipitated material. On cooling on an ice-bath, the solution deposited a mass of colourless needle crystals, identified as 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine bis-THF, \[
\text{2-SnCl$_3$-4-MeC$_6$H$_3$(p-MeC$_6$H$_4$)=NH.2THF,}
\]
M.Pt. (sealed tube): 70-100°C, THF lost; melts 228-230°C.

(Found: C 47.2, H 7.8, N 2.5, Cl 19.2%; C$_{23}$H$_{30}$NO$_2$SnCl$_3$ requires: C 47.8, H 5.2, N 2.4, Cl 18.4%)

$\nu_{\max}$ (Nujol mull): 3279s, 3215m,br, 3068w, 3040w, 1938vw, 1800vw, 1613s, 1604s, 1587vs, 1572m, 1551s, 1513mw, 1408m, 1380vs, 1368s, 1328vw, 1319mw, 1306w, 1289w, 1279vw, 1264w, 1240m, 1227mw, 1214m, 1190m, 1168mw, 1149s, 1122vw, 1077w, 1054s, 1040m, 1023s, 999mw, 960vw, 927s, 862s, 838s, 834sh, 823sh, 793m, 773vw, 760s, 728w, 678mw, 666w, 638w, 611m, 570w, 527vw, 483mw, 460vw, 445w, 436mw, 413w, 406w, 374vw, 363vw, 349mw, 328w cm$^{-1}$

vi) **Attempted reaction of 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine with iodine**

1.36g. 2-trichlorostannyl-4-methylphenyl(p-tolyl)methyleneamine (3.41 mmol.) was dissolved in 20 cm$^3$ dry THF and a solution of 0.796g. iodine (3.14 mmol.) in 8 cm$^3$ THF was added. The mixture was refluxed for 12 hours without visible effect. Removal of the solvent under vacuum yielded a dark brown semi-solid residue, the infra-red spectrum of which resembled that of the ortho-metallated starting material. The characteristic THF absorbtions at about 1050 and 850 cm$^{-1}$ (the asymmetric and symmetric C-O-C stretching vibrations respectively) were absent, implying that a THF adduct had not formed.
vii) Reaction of di-p-tolylmethyleneaminolithium with tin tetrachloride
(Mole ratio 2:1)

A solution of 28 mmol. di-p-tolylmethyleneaminolithium in 60 cm$^3$
ether/hexane was cooled to $-196^\circ$C and 1.625 cm$^3$ tin tetrachloride (14 mmol.)
were added. The mixture was allowed to warm to room temperature with
stirring, and was stirred overnight. The resulting yellow solution over
a cream-coloured precipitate was evaporated to dryness under vacuum, and
40 cm$^3$ dry toluene were added. The mixture was heated to 90$^\circ$C and
filtered, yielding a white solid (LiCl) and a dark orange-yellow solution,
which on concentration to about 25 cm$^3$ and cooling to $-10^\circ$C, deposited a
mass of microcrystalline yellow solid. The infra-red spectrum of this
material showed a sharp absorption attributable to $\nu$(N-H) at 3288 cm$^{-1}$,
and several absorptions in the C=N stretching region (1610 vs, 1583vs, 1551sh,
1534vs), suggesting that ortho-metallation may have occurred.
Analytical data, however, was inconsistent with the expected formula,
i.e. $\text{C}_2\text{H}_3\text{N}^+\text{SnCl}_2\text{C(p-tolyl)}_2^-\text{4-MeC}_6\text{H}_4\text{C(p-tolyl)=NH.}$

(Found: C 58.0, H 5.7, N 4.0, Cl 16.4%)

C$\text{_{30}}$H$\text{_{28}}$N$\text{_{2}}$SnCl$_2$ requires: C 59.5, H 4.6, N 4.6, Cl 11.7%)

$\nu_{\max}$ (Nujol mull): 3288 mw, 3257vw, 3176w, 3027mw, 1937vw, 1820vw, 1610vs,
1583vs, 1551sh, 1534vs, 1508s, 1499s, 1428s, 1401s, 1319mw, 1296m, 1288m,
1263s, 1219w, 1200mw, 1190s, 1168mw, 1146vw, 1088vw, 1043m, 1025m, 988vw,
979vw, 962vw, 956w, 930m, 863m, 854sh, 833vs, 826s, 817s, 785m, 745vs,
735sh, 702mw, 687w, 679sh, 650sh, 639w, 623vw, 601mw, 574vw, 545vw, 531vw,
497mw, 482sh, 478m, 437w, 410w, 337sh, 326w cm.$^{-1}$
viii) **Rearrangement of tris(diphenylmethyleneamino)tin(IV) chloride**

A solution of 30 mmol. tris(diphenylmethyleneamino)tin(IV) chloride in 50 cm$^3$ toluene was prepared in the manner described in Chapter 2. After filtration to remove the lithium chloride produced in the preparation, the solution was heated to boiling point and refluxed for one hour. The resulting bright yellow precipitate was then filtered off, washed with a little toluene, and dried under vacuum. The infra-red spectrum of the product showed a sharp N-H stretching absorption at 3332 cm$^{-1}$, and several absorptions in the C=N stretching region (1609vs, 1599vs, 1576vs, 1557s, 1543vs), consistent with an ortho-metallated structure. The mass spectrum contained, as peaks of highest m/e, fragments identified as $^{3}$Cl$_{3}$SnC$_{6}$H$_{4}$CPh=NH$^{+}$ (m/e 405), $^{2}$Cl$_{2}$SnC$_{6}$H$_{4}$CPh=NH$^{+}$ (m/e 370), and ClSnC$_{6}$H$_{4}$CPh=NH$^{+}$ (m/e 335). The dichlorotin containing peak was the most intense tin-containing peak in the spectrum, parallelling the ortho-metallated trichlorostannyl derivatives (q.v.). However, the analytical data were not consistent with the expected formula, i.e. $^{2}$SnCl(N=CPh)$_{2}$-C$_{6}$H$_{4}$CPh=NH.

(Found: C 56.5, H 3.4, N 4.8, Cl 7.2%;
C$_{39}$H$_{30}$N$_{2}$SnCl requires: C 67.4, H 4.3, N 6.1, Cl 5.1%)

$\gamma_{\text{max}}$ (Nujol mull): 3332m, 3085w, 3060m, 3028sh, 1960vw, 1830vw, 1609vs, 1599vs, 1576vs, 1557s, 1543vs, 1492m, 1447s, 1404m, 1369s, 136ls, 1325sh, 1292s, 1278s, 1261m, 1253m, 1204m, 1189w, 1154s, 1120m, 1078mw, 1049mw, 1033m, 1003w, 962sh, 955s, 919m, 913m, 900vw, 884vw, 858w, 820m, 800sh, 797s, 774s, 771s, 750m, 746m, 734sh, 728s, 709vs, 700sh, 691s, 658w, 646m, 628w, 620w, 607vw, 586vw, 558w, 543w, 488m, 477sh, 458m, 450mw, 426w, 410vw, 368mw, 331vw cm$^{-1}$
B. Attempted metallations of other related systems by tin tetrachloride

i) Reaction of N-methyldiphenylmethyleneamine with tin tetrachloride in the presence of triethylamine (Mole ratio 1:1:1)

2.34 ml. tin tetrachloride (20 mmol.) were added dropwise to a stirred solution of 2.44 cm$^3$ N-methyldiphenylmethyleneamine (20 mmol.) and 2.79 cm$^3$ triethylamine (20 mmol.) in 100 cm$^3$ dry toluene. The pale yellow-green solution darkened to yellow and a white precipitate formed. The mixture was heated to boiling and refluxed overnight. It then consisted of a yellow solution over a black liquid layer, which solidified on cooling to an intractable tar. Removal of solvent from the yellow solution yielded a yellow-brown oil, whose infra-red spectrum indicated that its major constituent was unreacted N-methyldiphenylmethyleneamine.

ii) Reaction of N-phenyldiphenylmethyleneamine with tin tetrachloride in the presence of triethylamine (Mole ratio 1:1:1)

1.17 cm$^3$ tin tetrachloride (10 mmol.) were added to a stirred solution of 2.57 g. N-phenyldiphenylmethyleneamine (10 mmol.) in 50 cm$^3$ dry toluene. A white precipitate of the adduct immediately formed. 1.48 cm$^3$ triethylamine (10 mmol.) were then added without visible effect. The mixture was heated to boiling and refluxed overnight. It then consisted of a pale green solution over a black liquid layer, which solidified on cooling to an intractable tar.

iii) Reaction of azobenzene with tin tetrachloride in the presence of triethylamine (Mole ratio 1:1:1)

2.34 cm$^3$ tin tetrachloride (20 mmol.) were added to a solution of 3.94 g. azobenzene (20 mmol.) and 2.79 cm$^3$ triethylamine (20 mmol.) in 100 cm$^3$ dry toluene. A cream precipitate slowly separated from the orange solution. The mixture was heated to boiling, and refluxed overnight.
It then consisted of an orange solution over a black liquid layer, which congealed to an intractable black tar on cooling. Concentration and cooling of the solution yielded an orange crystalline solid, identified as unreacted azobenzene from its infra-red spectrum and analytical data.

(Found: C 78.9, N 14.5%; \( \text{C}_{12}\text{H}_{7}\text{O}_{2} \) requires: C 79.2, N 15.4%).

5.3 Discussion

A. Preparation and structure of ortho-metallated derivatives of tin(IV)

The new compounds are listed in Table 36. They are all pale yellow or colourless crystalline solids. None show any indication of hydrolysis.

TABLE 36

<table>
<thead>
<tr>
<th>New ortho-metallated derivatives of tin(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: ( \text{o-SnCl}<em>{3}-\text{C}</em>{6}\text{H}<em>{4}\text{CPh=NH.C}</em>{6}\text{H}_{8} )</td>
</tr>
<tr>
<td>II: ( \text{2-SnCl}<em>{3}-\text{4-MeC}</em>{6}\text{H}_{3}\text{C(p-tolyl)=NH} )</td>
</tr>
<tr>
<td>III: ( \text{2-SnCl}<em>{3}-\text{4-ClC}</em>{6}\text{H}<em>{3}\text{C(p-ClC}</em>{6}\text{H}_{4})=\text{NH} )</td>
</tr>
<tr>
<td>Ia: ( \text{o-SnCl}<em>{3}-\text{C}</em>{6}\text{H}_{4}\text{CPh=NH.THF} )</td>
</tr>
<tr>
<td>IIa: ( \text{2-SnCl}<em>{3}-\text{4-MeC}</em>{6}\text{H}_{3}\text{C(p-tolyl)=NH.2THF} )</td>
</tr>
</tbody>
</table>
on exposure to air, although both I and III absorb atmospheric moisture which may be removed under vacuum. The di-p-tolylmethylenamine derivative II and the THF adduct of the diphenylmethylenamine derivative, Ia, appear to be completely stable to air, although the THF adduct of the di-p-tolylmethylenamine derivative, IIa, loses THF on air exposure. This may indicate a structural difference between the two THF adducts (q.v.). Both I and IIa probably contain solvent of crystallisation (respectively toluene and THF). In the former case this is demonstrated by the loss of toluene on heating, and in the latter case the infra-red spectrum shows two sets of C-O-C stretching vibrations, corresponding to free and coordinated THF.

The hydrolytic stability of these compounds is probably due to the higher coordination number of the tin atom, and is remarkably high in some cases; 2-SnCl₃-4-MeC₆H₃(p-CH₂C₆H₄)=NH (II) resists the action of boiling water, although it is slowly attacked by acids. The stability is further demonstrated by the failure of attempts to degrade this compound by iodine cleavage of the Sn-C bond.

The new compounds are insufficiently soluble in the absence of coordinating species for cryoscopic molecular weight determinations, but the monomeric 5-membered ring structure has been proven for compound II by X-ray crystallography, and the spectroscopic similarities between this compound and I and III are sufficiently great to justify the assumption of similar structures. Mössbauer data for compounds I-III confirm the structural similarity, and are consistent with a 5-coordinate environment for tin. No evidence was found for the type of equilibrium between monomeric 5-membered and dimeric 10-membered heterocycles observed for the ortho-metallated beryllium derivative described in section 5.1.
The structure of II is based on a trigonal bipyramid, with the imine nitrogen occupying an axial site, and the aromatic ring an equatorial position. This is discussed in detail in a later section.

There is little modification of the infra-red spectrum on formation of the THF adducts, and it may therefore be assumed that the 5-membered ring remains intact when the coordination number at tin is increased to six. Four isomeric configurations are now possible for the adduct (Fig. 5-1), two of which are optical isomers.

![Chemical structures](image)

**Figure 5-1**
In the enantiomeric forms (a), the $\text{SnCl}_3$ unit forms a trigonal pyramid as it does in the 5-coordinate parent compounds, so that the Sn-Cl stretching vibrations should show relatively little change between parent and THF adduct. In structures (b) and (c) however, the $\text{SnCl}_3$ group is T-shaped, and a different splitting pattern would be expected. On this basis, structures (a) seem most likely for the diphenylmethyleneamine derivative Ia, and (b) or (c) for the di-p-tolylmethylineamine derivative IIa, the infra-red spectrum of which does not show the strong $\nu_{\text{as}}(\text{SnCl}_3)$ absorption at $\sim 365 \text{ cm}^{-1}$. common to all the other new ortho-metallated compounds.

It has been suggested that a cis-configuration is preferred by electronegative ligands in octahedral tin (IV) complexes, where this is not precluded by steric factors, and on this basis structure (b) would probably be preferred for IIa.

It is interesting that the comparatively small structural difference between (a) and (b) should produce such a large change in stability between Ia and IIa. Thus Ia has a well-defined melting point, whereas IIa loses THF on heating and the residue melts at approximately the same temperature as the parent compound II.

The mechanism of formation of these ortho-metallated compounds is of interest. Both the preparative routes used (Eqn. 5.14) might be expected

$$\left((\text{RC}_6\text{H}_4)\text{CNM}_6\text{H}_4\right)_2 + \text{SnCl}_4 \rightarrow \left[\left((\text{RC}_6\text{H}_4)\text{CNM}_6\text{H}_4\right)_2\text{CNSnCl}_3\right] + \text{MCl}$$

$\text{M} = \text{Li}, \text{Me}_3\text{Si}$

$$5.14$$
to involve formation of the unrearranged diarylmethyleneaminotin(IV) trichloride, Ar$_2$CNSnCl$_3$, as an intermediate, although it might be possible that, in the preparation via the iminolithium, ortho-lithiation of the imine could occur directly at the aromatic ring, as is known to happen under mild conditions with other ligands, e.g. PhCH$_2$NHMe. However, no such rearrangement of diarylmethyleneaminolithiums has previously been observed, and the successful preparation of ortho-metallated tin(IV) derivatives from the iminotrimethylsilane indicates that the mechanism does involve rearrangement of the iminotin trichloride, although the temperature necessary to decompose the iminosilane-tin tetrachloride complex is such that the ortho-metallation occurs immediately, and no intermediate can be identified (cf. the preparation of stannylamines from silylamines$^{126}$ described in Chapter 1).

In the synthesis via imino-lithium, however, the initial stage of the reaction was carried out in diethyl ether at low temperatures, and the intermediates could be observed spectroscopically as ether complexes. The infra-red spectra of these materials, obtained as mixtures with lithium chloride, show medium absorptions in the region 1060-70 cm$^{-1}$, corresponding to the asymmetric C-O-C stretching vibration of coordinated diethyl ether. Free ether absorbs at 1129 cm$^{-1}$ (liquid film). The C=N stretching frequencies lie in the region 1550-90 cm$^{-1}$; somewhat low for terminally bonded methyleneamino groups but appropriate for methyleneamino bridges. Hence, if 6-coordinate tin is assumed, the intermediate may be formulated as (Ar$_2$CNSnCl$_3$.Et$_2$O)$_n$.

Extraction of these mixtures with hot toluene leads to the rearranged products. The duration of heating seems to have little effect on the rate of reaction, with the exception of the di-p-chlorophenylmethylenearino derivative, where reaction occurs only on prolonged heating. A
para-chlorine substituent would be expected to deactivate the aromatic ring to electrophilic attack in the ortho-position, so that this observation provides evidence for such a mechanism.

For the diphenyl- and di-p-tolylmethyleneamino derivatives the products crystallise from solution over several hours. Further crops are obtained if the mother liquor is pumped on briefly, and left to stand. All attempts to isolate intermediates by concentration of the solutions, however, resulted in uncharacterisable amorphous solids whose infra-red spectra bore some resemblance to those of the etherates mentioned earlier, except that the infra-red spectral band due to coordinated ether was either absent or considerably diminished in intensity. Analytical data gave low carbon and nitrogen and high chlorine analyses compared to the expected results for \((\text{Ar}_2\text{CnSnCl}_3)_n\), and it seems likely that a complex with tin tetrachloride of the type \(\text{Ar}_2\text{CnSnCl}_7\) is formed, presumably from the disproportionation of \(\text{Ar}_2\text{CnSnCl}_3\) in solution.

The ortho-metallated products have low solubilities in aromatic hydrocarbons, and it seems likely that they crystallise out as they are formed. However, it was observed that the THF adducts are quite soluble in these solvents, and the addition of diethyl ether appeared to increase the solubility of the ortho-metallated tin trichlorides in toluene, although diethyl ether adducts were not isolated.

It is thus likely that several equilibria exist in the reaction solution (Eqn. 5.15). Addition of THF before the product begins to form interferes with the mettallation process, since it enhances disproportionation of the mono-iminotin trichloride to tin tetrachloride, with which it forms a complex. Some mettallation occurs, however, but if a stronger base such as \(N,N,N',N'\)-tetramethylethylenediamine is added
the mettallation is blocked completely and the TMED.SnCl₄ adduct is precipitated. Such disproportionation reactions occur for the monodiarylmethyleneamino silicon and -germanium trichlorides (see Chapter 2), and it is therefore not unexpected to find it for the corresponding tin compounds, although no evidence was found for similar ortho-metallation reactions for the silicon and germanium systems. This is in keeping with the proposed mechanism of mettallation and the relative Lewis acidities of the Group IVB tetrachlorides.

Similar rearrangements appeared to occur for more highly substituted diarylmethyleneaminotin(IV) chlorides $\text{(Ar}_2\text{CN})\text{SnCl}_{4-n^\prime}, n = 2, 3$, but although there was spectroscopic evidence (mainly infra-red - the appearance of sharp $\nu(N-H)$ absorptions and modification of the remainder of the spectrum in accordance with the presence of ortho-metallated rings) for ortho-metallation, consistent analytical data could not be obtained.
In view of the ease of formation of 6-coordinate adducts from the ortho-metallated trichlorides, it might be expected that cyclised forms of the higher iminotin chlorides might have dimeric or polymeric structures (Fig. 5-2).

As has been stated, this ortho-metallation reaction may be related to the cyclopalladation of arylmethylenamines. Palladium also forms cyclic derivatives with a wide range of other aromatic ligands, but all attempts to form similar tin compounds failed. The ligands studied were N-methyl- and N-phenyldiphenylmethylenamine, and azobenzene, which were reacted with tin tetrachloride in refluxing toluene, triethylamine being added in an attempt to remove HCl (Eqn. 5.16). However, all that could be obtained were intractable tars and unreacted starting material. It is possible that the presence of a blocking substituent on the tin-bonded nitrogen atom may be important, since it prevents the formation of a 4-coordinate N-SnCl$_3$ group, which will be more electrophilic than tin in
a higher coordination number; for example the 5-coordinate amidine derivative N,N'-diphenylacetamidinotin(IV) trichloride (see Chapter 4) is stable to 200°C, showing no sign of ortho-stannylation (Eqn. 5.17). 

This is in contrast to the palladium system, where ortho-metallation of N-arylamidines is facile. There is, however, some evidence that at high temperatures the 2:1 adduct of N-methyldiphenylmethylenamine with tin tetrachloride rearranges by cyclometallation.

Such 5-membered rings involving dative bonds to tin(IV) are not unknown. The analogous saturated species shown in Figure 5-3 have been prepared by the reaction of diorganotin dibromides with an appropriately substituted aryllithium or arylcopper(I), and an X-ray crystal structure has been reported for the compound where R = Ph.

Directed stannylation may also occur in the formation of β-substituted ethyltin trihalides from αβ-unsaturated carbonyl compounds.
and halogenostannanes (produced in situ by the action of halogen acids on tin(II) dichloride or metallic tin; Eqn. 5.18).

\[
\text{HSnX}_3 + R^1R^2C\equiv CR^3 - CR^4 = O \rightarrow \text{Sn}^{IV} \text{Cl}_3
\]

However, the unique nature of the new reactions reported here lies in the directed electrophilic substitution of an aromatic ring by an \(\text{Sn}^{IV} \text{Cl}_3\) group. There appears to be no previous report of reactions of tin(IV) halides with aromatic hydrocarbons, and it may be assumed that in this case the directing group is also the activating agent. Work currently in progress suggests that this reaction may be extended to other systems, in spite of the initial failures reported here, and it is evident that this area will prove fertile.

**B. Spectroscopic and structural data**

1) **Mass spectra**

The mass spectra of the three ortho-metallated diarylmethyleneamino-tin(IV) trichlorides were recorded, but their THF adducts were not investigated by this method. The results obtained are listed in Table 37a-c, consisting of the major metal-containing fragments, together with the major identifiable organic fragments.

Each of the three compounds shows a clear parent peak, higher m/e fragments being due to recombination processes. There is no evidence of ditin-containing fragments such as might be generated by a dimeric or polymeric structure. The ortho-metallated ring appears to be relatively stable; the most prominent metal-containing fragments are due to loss of
TABLE 37

Mass spectra of the new ortho-metallated diarylmethyleneamino tin (IV) trichlorides

a) \(2-SnCl_3\cdot4-MeC_6H_3C(p-tolyl)=NH\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>489</td>
<td>0.7</td>
<td>(P-Cl + C_7H_7)</td>
<td>199</td>
<td>3.5</td>
<td>((P-Cl)^{2+})</td>
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<tr>
<td>433</td>
<td>13</td>
<td>[Structure]</td>
<td>193</td>
<td>12</td>
<td>(C_6H_4C_7H_7CN^+)</td>
</tr>
<tr>
<td>418</td>
<td>0.6</td>
<td>(P-CH_3)</td>
<td>178</td>
<td>6</td>
<td>((C_6H_4)_2CN^+)</td>
</tr>
<tr>
<td>398</td>
<td>70</td>
<td>(P-Cl)</td>
<td>165</td>
<td>14</td>
<td>?</td>
</tr>
<tr>
<td>383</td>
<td>0.5</td>
<td>(P-Cl-CH_3)</td>
<td>155</td>
<td>17</td>
<td>(SnCl^+)</td>
</tr>
<tr>
<td>363</td>
<td>5</td>
<td>(P-2Cl)</td>
<td>120</td>
<td>3.5</td>
<td>(Sn^+)</td>
</tr>
<tr>
<td>348</td>
<td>1</td>
<td>(P-2Cl-CH_3)</td>
<td>118</td>
<td>15</td>
<td>(C_7H_7CNH^+)</td>
</tr>
<tr>
<td>342</td>
<td>0.5</td>
<td>(P-C_7H_7)</td>
<td>91</td>
<td>25</td>
<td>(C_7H_7^+)</td>
</tr>
<tr>
<td>328</td>
<td>3</td>
<td>(P-3Cl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>312</td>
<td>1.5</td>
<td>(P-3Cl-CH_3-H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>307</td>
<td>2</td>
<td>(P-Cl-C_7H_7)</td>
<td></td>
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<tr>
<td>272</td>
<td>0.8</td>
<td>(P-2Cl-C_7H_7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>271</td>
<td>0.8</td>
<td>(P-2Cl-C_7H_7-H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>11</td>
<td>((C_7H_7)_2CNCl^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>236</td>
<td>3</td>
<td>(C_7H_7CNSn^+)</td>
<td></td>
<td></td>
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<tr>
<td>228</td>
<td>16</td>
<td>(C_7H_7CNCl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>0.5</td>
<td>(SnCl_3^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>100</td>
<td>((C_7H_7)_2CN^+) or (CH_3C_7H_7CNH^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

m/e values refer to the fragment containing the most abundant isotopes (i.e. \(^{35}C_l\) and \(^{120}Sn\)).
\[ \text{b) } \text{o-SnCl}_3 \cdot \text{C}_6 \text{H}_4 \text{C(Ph)=NH.C}_7 \text{H}_8 \]

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>461</td>
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<td>( \text{P-Cl + C}_7 \text{H}_7 )</td>
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<tr>
<td>405</td>
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<td></td>
</tr>
<tr>
<td>370</td>
<td>32</td>
<td>( \text{P-Cl} )</td>
</tr>
<tr>
<td>335</td>
<td>5</td>
<td>( \text{P-2Cl} )</td>
</tr>
<tr>
<td>300</td>
<td>2.5</td>
<td>( \text{P-3Cl} )</td>
</tr>
<tr>
<td>294</td>
<td>1.5</td>
<td>( \text{P-Cl-Ph + H} )</td>
</tr>
<tr>
<td>260</td>
<td>2</td>
<td>( \text{SnCl}_4^+ )</td>
</tr>
<tr>
<td>258</td>
<td>*</td>
<td>( \text{P-2Cl-Ph} )</td>
</tr>
<tr>
<td>225</td>
<td>10</td>
<td>( \text{SnCl}_3^+ )</td>
</tr>
<tr>
<td>190</td>
<td>6</td>
<td>( \text{SnCl}_2^+ )</td>
</tr>
<tr>
<td>180</td>
<td>100</td>
<td>( \text{Ph}_2 \text{CN}^+ ) or ( \text{Ph.C}_6 \text{H}_4 \text{CNH}^+ )</td>
</tr>
<tr>
<td>155</td>
<td>24</td>
<td>( \text{SnCl}^+ )</td>
</tr>
<tr>
<td>120</td>
<td>9</td>
<td>( \text{Sn}^+ )</td>
</tr>
<tr>
<td>104</td>
<td>27</td>
<td>( \text{PhCHN}^+ )</td>
</tr>
<tr>
<td>91</td>
<td>12</td>
<td>( \text{C}_7\text{H}_7^+ )</td>
</tr>
<tr>
<td>77</td>
<td>49</td>
<td>( \text{Ph}^+ )</td>
</tr>
</tbody>
</table>
c) \( \text{2-SnCl}_3 -4\text{ClC}_6\text{H}_3\text{C(p-ClC}_6\text{H}_4)=NH } \)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>484</td>
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<tr>
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<tr>
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<td>88</td>
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<tr>
<td>403</td>
<td>10</td>
<td>P-2Cl</td>
</tr>
<tr>
<td>384</td>
<td>0.4</td>
<td>?</td>
</tr>
<tr>
<td>368</td>
<td>2</td>
<td>P-3Cl</td>
</tr>
<tr>
<td>330</td>
<td>1.5</td>
<td>?</td>
</tr>
<tr>
<td>326</td>
<td>2</td>
<td>P-Cl-ClC_6\text{H}_4-H</td>
</tr>
<tr>
<td>283</td>
<td>8</td>
<td>(ClC_6\text{H}_4)_2\text{CNCl}^+</td>
</tr>
<tr>
<td>248</td>
<td>100</td>
<td>(ClC_6\text{H}_4)_2\text{CN}^+ or ClC_6\text{H}_3\cdot\text{ClC}_6\text{H}_4\text{CNH}^+</td>
</tr>
<tr>
<td>225</td>
<td>7</td>
<td>SnCl_3^+</td>
</tr>
<tr>
<td>219</td>
<td>5</td>
<td>(P-Cl)^2+</td>
</tr>
<tr>
<td>214</td>
<td>15</td>
<td>(ClC_6\text{H}_4)_2\text{CN}^+\text{-Cl} + H</td>
</tr>
<tr>
<td>177</td>
<td>30</td>
<td>C_6\text{H}_3\cdot\text{ClC}_6\text{H}_4\text{CN}^+</td>
</tr>
<tr>
<td>155</td>
<td>23</td>
<td>SnCl^+</td>
</tr>
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<td>138</td>
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<td>ClC_6\text{H}_4\text{CNH}^+</td>
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<td>120</td>
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<td>Sn^+</td>
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<td>ClC_6\text{H}_4^+</td>
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<tr>
<td>91</td>
<td>37</td>
<td>C_7\text{H}_7^+</td>
</tr>
</tbody>
</table>
chlorine or the non-metallated aryl group. The most intense peak corresponding to a metal-containing fragment is due to loss of one chlorine atom, i.e. $2\text{-SnCl}_2\text{-}4\text{-XC}_6\text{H}_3\text{C(p-XC}_6\text{H}_4\text{)}\text{=NH}^+$. The relatively high stability of this ion is probably due to extensive delocalisation of the positive charge over the aromatic $\pi$-systems.

The major breakdown pathways are by loss of halogen, non-metallated aryl group, or (for the di-p-tolyl derivative) methyl groups. Another important route is cleavage of the Sn-C bond, with loss of the organic group. Recombination processes involving metal-containing fragments (except for the abundant fragment due to loss of one chlorine atom) are rare, but reaction of organic fragments with chlorine is found.

ii) Proton nuclear magnetic resonance spectra.

The spectra were recorded on solutions in $d^6$-DMSO, THF, $d^6$-acetone, or CDCl$_3$. The THF adduct of the di-p-tolylmethyleneamine derivative IIa was sufficiently soluble in aromatic hydrocarbons for a spectrum to be obtained in $C_6D_6$. The spectra are listed in Table 38, and those of the 5-coordinate tin derivatives, I-III, in the range 1-3.5 $\tau$ (i.e. covering the aromatic protons) are illustrated in Figure 5-4a-c.

Each spectrum shows a clear N-H resonance, generally quite sharp, consistent with a strongly coordinated nitrogen lone pair with an associated low rate of imine proton exchange. In several cases $^1H-N-117,119\text{Sn}$ coupling is observed ($^{117}\text{Sn}$ and $^{119}\text{Sn}$ splitting could not be resolved). The coupling constants $J(1^H-117,119\text{Sn})$ are listed in Table 39. There is little variation between compounds, although $J$ would seem to be solvent dependent, the splitting decreasing slightly on going from $d^6$-DMSO to THF. This is probably due to complex formation.
### TABLE 38

$^1$H-NMR spectra for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides and their THF adducts

![Structural diagram](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^\text{T}_{\text{ppm}}$a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-H</td>
</tr>
<tr>
<td>I: d$^6$-acetone$^b$</td>
<td>2.00s</td>
</tr>
<tr>
<td>I: d$^6$-DMSO$^c$</td>
<td>-2.15s</td>
</tr>
<tr>
<td>II: d$^6$-DMSO</td>
<td>-2.26s</td>
</tr>
</tbody>
</table>

---

a: ppm values are given.

b: d$^6$-acetone.

c: d$^6$-DMSO.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>II</th>
<th>IIa</th>
<th>III:</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td></td>
<td></td>
<td>N-H</td>
<td>H&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>CDC&lt;sub&gt;3&lt;/sub&gt;b</td>
<td>1.58s 1.99s</td>
<td>2.19s</td>
<td>7.16s</td>
</tr>
<tr>
<td>d&lt;sup&gt;6&lt;/sup&gt;-DMSO&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-2.01s 2.00s</td>
<td>2.23s, 2.34sh,2.5m</td>
<td>7.27s</td>
</tr>
<tr>
<td>THF</td>
<td>-0.94s 1.84s</td>
<td>2.12s,2.27s,2.37sh,2.5m</td>
<td>7.33s</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;</td>
<td>2.02s 2.94s</td>
<td>3.22s</td>
<td>7.08s</td>
</tr>
<tr>
<td>d&lt;sup&gt;6&lt;/sup&gt;-DMSO</td>
<td>-1.85s 2.01s</td>
<td>2.25s</td>
<td>7.31s</td>
</tr>
</tbody>
</table>

III: ![Chemical Structure](image)

<table>
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<th>Solvent</th>
<th>III</th>
<th>ppm&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N-H</td>
</tr>
<tr>
<td>THF</td>
<td></td>
<td>-1.44s</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Relative to γ(TMS) = 10 ppm (external reference)

Relative intensities in parentheses

<sup>b</sup>: Noise to signal ratio too high for integration.

<sup>c</sup>: Run at 21°C. All other spectra run at ~45°C.

<sup>s</sup>: singlet  sh: shoulder  m: multiplet  br: broad.
TABLE 39

Coupling constants, $J(\text{H-N-}^{117,119}\text{Sn})$, for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$J(\text{H-N-}^{117,119}\text{Sn})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$d^6$-DMSO</td>
<td>38</td>
</tr>
<tr>
<td>II</td>
<td>$d^6$-DMSO</td>
<td>37</td>
</tr>
<tr>
<td>II</td>
<td>THF</td>
<td>31</td>
</tr>
<tr>
<td>III</td>
<td>THF</td>
<td>32.5</td>
</tr>
<tr>
<td>Ia</td>
<td>$d^6$-DMSO</td>
<td>36.5</td>
</tr>
<tr>
<td>IIa</td>
<td>$d^6$-DMSO</td>
<td>35.5</td>
</tr>
</tbody>
</table>
in solution (on standing, the $^6$DMSO adduct crystallises out), since $J$(Sn-H) has been shown to be dependant on the s-character of the tin orbitals and hence on the hybridisation and coordination number. The coupling constants here are all in the range 30-40 cps, which is a narrow enough range to suggest that the coordination number of the tin atom is the same in all the solutions. It is most probably six. Little can be derived from the magnitude of the coupling constants in the apparent absence of other $J$(H-N-Sn) values for comparison, but they are low compared to both $J(^1$H-C-117,119Sn) and $J(^1$H-C-N-117,119Sn) for the dialkylaminomethylstannanes, MeSn(NR$_2$)$_2$4-n.

Unexpectedly the chemically inequivalent methyl groups of the di-p-tolylmethyleneamine derivatives gave a single signal in both of the polar solvents used. However, in CDC$_3$ solution slight splitting of the methyl signal was observed (0.03 ppm), and in a non-polar solvent, C$_6$D$_6$, the two methyl groups of the THF adduct IIa were well resolved (separation 0.12 ppm).

The aromatic resonances show remarkably little variation between compounds, in spite of the changes in ring substitution (Fig. 5-4 a-c). Generally, they consist of a weak singlet to low field, and a strong, fairly broad singlet to higher field which overlies other weak, multiple absorptions. It is considered that the strong singlet corresponds to the aromatic protons of the unmetallated ring, and the low field absorption is produced by the aromatic proton adjacent to the electrophilic, i.e. deshielding, SnCl$_3$ group; the remaining signals from the metallated ring underlie the strong absorption. This is consistent with the integrations, and a similar pattern has been reported for some ortho-metallated transition metal carbonyl derivatives of azobenzene and benzyldeneaniline (N-phenylphenylmethyleneamine).
Aromatic proton resonances in the $^1$H-NMR spectra of some ortho-metallated diarylmethyleneaminotin(IV) trichlorides.

a) $\text{SnCl}_3 \text{C}_6\text{H}_4\text{C(Ph)}=\text{NH.C}_7\text{H}_8$ (I)  
b) $\text{SnCl}_3 \text{C}_6\text{H}_3\text{C(p-tolyl)}=\text{NH}$ (II)

d$^6$-DMSO soln.

i) d$^6$-DMSO soln.

ii) THF soln.

iii) THF soln.

Figure 5-4
The latter paper also reported a manganese derivative of N-methylphenylmethyleneamine (Fig. 5-5) which showed the NMR spectrum of the ortho-metallated ring in greater detail. It consisted of three complex resonances, which were assigned (in order of increasing field)

Figure 5-5

\[ H_A; H_B; H_C \text{ and } H_D. \] This is inconsistent with the assignment made here for the new tin compounds, but the report expressed some doubt as to whether \( H_B \) gave rise to the middle or low field absorption, and since the \( \text{SnCl}_3 \) group is considerably more electrophilic than the \( \text{Mn(CO)}_4 \) group, a different order might be expected anyway.

The spectrum of the related compound \( 2-\text{Me}_2\text{BrSn}(\text{CH}_6\text{CH}_2\text{NMe}_2) \) (Fig. 5-6) has also been assigned with the proton adjacent to the

Figure 5-6

metallation site \( (H_0) \) giving rise to the aromatic signal at lowest field; here, as in the manganese compound referred to above, the aromatic proton signals are much better separated than those of the ortho-metallated trichlorostannyldiaryl methyleneamines.
It is interesting that the non-metallated ring protons give only a single absorption, since for the parent diarylmethyleneamines and their unrearranged N-metallated derivatives the aromatic ring protons generally give much more complex spectra. This may be related to a reduction in steric interaction between the two aromatic rings when one of them is fixed in position by formation of the ortho-metallative chelate ring.

iii) **Infra-red spectra.**

a) **Azomethine stretching frequencies**

Assignment of $\nu(C=N)$ for these compounds is rendered necessarily tentative by the presence in the same region of the spectrum of several bands due to the aromatic ring stretching modes, $\nu(C=C)$. Each of the new compounds exhibits three major absorptions in the 1500-1650 cm$^{-1}$ region (the di-p-tolyl derivatives II and IIa exhibit further splitting, and for the diphenyl derivative I an additional peak due to toluene of crystallisation is found at 1587 cm$^{-1}$, but the three main bands can be picked out). These are listed in Table 40. There is relatively little variation between compounds, even when the coordination number of the tin atom changes.

The highest frequencies listed are at about the same positions as $\nu(C=N)$ for the parent methyleneamines, but the other bands are all at lower energies (see Chapter 2, Table 8 for comparison). This is similar to the effect found for the ortho-metallated N-phenylbenzaldimine derivatives of palladium,\textsuperscript{405} where a shift of $\nu(C=N)$ to lower energy relative to the parent imine of about 40 cm$^{-1}$ was observed. If a shift of similar magnitude occurs here, the lowest absorption listed ($\sim$ 1550 cm$^{-1}$), which
**TABLE 40**

**Major absorptions in the \( \gamma(\text{C=C}) \) and \( \gamma(\text{C=N}) \) region for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \gamma (\text{C=C, C=N}) ) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1598, 1572, 1548, (1605, 1578, 1557(^*))</td>
</tr>
<tr>
<td>II</td>
<td>1599, 1582, 1545</td>
</tr>
<tr>
<td>III</td>
<td>1600, 1569, 1545</td>
</tr>
<tr>
<td>Ia</td>
<td>1599, 1579, 1551</td>
</tr>
<tr>
<td>IIa</td>
<td>1604, 1587, 1551</td>
</tr>
</tbody>
</table>

\(^*\): Crude sample, without toluene of crystallisation, from reaction \( \text{Ph}_2\text{CNSiMe}_3/\text{SnCl}_4 \).
is also a little low for an aromatic $\nu$(C=C) vibration, may be identified as $\nu$(C=N).

This being the case, it is in direct contrast to the effect generally observed when a methyleneamine is coordinated to a strong Lewis acid such as a tin(IV) halide. In such a case, a shift of $\nu$(C=N) to higher energy is found. This effect was discussed in detail in the introduction to Chapter 2, where it was mentioned that it may be ascribed to C-N bond order changes, presumably accompanied by modification of the hybridisation at nitrogen.

In these ortho-metallated compounds, however, the formation of a planar and probably fairly rigid chelate ring will impose a constraint on the bond angle at nitrogen, with the result that the effect of drainage of electrons towards the SnCl$_3$ group may predominate and the weakened C=N bond absorbs at a lower energy.

b) Other vibrations

The most obvious sign of ortho-metallation for these compounds is the appearance in the infra-red spectrum of the $\nu$(N-H) absorption in the region 3275-3335 cm$^{-1}$. In all cases, this is strong and sharp, although for the THF adduct 2-SnCl$_3$-4-MeC$_6$H$_3$(p-tolyl)NH.2THF (IIa) an additional broad band appears at 3215 cm$^{-1}$, attributable to hydrogen-bonding effects within the crystal. This probably involves the uncoordinated molecule of THF, since the THF adduct of the diphenylmethyleneamine derivative, Ia, which contains no THF of crystallisation, shows no such effect.

Since the ortho-metallation process changes the substitution of one aromatic ring, it might be expected that the Ar-H out of plane bending
modes, which absorb in the region 900-675 cm\(^{-1}\), would show significant changes. However, there is relatively little difference in the spectra of 1,4-disubstituted and 1,2,4-trisubstituted benzenes, so that this does not provide a reliable indication of ortho-metallation for the di-p-chlorophenyl- and di-p-tolylmethylenamine derivatives. For the ortho-metallated diphenylmethylenamine derivatives, however, a strong absorption at \(\sim 730\) cm\(^{-1}\) which does not appear in the spectra of non-cyclised N-metallated derivatives may be assigned to \(\delta\) (C-H) for the metallated ring.

A prominent feature of the majority of the spectra is a medium to strong band, usually with several shoulders, in the region 350-400 cm\(^{-1}\), assignable to \(\nu\) (Sn-Cl). A pyramidal SnCl\(_3\) group, of symmetry \(C_{3v}\), would be expected to give rise to two Sn-Cl stretching vibrations, of which the symmetric vibration would have the lower energy. Here, because of the presence of the chelating ligand, the local symmetry of the SnCl\(_3\) group is lowered, and splitting of the degenerate asymmetric vibration into two vibrations might be expected, as is found in PhSnCl\(_3\) due to the rotational barrier about the Sn-C bond. The two \(\nu\) (Sn-Cl) absorptions for PhSnCl\(_3\) lie at 439 and 377 cm\(^{-1}\); the observed band for the new ortho-metallated compounds probably corresponds to the lower of these (several bands occur in the region 400-450 cm\(^{-1}\), one of which may correspond to the higher (and weaker) absorption). The only one of the new compounds for which this band is absent (or significantly modified; two much weaker absorptions appear in the same region) is the THF adduct of the di-p-tolylmethylenamine derivative Ila.

As was suggested in the general discussion, this may indicate a different arrangement of the SnCl\(_3\) group in this probably 6-coordinate species.
A cis-arrangement of the chlorine atoms (Fig. 5-7a) gives a similar

\[
\begin{array}{c}
\text{Cl-Sn-Cl} \\
\text{Cl-Sn-Cl}
\end{array}
\]

(a) (b) (c)

\[
\begin{array}{c}
\text{Cl-Sn-Cl} \\
\text{Cl-Sn-Cl}
\end{array}
\]

Figure 5-7

pyramidal SnCl\(_3\) group to that found in the 5-coordinate parent compound (Fig. 5-7c), and this type of arrangement may be inferred for the THF adduct of the diphenylmethylenamine derivative, Ia, which does show a band corresponding to \(\nu_{\text{as}}(\text{SnCl}_3)\) in its spectrum. The alternative trans-arrangement (Fig. 5-7b) therefore seems likely for the THF adduct of the di-p-tolylmethylenamine derivative, IIa. A far infra-red spectral study on these compounds should further elucidate this.

The THF adducts both show bands corresponding to the C-O-C stretching vibrations of their THF molecules. These are listed in Table 4.1, together with the frequencies for free THF. The absorptions shift to lower energy on adduct formation, as might be expected since some weakening

\[
\begin{array}{c|c|c}
\text{Compound} & \nu_{\text{as}} \text{cm}^{-1} & \nu_{\text{s}} \text{cm}^{-1} \\
\hline
\text{Ia: o-SnCl}_3\text{C}_6\text{H}_4\text{CPh}=\text{NH}.\text{THF} & 1017 & 847 \\
\text{IIa: 2-SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tol)=NH}.\text{THF} & 1054, 1023 & 862, 838 \\
\text{THF (liq. film)} & 1076 & 917
\end{array}
\]
of the C-O bonds should accompany formation of the dative bond. The existence of two chemically distinct THF molecules in the di-p-tolyl methyleneamine derivative IIa is clearly shown by the presence of two sets of $\nu$(COC) absorptions; one THF molecule appears to be more strongly bonded than the other, and its $\nu$(COC) frequencies are quite close to those of the diphenyl analogue, Ia. This is presumably the THF molecule directly coordinated to the tin atom. The other has higher energy vibrations, but the C-O bonds are still weaker than those in free THF; this may be due to hydrogen bonding to the N-H group, which is indicated by the $\nu$(N-H) absorption.

iv) Crystallographic data

The crystal and molecular structure of the di-p-tolylmethyleneamine derivative $2$-$\text{SnCl}_3$-$4$-$\text{MeC}_6\text{H}_3$-$\text{C(p-tolyl)}$-$\text{NH}$, II, has been determined in an X-ray diffraction study by G. Whitehead and H.M.M. Shearer. The molecule is illustrated in Figure 5-8, and relevant structural parameters are listed in Table 42.

The 5-membered metallocycle is planar, and coplanar with the aromatic ring with which it shares an edge. The non-metallated p-tolyl group is twisted with respect to the plane defined by the other two rings. A similar ring system, containing a manganese atom, has been described in the crystal structure of $o$-$\text{Mn(CO)}_4$-$\text{C}_6\text{H}_4$-$\text{CH=NPh}$, but in this compound the metallocycle makes an angle of 3\degree with the metallated phenyl ring. The C=N bond distance (1.285 (10) $\AA$), however, is similar to that found here (1.280 (7) $\AA$), and both may be compared to that of the coordinated diphenylmethyleneamine molecule in the tin(II) compound $\text{Ph}_2\text{CNH.}(\text{Ph}_2\text{CNSn}^{\text{II}}\text{Cl})_2.\text{C}_7\text{H}_8$ (1.274 (12) $\AA$; ref. 378 and Chapter 3).
<table>
<thead>
<tr>
<th>Bond lengths, Å</th>
<th>Bond angles, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-C(2) 1.474(8)</td>
<td>SnNC(1) 114.2(4)</td>
</tr>
<tr>
<td></td>
<td>NC(1)C(9) 117.0(5)</td>
</tr>
<tr>
<td>C(1)-N 1.280(7)</td>
<td>C(1)C(9)C(14) 117.2(5)</td>
</tr>
<tr>
<td>C(1)-C(9) 1.487(8)</td>
<td>C(9)C(14)Sn 114.6(4)</td>
</tr>
<tr>
<td>C(9)-C(14) 1.391(7)</td>
<td>C(14)SnN 76.5(2)</td>
</tr>
<tr>
<td>Sn-C(14) 2.116(5)</td>
<td>SnC(12) 88.1(1)</td>
</tr>
<tr>
<td>Sn-N 2.260(5)</td>
<td>NSnCl(2) 90.4(1)</td>
</tr>
<tr>
<td>Sn-Cl(1) 2.416(2)</td>
<td>SnC(12) 96.7(1)</td>
</tr>
<tr>
<td>Sn-Cl(2) 2.315(2)</td>
<td>C(14)SnCl(2) 123.2(2)</td>
</tr>
<tr>
<td>Sn-Cl(3) 2.318(2)</td>
<td>C(14)SnCl(3) 126.6(2)</td>
</tr>
</tbody>
</table>

Estimated standard deviations in parentheses.

Cl(1)SnCl(2) 94.1(1)
Cl(1)SnCl(3) 94.7(1)
Cl(1)SnN 173.1(1)
Molecular structure of $2\text{-SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tolyl)=NH}$.
The chelate ring dimensions for the new ortho-metallated tin(IV) compound are compared with those of the manganese compound referred to above in Figure 5-9. The smaller size of the ring in the manganese derivative is clearly seen; this is mainly due to the smaller size of the manganese atom, but the markedly shorter Ar-C distance may imply some π-delocalisation in the manganese derivative. For the tin compound, this distance (C(1)-C(9)) is essentially the same as that to the unmetallated aryl group (C(1)-C(2): 1.474(8) Å). There also appears to be less distortion of the adjoining aromatic ring in the tin compound, although this is on the limits of the experimental accuracies. The CMN angles are fairly close; 79.4(3)° for the manganese compound and 76.5(2)° for that of tin. They may also be compared with 75.3(4)° for the corresponding angle in the ring-closed N,N-dimethylbenzylamine derivative o-Ph$_2$Sn$_2$BrC$_6$H$_4$CH$_2$NMe$_2$ (Fig. 5-3).

In the new tin complex, the tin atom forms the centre of a slightly distorted trigonal bipyramid; the metallated aryl group occupies one equatorial position and the nitrogen occupies an axial site. This arrangement appears to be dictated by two factors: it is commonly observed that the less electronegative ligands tend to occupy equatorial positions in a trigonal bipyramidal arrangement, so that the metallated
aromatic ring occupies this position; the electronegativities of nitrogen and chlorine are quite close, so the nitrogen atom adopts the position best able to accommodate the small Sn–NC angle required by the chelate ring, i.e. the axial position. This angle is however only 76.5°, compared to 90° in a perfect trigonal bipyramid; the observed distortion of the molecule is probably mainly due to this. The Cl(1)–Sn–N axis is not linear, the angle at tin being 173.1(1)°, and the tin atom does not lie in the plane defined by the equatorial ligands; it is on the opposite side of this plane to the nitrogen atom. A similar distortion of the trigonal bipyramid is found in the structure of o-Ph₂SnBr.C₆H₄CH₂NMe₂; the angle between axial bonds in this structure is 171.0(1)°.447

The Sn⁴–N distance, 2.260(5)Å, is considerably shorter than the dative Sn²–N distance in the diphenylmethylenamine complex Ph₂CNH.(Ph₂CNSnCl)₂·C₇H₈ (2.474(8)Å).378 This will be due to the smaller size of the tin atom in its higher oxidation state, but the bond is also short for a Sn⁴–N dative bond; for example the bonds in the bipyridyl complex bipy.P₃SnCl₂ (2.344(6) and 2.375(6)Å)73 and the nitrile complex cis-(MeCN)₂SnCl₄ (average 2.311 (24) Å).74 It is also considerably shorter than the Sn⁴–N bond in the corresponding saturated metalloercycle in the compound o-Ph₂SnBr.C₆H₄CH₂NMe₂ (2.511(12) Å).447 It is, however, longer than the non-dative Sn²–N bonds in the 4-coordinate compounds (Me₂N)₂Sn⁴ (2.045 Å)266 and (Ph₂CN)₄Sn⁴ (2.068 (27)Å).301,302

The Sn–C(14) distance, 2.116(5) Å, is similar to other Ar–Sn distances in the literature, e.g. 2.09(3) Å (Ph₃SnNCS)100 and 2.11(5) Å (Ph₂SnCl₂),423 but it is still shorter than the corresponding bond in o-Ph₂SnBr.C₆H₄CH₂NMe₂ (2.150 (12)Å).447
The two equatorial Sn-Cl distances (to Cl(2) and Cl(3)) are equal to within the accuracy of the experiment, and their average, 2.317 (1)Å, compares quite well with other equatorial Sn—Cl distances in trigonal bipyramidal complexes, e.g. 2.321(1) Å for the anion Me₂SnCl₃⁻⁶¹ and 2.316 (6) Å (average) for AmSnIVCl₃ (ref. 401 and previous chapter). It is also close to 2.318 (15) Å found in the 4-coordinate species Ph₃SnCl.⁴²²

The axial distance Sn-Cl(1), 2.416(2) Å, is longer than the equatorial Sn-Cl distances, an effect commonly observed where a particular ligand occupies both axial and equatorial sites in a trigonal bipyramidal structure. It may be compared to other axial Sn—Cl distances; 2.54 (2) Å for Me₂SnCl₃⁻⁶¹ 2.42 (4) Å for py.Me₃SnCl⁶³ᵃ,ᵇ and 2.335(10) Å for AmSnCl₃.⁴⁰¹ The considerable variation suggests that the axial Sn-Cl bond lengths are particularly sensitive to the substitution and degree of distortion of the structure.

C. Summary.

The attempted preparation of mono-diarylmethyleneaminotin(IV) trichlorides reveals that these compounds, isolable only as probably associated ether adducts, show a strong tendency to rearrange via ortho-metallation, giving rise to 5-membered heterocycles containing pentacoordinate tin(IV), apparently by a process involving electrophilic attack on the aromatic ring by the SnCl₃ group. The structures of the resulting compounds are based on a trigonal bipyramid, with the ortho-metallative chelate ring bridging between axial (nitrogen) and equatorial (aromatic ring) positions. The tin atom readily expands its coordination number to six by adduct formation with THF.
APPENDICES
Appendix 1

Mössbauer Data

The Mössbauer spectra of several of the new tin compounds described in this thesis have been recorded by Dr B. Fitzsimmons of Birkbeck College, London. Some reference has already been made to the initial results of this study; the results obtained to date are listed in Table 43.

The very much greater isomer shifts (δ) of the compounds \( \text{Ph}_2\text{CNH.SnCl}_2 \) and \( \text{Li}^{(\text{Bu}_2\text{CN})}_3\text{Sn} \) clearly label them as tin(II) derivatives; the quadrupole splitting (\( \Delta E \)) for the latter is significantly greater than for most other tin(II) compounds, a feature paralleled by the recently-prepared tin(II) amines.\(^{104,105}\)

The two tetrakis(methyleneamino)tins, \( (\text{Bu}_2\text{CN})_4\text{Sn}^{\text{IV}} \) and \( (\text{Ph}_2\text{CN})_4\text{Sn}^{\text{IV}} \), both exhibit zero quadrupole splitting, consistent with a tetrahedral arrangement of ligands, which, having cubic symmetry, gives rise to a zero electric field gradient at the tin nucleus with consequent absence of quadrupole splitting. Admittedly there exists a large group of tin compounds which lack cubic symmetry but for which quadrupole splitting cannot be resolved, but in this case the tetrahedral geometry has been proven for \( (\text{Ph}_2\text{CN})_4\text{Sn}^{\text{IV}} \) by crystal structure\(^{302}\) (see also Chapter 2).

It might be expected that the diphenylmethyleneaminotin(IV) chlorides, if they were monomeric, would show only a small quadrupole splitting, if any, since the tetrahedral arrangement of ligands of quite close electronegativities should generate only a small electric field gradient at the tin nucleus; the observed quadrupole splittings may therefore indicate association, with coordination numbers of five or six at tin. The significantly different values of \( \Delta E \) may in fact be due to different coordination numbers in these two compounds.
TABLE 43.
Mössbauer spectral parameters \(^a\) for some new organonitrogen derivatives of tin(II) and tin(IV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta E \text{ mm.s.}^{-1})</th>
<th>(\delta \text{ mm.s.}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}(^t\text{Bu}_2\text{CN})_3\text{Sn}^{\text{II}})</td>
<td>2.27</td>
<td>3.44(^b)</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{CNH.Sn}^{\text{II}}\text{Cl}_2)</td>
<td>1.51</td>
<td>3.52(^b)</td>
</tr>
<tr>
<td>((^t\text{Bu}_2\text{CN})_4\text{Sn}^{\text{IV}})</td>
<td>0</td>
<td>1.16(^b)</td>
</tr>
<tr>
<td>((\text{Ph}_2\text{CN})_4\text{Sn}^{\text{IV}})</td>
<td>0</td>
<td>0.805(^b)</td>
</tr>
<tr>
<td>(\left[(\text{Ph}_2\text{CN})_2\text{Sn}^{\text{IV}}\text{Cl}_2\right]_n)</td>
<td>0.88</td>
<td>0.98(^b)</td>
</tr>
<tr>
<td>(\left[(\text{Ph}_2\text{CN})_3\text{Sn}^{\text{IV}}\text{Cl}\right]_n)</td>
<td>1.47</td>
<td>1.08(^b)</td>
</tr>
<tr>
<td>(3\text{Sn}^{\text{IV}}\text{Cl}_3-4\text{MeC}_6\text{H}_3(p-\text{tol})=\text{NH})</td>
<td>1.58</td>
<td>1.66(^b)</td>
</tr>
<tr>
<td>(\text{Sn}^{\text{IV}}\text{Cl}_3\text{C}_6\text{H}_4\text{CPh}=\text{NH})</td>
<td>1.588</td>
<td>0.874(^c)</td>
</tr>
<tr>
<td>(3\text{Sn}^{\text{IV}}\text{Cl}_3-4\text{CIC}_6\text{H}_3(p-\text{ClC}_6\text{H}_4)=\text{NH})</td>
<td>1.730</td>
<td>0.716(^c)</td>
</tr>
<tr>
<td>(3\text{Sn}^{\text{IV}}\text{Cl}_3-4\text{CIC}_6\text{H}_3(p-\text{ClC}_6\text{H}_4)=\text{NH})</td>
<td>1.440</td>
<td>0.764(^c)</td>
</tr>
</tbody>
</table>

\(^a\): \(\Delta E\) is the quadrupole splitting, \(\delta\) is the chemical isomer shift.

\(^b\): Relative to a \(\text{BaSnO}_3\) absorber.

\(^c\): Relative to a \(\text{CaSnO}_3\) absorber.

Spectra were measured at 78°K.
The similarity of the quadrupole splittings of the three ortho-metallated compounds indicates that the 5-coordinate structure, established for the di-p-tolylmethyleneamine derivative by a crystal structure determination (see also Chapter 5), is common to all of them. It can be shown that the observed values are consistent with the proposed structures by the method of partial quadrupole splittings.
Appendix 2.
Experimental Details

1. General.

The majority of the new compounds described in this thesis, and many of the starting materials, were sensitive to atmospheric exposure, either through hydrolysis or oxidation. All operations were therefore carried out under vacuum or an atmosphere of pure dry nitrogen. Liquids and solutions were transferred as required by syringe against a counter-current of nitrogen. Filtrations made use of standard filter-stick techniques, flask connections being exchanged rapidly also against a counter-current of nitrogen to minimise contamination by air. Air-sensitive solids were handled in a glove box.

2. Nitrogen supply.

Nitrogen gas was supplied as the boil-off from a tank containing liquid nitrogen. Traces of oxygen were removed by passage through a furnace containing copper wire at 400°C, and water was removed by a trap cooled by liquid air and a sulphuric acid bubbler (the latter was later replaced by a $\text{P}_2\text{O}_5$ tower). The purified gas was then delivered to a multiple outlet system.

3. Glove Box.

The purity of the nitrogen atmosphere was maintained by continuous recycling through a series of traps: a furnace containing copper wire at 400°C to remove oxygen, a trap cooled with liquid air to remove water and other volatiles, a $\text{P}_2\text{O}_5$ tower to remove residual water, and a KOH tower to remove acid gases. All external tubing was of PVC, and all joints
in the glove box structure were sealed with silicone putty. The
gloves used were of 'Butasol' rubber.

4. **Solvents.**

Hydrocarbon solvents and diethyl ether were dried and stored over extruded sodium wire. THF was dried over KOH, followed by potassium metal, and was freshly-distilled before use. Chloroform for basicity studies was washed several times with distilled water before drying over anhydrous calcium chloride and distillation onto activated molecular sieve. It was then stored under an atmosphere of dry nitrogen. Deuterated solvents for NMR work were commercial samples, stored under dry nitrogen.

5. **Starting Materials.**

Tin tetrachloride and silicon tetrachloride were purified by vacuum distillation. Germanium tetrachloride and anhydrous tin dichloride were fresh commercial samples.

Amines were purified by drying over calcium hydride, followed by vacuum distillation.

Solutions of alkylolithiums were standardised against a 0.1M solution of sec-butanol in xylene using 1,10-phenanthroline as indicator.

Solutions of diarylmethyleneaminolithiums were prepared by adding a solution of n-butyllithium in hexane to a solution of the appropriate methyleneamine in ether, mole ratio 1:1, at -196°C. The mixture was then allowed to warm to room temperature and was stirred for ~15 minutes before use to complete the lithiation.
Solutions of di-t-butyllithium were prepared by mixing hydrocarbon or ether solutions of t-butyllithium and t-butyl cyanide, mole ratio 1:1, at -196°C and allowing the mixtures to warm to room temperature. The resulting solutions were stirred for ~20 minutes before use.

The methyleneamines used were prepared as described in the literature. N,N'-diphenylacetamidine was a commercial product used without further purification.

6. Instrumentation.
   a) Infra-red spectra
   I.R. spectra in the range 4000-250 cm⁻¹ were recorded on a Perkin-Elmer 457 or 577 grating spectrometer. Samples were in the form of Nujol mulls or neat liquids, sandwiched between KBr plates.
   b) ¹H-nuclear magnetic resonance spectra
   These were recorded on a Varian A56/60D spectrometer operating at 60 Mc. Samples were either neat liquids or concentrated solutions in an appropriate solvent. Tetramethylsilane was used as an external reference standard.
   c) Mass spectra.
   Mass spectra were recorded on an A.E.I. MS9 mass spectrometer at 70 eV and an accelerating potential of 8 kV, with a source temperature of 150-250°C and electromagnetic scanning. Samples were introduced by direct insertion into the ion source.
   d) Molecular weights
   These were determined cryoscopically in benzene, where solubility permitted, using a conventional Beckmann apparatus. Calibration for
the freezing-point constant of benzene was obtained using freshly-
sublimed biphenyl.

7. Analytical methods.

Carbon, hydrogen, and nitrogen were determined using a Perkin-
Elmer 240 Elemental Analyser. Nitrogen was also determined by the
Kjeldhal method.

Chlorine was determined by oxygen flask combustion followed by
potentiometric titration of the chloride ions.

Lithium was determined by decomposition in HClO₄, followed by
Atomic Absorption Spectroscopy on an aqueous solution of the residue.

Samples of air-sensitive compounds for analysis were handled in
small gelatine capsules (for chlorine analysis) or glass phials (for
nitrogen or lithium), filled in a glove box. For C, H and N analysis
samples were sealed into pre-weighed aluminium capsules.
REFERENCES

'A man will turn over half a library to make one book.'

Dr Samuel Johnson, Lexicographer, wit, and amateur chemist.
1. J.G.A. Luijten, F. Rijkens and G.J.M. van der Kerk
17. J.D. Donaldson Progr. Inorg. Chem. 1967 8 287
21. F.P. van Remoortere, J.J. Flynn, F.P. Boer and P.P. North
    Inorg. Chem. 1971 10 1511
b. E.O. Fischer and S. Schreiner Chem. Ber. 1959 92 938
32. E. Amberger and M.R. Kula Angew. Chem. 1963 75 476
34. R. Gsel and M. Zeldin ibid, 1975 37 1133
38. J. Potenza and D. Mastropaolo Acta Crystallogr. (B) 1973 29 1830
41. K.D. Bos 'Organic and Organometallic Chemistry of Divalent Tin'
   Doctoral Thesis, University of Utrecht, 1976

   12 930

43. R. Hoppe and W. Hahn Naturwissenschaften 1962 49 254

   and references therein


   J. Organometal. Chem. 1973 59 1

47. A.G. Davies, H.J. Milledge, D.C. Puxley, and P.J. Smith


   Rec. Trav. chim. 1963 82 90


54. W.P. Neumann, R. Schick and R. Köster Angew. Chem. 1964 76 380


56. V.I. Gol'danskii, E.F. Makarov, R.A. Stukan, V.A. Trukhtanov and
   V.V. Khrapov Dokl. Akad. Nauk. SSSR 1963 151 351


60. R.F. Bryan J. Amer. Chem. Soc. 1964 86 733


63a. I.R. Beattie, G.P. McQuillan and R. Hulme Chem. and Ind. 1962 1429


64. A. Tzschach and K. Pönicke Z. anorg. allg. Chem. 1975 413 136


68. G. Engel Naturwissenschaften 1933 21 704


70. R.S. Tobias Trans. N.Y. Acad. Sci. 1969 31 913


77a. H. Lüth and E.L. Amma ibid 1969 91 7515
   b. P.F. Rodesiler, Th. Auel, and E.L. Amma ibid 1975 97 7405
78. G.S. Brownlee, A. Walker, S.C. Nyburg and J.T. Szymanski
    Chem. Commun. 1971 1073
82. E.A.V. Ebsworth Chem. Commun. 1966 530
85. P. Kulmiz J. Prakt. Chem. 1860 80 60
88. R.A. Bullard and W.B. Robinson J. Amer. Chem. Soc. 1927 49 1368
89. R. Schwarz and A. Jeanmaire Ber. 1932 65 1443
     b. E. Bannister and G.W.A. Fowles ibid 1958 4374
91. G. Mack and E. Parker U.S 2,618,625 Nov. 18 1952 (Chem. Abs. 47 1977g)
92. G. Mack and E. Parker U.S. 2,634,281 Apr. 7 1953 (Chem. Abs. 48 1420f)
94. J.G.A. Luijten and G.J.M. van der Kerk 'Investigations in the field
275.


98. E. Wiberg and R. Rieger Ger. 1,121,050 (Cl.120) Appl. Dec. 9 1960 (Chem. Abs. 56 14328b)


106. Y.M. Chow ibid 1971 10 1938


110. W.J. Kroenke and M.E. Kenney ibid 1964 3 251


114. T.L. Gilchrist and C.W. Rees 'Carbenes, Nitrenes and Arynes'
Nelson, London 1969

115. J.D. Cotton, C.S. Cundy, D.H. Harris, A. Hudson, M.F. Lappert and


1969 366 180

123. O. Schmitz-Dumont and H.-J. Götze ibid 1969 371 38

124. O. Schmitz-Dumont and H.-J. Götze ibid 1968 357 139

1839

126. E.W. Abel, D. Brady and B.R. Lerwill Chem. and Ind. 1962 1333

127. W.L. Lehn J. Amer. Chem. Soc. 1964 86 305


1964 19b 447


134. F.E. Brinckman and H.S. Haiss Chem. and Ind. 1963 1124
137. U. Wannagat, E. Bogusch and R. Braun ibid 1969 19 367
143. A.G. Davies, T.N. Mitchell and W.R. Symes J. Chem. Soc. (C) 1966 311
144. W. Stamm J. Org. Chem. 1965 30 693
146. R.C. Mehrotra and V.D. Gupta Indian J. Chem. 1967 5 643
149. D.P. Gaur, G. Srivastava and R.C. Mehrotra ibid 1974 65 195
150. S. Sakai, Y. Fujimura and Y. Ishii ibid 1973 50 113
159. E. Wenschuh, W.D. Riedmann, L. Korecz and K. Burger Z. anorg. allg. Chem. 1975 413 143
164. W.P. Neumann and E. Heymann Annalen 1965 683 24
165. W.P. Neumann and E. Heymann Angew. Chem. Inter. Edit. 1963 2 100
166. W.P. Neumann, H. Niermann and R. Sommer Angew. Chem. 1961 73 768
169. W.P. Neumann and E. Heymann Annalen 1965 683 11
170. A.J. Bloodworth and A.G. Davies Chem. and Ind. 1965 900
171. A.J. Bloodworth and A.G. Davies ibid 1965 1868
175. A.G. Davies and J.D. Kennedy J. Chem. Soc. (C) 1968 2630
177. T.A. George, K. Jones and M.F. Lappert J. Chem. Soc. 1965 2157
188. J. Konnert, D. Britten and Y.M. Chow ibid 1972 B28 180
192. K. Jones and M.F. Lappert ibid 1965 3 295
195. J. Lorberth and M.-R. Kula ibid 1964 97 3444
196. J. Lorberth ibid 1965 98 1201
197. J. Lorberth, H. Krapf and H. Nüth ibid 1967 100 3511
203. D.J. Peterson U.S. 3,794,670 (Chem. Abs. 80 108670j)
204. J. Lorberth, Dissertation, Munich 1965
205. W.P. Neumann and B. Schneider Angew Chem. Inter. Edit. 1964 3 751
206. W.P. Neumann, B. Schneider and R. Sommer Annalen 1966 692 1
207. W.P. Neumann, J. Pedain and R. Sommer ibid 1966 694 9
208. R. Sommer, W.P. Neumann and B. Schneider Tetrahedron Lett. 1964 3978
210. R. Sommer, B. Schneider and W.P. Neumann Annalen 1966 692 12
212. H.M.J.C. Creemers, J.G. Noltes and G.J.M. van der Kerk ibid 1964 83 1284
213. H.M.J.C. Creemers and J.G. Noltes ibid 1965 84 590
214. W.P. Neumann Angew. Chem. 1964 76 849


221. T.A. George and M.F. Lappert Chem. Commun. 1966 463

222. T.A. George and M.F. Lappert J. Chem. Soc. (A) 1969 992


226. H.W. Roesky and H. Wiezer ibid 1974 107 3186


229. G. Chandra, T.A. George and M.F. Lappert J. Chem. Soc. (C) 1969 2565


239. T.A. George and M.F. Lappert  J. Organometal. Chem. 1968 14 327
241. K. Itoh, Y. Fukumoto and Y. Ishii  ibid 1968 3199
245. J.-C. Pommier and A. Roubineau  ibid 1969 17 P25
246. J.-C. Pommier and A. Roubineau  ibid 1973 50 101
247. J.M. Brocas and J.-C. Pommier  ibid 1975 92 67
256. S. Kozima, T. Hitomi, T. Akiyama and T. Isida  ibid 1975 92 303
261. K. Hedberg J. Amer. Chem. Soc. 1955 77 6491
269. H.-J. Götze ibid 1973 47 C25
278. S. Bell and A.D. Walsh Trans. Farad. Soc. 1966 62 3005
279. C.G. Pitt and M.S. Forder J. Amer. Chem. Soc. 1967 89 6792
284. E.W. Abel, D.A. Armitage and D.B. Brady  ibid 1966 62 3459
286. Ref. 2, Quoting J.C. Baldwin, M.F. Lappert and K. Jones, unpublished work.
293. J. Keable, D.G. Othen and K. Wade  ibid 1976 1
301. N.W. Alcock, M. Pierce-Butler, G.R. Willey and K. Wade
   J.C.S. Chem. Commun. 1975 183

   1975 2469


   1976 15 236


312. W.T. Reichle ibid 1964 3 402

   1968 4677


315. J.A. Feiccabrino and E.J. Kupchick ibid 1973 56 167

316. Yu. I. Dergunov, A S. Gordetsov, I.A. Vostokov and V.F. Gerega
   J. Gen. Chem. USSR 1974 44 2127

317. E.Z. Zhuravlev, V.D. Selimanov, V.F. Gerega and Yu. I. Dergunov ibid
   1973 43 1089

318. E.Z. Zhuravlev, V.F. Gerega, V.D. Selimanov, P.V. Mulyanov and
   Yu. I. Dergunov ibid 1975 45 1030


   1966 5 514
321. R. Sommer and W.P. Neumann *ibid* 1966 5 515
326. A.M. Domingos and G.M. Sheldrick *ibid* 1974 69 207
341. F. Kerek, G. Ostrogovich and Z. Simon J. Chem. Soc. (B) 1971
347. R.A. Walton, Quart Rev. 1965 19 141
349. B. Swanson, D.F. Shriver and J.A. Ibers Inorg. Chem. 1969 8 2182
351. H.M.M. Shearer, unpublished results.
354. I. Pattison and K. Wade ibid 1968 57


368. F.A. Miller and G.L. Carlson  ibid 1961 17 977

369. G.L. Carlson  ibid 1962 18 1529


376a. S. Wallwork and co-workers, unpublished results


378. Ref. 350


381. B. Fitzsimmons, personal communication.

382. K. Manning, E.A. Petch, H.M.M. Shearer, K. Wade and G. Whitehead
       J.C.S. Chem. Commun. 1976 107

383. C. Summerford and K. Wade

384. H.J. Coerver and C. Curran
       J. Amer. Chem. Soc. 1958 80 3522

385. H.C. Brown and M. Kubota
       ibid 1961 83 4175

386. D. Cook
       Canad. J. Chem. 1962 40 480

       Inorg. Chem. 1972 11 204

388. Chemical Society Specialist Periodical Reports: 'Spectroscopic
       Properties of Inorganic and Organometallic Compounds'
       Vols. 1-7


390. I. Pattison and K. Wade
       J. Chem. Soc. (A) 1967 1098

391. K. Wade and B.K. Wyatt
       ibid 1967 1339

392. J.R. Jennings, I. Pattison, K. Wade and B.K. Wyatt
       ibid 1967 1608

393. H. Bürgler, W. Sowodny and U. Wannagat
       J. Organometal. Chem. 1965 3 113

394. D.H. Olsen and R.E. Rundle
       Inorg. Chem. 1963 2 1310

395. B. Kamenar and D. Gredenic

396. J.K. Stalick, D.W. Meek, B.Y.K. Ho, and J.J. Zuckerman
       J.C.S. Chem. Commun. 1972 630

397. R.E. Rundle and D.H. Olsen
       Inorg. Chem. 1964 3 596

398. N.G. Bokii, G.N. Zakharova and Yu. T. Struchkov

401. Ref. 350
402. K.G. Shields, R.C. Secombe and C.H.L. Kennard
403. N.D. Cameron and M. Kilner J.C.S. Chem. Commun. 1975 687
405. H. Onoue and I. Moritani ibid 1972 43 431
408. M. Kilner and co-workers, unpublished results
409. T. Inglis, M. Kilner, T. Reynoldson and E.E. Robertson
412. J.D. Wilkins J. Organometal. Chem. 1974 80 349
413. W. Bradley and E. Leete J. Chem. Soc. 1951 2147
414. W. Bradley and I. Wright ibid 1956 640
       1975 14 2023
416. F.A. Cotton and L.W. Shire ibid 1975 14 2027
418. Ref. 388
       1579
420. M.G.B. Drew and J.D. Wilkins ibid 1974 1973
422. Ref. 398.
439. K. Wade and D.G. Othen, work in progress.
442. E.V. van den Berghe and G.P. van der Kelen J. Organometal. Chem. 1968 11 479
448. S.C. Watson and J.F. Eastham ibid 1967 9 165