Studies in the organonitrogen chemistry of tin and neighbouring elements

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STUDIES IN THE ORGANONITROGEN CHEMISTRY OF TIN AND NEIGHBOURING ELEMENTS

by

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

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To my parents.

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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.
J.Chem.Soc. Dalton Trans. 1976 1.

'New route to aryltin(IV) halides by spontaneous cyclometallation of benzylideneaminotin(IV) halides; structure of the ortho-metallated ketimine o-$SnCl_3$-p-$MeC_6H_3C(=NH)$p-C_6H_4Me.'
By B. Fitzsimmons, D.G. Othen, H.M.M. Shearer, K. Wade and G. Whitehead.
J.C.S. Chem. Commun., in the press.

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'

By D.G. Othen and K. Wade. 1st European Conference on Organometallic Chemistry, Warsaw, September 1976, Abstract II.3.1.

'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 $^tBu_2CNH.^tBu_2CNSn^{II}_2Cl_3$ 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 $^tBu_2CNH.^tBu_2CNSn_2^{II}Cl_3$ and $^tBu_2CNH_2^+.(^tBu_2CN)_2Sn_3^{II}Cl_5^-$.

The new M^{IV} derivatives are monomeric, except for the iminotin chlorides $[(Ph_2CN)_nSn^{IV}Cl_{4-n}]_m$ (n = 2,3; m $\geqslant$ 2). The Sn^{II} derivatives are mostly di- or oligomeric, containing three-coordinate tin. Association appears to involve bridging methyleneamino groups. The adducts $R_2CNH.(R_2CN)_nSn_2^{II}Cl_{4-n}$ 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 $N\rightarrow M$ $(p\rightarrow d)$ π-bonding.

The N,N'-diphenylacetamidino ('Am') derivatives $(Am_2SiCl_2)_2$, $(Am_2GeCl_2)_n$, $AmSn^{IV}Cl_3$ and $(AmSn^{II}Cl)_2$ are described. Attempts to prepare $AmMCl_3$ (M = Si, Ge) afforded Am_2MCl_2, apparently by disproportionation. $AmSn^{IV}Cl_3$ is monomeric, containing 5-coordinate tin. The associated amidino species are believed to contain bridging amidino groups.

Evidence was found for formation of Ph_2CNMCl_3 (M = Si, Ge), but attempts to prepare $Ar_2CNSn^{IV}Cl_3$ led to ortho-metallated products 2-$Sn^{IV}Cl_3$-4-$XC_6H_3C(p\text{-}XC_6H_4)$=NH, apparently by electrophilic attack on the aromatic ring by the $SnCl_3$ group. The products (containing five-coordinate tin) readily form adducts with Lewis bases. Initial attempts to form similar ortho-metallated species from Ph_2C=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 $\gt C{=}N-$ group should be named as derivatives of the (unknown) parent compound methyleneamine, $CH_2{=}NH$. Thus compounds of the type $RCH{=}N{-}M$ would be alkyl- or arylmethyleneamino (also known as 'aldimino') derivatives of M, and $R_2C{=}N{-}M$, 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 N,N'-diphenylacetamidino group, $Ph{-}N{=}CCH_3{-}NPh-$.

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[1] and 1966[2], and were mentioned in wider surveys in 1969[3] and 1972[4]. The structural chemistry of tin compounds has been reviewed, from various viewpoints, in 1965[8], 1966[9], 1967[10], 1969[11] and 1973[12]. Discussion of these matters in a broader context may also be found in a number of books concerning the chemistry of tin.[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 [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.[17]

Stereochemical configurations of di- and tetravalent tin

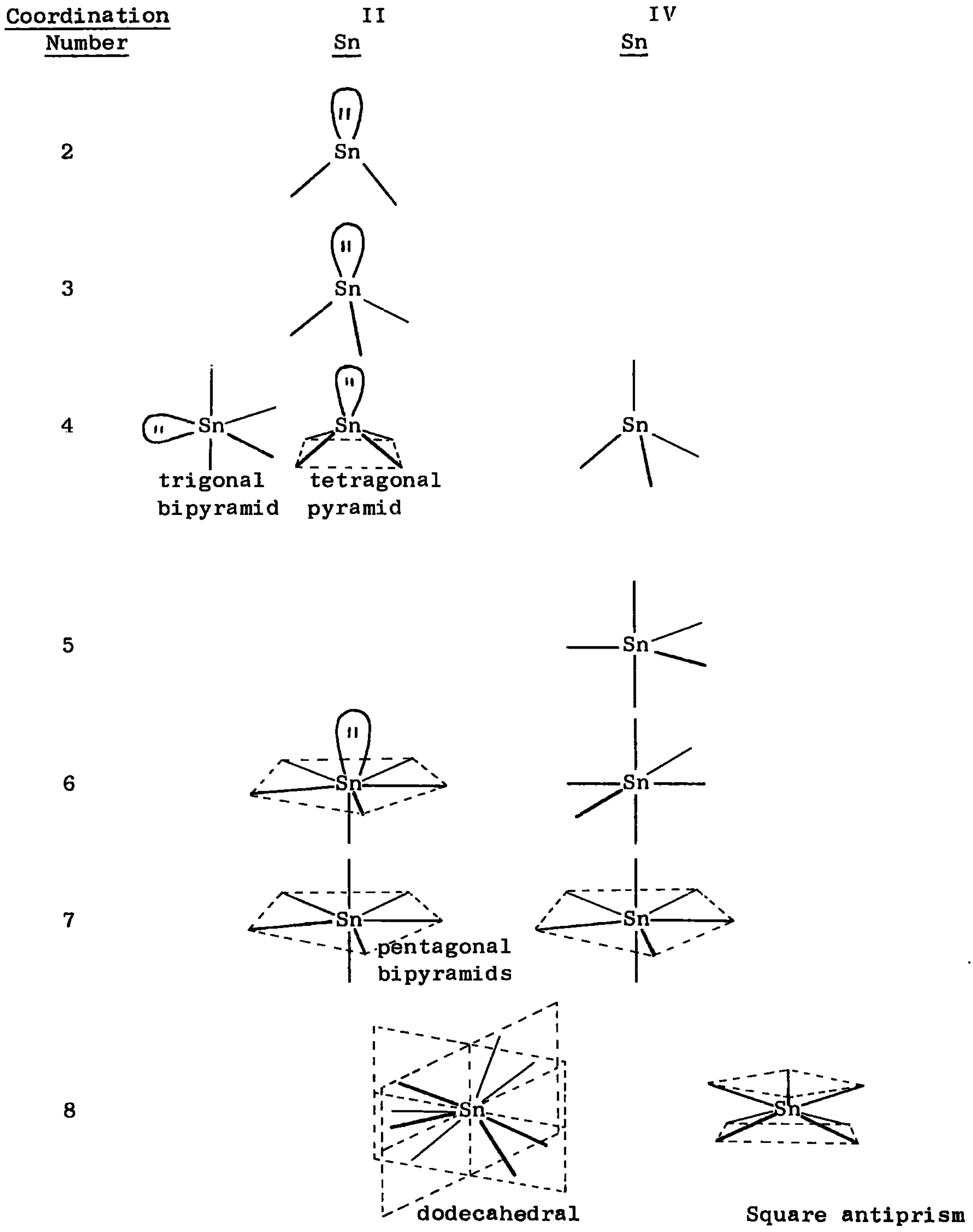


Figure 1.1

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 $SnCl_2.2H_2O$[18], $KSnCl_3$[18], and anhydrous $SnCl_2$[20], 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. $(C_5H_5)_2Sn^{II} \longrightarrow BF_3$[30]. 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 (sp^3d hybidisation - trigonal bipyramid), six (sp^3d^2 - 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[359] 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 R_2Sn^{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 σ-bonded organotin(ii) compound, presumably stabilised by steric effects.

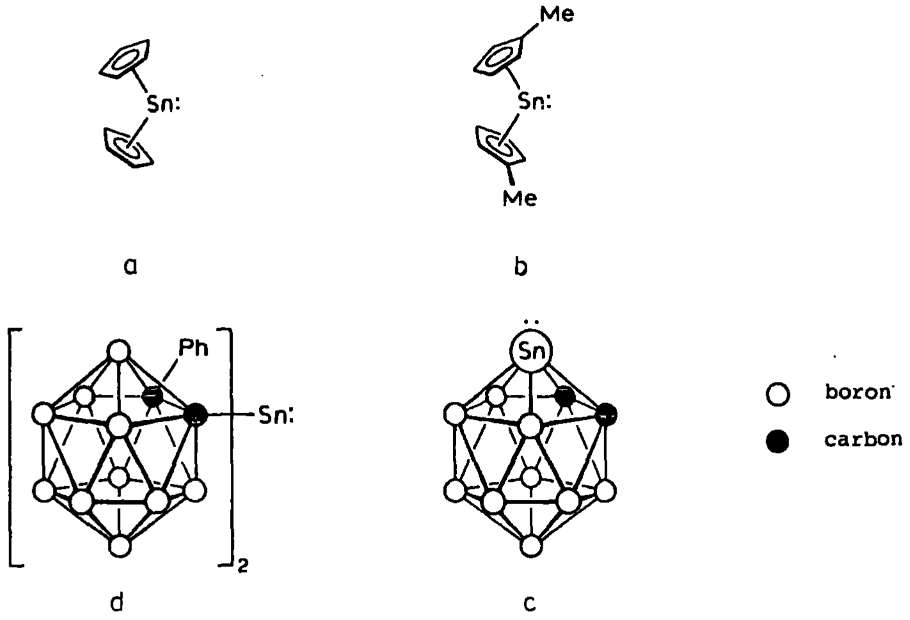


Figure 1-2: Structures of organotin (ii) compounds.

Since then, however, the compound bis(bis(trimethylsilyl)methyl)tin(ii), [(Me$_2$Si)$_2$CH]$_2$Sn^{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).

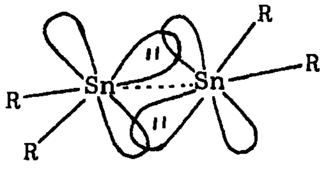


Figure 1-3

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).

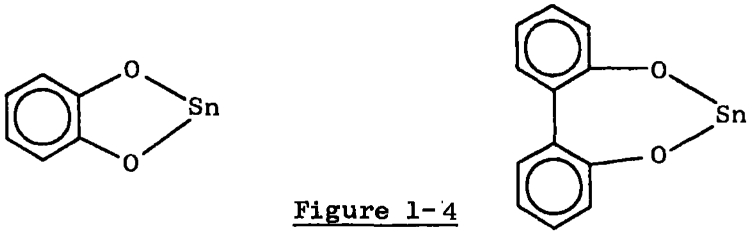


Figure 1-4

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).

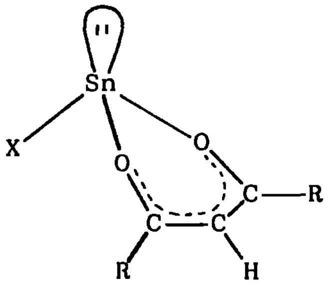
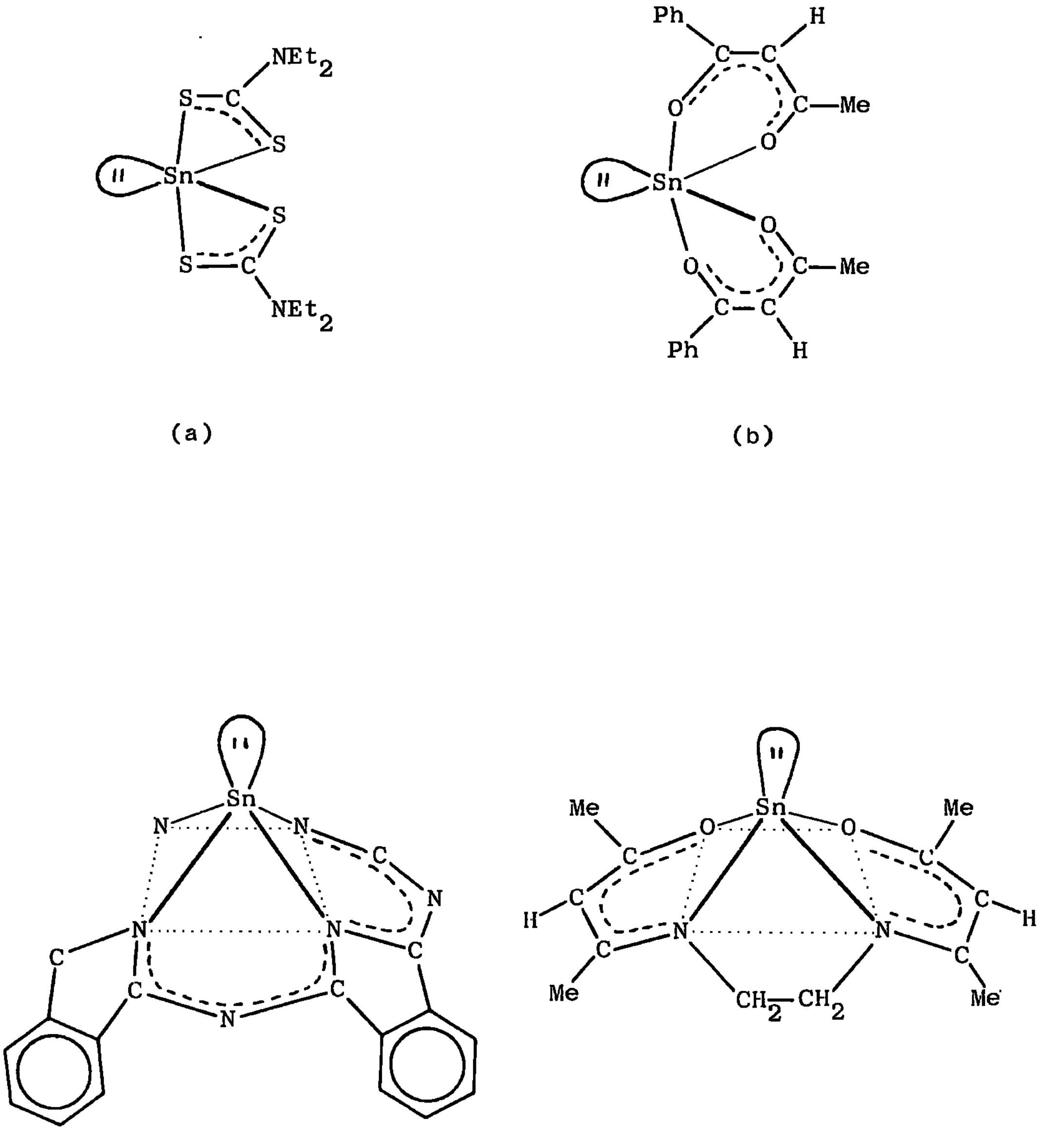


Figure 1-5



(a)

(b)

(c)

(d)

Figure 1-6

Higher coordination numbers are considerably rarer. The anion in the ethylenediaminetetraacetic acid complex $Sn^{II}(Sn^{II}EDTA.H_2O)H_2O$ has been shown[21] 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 $(C_6H_6)Sn^{II}(AlCl_4)_2\ C_6H_6$[77a,b], 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.

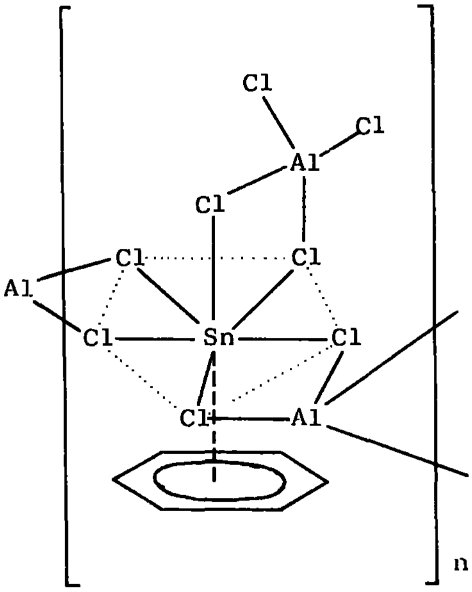


Figure 1-7

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 cystalline SnF_4, which has a structure based on octahedrally-coordinated tin[43]), the organotin halides in the gas phase[44], 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 tetrahedron[45], 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 properties[46]), 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 difluoride[48] and dichloride[47]. The former has a structure containing pure octahedral coordination at tin. It consists of infinite sheets of alternating Me_2Sn groups and fluorine atoms, in a square array (Fig. 1-8a). The chloride structure consists of infinite chains of Me_2Sn 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.

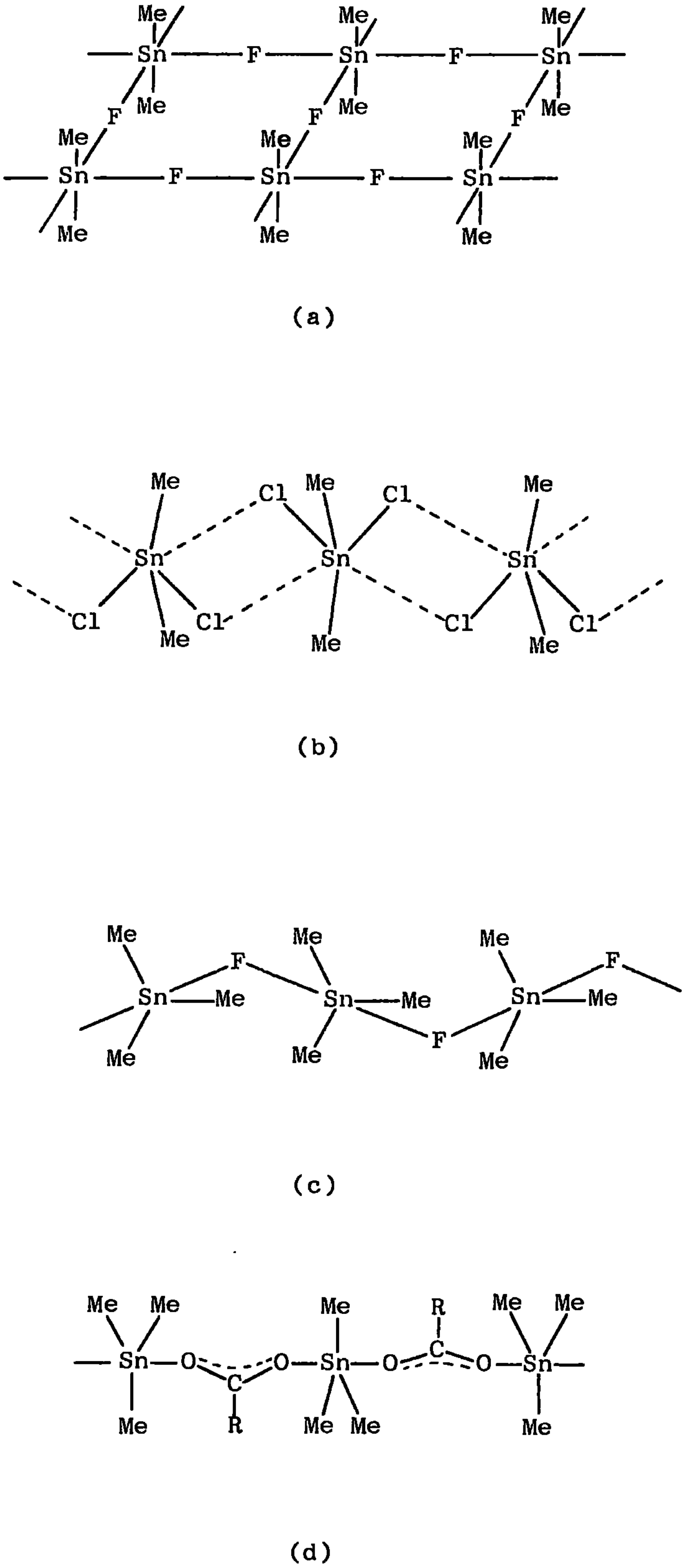
ii) Penta-coordinate Tin (iv)

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.[12] This is commonly observed in compounds of the type R_3SnX 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[49] and the trimethyltin carboxylates[50] (Fig.1-8, c and d). One of the best examples of this type of structure is trimethyltin cyanide[86], which has a linear chain structure of alternating planar Me_3Sn 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≡N..Ge interactions.[95]

Polymeric chain structures have also been observed or inferred for Me_3SnOH[51] (explaining its unusual resistance to dehydration), the trialkyltin imidazoles, triazoles, and tetrazoles (section 1.33), trimethyl-[191] and triphenyltin isothiocyanates[100] (bridging through -NCS...Sn), trimethyltin dicyanamide $Me_3SnN(CN)_2$[106] (bridged by Sn-NCNCN-Sn), Me_3SnNO_3[52], Me_3SnN_3 (Mössbauer study)[107], Me_3SnClO_4[52], Me_3SnBF_4[53], Me_3SnAsF_6[53], and the trialkyltin tetrachloroaluminates.[54]. Trimethyltin chloride and bromide are also believed to associate in the solid, through less strongly than the fluoride.[55]

Interestingly, in the mixed-crystal complexes $Me_3SnOH.Me_3SnNXY$ (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 $(R_2SnO)_n$, which are insoluble polymeric solids, in marked contrast to the corresponding oligomeric (containing 4-coordinate silicon) silicon compounds, have been shown by Mössbauer studies[56] to contain 5-coordinate tin, and the structure in Figure 1-9b has been postulated.


(a)

(b)

(c)

(d)

Figure 1-8

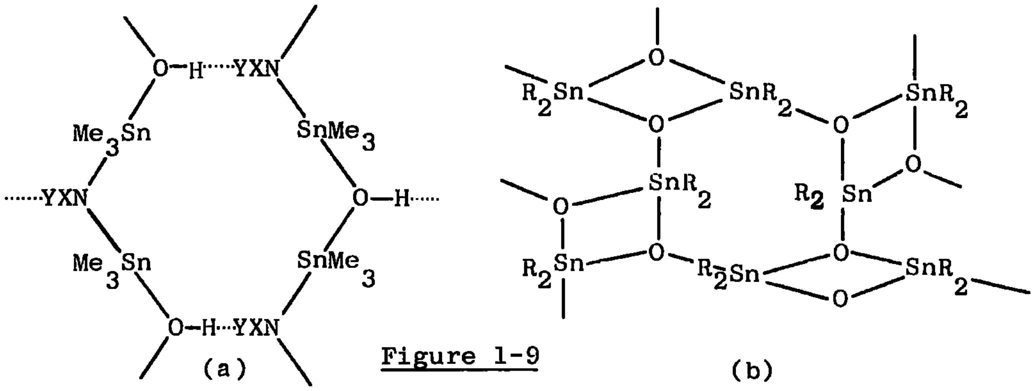


Figure 1-9

Four-membered cyclostannoxane rings are also observed in the dimeric di- and tristannoxanes.[57,58,59] These compounds have an unusual 'ladder' structure, for example tetramethyl-1,3-diisothiocyanatodistannoxane[58] (Fig.1-10).

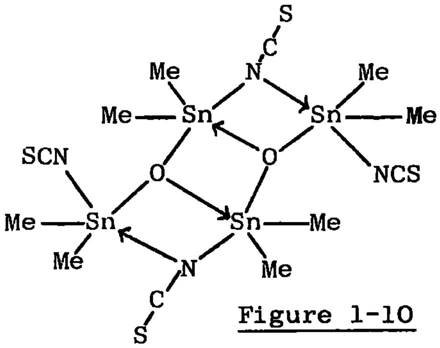


Figure 1-10

Apart from such complex materials, there are a great many monomeric 5-coordinate compounds of tin, for example the complex anions $SnCl_5^-$[60], $Me_2SnCl_3^-$[61] and $Me_3SnCl_2^-$[62], 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, $Me_3SnCl.py$[63a,b], 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[64], $RSn(OCH_2CH_2)_3N$, have an unusual cage structure with an internal dative N→Sn bond. (Figure 1-11b). The compound di-μ-acetato-bis-diphenyltin[65] contains a Sn-Sn bond, bridged by the two acetate groups (Fig.1-11c).

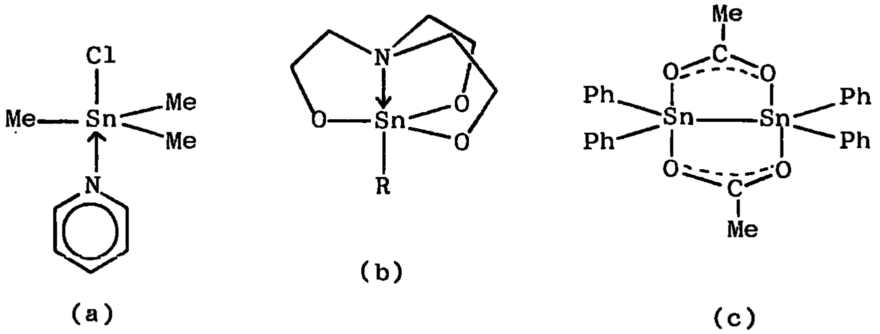


Figure 1-11

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 R_2SnX_2, where X is capable of bridging. Thus dimethyltin bis (fluorosulphate), $Me_2Sn(FSO_3)_2$, has a structure based on a distorted form of the Me_2SnF_2 structure, with fluorosulphate bridges,[67] 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 dicyanide[188](Fig.1-12(a)) and dimethyltin bis-dicyanamide[106] have structures based on a slightly distorted variant of the Me_2SnF_2 structure. Here, unlike the Me_3SnCN structure, the cyanide groups are not disordered. Again, the corresponding silicon and germanium cyanides[188](Fig.1-12(b))

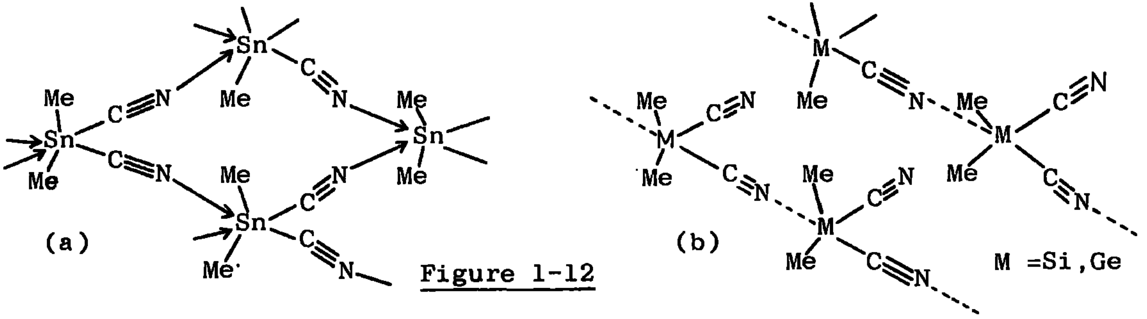


Figure 1-12

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[189,190] has been found to be similar to that of Me_2SnCl_2, 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[68]. 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 substitutents on the tin atom. Thus, while Me_3SnCl forms a stable 1:1 trigonal bipyramidal adduct with pyridine, attempts to prepare the 1:2 complex have failed.[69] 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, $(Me_2SnCl_2)_2$.ter, which has been shown to have an ionic structure containing both 5- and 6- coordinate tin (Fig.1-13).

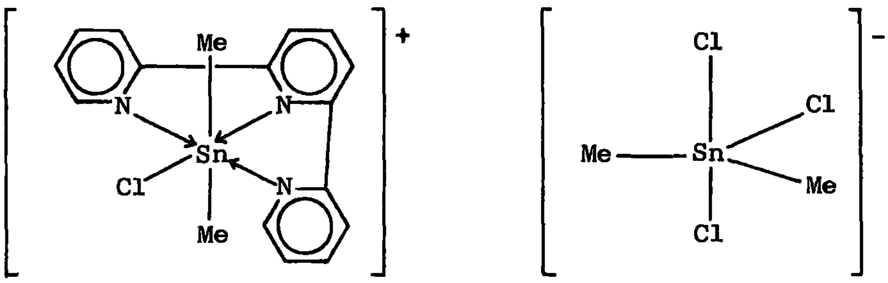
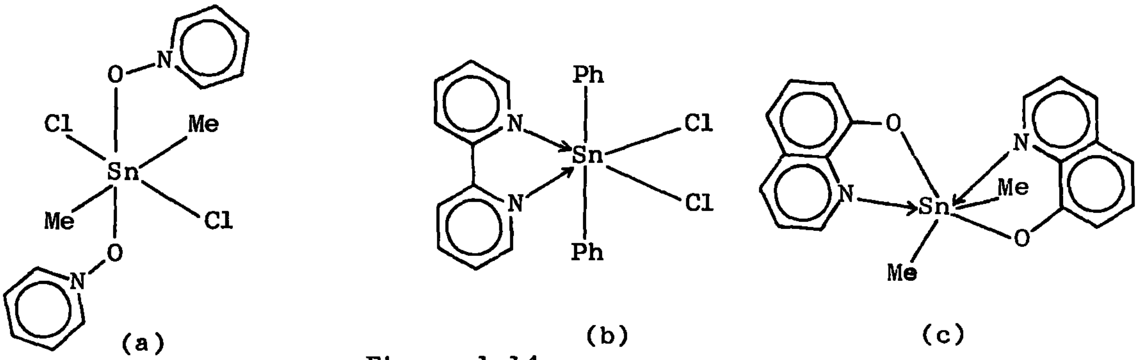


Figure 1-13

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[12] 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. $SnCl_4.2CH_3CN$[74]), 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.$SnCl_4.2py$[75]). A semi-quantitative stereochemical model has been applied to octahedral tin complexes[76], and reaches similar conclusions, as does a separate study[70] which rationalises the commonly observed trans-configuration for the methyl-groups in Me_2Sn^{IV} octahedral derivatives. Examples are the 1:2 adduct of Me_2SnCl_2 with pyridine-N-oxide[71] (Fig.1-14(a)) and the complex of 2,2'-bipyridyl with Ph_2SnCl_2[73] (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)).



(a) (b) (c)

Figure 1-14

It has been suggested[12] 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 $RSn(OOCR')_3$[10], and has been established crystallographically for methyltin trinitrate[78] and for tris (tropolonato) monochloro- and monohydroxytin (iv)[79], all of which are compounds of the type $XSnL_3$ 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 $Me_2Sn(NCS)_2$.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 (dimethylsulphoxy)nitratodiphenyl tin (iv) nitrate[81] (Figure 1-15(c)).

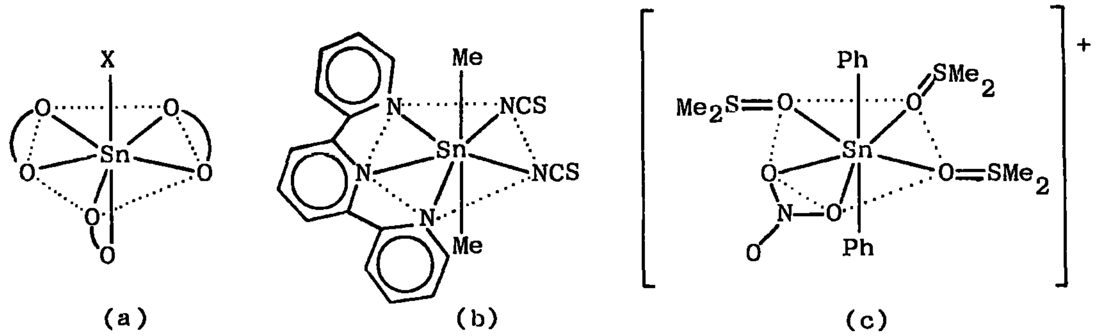


Figure 1-15

A distorted pentagonal bipyramidal structure has been found for the ethylenediaminetetraacetic acid complex $Sn^{IV}EDTA.H_2O$[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(phthalocyaninato)tin(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, $Sn(NO_3)_4$, has a structure based on a dedecahedron 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.

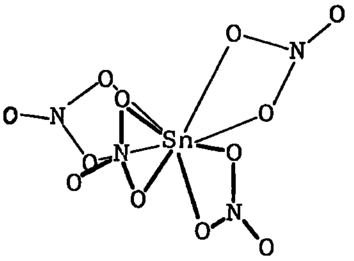


Figure 1-16

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[85] has never been repeated. In 1896 the compound N-tributylstannyl-N-phenylformamide was prepared from the corresponding mercury (ii) derivative and bis(tributylstannyl) sulphide[87]. 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[88], 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, $ClSn(NH_2)_3$[89]. (This was confirmed and the system further investigated in 1958[90].) In 1936 a series of tin phthalocyanine derivatives was prepared.[108]

In the early 1950's, reports began to appear of N-organotin-substituted sulphonamides[91,92] (investigated as potential resin stabilisers) and carbonimides[93,94]. In 1959, further liquid ammonia work yielded the compound amino -dimethylstannylsodium, Me_2SnNH_2Na[97], but it was not until 1961, when the synthesis of aminostannanes was achieved by the reaction of N-lithioamides with organotin halides[98,99], 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, phtlalocyanines and other tetrapyrroles, imidazoles, triazoles, tetrazoles,phosphorous-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 derivates of the type $Sn^{II}(NR.CO.OR')_2$ were reported, [101,102] there existed only the 1939 account of phthalocyaninatotin(ii)[108]. Today, however, with the recent synthesis of the highly reative bis(dialkylamino)tins[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[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)[108,109]. The crystal structure was reported in 1970[40], disproving the earlier conjecture that the molecule was planar[110]. As stated in Section 1.22, the structure is a tetragonal pyramid, the tin atom lying 1.11Å 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[101,102] 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).

$$(RC_5H_4)_2Sn + HNR'R'' \longrightarrow 2\ RC_5H_4 + (R'R''N)_2Sn \qquad 1.1$$

$$SnCl_2 + 2LiNR'R'' \longrightarrow 2\ LiCl + (R'R''N)_2Sn \qquad 1.2$$

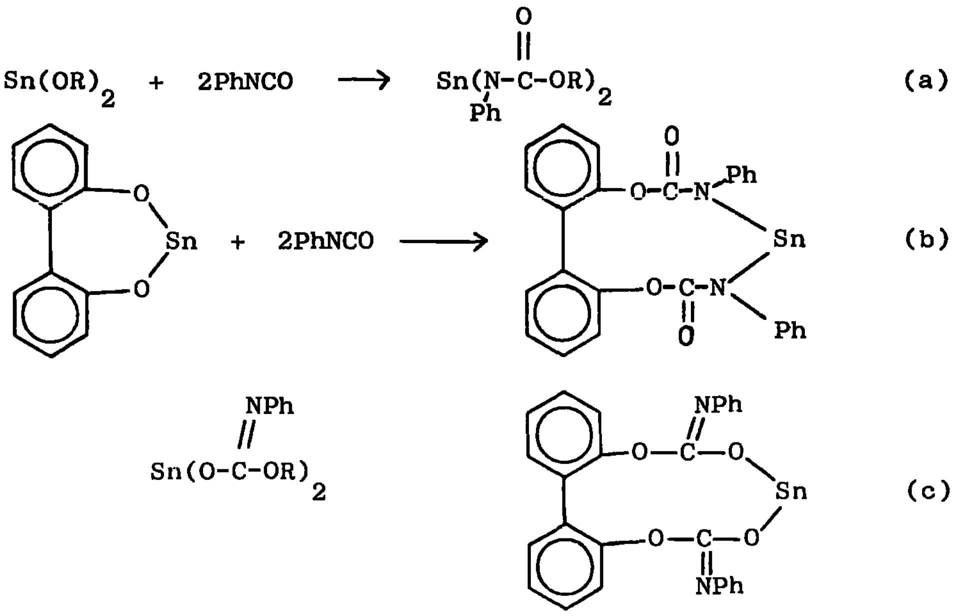


Figure 1-17

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)[66], 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.[111] 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.

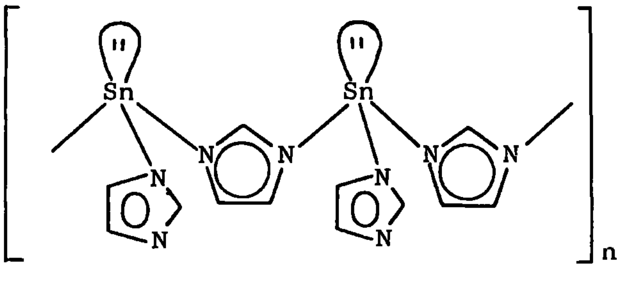


Figure 1-18

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 $[(Me_3Si)_2N]_2\,Sn^{II}$ 103,104 and $(^tBu.Me_3SiN)_2Sn^{II}$ 103 are stable, volatile, coloured (yellow or red), diamagnetic, soluble in hydrocarbons, and apparently monomeric in solution[103], although this has been disputed.[104] Certainly the less sterically hindered bis(dimethylamino)tin(ii)[105] is dimeric in solution, a bridged structure being postulated (Fig.1-19).

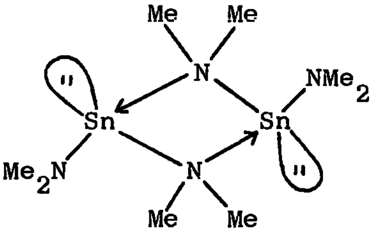


Figure 1-19

A number of compounds with tin(ii) in a heterocyclic ring have also been prepared (Fig.1-20a [104], b [112,138], c [104] and d [104]). 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.

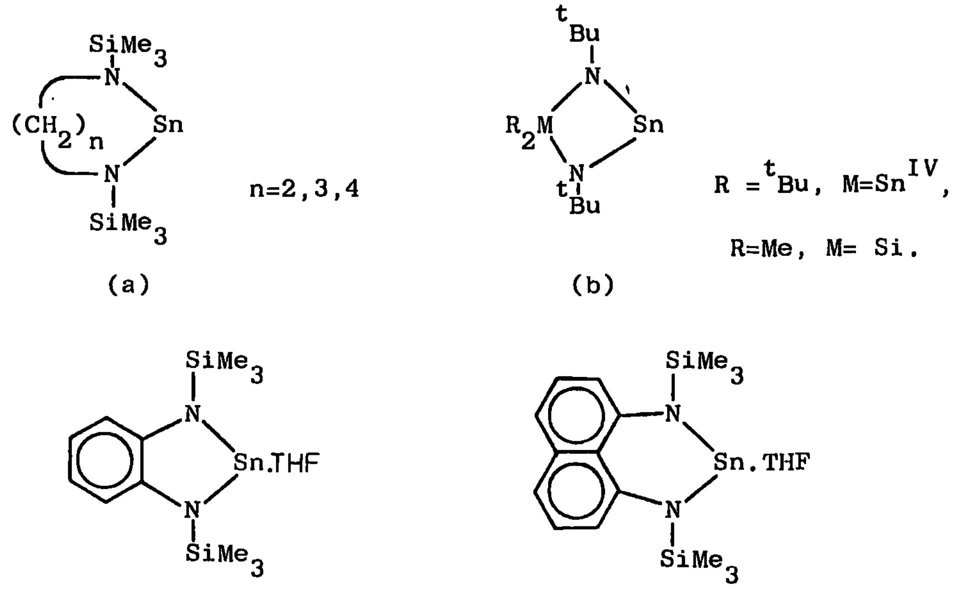
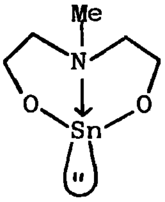
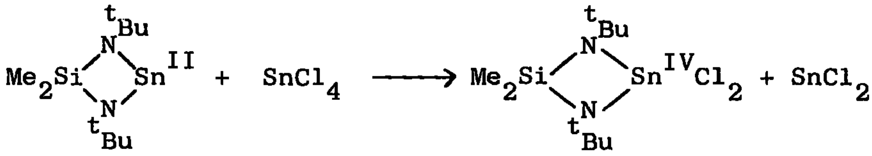


Figure 1-20

TABLE 1

Reactions of $(R_2N)_2Sn^{II}$

$R' = Me_3Si$

		Reference
Protolysis:		
(i)	$(R_2N)_2Sn + HX \longrightarrow 2R_2NH + SnX_2$, X=OEt,	103,104,105
	$R = Me, R'$ OMe,	104
	Cl, C_5H_5	103
(ii)	$[(Me_2N)_2Sn]_2 + 2\,(HOC_2H_4)_2NMe \longrightarrow$ 	105
Metathesis:		
(iii)	$(R'_2N)_2Sn + Sn^{II}Y_2 \longrightarrow 2\ YSnNR'_2$, $Y = C_5H_5$	103, 104
(iv)	$(R'_2N)_2Sn + 2\,LiCHR'_2 \longrightarrow Sn^{II}(CHR'_2) + 2LiNR'_2$	103,29
(v)		112
Complex Formation:		
(vi)	$[(Me_2N)_2Sn^{II}]_2 + 2py \longrightarrow 2(Me_2N)_2Sn^{II}.py$	105
Addition to Unsaturated species:		
(vii)	$(R'_2N)_2Sn + 2Ph\text{-}N{=}C{=}O \longrightarrow [Sn(NPh.CO.NR'_2)_2]_n$?	103
	Structure not confirmed.	
Oxidation:		
(viii)	$(R'_2N)_2Sn^{II} + O_2 \longrightarrow [(R'_2N)_2Sn^{IV}O]_n$	104
(ix)	$(R'_2N)_2Sn^{II} + C_5H_5(CO)_2FeMe \longrightarrow C_5H_5(CO)_2Fe\text{-}Sn^{IV}(NR'_2)_2\text{-}Me$	103
(x)	$(R'_2N)_2Sn^{II} + R''\text{—}X \longrightarrow (R'_2N)_2Sn^{IV}X.R''$	113
	R'' = Alkyl Aryl	
	X = Cl, Br, I	

The sterically crowded materials are generally low melting point solids or liquids, unlike the dimeric $[(Me_2N)_2Sn]_2$(M.Pt.92°C[105]). 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 Sn^{IV}—N bond has been attributed to weakness combined with high polarity[2]. The same is probably true of the Sn^{II}–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, (vii). Complex formation with bases, in constrast, is little known for Sn^{IV}–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 $[(Me_3Si)_2N]_2Sn^{II}$ yields the tris(dialkylamino)tin^{III} radical, $[(Me_3Si)_2N]_3Sn^{\bullet}$, 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 (1) photoelectron spectroscopy investigation[116] showed that, in the tin (ii) amides $(Me_3Si.RN)_2Sn^{II}$ ($R=Me_3Si$, ^tBu), the s^2 lone pair is more tightly bound than in the dialkyls, which do show basic behaviour. No evidence was discovered for $N \rightleftharpoons Sn^{II}$ ($p \rightarrow d$) π-bonding, although $N \rightleftharpoons Si$ 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, ν_{as} ($\mathrm{Sn^{II}N_2}$)has identified for a number of compounds[104,105]; it appears to lie in the range 360-440cm^{-1} (cf. 690cm^{-1} for ν_{as}($\mathrm{Sn^{IV}N_2}$)-Section 1.33 i c). ν_s($\mathrm{Sn^{II}N_2}$) has been suggested to lie about 10-22cm^{-1} below ν_{as}.

The oxidation state of most of the $\mathrm{Sn^{II}}$-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. $\mathrm{Sn^{II}}$ compounds generally have a much higher electron density in the 5s orbital than $\mathrm{Sn^{IV}}$ compounds, due to the lone pair, and therefore have a higher isomer shift. The isomer shifts for $\mathrm{Sn^{II}}$ and $\mathrm{Sn^{IV}}$ compounds fall into two groups, with the dividing line formed approximately by the value for α-Sn(grey tin) (there is in fact a slight overlap of the two groups[41], for example the I.S value for $[(\mathrm{Me_3Si})_2\mathrm{CH}]_2\mathrm{Sn^{II}}$ is very close to that of α-Sn[128], but in general the isomer shift forms a good guide to oxidation state).

C. Organonitrogen Derivatives of Tetravalent Tin

i) Compounds containing Tin bonded to 3-covalent Nitrogen

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

a) Preparative Aspects

The non-appearance of the stannylamines until 1961 is probably due to the fact that, unlike silicon and germanium, the tin(iv) halides do not undergo aminolysis[118] 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[89,90] (Eqn.1.4),

$$R_2NH + SnX_4 \longrightarrow R_2NH.SnX_4 \not\longrightarrow R_2NSnX_3 + HX \qquad 1.3$$

$$SnX_4 + 2NH_3 \longrightarrow NH_4X + [X_3SnNH_2] \longrightarrow XSn(NH_2)_3 \qquad 1.4$$

$X = Cl, Br.$

and a range of preparations are now available based on the reaction of organotin halides[119,120,121] or phenyls[121,122,123] with liquid ammonia in the presence of alkali metal amides (Eqn.1.5).

$$R_3SnX + NH_3 \xrightarrow{KNH_2} [R_3SnNH_2] + \overset{K}{HX}$$

$X = Hal, Ph.$ $\swarrow$ (disproportionates) 1.5

$$(R'_3Sn)_2NH \text{ or } (R''_3Sn)_3N$$

$R' = {}^nPr, {}^iPr, {}^iBu$, neopentyl, cyclohexyl; $R'' = Me, Et, {}^nPr$.

The products depend upon the alkyl substituents on tin; if $R = {}^tBu$, the primary stannylamine is stable to disproportionation[121]. If starting materials such as tetraphenyltin or hexaphenylditin[123,124,125] are used, complete substitution can be effected, giving rise to alkali metal salts of the hexaaminostannate anion $Sn(NH_2)_6^{2-}$.

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[98,99,120,126,130,131,154]. Lithium nitride, Li_3N has also been used in the preparation of tris (trialkylstannyl)amines[127].

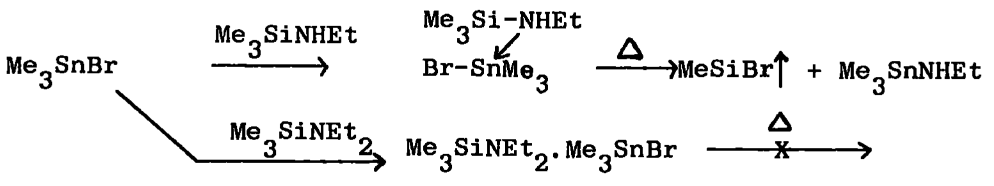
Sodium dialkylamides have been used, for example in the preparation of silylstannylamines[128] (Eqn.1.7) and the synthesis of $(Me_3Sn)_3N$ from trimethyltin alkoxides[129] (Eqn.1.8), but in general the lithium reagents are superior.

$$R_{4-n}SnX_n \quad + \quad nLiNR'R'' \longrightarrow nLiX \quad + \quad R_{4-n}Sn(NR'R'')_n \qquad 1.6$$

$$(Me_3Si)_2NNa \quad + \quad R_3SnCl \longrightarrow \underset{R\,=\,Me,\ {}^{n}Bu}{(Me_3Si)_2NSnR_3} \quad + \quad NaCl \qquad 1.7$$

$$Me_3SnOR \quad + \quad NaNH_2 \longrightarrow NaOR \quad + \quad [Me_3SnNH_2] \longrightarrow (Me_3Sn)_3N \quad + \quad NH_3 \qquad 1.8$$

Diethylaminomagnesium bromide has been used as an aminating agent[132,140] 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[126] (Eqn. 1.9).



$$Me_3SnBr \xrightarrow{Me_3SiNHEt} \begin{matrix} Me_3Si{-}NHEt \\ \swarrow \\ Br{-}SnMe_3 \end{matrix} \xrightarrow{\Delta} MeSiBr\uparrow \; + \; Me_3SnNHEt \qquad 1.9$$

$$Me_3SnBr \xrightarrow{Me_3SiNEt_2} Me_3SiNEt_2.Me_3SnBr \;\overset{\Delta}{\not\longrightarrow}$$

Transmetallations involving sodium sulphonamides[91,92,93] (which are easily prepared by the reaction of the parent sulphonamide with sodium hydroxide) have been used to prepare N-organostannyl sulphonamides,

$R_{4-n}Sn(NR'SO_2R'')_n$ (n=1,2). 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-diphenyltriazen with phenyltin chlorides has been used to prepare some unusual triazen derivatives of tin[134] (Eqn.1.10).

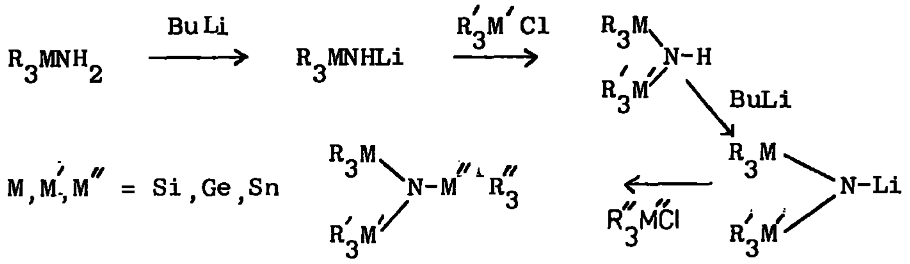
$$Ph_nSnCl_{4-n} + m\ AgN_3Ph_2 \longrightarrow mAgCl + Ph_nSnCl_{4-(m+n)}.(NPh\text{-}N{=}NPh)_m \qquad 1.10$$

$$n=0,1,3;\ m = 1,2.$$

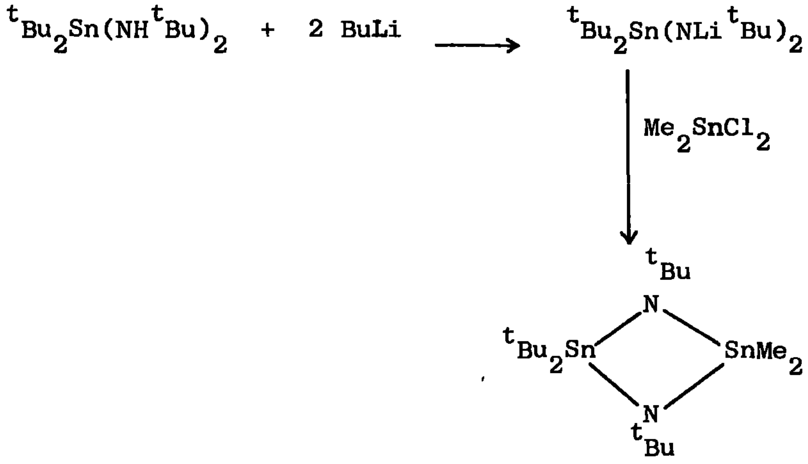
$$PhHgNS_7 + Me_3SnCl \longrightarrow PhHgCl + Me_3SnNS_7 \qquad 1.11$$

The early preparation of N-tributylstannyl-N-phenylformamide from a mercuric compound has already been mentioned (Section 1.31). A mercury derivative has also been used in the preparation of an N-trimethylstannyl substituted sulphur-nitrogen ring[289] (Eqn.1.11).

An advantage of the use of organolithiumreagents 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 amines[135,136,137,138,139] and bis-stannylamines[138,139] (Eqn.1.12), as well as tin-nitrogen cyclic compounds[138,139] (Eqn.1.13)



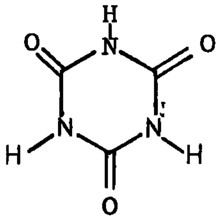
1.12



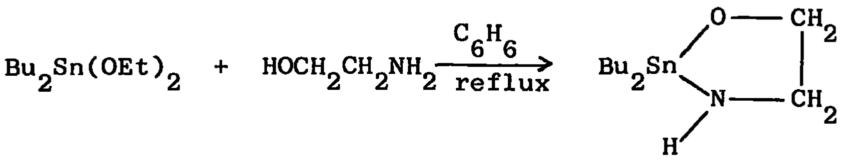
1.13

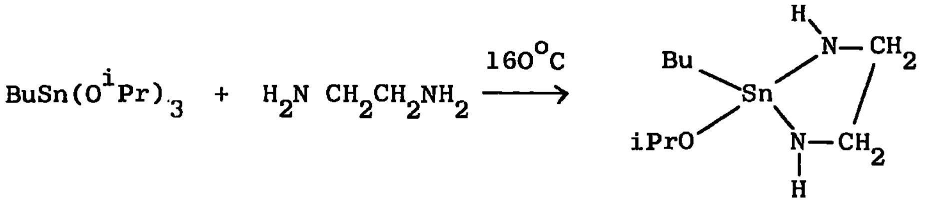
Although it is not applicable to preparation of the very hydrolytically-sensitive stannylamines, the reaction between trialkyltin oxides, hydroxides, or alkoxides and the N-H bond, with elimination of water or alcohol, has been used in a number of cases where the N-H proton has acidic character or where 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[93,141], carboxamides,[93,142,143,145], ureas and isocyanurates, [143,145], imidazoles and triazoles,[96,140,185] and alkanolamines[146, 147,148,149,150]. Some amino-derivatives have even been prepared in this way, using alkyltin trialkoxides[145]. 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[143,144] (Eqn.1.18).

$$Et_3SnOH \quad + \quad CH_3C_6H_4SO_2NH_2 \xrightarrow{EtOH} CH_3C_6H_4SO_2NHSnEt_3 \quad (93) \qquad 1.14$$



$$+ \quad 3(Bu_3Sn)_2O \xrightarrow[reflux]{C_6H_6} (Bu_3SnNCO)_3 \quad (144) \qquad 1.15$$


(146) 1.16


(145) 1.17

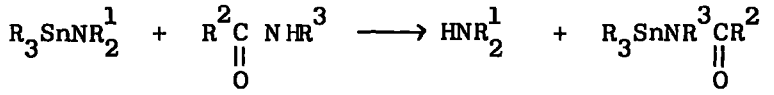
$$R_3SnOH + NH_2\overset{O}{\overset{\|}{C}}NHR' \longrightarrow R_3SnNCO + R'NH_2 + H_2O$$ 1.18

$$R_3SnNR'_2 + R_2NH \longrightarrow R_3SnNR_2 + R'_2NH$$ 1.19

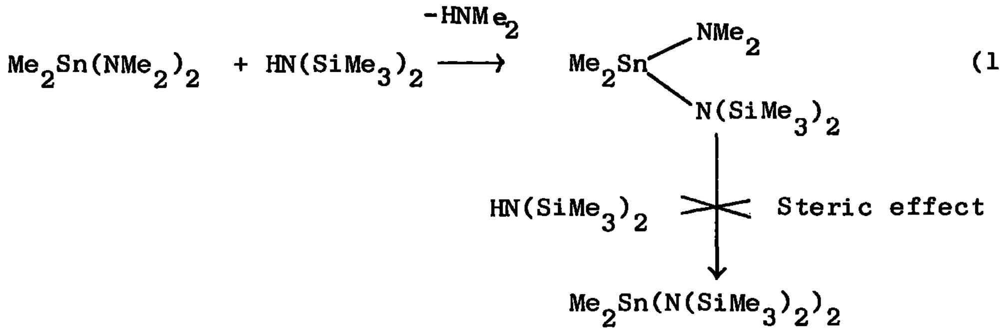
Another example of the exchange process is transamination. The general process for secondary amines is indicated in Eqn.1.19.

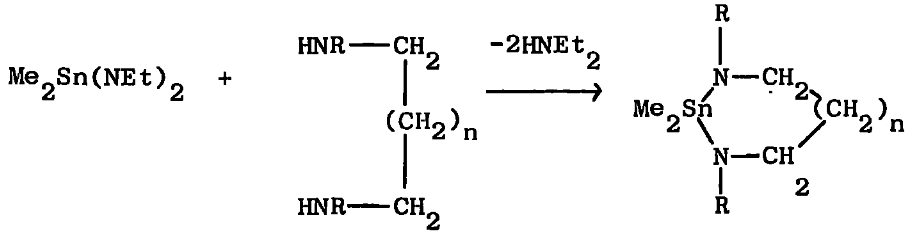
This reaction appears to be volatility controlled and the displacement series $Bu_2N > Et_2N > Me_2N$ has been demonstrated.[131] This method has been used as a route to organotin derivatives of hydrazines[151], amides[152], silylaminostannanes[153], aziridines[154], sulphamides[155], sulphinamides[159] and to tin-nitrogen heterocycles.[150,156,157.]

Examples are given in equations 1.20 - 23.


(152) 1.20

$$R_3SnNR^1_2 + R^2\underset{\underset{O}{\|}}{C}NHR^3 \longrightarrow HNR^1_2 + R_3SnNR^3\underset{\underset{O}{\|}}{C}R^2$$

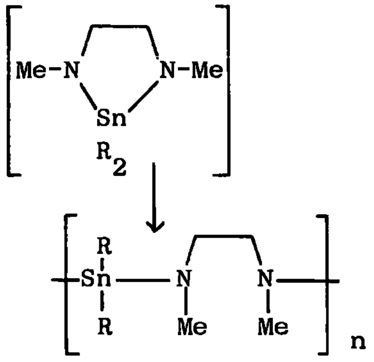

(153) 1.21


(156) 1.22

R = Me,n=1; R = Me_3Si, n = 0,1,2

$$(NH_2)_2SO_2 + 4\ Me_3SnNMe_2 \xrightarrow{-\ 4HNMe_2} (Me_3Sn)_2NSO_2N(Me_3Sn)_2 \qquad (155) \qquad 1.23$$

$$R_2Sn(NEt_2)_2 + MeNHCH_2CH_2NHMe \xrightarrow{-2HNEt_2}$$



1.24

Interestingly, the attempted preparation of th ethylenediamine derivative in equation 1.24 gave a polymeric product.[157] 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 polymeric 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[130,131] (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[131] that condensation to form the more highly substituted amine must occur very quickly, when steric factors allow it.

$$Me_3SnNR'_2 + R''NH_2 \longrightarrow Me_3SnNHR'' + R'_2NH \qquad 1.25$$

$$R' = Me,Et; \quad R'' = Aryl$$

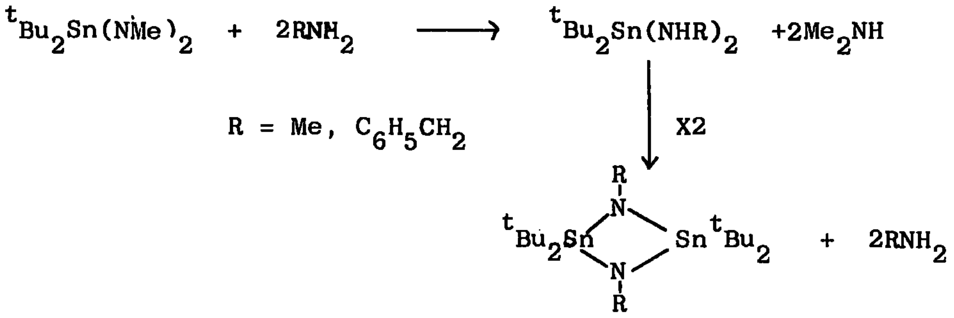
$$2Me_3SnNR'_2 + R''NH_2 \longrightarrow (Me_3Sn)_2NR'' + 2R'_2NH \qquad 1.26$$

$$R' = Me,Et; \quad R'' = Me,Et.$$

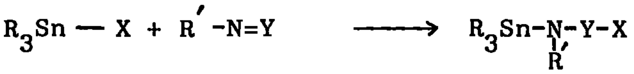
$$3Me_3SnNMe_2 + NH_3 \longrightarrow (Me_3Sn)_3N + 3Me_2NH \qquad 1.27$$

The reaction of distannazanes with primary amines has been used to obtain cyclostannazanes[130,131] (Eqn.1.28), and the condensation reaction has been utilised to provide a synthesis of a 4-membered Sn_2N_2 ring[158] (Eqn.1.29)

1.28



1.29



$$R_3Sn - X + R'\text{-}N{=}Y \longrightarrow R_3Sn\text{-}\underset{R'}{N}\text{-}Y\text{-}X$$

1.30

The majority of other preparations involve the addition of an 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 Sn-N bonded product is capable of further reaction with an excess of unsaturated reactant,to form a wide range of materials.[168,171,173.]

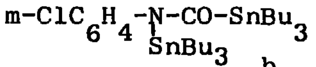
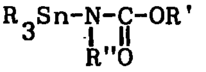
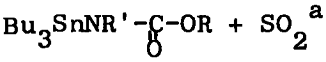
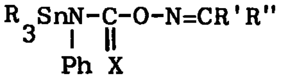
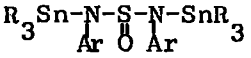
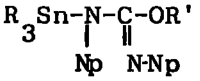
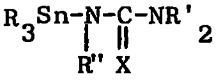
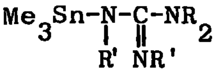
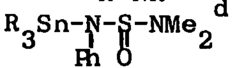
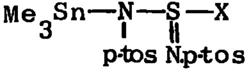
It is of interest that, while the reaction of organotin hydrides with isocyanates yields an Sn-N bonded material, isothiocyanates yield compounds containing an Sn-S bond[160,161] (Eqn.1.31)

$$R_3SnH + R'NCS \longrightarrow R'\text{-}N{=}CH\text{-}S\text{-}SnR_3 \qquad 1.31$$

However, the stannylamines react with both isocyanates and isothiocyanates to produce Sn-N bonded products. This presumably reflects the stabilising effect of the thiourea structure on the C=S bond.

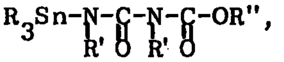
TABLE 2

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

	Reactants	Products	Reference
(i)	$R_3Sn\text{-}H + R'\text{-}N{=}C{=}O$	$R_3Sn\text{-}NR'\text{-}CH{=}O$	160,161
(ii)	$R_3Sn\text{-}X + Ph\text{-}N{=}N{=}N$ $X = H, Li$	$R_3SnNXPh + N_2$ [a]	162
(iii)	$Ph_3Sn\text{-}H + Ph\text{-}N{=}N\text{-}Ph$	$Ph_3SnNHNHSnPh_3$	163
(iv)	$R_3Sn\text{-}H + R'\text{-}CH{=}N\text{-}R''$	$R'\text{-}CH_2\text{-}NR''\text{-}SnR_3$ [c]	164,165,166
(v)	$Bu_3SnSnBu_3 + m\text{-}ClC_6H_4N{=}C{=}O$	 $m\text{-}ClC_6H_4\text{-}\underset{SnBu_3}{N}\text{-}CO\text{-}SnBu_3$	167
(vi)	$R_3SnOR' + R''N{=}C{=}O$ $R' = \text{Alkyl}, R_3Sn$	 $R_3Sn\text{-}\underset{R''}{N}\text{-}\underset{\overset{\Vert}{O}}{C}\text{-}OR'$ [b]	168-174,253, 303.
(vii)	$Bu_3SnOSO_2R + R'N{=}C{=}O$	 $Bu_3SnNR'\text{-}\underset{\overset{\Vert}{O}}{C}\text{-}OR + SO_2$ [a]	175
(viii)	$R_3SnON{=}CR'R'' + Ph\text{-}N{=}C{=}X$ $X = O, S$	 $R_3Sn\underset{Ph}{N}\text{-}\underset{\overset{\Vert}{X}}{C}\text{-}O\text{-}N{=}CR'R''$	327
(ix)	$(R_3Sn)_2O + Ar\text{-}N{=}S{=}N\text{-}Ar$	 $R_3Sn\text{-}\underset{Ar}{N}\text{-}\underset{\overset{\Vert}{O}}{S}\text{-}\underset{Ar}{N}\text{-}SnR_3$	175
(x)	$R_3SnOR' + Np\text{-}N{=}C{=}N\text{-}Np$ $R' = \text{Alkyl}, SnR_3$; Np = 1-naphthyl	 $R_3Sn\text{-}\underset{Np}{N}\text{-}\underset{\overset{\Vert}{N\text{-}Np}}{C}\text{-}OR'$	253,303
(xi)	$R_3SnNR'_2 + R''N{=}C{=}X$ $X = O, S$	 $R_3Sn\text{-}\underset{R''}{N}\text{-}\underset{\overset{\Vert}{X}}{C}\text{-}NR'_2$	130,176,177
(xii)	$Me_3SnNR_2 + R'\text{-}N{=}C{=}N\text{-}R'$	 $Me_3Sn\text{-}\underset{R'}{N}\text{-}\underset{\overset{\Vert}{NR'}}{C}\text{-}NR_2$	176,177,178
(xiii)	$R_3SnNMe_2 + PhN{=}S{=}O$	 $R_3Sn\text{-}\underset{Ph}{N}\text{-}\underset{\overset{\Vert}{O}}{S}\text{-}NMe_2$ [d]	177,234
(xiv)	$Me_3SnX + p\text{-}tos\text{-}N{=}S{=}N\text{-}p\text{-}tos$ $X = Me, NMe_2, OMe.$	 $Me_3Sn—\underset{p\text{-}tos}{N}—\underset{\overset{\Vert}{Np\text{-}tos}}{S}—X$	234,254

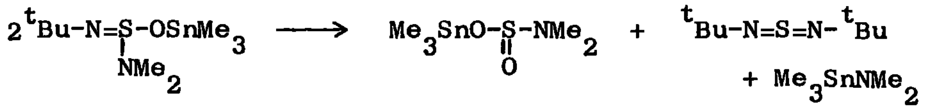
NOTES To Table 2:

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  $R_3Sn\text{-}\underset{R'}{N}\text{-}\underset{\overset{\Vert}{O}}{C}\text{-}\underset{R'}{N}\text{-}\underset{\overset{\Vert}{O}}{C}\text{-}OR''$, which may eliminate CO_2 to give a urea derivative.

c) Catalysts, e.g. $ZnCl_2$, suppress side reactions when R',R" contain unsaturated groups.

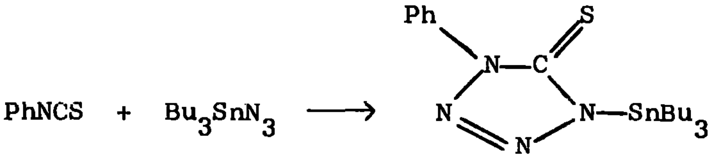
d) When R = ${}^tBu$,[234] addition occurs across the S=O bond, followed by rearrangement:



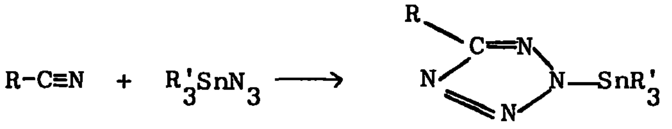
$$2\,{}^tBu\text{-}N{=}\underset{NMe_2}{S}\text{-}OSnMe_3 \longrightarrow Me_3SnO\text{-}\underset{\overset{\Vert}{O}}{S}\text{-}NMe_2 + {}^tBu\text{-}N{=}S{=}N\text{-}{}^tBu + Me_3SnNMe_2$$

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).

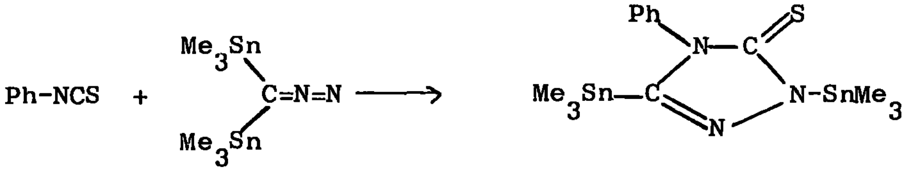
Organotin derivatives of nitrogen-containing heterocycles have been prepared by the reaction of trialkyltin azides[179,180,185] and bis(trialkylstannyl) diazomethanes[181] with unsaturated species (Eqns. 1.32-35).



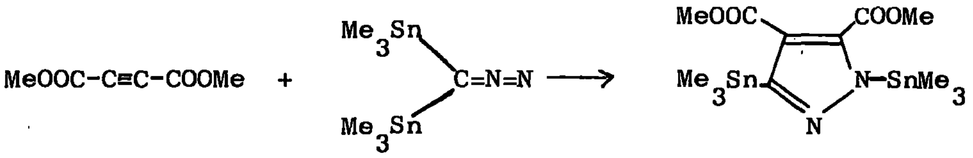
(179) 1.32



(180) 1.33



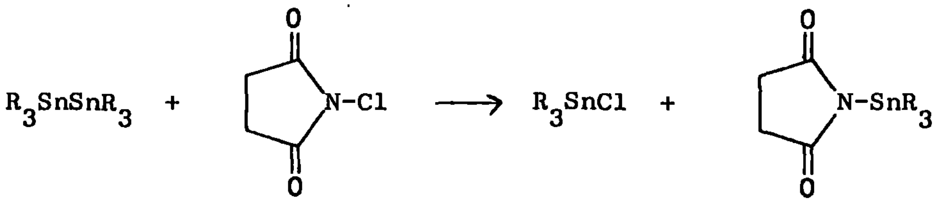
(181) 1.34



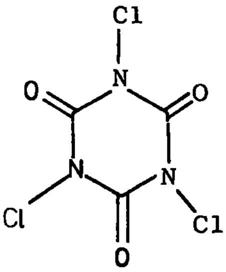
(181) 1.35

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 uracil[183] and succinimide[184] 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]



(184) 1.36



$$\xrightarrow{Me_3SnCl} Me_3SnN_3C_3O_3Cl_2 + Cl_2$$

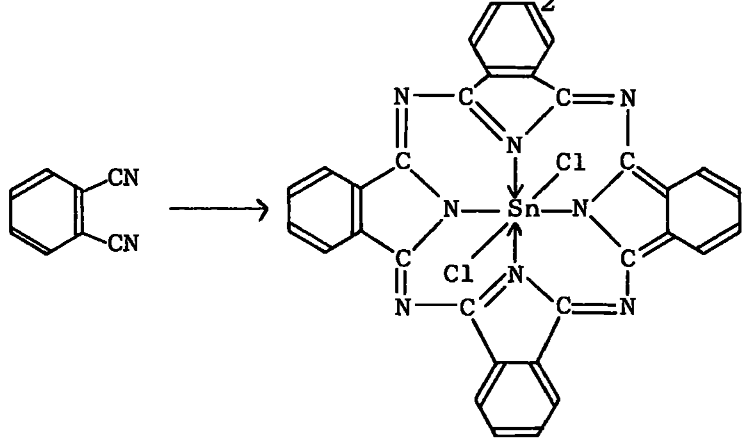
$$\xrightarrow{2Me_4Sn} (Me_3Sn)_2N_3C_3O_3Cl + 2MeCl$$

$$\xrightarrow{Me_2SnCl_2} Me_2Sn(N_3C_3O_3Cl_2)_2 + 2Cl_2 \quad (183) \quad 1.37$$

$$\xrightarrow{SnCl_4} Cl_3SnN_3C_3O_3Cl_2 + Cl_2$$

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.[108] However, the usual method, like most metallophthalocyanine preparations, is by reaction of the central unit of the product (in this case $SnCl_2$) with phthalonitrile[108,109] (Eqn. 1.38)

$SnCl_2$ + 4



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

$$R_3SnNR'_2 + HA \longrightarrow R_3SnA + HNR_2' \qquad 1.39$$

$$Me_3SnNEt_2 + MeOH \xrightarrow{-50^oC} Me_3SnOMe + HNMe_2 \qquad 1.40$$

reactions of stannylamines to be extensively investigated.[176,192] In a number of instances it provides easy access to compounds which are difficult to obtain by other routes; for example trimethyltin methoxide[193] (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 procede under mild conditions.

Similar reactions not shown in the table are those with nitroalkanes and α-hydrogen-containing nitriles.

Stannylamines react with benzonitrile by addition across the $C\equiv N$ bond (see Table 5). However, nitriles possessing an α-hydrogen react as protic species with elimination of amine[192] (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.

$$\begin{tikzcd} R_3SnNR'_2 + R''R'''CHCN \arrow[r] & R_3SnCR''R'''CN + HNR'_2 \arrow[d, "\text{Redistribution}"] & 1.41 \\ & \text{Mixture of products} & \end{tikzcd}$$

A similar observation is made for the reaction with nitromethane,[192] although a clean reaction is obtained if the isopropyl compound, Me_2CHNO_2, is used.

The reaction with acetone has been claimed to proceed via abstraction of α-hydrogen,[192] 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

	Reactants	Products *	References
(i)	$R_3SnNR'_2$ + HCl	$R_3SnCl + R_2'NH_2{}^+Cl^-$	132,176,192
(ii)	$R_3SnNR'_2$ + 'H_2CO_3' ($H_2O + CO_2$)	$(R_3Sn)_2CO_3$	120,132,192
(iii)	$R_{4-n}Sn(NR'_2)_n + R''OH$ n = 1-4	$R_{4-n}Sn(OR'')_n$	99,192,193,194,195
(iv)	R_3SnNMe_2 + Ph_2MH R = Me,Et; M = P,As	R_3SnMPh_2	176,192
(v)	$R_{4-n}Sn(NEt_2)_n$ + HCN n = 1,2; R= Me,Et,Bu,Ph	$R_{4-n}Sn(CN)_n$	196
(vi)	$R_{4-n}Sn(NR'_2)_n + HN_3$ n = 1-4	$R_{4-n}Sn(N_3)_n$	197
(vii)	$R_3SnNR'_2$ + H-C≡CR" R" = Pr,Bu,Ph,C_6F_5,$-(CH_2)_2CHMe_2$, $-CMe{=}CH_2$	$R_3Sn-C{\equiv}C-R''^a$	176,192,198,199
(viii)	$R_3SnNR'_2$ + C_5H_6	$R_3SnC_5H_5$	176, 192
(ix)	R_3SnNMe_2 + C_6F_5H	$R_3SnC_6F_5$	199
(x)	$R_3SnNR'_2$ + $R''CHN_2$ R" = H, COOEt, COR"'	$R_3SnR''CN_2{}^b$	200, 201
(xi)	R_3SnNEt_2 + HCX_3 X = Cl, Br	R_3SnCX_3	202
(xii)	$Bu_3SnNR_2 + R'_2CH\underset{\underset{O}{\|}}{C}-NR''_2$ R" ≠ H	$Bu_3SnCR'_2\underset{\underset{O}{\|}}{C}NR''_2{}^c$	152
(xiii)	$Bu_3SnNEt_2 + CH_3O.SO.Ph$	$Bu_3SnCH_2O.SO.Ph$	203

* Amine may be assumed, unless otherwise indicated.

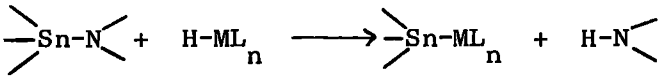
NOTES:

a) If R" = H, disubstitution will occur, forming $R_3Sn-C{\equiv}C-SnR_3$

b) If R"=H, disubstitution will occur, forming $(R_3Sn)_2CN_2$

c) If R"=H, transamination will occur, forming $Bu_3SnNR''\underset{\underset{O}{\|}}{C}CR'_2H$

A reaction related to protolysis is that with metal hydrides. The general reaction is given in Equation 1.42.



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)

$$\begin{tikzcd}
R_3SnNPh.CHO + R_2'SnH_2 \arrow[r] & R_3Sn\text{-}SnR_2'H + HNPhCHO \arrow[d, "R_3''SnNPhCHO"] \\
 & R_3Sn\text{-}R_2'Sn\text{-}SnR_3''
\end{tikzcd} \qquad (211) \quad 1.43$$

$$3\ R_3SnNPhCHO + PhSnH_3 \longrightarrow (R_3Sn)_3SnPh + 3HNPhCHO \qquad (212) \quad 1.44$$

$$nR_2SnH_2 + nR_2Sn(NEt_2)_2 \longrightarrow 2nHNEt_2 + \left[SnR_2 \right]_{2n} \qquad (207) \quad 1.45$$

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[215,216,217] (not silicon - silicon hydrides do not react), platinum,[218] and tungsten.[218]

In contrast, dialkylaminotins react with aluminium and boron hydrides by a metathetical process forming tin hydrides and amino-alanes or boranes.[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

$$R_{4-n}Sn(NEt_2)_n + nBu_2AlH \longrightarrow R_{4-n}SnH_n + nBu_2AlNEt_2 \qquad 1.46$$

$$2R_{4-n}Sn(NEt_2)_n + n(BH_3)_2 \longrightarrow 2R_{4-n}SnH_n + 2nH_2BNEt_2 \qquad 1.47$$

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

Figure 1-21

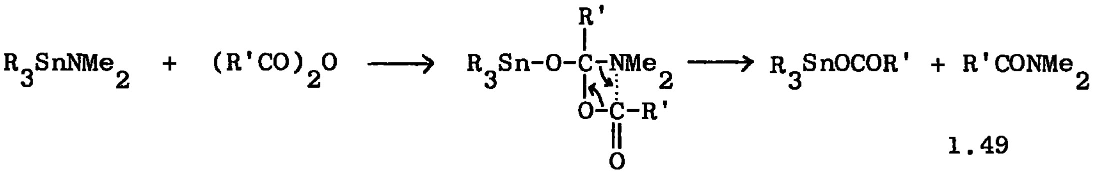
The basicity of the nitrogen in stannylamines is shown by the formation of stable complexes such as $Sn(NEt_2)_4 \cdot VOCl_3$[220] (see also Section (c)). The tin does not appear to be particularly acidic, however. Although a number of Sn-N compounds contain 5-coordinate tin by association with donor 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.[192]

The generalised metathetical reaction in Equation 1.48 is known for a large number of systems. Representative examples are given in Table 4.

$$R_3Sn{-}N\!\lessdot \quad + \quad X{-}Y \longrightarrow R_3Sn{-}X \quad + \quad Y{-}N\!\lessdot \qquad 1.48$$

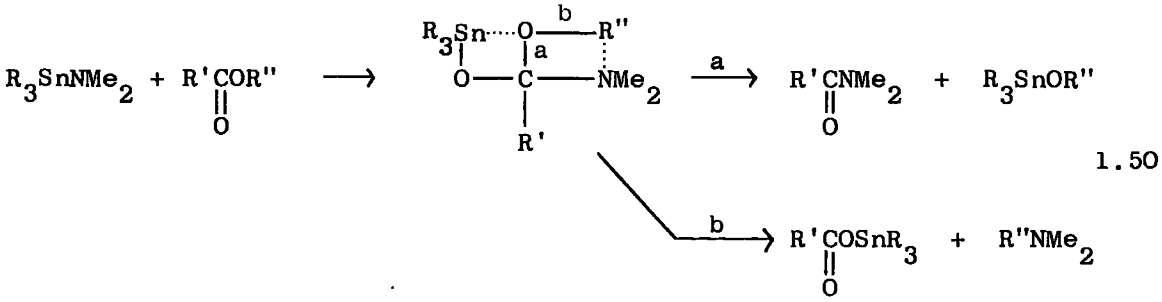
The reactions commonly proceed smoothly and cleanly under mild conditions,[222] although violent reaction is met with in some cases, particularly where the product is trimethyltin fluoride. The ease of reaction has been ascribed to the high donor strength of the stannylamines, the weak and polar Sn-N bond, and the high heats of formation of many of the organotin products, especially the above-mentioned fluoride.[221] 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.[108,109]

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).



$$R_3SnNMe_2 + (R'CO)_2O \longrightarrow R_3Sn{-}O{-}\overset{R'}{\underset{O-\underset{\underset{O}{\|}}{C}-R'}{C}}{-}NMe_2 \longrightarrow R_3SnOCOR' + R'CONMe_2 \qquad 1.49$$

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



1.50

TABLE 4

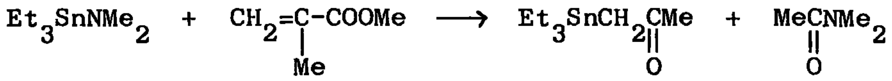
Metathetical Reactions of Stannylamines

	Reactants	Products	Reference
(i)	Me_3SnNMe_2 + C_6F_6	Me_3SnF + $C_6F_5NMe_2$	221,222
(ii)	Me_3SnNMe_2 + $CF_2 = CFCl$	Me_3SnF + $CFCl = CFNMe_2$	221,222
(iii)	Me_3SnNMe_2 + $HN(CF_3)_2$	Me_3SnF + $CF_3NHCF_2NMe_2$	221,222
(iv)	Bu_3SnNEt_2 + RX	Bu_3SnX + $RNMe_2$ *	313
	R = $PhCH_2$, X = Cl,Br; R = $CH_2{=}CHCH_2$, X = Cl,Br,I		
(v)	$Me_3SnN<$ + $X{-}B<$	Me_3SnX + $>N{-}B<$	
	X = F, ^{n}Bu, Ph, OMe		221,222
	Cl		221,222,223
	Br		224
	H		219,222
(vi)	$2Me_3SnNMe_2$ + $(AlEt_3)_2$	$2Me_3SnEt$ + $(Et_2AlNMe_2)_2$	221,222
(vii)	$Me_3Sn{-}N<$ + F-M	Me_3SnF + $>N{-}M$	
	M = As, Sb		221,222
	P		221,222,225
	S^{VI}		228
(viii)	$Me_3Sn{-}N<$ + $Cl{-}Si{\equiv}$	Me_3SnCl + $>N{-}Si{\equiv}$	221,222,226,227
(ix)	Et_3SnNMe_2 + Cl_2	Et_3SnCl + $ClNMe_2$	221,222
(x)	$R_3SnN<$ + $(R'_2CO)_2O$	$R_3SnOCOR'$ + $>NCOR'$	221,222,229,230
(xi)	R_3SnNMe_2 + R'COOR"	R_3SnOR'' + $R'CONMe_2$	221,222,229

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

$$Bu_3SnNEt_2 + BuX \longrightarrow Bu_3SnX + BuNEt_2, Bu_2NEt, Bu_3N, Et_3N$$

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)



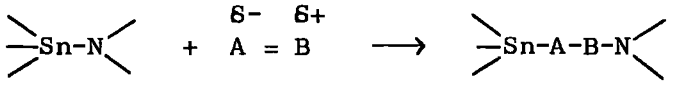
$$Et_3SnNMe_2 + CH_2{=}\underset{Me}{\underset{|}{C}}{-}COOMe \longrightarrow Et_3SnCH_2\underset{O}{\underset{\|}{C}}Me + Me\underset{O}{\underset{\|}{C}}NMe_2 \qquad 1.51$$

Attempted reaction of trimethyltin dimethylamide with chlorides containing hydrogen may lead to dehydrochlorination and formation of the complex $Me_3SnCl.HNMe_2$, 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.

$$Cl_2HIr^{III}(PPh_3)_3 + Me_3SnNMe_2 \longrightarrow ClIr^{I}(PPh_3)_3 + Me_3SnCl.HNMe_2 \qquad 1.52$$

$$^{n}BuCl \xrightarrow{Me_3SnNMe_2} \underset{5.2\%}{cis\text{-}MeCH{=}CHMe} + \underset{88.5\%}{trans\text{-}MeCH{=}CHMe} + \underset{6.3\%}{EtCH{=}CH_2} \qquad 1.53$$

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



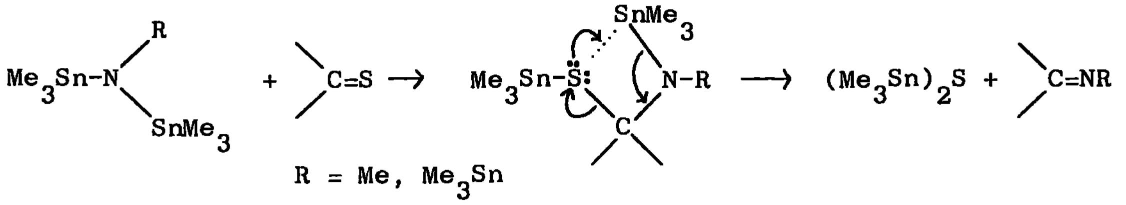
$$>Sn{-}N< + \overset{\delta-}{A} = \overset{\delta+}{B} \longrightarrow >Sn{-}A{-}B{-}N< \qquad 1.54$$

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'.[233] 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.[235] 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[235,240,241] (Eqn. 1.55).



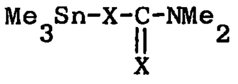
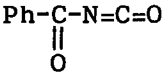
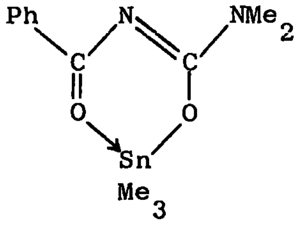
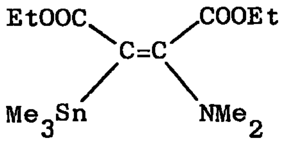
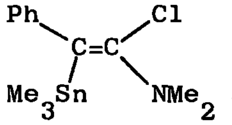
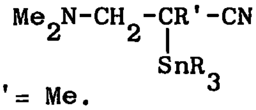
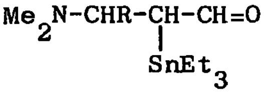
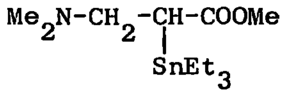
R = Me, Me_3Sn

1.55

Amine groups attached to the thiocarbonyl moiety lower the reactivity; thus while thiobenzophenone, $Ph_2C=S$, reacts at room temperature, N,N'-dimethyl thiobenzamide, $PhCS.NMe_2$, requires forcing conditions and N,N,N',N'-tetramethylthiourea, $(NMe_2)_2C=S$, does not react at all.[241] This reaction was also investigated for OCS, CS_2 and 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

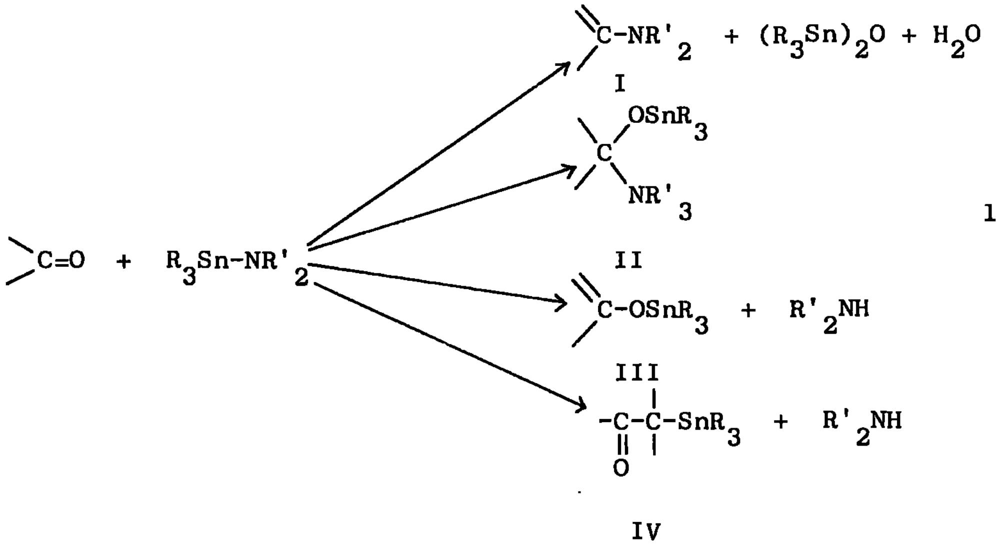
Reactants	Products	Reference
(i) Me_3SnNMe_2 + CX_2 X = O,S	 $Me_3Sn\text{-}X\text{-}\underset{\displaystyle X}{\overset{}{C}}(=X)\text{-}NMe_2$	130,177
(ii) Me_3SnNMe_2 + $O=C=S$	$Me_3Sn\text{-}S\text{-}CO\text{-}NMe_2$	235
(iii) Me_3SnNMe_2 + $CH_2=C=O$	$Me_3SnCH_2\text{-}CO\text{-}NMe_2$	177,232
(iv) Me_3SnNMe_2 + $Ph\text{-}C\equiv N$	$Me_3Sn\text{-}N=CPh\text{-}NMe_2$ *	176,177
(v) Me_3SnNMe_2 +  $Ph\text{-}C(=O)\text{-}N=C=O$		236
(vi) Me_3SnNMe_2 + SO_2	$Me_3Sn\text{-}O\text{-}SO\text{-}NMe_2$	177
(vii) Me_3SnNMe_2 + $EtOOC\text{-}C\equiv C\text{-}COOEt$		238,239
(viii) Me_3SnNMe_2 + $PhC\equiv CCl$		238,239
(ix) R_3SnNMe_2 + $CH_2=CR'CN$ R=Me,R'= H; R = Et, R'= Me.	 $Me_2N\text{-}CH_2\text{-}CR'(SnR_3)\text{-}CN$	238,239
(x) Et_3SnNMe_2 + $R\text{-}CH=CH\text{-}CH=O$ R = H, Me Ph.	 $Me_2N\text{-}CHR\text{-}CH(SnEt_3)\text{-}CH=O$	238,239
(xi) Et_3SnNMe_2 + $CH_2=CH\text{-}COOMe$	 $Me_2N\text{-}CH_2\text{-}CH(SnEt_3)\text{-}COOMe$	238,239
(xii) Me_3SnNMe_2 + $(CF_3)_2C=O$	$Me_3Sn\text{-}O\text{-}C(CF_3)_2\text{-}NMe_2$	243

* Reaction does not occur with alkyl cyanides unless they contain electron-withdrawing groups (e.g. CCl_3CN [237]). If α-hydrogen is present, protolysis may occur. $^{t}BuCN$ does not react at all.[237]

usual insertion products.[241] However, other workers have found that if bis(tributylstannyl)amines are used, elimination of the oxide may occur[242] (Eqn. 1.56).

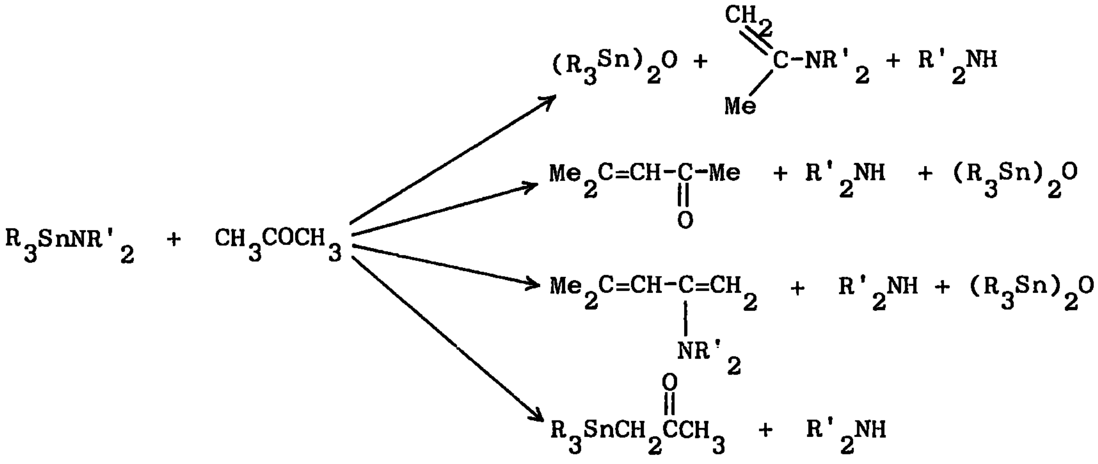
$$\text{R-CO-R'} + (\text{Bu}_3\text{Sn})_2\text{NEt} \longrightarrow \text{RR'C=NEt} + (\text{Bu}_3\text{Sn})_2\text{O} \qquad 1.56$$

$$\text{R} = \text{Me,Et, R'} = \text{C}_{1-4}\text{alkyl; R} = \text{Ph,R'} = \text{Me, }{}^{i}\text{Pr.}$$

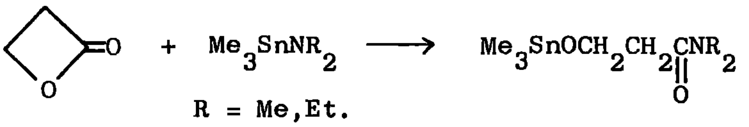


1.57

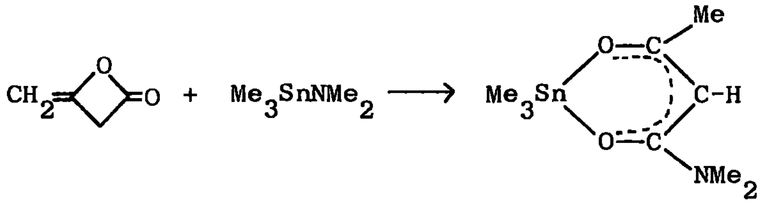
The reaction of mono-trialkylstannylamines with aliphatic ketones and aldehydes has also been shown to be complex.[244-7] The possible reaction products are shown in Equation 1.57. The distribution of products seems to be very sensitive to substituent effects (both steric and electronic),[246] and is 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.[247] 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.[192,245] The distribution of products is again sterically sensitive (to the substituents on the tin amine) (Eqn. 1.58).



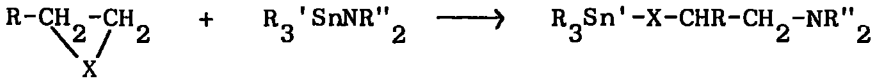
Insertion reactions also occur with ring-systems containing polar bonds, with opening of the ring as a result (Equations 1.59-61).



R = Me,Et. (237,248) 1.59



(249) 1.60



(237,250) 1.61

X = S,O; where X = O, $LiNEt_2$ was used as catalyst.

$$2(Me_3Sn)_3N + S_4N_4 \longrightarrow 3Me_3Sn\text{-}N{=}S{=}N\text{-}SnMe_3 + S \qquad 1.62$$

$$4Me_3SnNMe_2 + S_4N_4 \longrightarrow 2(Me_2N)_2S + 2Me_3Sn\text{-}N{=}S{=}N\text{-}SnMe_3 \qquad 1.63$$

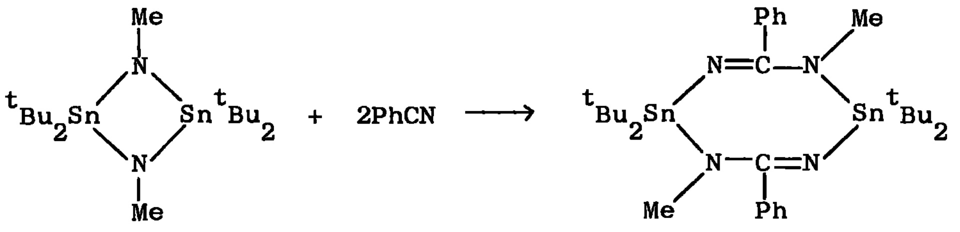
A basically similar, although rather more complex, reaction is that with the sulphur-nitrogen cage, S_4N_4.[226,251,254] (Eqns 1.62,63).

The photo-cleavage of the Sn-N bond in primary stannylamines has also been studied.[252] The overall reaction (which is a multi-step free-radical process) is given in Equation 1.64.

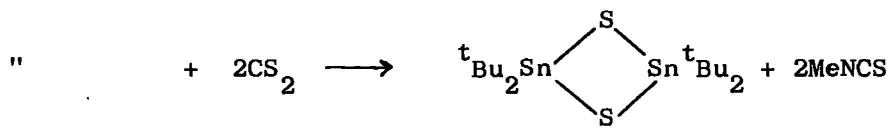
$$2Me_3SnNEt_2 \xrightarrow[C_6H_6]{h\nu} Me_3Sn{-}SnMe_3 + Et_2NH + MeCH{=}NEt \qquad 1.64$$

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 $R_3SnNR'_2 > R_3SnNR'COR'' > R_3SnNR'SO_2R''$ has been demonstrated,[141] in agreement with the suggestion that the dominant factor in these reactions is the nucleophilicity of the nitrogen atom.

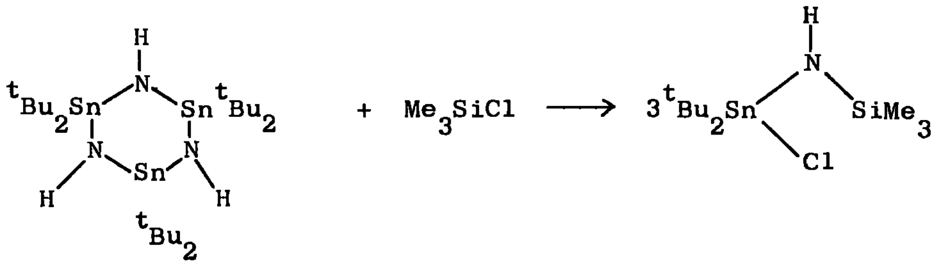
Generally speaking, heterocycles containing the Sn-N bond show much the same types of reaction as the simple amines. Some examples are given in Equations 1.65-68. Ring expansion and ring cleavage are observed, but the basic chemistry is essentially that found for the stannylamines.



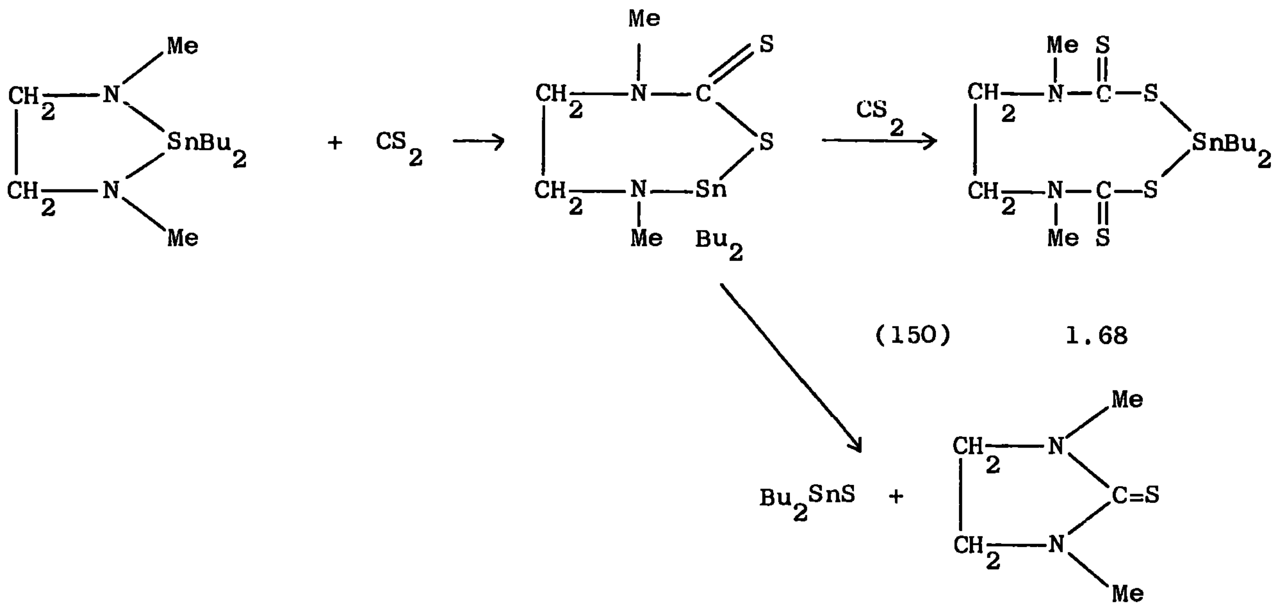
(139) 1.65



(139) 1.66



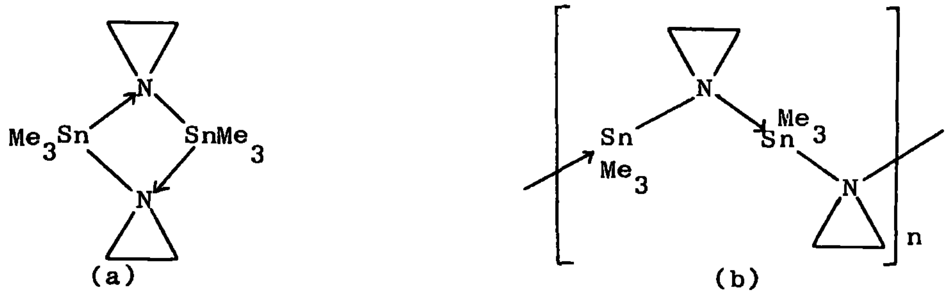
(138,139) 1.67



(150) 1.68

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[131] 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,[154] 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_3Sn 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



(a) (b)

Figure 1-22

being only moderately sensitive to atmospheric moisture. A Mössbauer study,[154] on this and its homologues derived from cyclic amines of three to seven members, shows a considerably higher ^{119m}Sn quadrupole splitting (~2.3mm.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)[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,[160] and in the latter the lowering of ν (C=O) relative to the parent formamide has been ascribed to strong C=O→Sn interactions[255] (Fig. 1-23a). Intermolecular coordination of this type has been confirmed by Mössbauer studies,[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

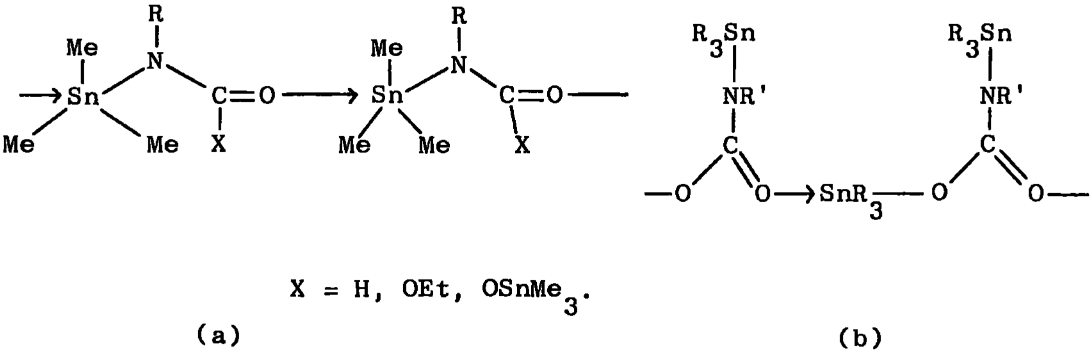


Figure 1-23

N-triorganostannylsulphinamides.[159] A similar polymeric structure has been obtained by X-ray diffraction for N-(trimethylstannyl)-N-nitro-methylamine[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.

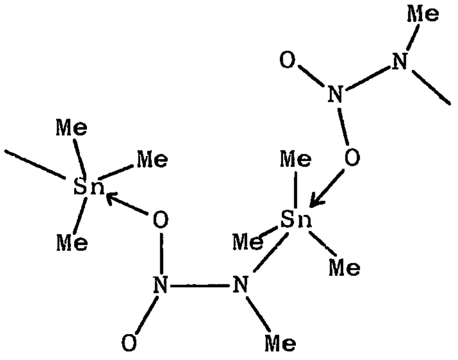


Figure 1-24

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).

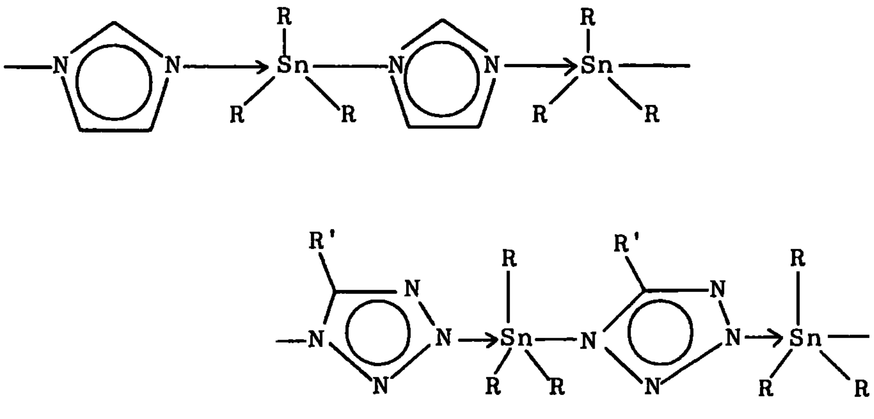


Figure 1-25

The 5-coordinate structure has been confirmed by Mössbauer work.[258,259] The degree of association appears to be dependent on the ring substituents.[185,256] The 1,3-arrangement of nitrogens is important; pyrole, pyrazole, and 1,2,5-triazole derivatives are monomeric and reactive.[140,185]

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[108,109] and similar compounds, although the effect of delocalisation over the almost planar system[260] 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 σ-bond (Fig. 1-26a), or may involve (p→d)π-bonding (Fig. 1-26b). In the former case a tetrahedral

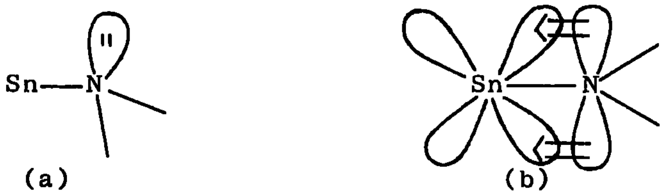


Figure 1-26

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[82] that sufficient overlap can occur in pyramidal systems for substantial (p→d)π-bonding to be at least possible). Structures planar at nitrogen have been observed for trisilylamine and several other silyl amines,[261,262] and also for the very unstable trigermylamine[263] (mostly by electron-diffraction techniques). (p→d)π-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[262] that this is because 2p-4d overlap is less favoured than 2p-3d, with a weaker π-bond as a result. On this basis, N-Sn (p→d)π-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 $(Me_3Sn)_3N$[264] and $^tBu_3SnNH_2$[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 $Sn(NEt_2)_4$, which shows the bonds at nitrogen to be nearly coplanar.[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 π-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.$(Me_3Sn)_3N$[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 $(Me_3Sn)_3N$[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 $\nu(Sn\text{-}N)$ = 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 $(Bu_3Sn)_2NEt$, several tributylstannylamines Bu_3SnNRR', and some bis(dialkylamino) dibutyltins $Bu_2Sn(NR_2)_2$.[268] Assignments have also been made for a number of hexaalkyldistannazanes $(R_3Sn)_2NH$.[269]

Generally, for $R_3SnNR'_2$ $\nu(Sn\text{-}N)$ falls in the region 560-600cm^{-1}. For $R_2Sn(NR'_2)_2$ $\nu_{as}(SnN_2)$ ~690 cm^{-1}, $\nu_s(SnN_2)$ ~600 cm^{-1}, and for $(R_3Sn)_2NR'$ $\nu_{as}(NSn_2)$ ~700cm^{-1}, $\nu_s(NSn_2)$ ~590 cm^{-1}. These values may be compared with $\nu_{as}(NSi_2)$ 900-1000cm^{-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_3SnNMe_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_3SnNMe_2[277]). Indeed, the apparent absence of this feature in the spectra of the N-methylaminostannanes lead to the proposal[153] that this was due to rapid amine exchange, even at low temperatures. A detailed study,[271] 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.[272]

Detailed ^{1}H-NMR studies have been carried out on the series $R_nSn(NEt_2)_{4-n}$ R= Me, Ph, n = 0-3;[273] $Me_{4-n}Sn(NEt_2)_n$ n = 1-3;[153] $Me_{4-n}Sn(NR_2)_n$ R = Me, Et, n = 1-4;[272] and $Me_{3-n}Sn(NMe_2)_nN(SiMe_3)_2$ n = 0-2.[153]

^{119}Sn-NMR has also been exploited,[272] 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→d) π-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_3MNMe_2 and $M(NMe_2)_4$ (M = 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,[258,259] N-organostannyl cyclic amines,[154] tin(iv) phthalocyanines and porphins[275,276] 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 $Sn(NMe_2)_4$ 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,[282,283,284] or the change in ^{1}H-chemical shift for similar solutions of chloroform.[282,285] The amine series $Me_2M(NEt_2)_2$[282,284,285] and $(Me_3M)_3N$[284] (M = Si, Ge, Sn) have been compared in this way, and it is generally found that basicity increases Si $<$ Ge $<$ Sn. Indeed, $(Me_3Si)_3N$ was found to have no basic properties at all, whereas $(Me_3Sn)_3N$ was the strongest base examined (it even reacted with Me_3SnBr to form an ammonium salt, $(Me_3Sn)_4N^+Br^-$).[284] This would seem to argue for a marked decrease in π-bonding down the group.

Reports of other physical properties are rather rarer. Dipole moments for a series of amino-stannanes have been measured.[204] The partial moment of $Sn-NEt_2$ was calculated as 1.7D. The molecular refraction of the Sn-N bond in N-tributylstannylsuccinimide has been calculated as 4.02.[288]

Thermochemical data are also sparse. The Sn-N bond energy has been derived from the heat of hydrolysis of liquid Me_3SnNMe_2[286] and found to be ~40 $kcal.mole^{-1}$; a separate determination (from the heats of combustion and formation) for Et_3SnNEt_2[287] gave the value 62 $kcal.mole^{-1}$. These may be compared with the values for Et_3SiNEt_2 (90kcal.$mole^{-1}$) and Et_3GeNEt_2 (80 kcal.$mole^{-1}$),[287] showing the comparative weakness of the Sn-N bond.

ii) <u>Compounds containing Tin bonded to 2-covalent Nitrogen.</u>

The N-organostannylmethyleneamines (or ketimines) $R_{4-n}Sn(N=CR'_2)_n$ 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 Ph_2CNSnR_3 R = Me, Ph,[290] Bu[298]; $^tBu_2CNSnMe_3$[291]; $(p\text{-}MeC_6H_4)_2CNSnMe_3$;[291] $Me_{4-n}Sn(N{=}C(CF_3)_2)_n$ n = 1-4;[291,292] and $(Ph_2CN)_4Sn$[293] (see also this work). The di-p-tolylketimine derivative has also been prepared by transamination[291] (Eqn. 1.70).

$$R_{4-n}SnCl_n \;+\; nLiN=CR'_2 \longrightarrow R_{4-n}Sn(N{=}CR'_2)_n \;+\; nLiCl \qquad 1.69$$

$$Me_3SnNMe_2 \;+\; HN{=}C\ (C_6H_4p\text{-}Me)_2 \longrightarrow (p\text{-}MeC_6H_4)_2CNSnMe_3 \;+\; HNMe_2 \qquad 1.70$$

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).

$$Me_{4-n}Sn(NCR_2)_n \;+\; nHA \longrightarrow Me_{4-n}SnA_n \;+\; nHNCR_2 \qquad 1.71$$

n = 1, A = OH, $-C{\equiv}CPh$, C_6F_5.[291]

n = 2, A = Cl[294]

The reaction of HCl with $Me_2M\ (N{=}C(CF_3)_2)_2$, M = 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 M-Sn bonded species[291] (Eqns. 1.72, 1.73).

$$Me_3SnN{=}C(CF_3)_2 + \pi\text{-}C_5H_5Mo(CO)_3H \longrightarrow C_5H_5Mo(CO)_3SnMe_3 + HNC(CF_3)_2 \quad 1.72$$

$$Me_3SnN{=}C{}^tBu_2 + trans\text{-}(PPh_3)_2PtClH \longrightarrow trans\text{-}(PPh_3)_2PtClSnMe_3 + HNC{}^tBu_2 \quad 1.73$$

$$Me_3SnN{=}C(CF_3)_2 + trans\text{-}(PPh_3)_2PtClH \longrightarrow \underset{I}{trans\text{-}(PPh_3)_2PtSnMe_3.N{=}C(CF_3)_2}$$

$$+ \underset{II}{(PPh_3)_2Pt.HN{=}C(CF_3)_2} + Me_3SnCl \quad 1.74$$

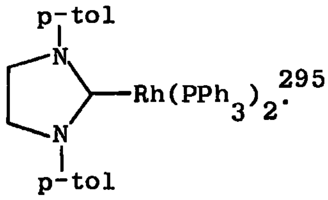
The presence of halogens in the system may lead to competing reactions involving elimination of trialkyltin halide[291] (Eqn. 1.74). Product I is the same as that obtained by reaction with the zero-valent platinum complex in Equation 1.75, where insertion of the transition metal into the Sn-N bond occurs.[296]

$$(Ph_3P)_3Pt + Me_3SnN{=}C(CF_3)_2 \longrightarrow Me_3Sn\text{-}Pt(PPh_3)_2\text{-}N{=}C(CF_3)_2 + PPh_3 \quad 1.75$$

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

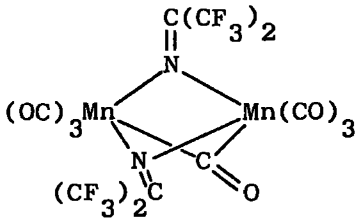
$$Me_3SnN{=}CR_2 + LM\text{-}Cl \longrightarrow Me_3SnCl + LM\text{-}N{=}CR_2 \quad 1.76$$

R=CF_3, LM= $(\pi\text{-}C_5H_5)_2TiCl$,[291] cis-$(PPh_3)_2PtCl$,[291,296]



R = Ph, LM = cis-$(PPh_3)_2PtCl$.[291]

$R_3SnN{=}C(CF_3)_2$ + $Mn(CO)_5Br$ $\longrightarrow$



+ R_3SnBr 1.77

R = Me, Et.

$$Me_3Sn\text{-}N{=}C(CF_3)_2 + Br_2 \longrightarrow Me_3SnBr + BrN{=}C(CF_3)_2 \quad 1.78$$

The Sn-N bond is also cleaved by bromine[291] (Eqn. 1.78).

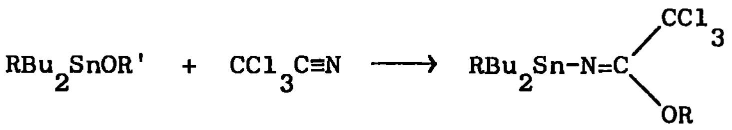
Ketiminotin compounds also react with unsaturated 1,2-dipoles, in the same manner as other Sn-N compounds, although they are less reactive than the aminostannanes.[291] Reactivity has been found to decrease in the sequence $Me_3SnNR_2 > Me_3SnN{=}CPh_2 > Me_3SnN{=}C(CF_3)_2$. The reactions are summarised 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).

$$\begin{tikzcd} R_3SnN{=}CR'_2 \ + \ X{=}Y \arrow[r, "slow"] \arrow[d, "H_2O", "Trace"'] & R_3Sn\text{-}X\text{-}Y\text{-}N{=}CR'_2 \\ H\text{-}N{=}CR'_2 \ + \ X{=}Y \arrow[r, "fast"] & H\text{-}X\text{-}Y\text{-}N{=}CR'_2 \arrow[u, "R_3Sn\text{-}N{=}CR'_2\ (\leftarrow HN{=}CR'_2)"'] \end{tikzcd} \qquad 1.79$$

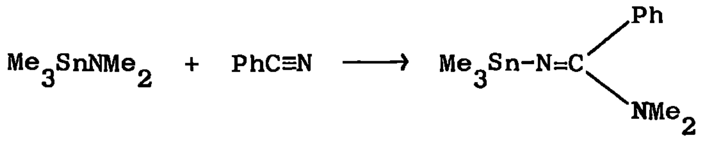
N-metallated ketimines are of particular interest since their structures should reflect the extent of N→M dative π-bonding in the M-N=C bond angle. This has been followed by a number of spectroscopic techniques, and the results are discussed in Chapter 2. The crystal structure of $(Ph_2CN)_4Sn$ has been 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).



$$RBu_2SnOR' + CCl_3C{\equiv}N \longrightarrow RBu_2Sn\text{-}N{=}C(CCl_3)(OR) \qquad (253,303) \qquad 1.80$$

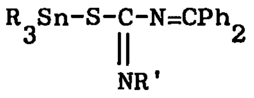
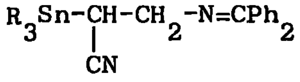
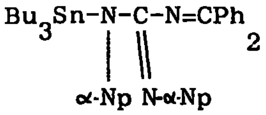
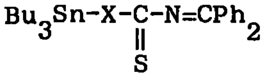
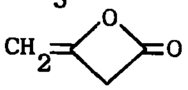
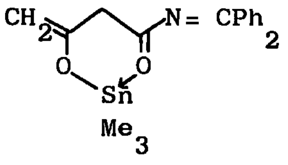
R = Bu, OMe; R' = Me, Bu_3Sn.



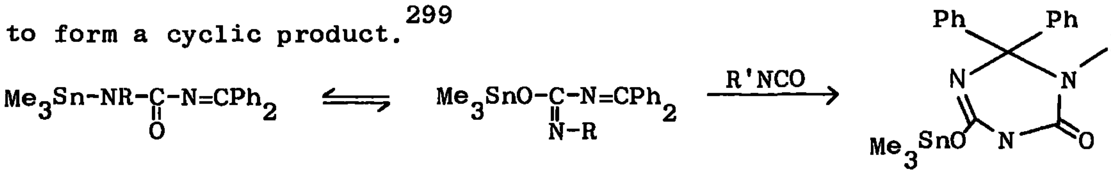
$$Me_3SnNMe_2 + PhC{\equiv}N \longrightarrow Me_3Sn\text{-}N{=}C(Ph)(NMe_2) \qquad (176,177) \qquad 1.81$$

TABLE 6

Reactions of N-Stannylketimines with Unsaturated Species

	Reactants	Products	Reference
(i)	$R_3SnN=CR'_2 + R''NCO$	$R_3Sn-NR''-CO-N=CR'_2$ *	
		R = Me, R' = Ph, CF_3, R" = Ph, Me	291,299
		R = Bu, R' = Ph, R" = Me, Et, Bu, Ph	298
(ii)	$R_3SnN=CPh_2$ + R'NCS	 $R_3Sn-S-\underset{NR'}{\underset{\Vert}{C}}-N=CPh_2$	298,299
		R=Me, Bu R' = Me, Ph	
(iii)	$R_3SnN=CPh_2 + CH_2=CH-CN$	 $R_3Sn-\underset{CN}{\underset{\vert}{C}H}-CH_2-N=CPh_2$	291,298
		R = Me, Bu.	
(iv)	$Bu_3SnN=CPh_2$ + α-Np-N=C=N-α-Np	 $Bu_3Sn-\underset{\alpha\text{-}Np}{\underset{\vert}{N}}-\underset{N\text{-}\alpha\text{-}Np}{\underset{\Vert}{C}}-N=CPh_2$	298
(v)	$Bu_3SnN=CPh_2$ + PhN=S=O	$Bu_3Sn-NPh-SO-N=CPh_2$	298
(vi)	$Bu_3SnN=CPh_2 + SO_2$	$Bu_3Sn-O-SO-N=CPh_2$	298
(vii)	$Bu_3SnN=CPh_2 + CCl_3C\equiv N$	$Bu_3Sn-N=C(CCl_3)-N=CPh_2$	298
(viii)	$Bu_3SnN=CPh_2$ + X=C=S	 $Bu_3Sn-X-\underset{S}{\underset{\Vert}{C}}-N=CPh_2$	298
		X = O,S	
(ix)	$Bu_3SnN=CPh_2$ + RR'C=O	$Bu_3Sn-O-CRR'-N=CPh_2$	298
	R=H, R'= CCl_3, CBr_3, Me, Et, ^{i}Pr, ^{n}Pr, Ph; R=R'=CCl_3; R=CCl_2F, R'=$CClF_2$		
(x)	$Me_3SnN=CPh_2$ + 		300

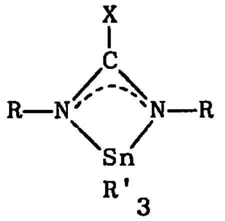
*: Further reaction with another mol. of RNCO gives (4π + 2π) cycloaddition to form a cyclic product.[299]



$Me_3Sn-NR-\underset{O}{\underset{\Vert}{C}}-N=CPh_2 \rightleftharpoons Me_3SnO-\underset{N-R}{\underset{\Vert}{C}}-N=CPh_2 \xrightarrow{R'NCO}$

The isothiocyanate system gives only the normal insertion product.

The latter is an example of an unsymmetrically substituted amidine; it appears to be monomeric[177] and has also been prepared from the N-lithioamidine and Me_3SnCl.[304] Although the symmetrically substituted amidino-tins seem to have a 5-coordinate, probably delocalised, structure[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



X = R″, NR″$_2$.

Figure 1-27

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, -N=N-, and the nitroso-derivatives, -N=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.[305]

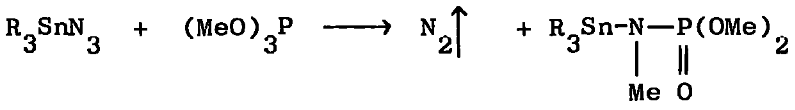
Nitroso-trimethyl- and triphenylstannanes have been prepared as blue and dark green solutions in THF by the reaction of triorganostannyllithiums with nitrosyl chloride at low temperatures. The solutions decompose at $>-10^{\circ}C$. Their UV and IR spectra were recorded together with those of the corresponding silicon, germanium, and lead compounds.[306]

Other examples of the Sn-N=X system are the phosphinimines, $R_3Sn\text{-}N{=}PR'_3$. 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.

$$R_3SnN_3 + R'_3P \xrightarrow{\Delta} R_3Sn\text{-}N{=}PR'_3 + N_2\uparrow \qquad 1.82$$

$R = Ph,\ R' = Ph,\ {}^{n}octyl,\ {}^{n}Bu.$[309]

$R = Et,\ {}^{n}Bu,\ R' = Ph,\ {}^{n}Bu,\ NMe_2.$[197]



$$R_3SnN_3 + (MeO)_3P \longrightarrow N_2\uparrow + R_3Sn\text{-}\underset{\displaystyle Me}{\underset{|}{N}}\text{—}\underset{\displaystyle O}{\underset{\|}{P}}(OMe)_2 \qquad 1.83$$

$$2Me_3SnN_3 + R_3P \longrightarrow Me_4Sn + Me_2Sn(N_3)\text{-}N{=}PR_3 + N_2\uparrow \qquad 1.84$$

$R = Me,\ Et,\ Ph.$

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)[309] and thermally stable. Their reactions, in so far as they have been investigated,[197] resemble those of the stannylamines (Eqns. 1.85-87).

$$R_3Sn\text{-}N{=}PR'_3 + 2HCl \longrightarrow R_3SnCl + R_3'P{=}NH_2{}^+Cl^- \qquad 1.85$$

$$R_3Sn\text{-}N{=}PR'_3 + 2R''I \longrightarrow R_3SnI + R'_3P{=}NR''_2{}^+I^- \qquad 1.86$$

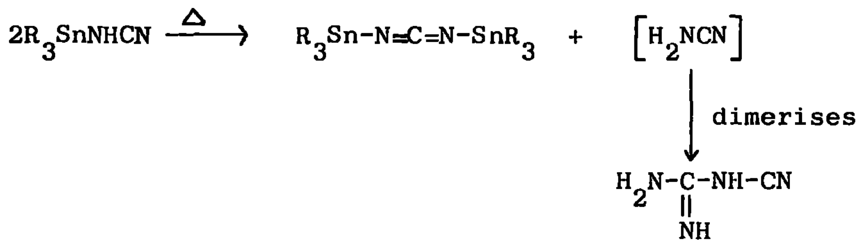
$$R_3Sn\text{-}N{=}PR'_3 + R''OH \longrightarrow R_3SnOR'' + R'_3P{=}NH \qquad 1.87$$

Some ^1H-NMR and IR data have been reported,[308,309] 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.[308]

No N-stannyl sulphinimines, $R_3Sn\text{-}N{=}SR'_2$ appear to have been reported, although the N,N'-bis(trialkylstannyl)sulphur diimides, $R_3Sn\text{-}N{=}S{=}N\text{-}SnR_3$, are well known.

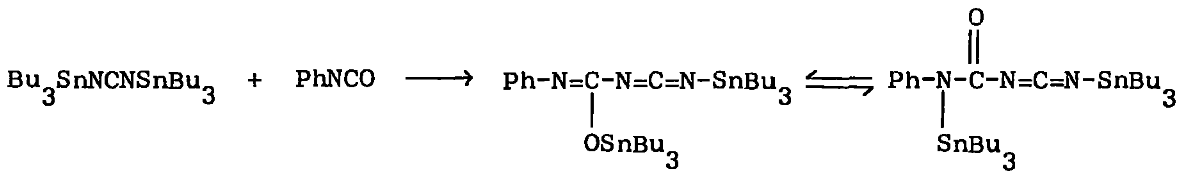
The latter compounds are an example of Sn-N derivatives containing cumulated double bonds, although in this instance the system is bent at sulphur, due to the sulphur lone pair. Linear heterocumulenes include the N-stannylketenimines, and the carbo-diimides.

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-chalcogen. 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[314,315] (Eqn. 1.88).



$$2R_3SnNHCN \xrightarrow{\Delta} R_3Sn\text{-}N{=}C{=}N\text{-}SnR_3 + \underset{\underset{\displaystyle H_2N\text{-}\underset{\underset{\displaystyle NH}{\|}}{C}\text{-}NH\text{-}CN}{\downarrow\ \text{dimerises}}}{[H_2NCN]}$$

1.88



$$Bu_3SnNCNSnBu_3 + PhNCO \longrightarrow Ph\text{-}N{=}\underset{\underset{\displaystyle OSnBu_3}{|}}{C}\text{-}N{=}C{=}N\text{-}SnBu_3 \rightleftharpoons Ph\text{-}\underset{\underset{\displaystyle SnBu_3}{|}}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}N{=}C{=}N\text{-}SnBu_3$$

1.89

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 π-system, although they do show some reactions similar to those of the more typical Sn-N systems, for example that with phenyl isocyanate[316] (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[319] (Fig. 1-28), further emphasising the 'pseudochalcogen' 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 of trialkylstannyl methoxides or acetates with the trimethylsilyl analogue.[323]

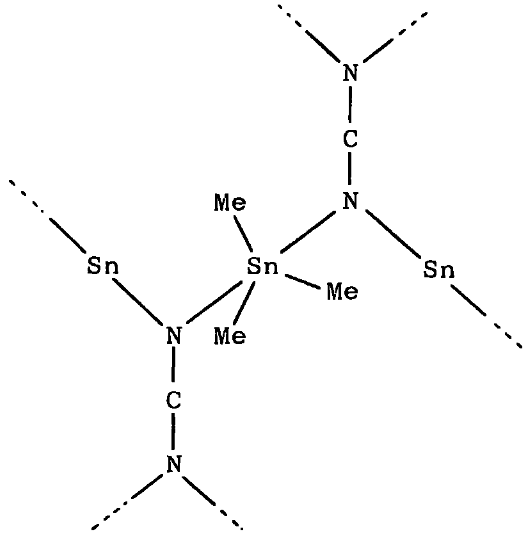
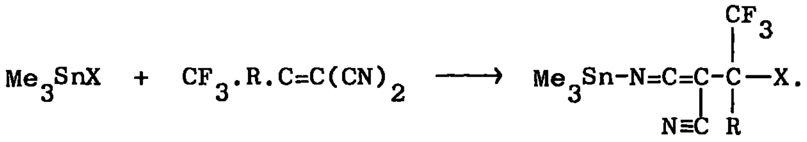
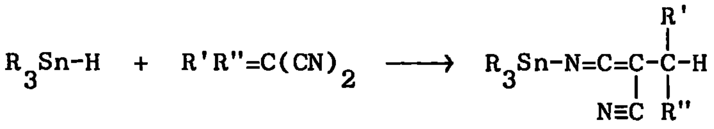


Figure 1-28



$$Me_3SnX + CF_3.R.C{=}C(CN)_2 \longrightarrow Me_3Sn{-}N{=}C{=}\underset{N\equiv C}{C}{-}\overset{CF_3}{\underset{R}{C}}{-}X. \qquad (322) \qquad 1.90$$

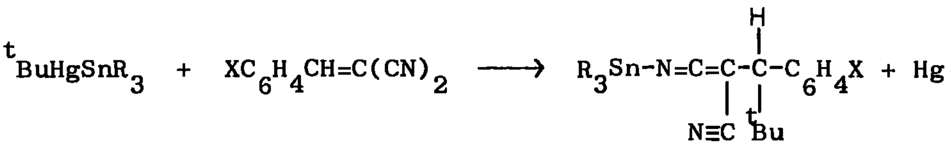
$R = CF_3$, X = SMe, $AsMe_2$, C_3H_5, C_4H_7; $R = CF_2Cl$, X = SMe



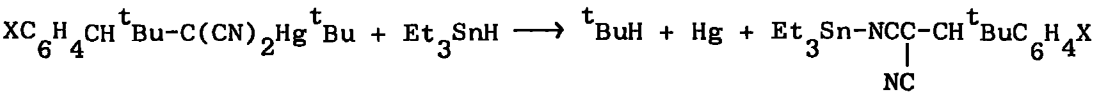
$$R_3Sn{-}H + R'R''{=}C(CN)_2 \longrightarrow R_3Sn{-}N{=}C{=}\underset{N\equiv C}{C}{-}\overset{R'}{\underset{R''}{C}}{-}H \qquad (320) \qquad 1.91$$

R = Et,Bu; R'= H,R" = Me, Ph,OEt, Furyl, p-XC_6H_4(X = Me_2N, MeO,Cl,NO_2);

R' = R" = Me,Ph.



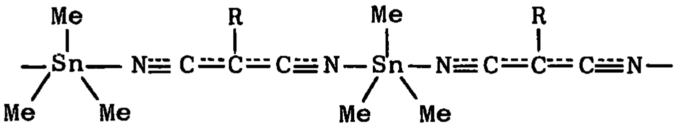
$$^tBuHgSnR_3 + XC_6H_4CH{=}C(CN)_2 \longrightarrow R_3Sn{-}N{=}C{=}\underset{N\equiv C}{C}{-}\overset{H}{\underset{^tBu}{C}}{-}C_6H_4X + Hg \quad (323) \quad 1.92$$



$$XC_6H_4CH^tBu{-}C(CN)_2Hg^tBu + Et_3SnH \longrightarrow {}^tBuH + Hg + Et_3Sn{-}NC\underset{NC}{C}{-}CH^tBuC_6H_4X$$

(323) 1.93

The products are involatile viscous oils or white solids. The fluorinated materials are stable to air and moisture,[322] although the others are moisture sensitive. They decompose above 50°C. The cryoscopic molecular weights (in benzene) increase with concentration,[320,322] suggesting 5-coordinate tin with association through the cyanide group, perhaps with a delocalised π -system (Fig. 1-29).



<u>Figure 1-29</u>

The non-fluorinated compounds are hydrolysed by alcohols,[321,323] and react with alkyl and acyl halides and bromine[321] (Eqn. 1.94).

$$R'CH_2C(CN){=}C{=}NSnR_3 \; + \; R''X \longrightarrow R'CH_2C(CN){=}C{=}N\text{-}R'' \; + \; R_3SnX \qquad 1.94$$

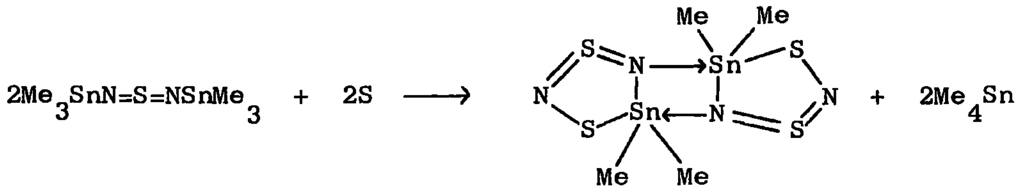
$$R''\text{-}X = CH_2{=}CH\text{-}CH_2Br;\; CH_3CH{=}CH\text{-}CH_2Cl;\; Ph\text{-}CH_2Cl;\; PhCOCl;\; CH_3COCl;\; Br_2$$

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[226,251,254] (Eqn. 1.95)

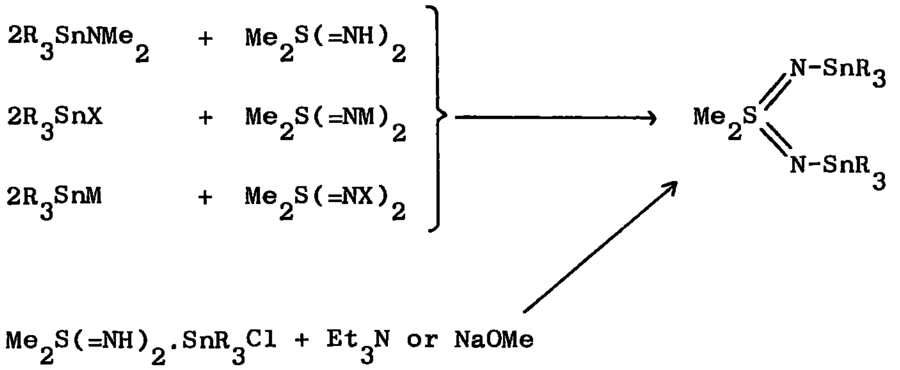
$$S_4N_4 \begin{array}{l} \xrightarrow{4Me_3SnNMe_2} 2(Me_2N)_2S + 2Me_3SnN{=}S{=}NSnMe_3 \\ \xrightarrow{2(Me_3Sn)_3N} 2S + 3Me_3SnN{=}S{=}NSnMe_3 \\ \xrightarrow{2(Me_3Sn)_2NSiMe_3} 2S + 2Me_3SnN{=}S{=}NSiMe_3 \\ \qquad\qquad\qquad\quad + Me_3SnN{=}S{=}NSnMe_3 \end{array} \qquad 1.95$$

The products are yellow crystalline solids, hydrolytically sensitive and soluble in organic solvents. They undergo exchange with chlorosilanes,[227,254] eliminating trimethyltin chloride, and on heating with sulphur give an unusual dimeric tin-nitrogen heterocycle[251] (Eqn. 1.96).



1.96

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

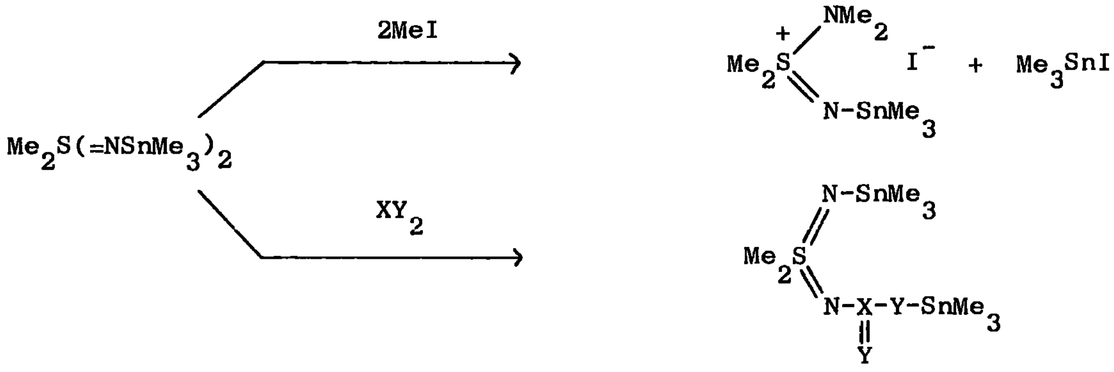


1.97

R = Me, Ph; X = Cl, Br; M = 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.

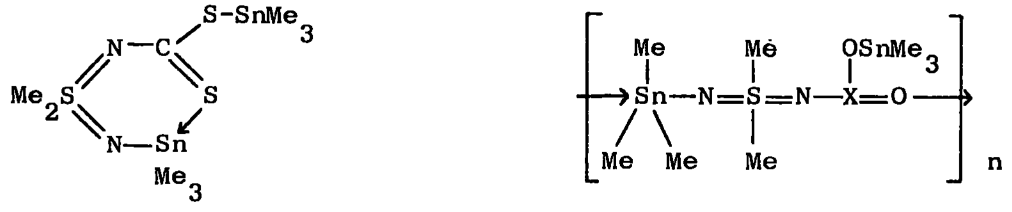
The di-substituted compounds are monomeric, colourless, crystalline solids. If R = Ph, the material is only slowly hydrolysed, and is generally unreactive. If R = Me, the material is very moisture sensitive, and reacts readily with alkyl halides and unsaturated species, towards which it is monofunctional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



1.98

$XY_2 = CO_2, CS_2, SO_2.$

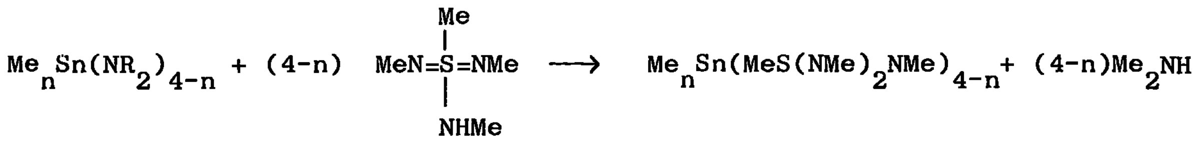
The latter reaction is believed to produce only the 1:1 adduct because the product is stabilised by association, either intramolecular ($XY_2 = CS_2$, Fig. 1-30(a)) or intermolecular ($XY_2 = CO_2, SO_2$, Fig. 1-30(b)).



(a) (b)

Figure 1-30

No derivatives of sulphur triimide, $S(=NH)_3$, appear to have been reported. However a number of methyl sulphur diimide amides are known.[325] The usual preparative routes for Sn-N compounds are followed (Eqns. 1.99-102).



$$Me_nSn(NR_2)_{4-n} + (4-n)\ MeN{=}\overset{\overset{Me}{|}}{\underset{\underset{NHMe}{|}}{S}}{=}NMe \longrightarrow Me_nSn(MeS(NMe)_2NMe)_{4-n} + (4-n)Me_2NH$$

$R = Me, Et;\quad n = 0\text{-}3$ 1.99

$$Me_nSnCl_{4-n} + (4-n)\ MeS(NMe)_2NMeNa \longrightarrow (MeS(NMe)_2NMe)_{4-n} + (4-n)NaCl \qquad 1.100$$

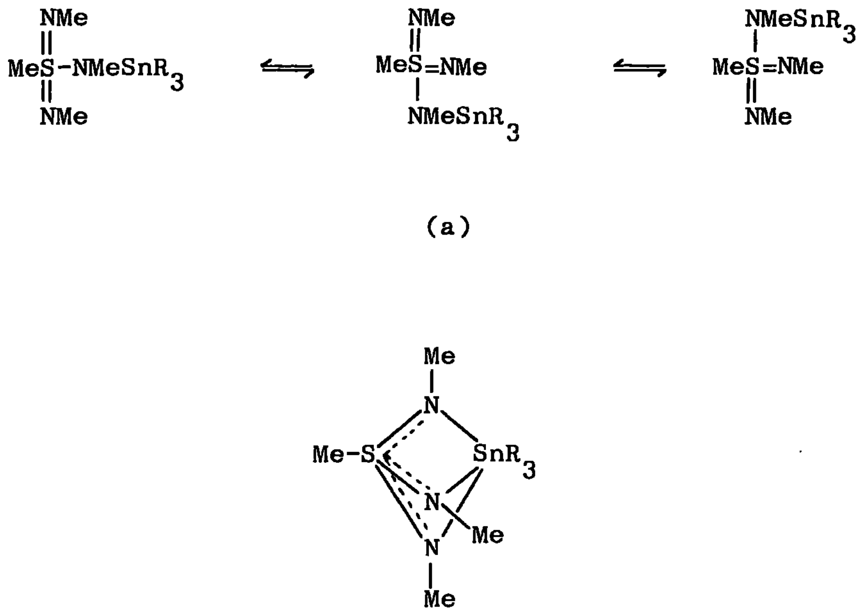
$$Ph_3SnCl + MeS(NMe)_2NMeNa \longrightarrow Ph_3Sn(MeS(NMe)_2NMe) + NaCl \qquad 1.101$$

but:

$$Ph_nSnCl_{4-n} + (4-n)MeS(NMe)_2NMeNa \longrightarrow Ph_nCl(MeS(NMe)_2NMe)_{3-n} + (3-n)NaCl$$

$n = 1,2$ 1.102

Except for $Me_3Sn(MeS(NMe)_2NMe)$, 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 ^1H-NMR spectra are interpreted in terms of a fluxional system (Fig. 1-31(a)), rather than the symmetrical delocalised form (Fig. 1-31(b)).



(a)

(b)

Figure 1-31

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,[5] and a review of the Group IIIB and IVB pseudohalides appeared at about the same time.[6] A more general survey of organometallic pseudohalides was published in 1967.[7]

Certain aspects of their structural properties, particularly the extent of N→Sn (p→d)π-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→M dative π-bonding (Fig. 1-32(a)), and would progressively approach linearity as the extent of N-M π-interaction increased (Fig.1-32(b)), 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 π -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 π -bonded and non-π-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)π -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 H_3GeNCS has a bent skeleton,[365] while Cl_3SiNCO and Cl_3SiNCS were considered to be linear at nitrogen.[367] In contrast to the electron diffraction study, the vibrational spectrum of $Si(NCO)_4$[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, H_3SiN_3 was found to be bent.[366]

Bonding possibilities for some metal pseudohalides.

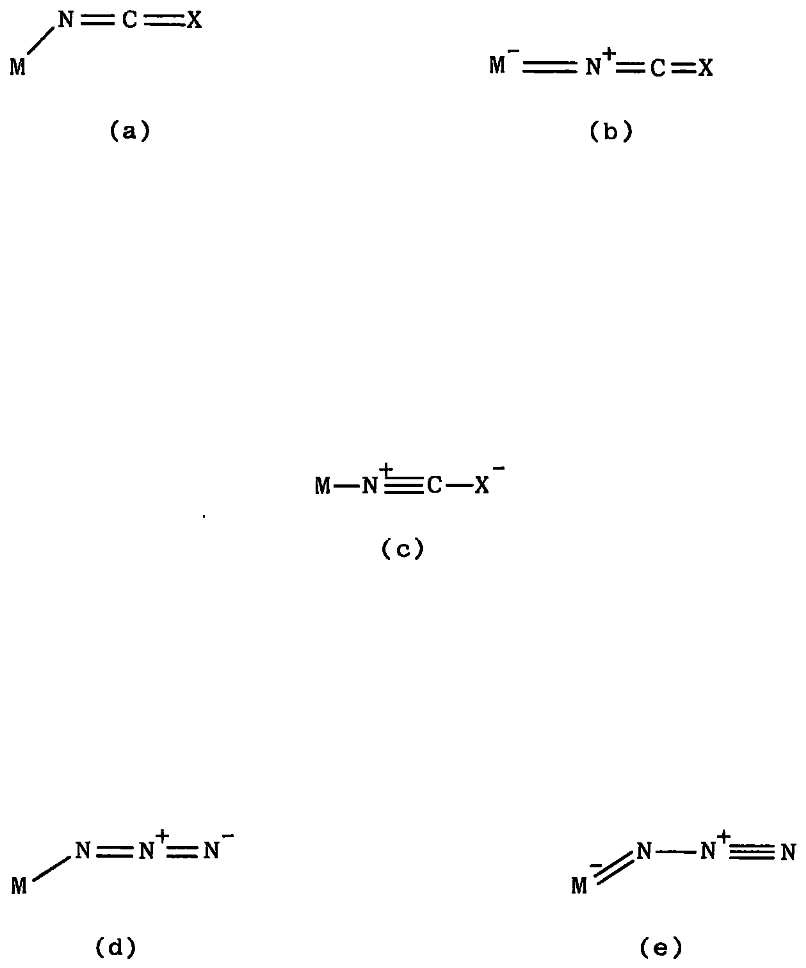


Figure 1-32

TABLE 7

Structural Data for Some Silicon & Germanium Pseudohalides

Compound	$M\hat{N}Y^{o}$	M-N Å	Δ(M-N) Å	Reference
H_3SiNCS [a]	linear	1.71	0.16	360
Me_3SiNCS [b]	154	1.78	0.09	362
Me_3SiNCO [b]	150	1.76	0.11	362
$Si(NCO)_4$ [b]	146.8	1.69	0.18	361
H_3GeNCO	141.3	1.83	0.09	363[b],364[a]
$H_3GeNCNGeH_3$ [b]	138	1.81	0.11	363
H_3GeN_3 [b]	119	1.85	0.07	363

a: Microwave spectrum; b: Electron diffraction.

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

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 Me_3SnNCS,[191] Ph_3SnNCS,[100] $Me_2Sn(NCS)_2$,[189,190] $Me_3SnN{=}C{=}NSnMe_3$,[319] $Me_3SnN(CN)_2$,[106] and $Me_2Sn(N(CN)_2)_2$.[106] 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[191] that this is due to the importance of valence bond extremes involving linearity at nitrogen (Fig. 1-33(a) and (b)), rather than (p→d) π-bonding. N→Sn π-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

The decrease in stability of the triphenyl monoazides down the group has been ascribed to a decrease in (p→d) π-bonding.[312] Infra-red spectroscopic studies[370] 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→M (p→d)π-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[371] on the azides Me_3MN_3 (M=Si,Ge,Sn,Pb), carried out in solution where the effect of association should be reduced, suggested that, whereas (p-d)π-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.

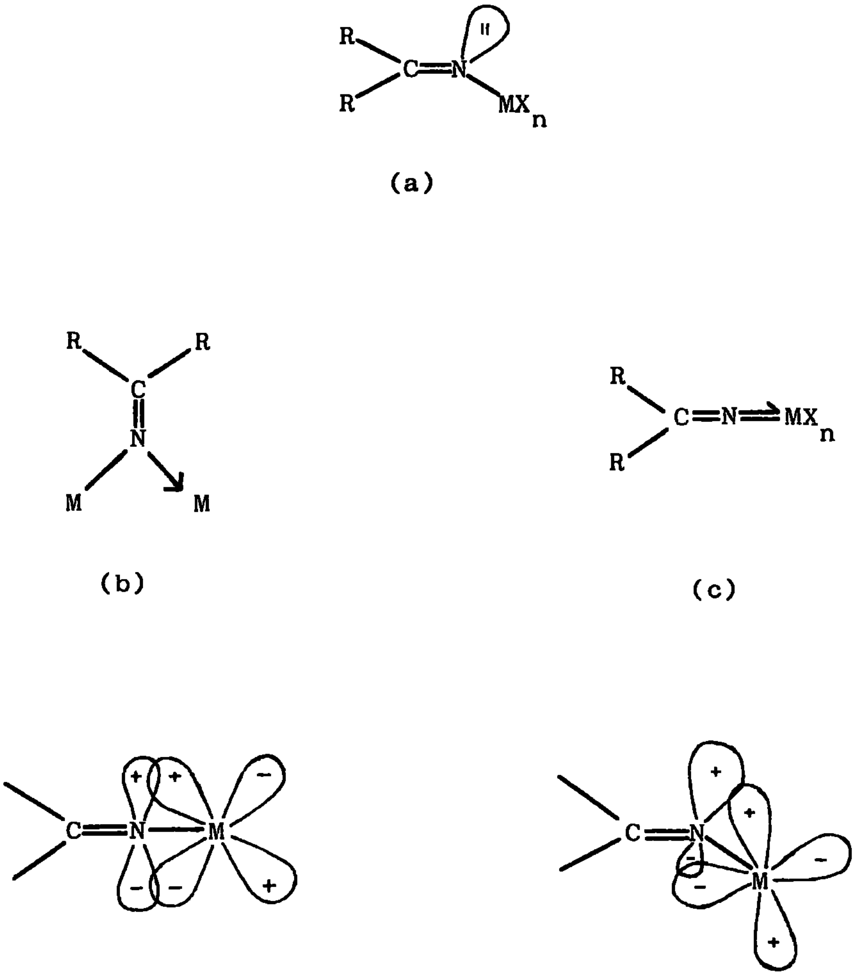
2.2 Bonding and Structure in Methyleneamino derivatives

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→M dative π-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 $C\hat{N}M$ angle of $\sim 120^o$ (Fig. 2-1a). 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. $(Ph_2CN)_3P$[351]).

If it is coordinatively unsaturated, however, donation of the nitrogen lone-pair may occur, either through bridging to a second metal atom (Fig. 2-1b) with the formation of a dimeric or oligomeric species, or through N→M dative π-bonding (Fig. 2-1c). 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,[82] from overlap integral calculations on silicon systems, that quite substantial (p→d) π-bonding is at least possible in the bent form (Fig. 2-1e), 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,[336] diphenylmethyleneamino-dimesitylborane,[337] tris(di-t-butylmethyleneamino)borane,[350] lithium tetrakis(di-t-butylmethyleneamino)alane,[338] and tris(diphenylmethyleneamino)-phosphine.[351] 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 $C\hat{N}B$ 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,[330,339] 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

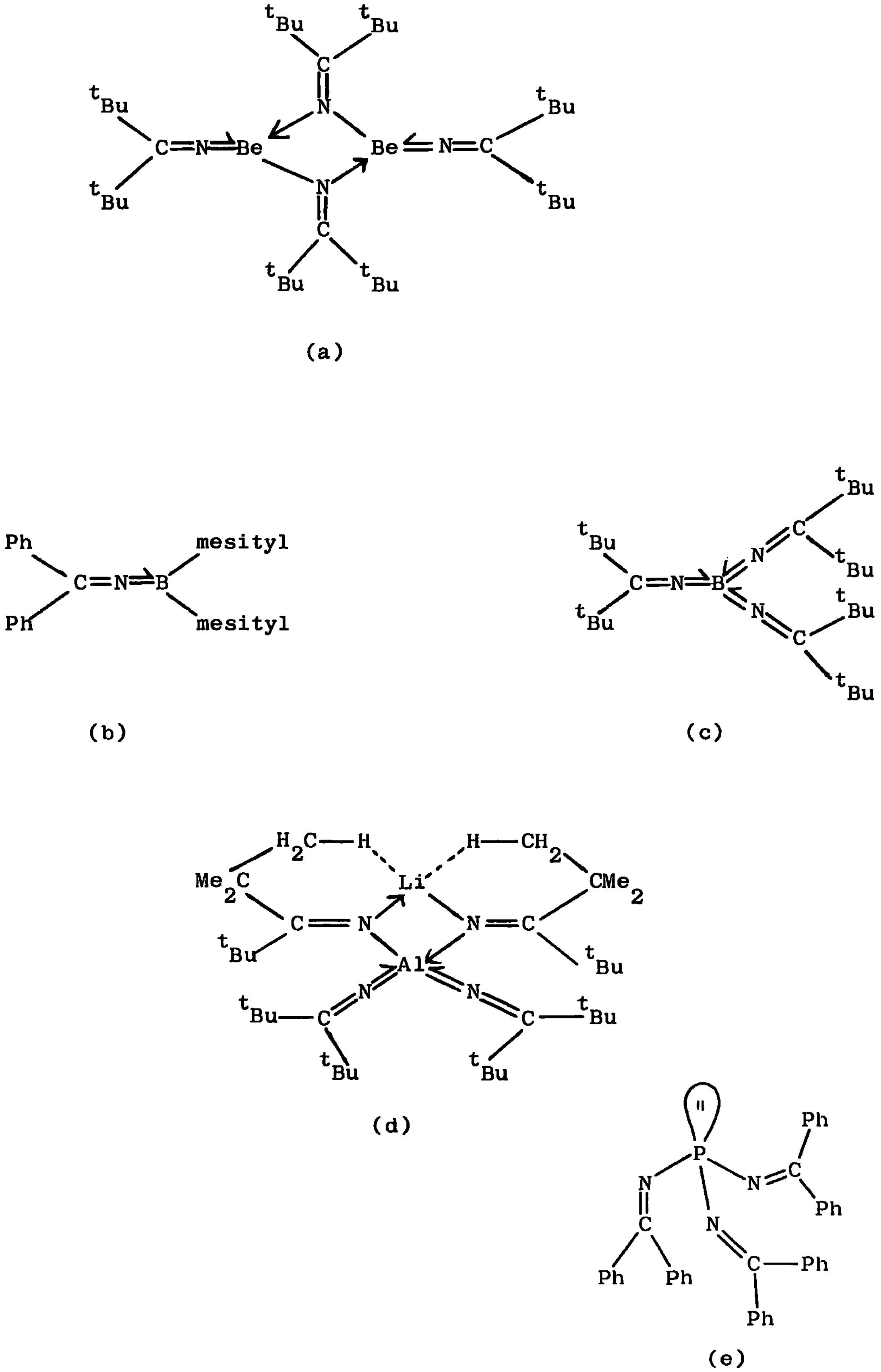


Figure 2-2

additional point of interest in the structure of the lithium compound

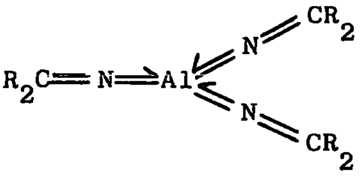


Figure 2-3

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

The tris-iminophosphine $(Ph_2CN)_3P$ has a pyramidal structure with all the imino groups bent at nitrogen, showing little evidence of N→P π-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 α-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

Figure 2-4

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

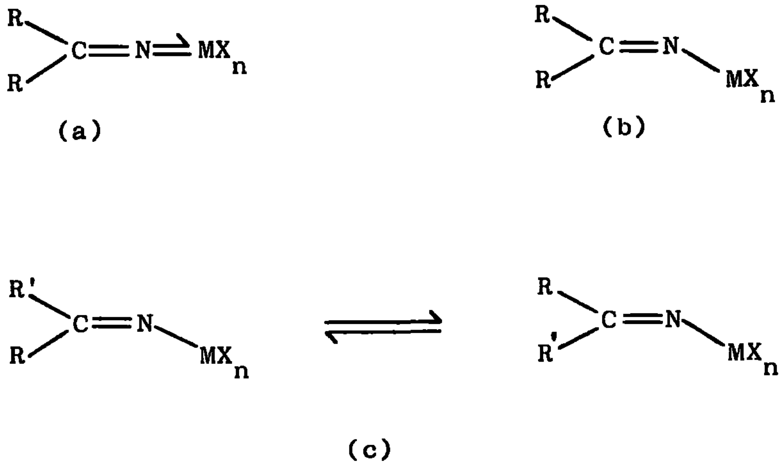
The imines used in the course of this work were di-t-butylmethyleneamine (which possesses no α-hydrogen), and diphenylmethyleneamine together with some of its p,p'-disubstituted derivatives (di-p-tolyl and di-p-chloro). Other workers have made use of bis(trifluoromethyl)methyleneamine.[291,292]

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-$CH_3C_6H_4$). 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.



(a) (b)

(c)

Figure 2-5

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 $^{t}Bu_2C{=}N{-}NMe_2$ has been found to exhibit two ^{t}Bu resonances in its ^{1}H-NMR spectrum at temperatures as high as 136°C,[329] 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 $^{t}Bu_2CNH$ shows only a single ^{t}Bu absorption at room temperature, but on cooling to -30°C this splits into two signals of equal intensity.[330]

Syn-anti isomerism in methyleneamines and the associated inversion process at nitrogen has attracted considerable interest, and has been reviewed.[340] The mechanism has been studied,[341] and the magnitude of the inversion barrier has been determined for several N-alkylated and -arylated compounds.[333,334] 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).[342]

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 $p\text{-}CF_3C_6H_4(Ph)C{=}NGeMe_3$[343] the methyl groups show a single sharp absorption at temperatures $> -70°C$. At -110°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,[343] which may account for the low rate of inversion of $^tBu_2CNNMe_2$, 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 π-interaction, $R_2C{=}N{\rightleftharpoons}M$.

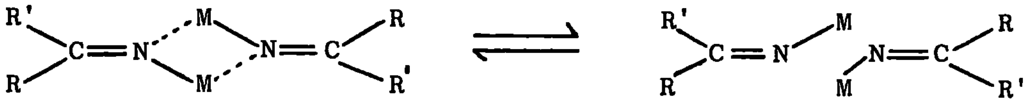


Figure 2-6

B. Infra-red Spectroscopy

The azomethine stretching frequencies, ν(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→M dative π-bonding.

TABLE 8

ν(C=N) for some methyleneamines, $R_2C{=}NH$

R	ν(C=N)cm^{-1}	Ref.
Ph	1603	335
p-$CH_3C_6H_4$	1597	345
p-ClC_6H_4	1590	344
^tBu	1604	a

a: This work. Previously reported as 1610 cm^{-1}.[344]

For N-metallated methyleneamines, $R_2C{=}N{-}MX_n$, linearity in the CNM skeleton has been found to lead to an increase in ν(C=N) relative to the parent imine. For derivatives of the lighter metals and metalloids, this increase may be as much as 100-140cm^{-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 π-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 ν(C=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 ν(C=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 π-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

TABLE 9

ν(C=N) for some methyleneamine derivatives of metals and metalloids.

Compound	ν(C=N)cm^{-1}	Ref.
$[(^tBu_2C{=}N)_2Be]_2$	1739, 1637	336
$Ph_2C{=}NB(C_6H_2Me_3)_2$	1792	383
$(^tBu_2C{=}N)_3B$	1730	329
$Li(^tBu_2C{=}N)_4Al$	1700,1642,1602	338
$(Ph_2C{=}N)_3P^{III}$	1607	346

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 $(^tBu_2CN)_3B$). The phosphorus derivative, which appears to contain little or no (p-d) π-bonding, the CNP angles being 120°, shows little variation in ν(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 ν(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 $\gt C=N-$ 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 $C > Pb \gg Ge > Sn \approx Si$,[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 π-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 π-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 $Si > Ge > Sn$, the inference being that $N \rightarrow M$ ($p \rightarrow d$) π-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

ν(C=N) frequencies for some diphenylmethyleneamino derivatives of the Group IVB elements.[290]

Compound	M	ν(C=N)cm^{-1}
Ph_2CNMMe_3	Si	1642
	Ge	1630
	Sn	1613
Ph_2CNMPh_3	Si	1662
	Ge	1633
	Sn	1613

(cf. Ph_2CNH : ν(C=N) = 1603 cm^{-1})

TABLE 11

ν(C=N) frequencies for some related imino-beryllium and magnesium derivatives.

Compound	ν(C=N)cm^{-1}		Ref.
	Terminal	Bridging	
$[(Ph_2CN)_2Be]_n$	1732	1627	353
$[(Ph_2CN)_2Mg]_n$	1650	1612	329
$[(^tBu_2CN)_2Be]_2$	1721	1631	380
$[(^tBu_2CN)_2Mg]_2$	1665	1604	329

Substituent effects

In the generalised methyleneamine derivative $R_2C{=}\dot{N}{-}M\ddot{X}_n$ the substituents X on the metal M may influence the metal-nitrogen bond (and hence the ν(C=N) frequency) by both σ and π effects. Electron-releasing groups will tend to weaken the metal-nitrogen σ-bond by reducing its polarity, while electron-withdrawing groups tend to strengthen it. The resulting increase in polarity may also encourage N→M dative π-bonding.

The π-bonding ability of X may also be important; apart from competing with the nitrogen lone pair for the metal orbitals, X→M π-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 ν(C=N); although Table 8 shows comparatively little difference between the parent imines (an exception is $(CF_3)_2C{=}NH$, with $\nu(C{=}N) = 1702\text{cm}^{-1}$),[373] there is often considerable variation between derivatives of different imines with similar structures, pointing to differing N→M π-bonding abilities.

C. Ultra-Violet Spectroscopy.

The presence of the potential chromophore C=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 200-400mμ, corresponding to the $n\rightarrow\pi^*$ transition of a nitrogen non-bonding electron and the $\pi\rightarrow\pi^*$ transition of the $C{=}N{\rightleftharpoons}M$ π-system. (Fig. 2-7).

If the nitrogen lone pair is involved in $(p\rightarrow d)$ π-bonding, a shift in the $n\rightarrow\pi^*$ transition would be expected if π-electron donating groups (e.g. Ph, vinyl, -OR, $-NR_2$) 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 $N\rightleftharpoons Si$ π-bonding. However, it has been suggested[329] that, if the energies of both the π^* and n levels were lowered to about the same extent by substitution at nitrogen, the $n\rightarrow\pi^*$ transition will not significantly alter on further substitution, in which case the results could accomodate both linear and bent C=N-Si units.

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

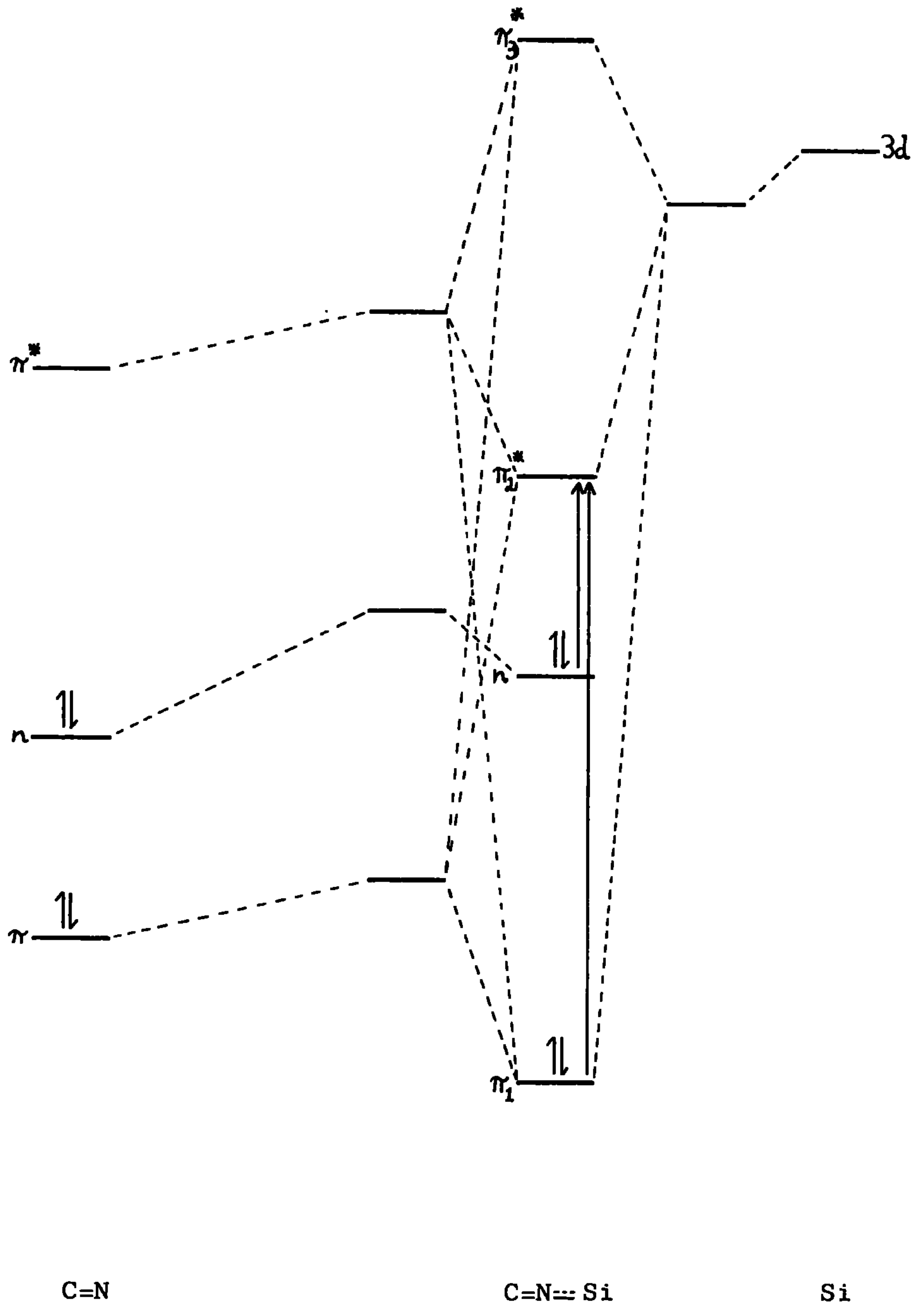


Figure 2-7

From: L. Chan and E.G. Rochow, J. Organometal.Chem. 1967, 9, 231.

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), $(Ph_2CN)_4Sn^{IV}$, M.Pt. 170-180° (sealed tube).

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

$C_{52}H_{40}N_4Sn$ requires: C 74.4, H 4.8, N 6.7, Cl 0%.)

ν_{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, 1030 mw, 1002 vw, 997 vw, 989 w, 974 w, 940 m, 923 mw, 911 m, 888 vw, 856 w, 846 sh, 791 m, 787 s, 774 vs, 739 m, 707 vs, 701 vs, 675 m, 654 s, 623 w, 618 w, 611 w, 516 mw, 468 w, 454 vw, 441 m, 432 mw.cm^{-1}.

ii) Reaction of diphenylmethyleneaminolithium with tin tetrachloride (Mole ratio 3:1)

A solution of 30mmol.Ph_2CNLi in 50ml dry diethyl ether/hexane was cooled to -196° and 1.17 ml. tin tetrachloride (10mmol.) was added. The mixture was allowed to warm to room temperature with stirring, and was then stirred at room temperature for ~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 ml. dry toluene. The mixture was heated to ~90° and filtered while hot, giving a white solid (LiCl) and a dark yellow solution. The latter on standing at -10°, deposited a yellow crystalline mass, which on isolation and drying formed a yellow powder identified as tris(diphenylmethyleneamino)tin(iv) chloride $[(Ph_2CN)_3Sn^{IV}Cl]_n$, M.Pt. 140-5° (sealed tube).

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

$C_{39}H_{30}N_3SnCl$ requires: C 67.4, H 4.3, N 6.1, Cl 5.1 %)

ν_{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}.

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

A solution of 30 mmol. diphenylmethyleneaminolithium in approximately 50ml. dry ether/hexane was cooled to -196° and 1.76 ml. tin tetrachloride (15 mmol.) was added. The mixture was allowed to warm to room temperature with stirring, then stirred for ~3½ 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 ~90°, and filtered while hot, leaving a white filter cake of lithium chloride. On cooling, the resulting deep yellow solution deposited colourless needle crystals of <u>bis(diphenylmethyleneamino)tin(iv) dichloride</u>, $[(Ph_2CN)_2Sn^{IV}Cl_2]_n$, M.Pt. 185-190° (sealed tube).

(Found: C 60.6, H 3.4, N 5.2, Cl 11.4%

$C_{26}H_{20}N_2SnCl_2$ requires: C 56.1, H 3.6, N 5.0, Cl 12.7%)

ν_{max}(Nujol mull): 3080sh, 3055mw, 3020mw, 1960vw, 1900vw, 1817vw, 1607s, 1590s, 1567sh, 1553vs, 1489m, 1446s, 1402w, 1319w, 1310w, 1291mw, 1272m, 1181mw, 1161w, 1146vw, 1075mw, 1029mw, 1001mw, 972vw, 951mw, 938mw, 914mw, 892sh, 850w, 788m, 780ms, 773m, 729ms, 712s, 702sh, 696vs, 670m, 661m, 624vw, 617vw, 532mw, 468w, 456w, 435w, 367vw, 348vw 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, $Ph_2CNSnCl_3$. 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 ~50ml. dry ether/hexane was cooled to -196° 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 diphenylmethyleneaminogermanium trichloride $Ph_2CNGeCl_3$.

ν_{max}(Thin film): 3108sh, 3091w, 3069mw, 3038w, 2968w, 2938w, 2870vw, 1973vw, 1910vw, 1818vw, 1730vw, 1624sh, 1609vs, 1593vs, 1571vs, 1565sh, 1495mw, 1451s, 1318s, 1284vs, 1257sh, 1186m, 1164mw, 1079mw, 1033m, 1006mw, 978vw, 947s, 916m, 850w, 788vs, 752w, 706vs, 700vs, 695s, 631mw, 621vw, 546mw, 434vs, 405vs. 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 $(Ph_2CN)_2GeCl_2$, M.Pt. 110-125°.

(Found: C 60.1, H 3.7, N 5.5, Cl 15.0 % M = 540
$C_{26}H_{20}N_2GeCl_2$ requires: C 62.0, H 4.0 , N 5.6, Cl 14.1%; M = 504)

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

vi) Reaction of diphenylmethyleneamine with silicon tetrachloride in the presence of triethylamine (Mole ratio 1:1:1)

3.65ml. diphenylmethyleneamine (21.84 mmol.) was added to a solution of 2.5ml. silicon tetrachloride (21.84 mmol.) in 60ml. 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 20ml. 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 20ml. dry hexane. Concentration and cooling of the resulting yellow solution yielded a pale yellow semi-crystalline solid, identified as bis(diphenylmethyleneamino) dichorosilane, $(Ph_2CN)_2SiCl_2$, 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%;
$C_{26}H_{20}N_2SiCl_2$ requires: C 67.1, H 4.4, N 6.1, Cl 15.5%).

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

To 4.5g. bis(diphenylmethyleneamino)dichlorosilane (~10 mmol.) were added 10ml. 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° 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, $Ph_2CNSiCl_3$.

(Found: C 52.4 %; $C_{13}H_{10}NSiCl_3$ requires C 51.3%)

ν_{max}(Nujol mull): 3085sh, 3063w, 3031w, 1954vw, 1920vw, 1819vw, 1650vs, 1599s, 1582m, 1452s, 1404vw, 1326mw, 1279s, 1198sh, 1184mw, 1168m, 1078m, 1033mw, 1004w, 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^o. 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), $(^tBu_2CN)_4Sn^{IV}$, M.Pt. 110-120^o dec. (sealed tube).

(Found: C 63.6, H 10.6, N 8.2, Cl 0%; M = 653.
$C_{36}H_{72}N_4Sn$ requires: C 63.5, H 12.3, N 8.7, Cl 0%; M = 679).

ν_{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^o. 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, $(^tBu_2CN)_3Sn^{IV}Cl$, B.Pt. $95-125^o$/0.5mm Hg. w. extensive decomposition.

(Found: C 54.7, H 8.2, N 7.8, Cl 6.9 %; M = 360 dec.

$C_{27}H_{56}N_3SnCl$ requires: C 56.4, H 9.4, N 7.3, Cl 6.2 %; M = 574.2)

ν_{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, ^tBuCN, and di-t-butylmethyleneamine, $^tBu_2CNH$, 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 3.51ml. 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, $(^{t}Bu_2CN)_2Sn^{IV}Cl_2$, 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 %.

$C_{18}H_{36}N_2SnCl_2$ requires: C 45.9, H 7.7, N 6.0, Cl 15.1 %).

ν_{max} (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 3.51ml. 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.

$LiSnCl_3$ 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 $(^{t}Bu_2CN)_2SnCl_2$.

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

A solution of 0.973g. tris(di-t-butylmethyleneamino)tin(iv)chloride (1.69 mmol.) in 10ml. dry pentane was added to a solution of 0.920g lithium tris(di-t-butylmethyleneamino)tin(ii) (1.68 mmol.) in 20ml. dry pentane at 0^{o}. 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 $\sim$5ml. and left at $\sim -10^{o}$ for several weeks, over which time it deposited large colourless cubic crystals of <u>hexakis(di-t-butylmethyleneamino)ditin(iv),</u> $(^{t}Bu_2CN)_6Sn_2^{IV}$, m.pt. 110-20^{o} (sealed tube).

(Found: C 62.6, H 9.8, N 7. 2%; M = 538 dec.

$C_{54}H_{108}N_6Sn_2$ requires: C 60.1, H 10.0, N 7.8 %; M = 1078)

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

vi) <u>Thermal decomposition of bis(di-t-butylmethyleneamino)tin(iv)dichloride</u>

On standing at room temperature for ~10 days (or on heating to ~60°) 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 <u>bis(di-t-butylmethyleneaminotin(ii)-chloride)hydrochloride</u>, $({}^{t}Bu_2CNSn^{II}Cl)_2.HCl$ or $({}^{t}Bu_2CN)_2HSn_2Cl_3$, M.Pt.: 100-130°, loss of ${}^{t}Bu_2CNH$, melts 149-153 °dec. (sealed tube).

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

$C_{18}H_{37}N_2Sn_2Cl_3$ requires: C 34.6, H 5.9 , N 4.5, Cl 17.0 %)

ν_{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. cm^{-1}.

The supernatant liquor exhibited a band in the infra-red spectrum at 2218 cm^{-1}, corresponding to $\nu(C\equiv N)$ 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° deposited a small amount of pale leafy crystals, apparently <u>tris(di-t-butylmethyleneaminotin(ii)chloride)dihydrochloride,</u> $({}^{t}Bu_2CNSn^{II}Cl)_3.2HCl$ or $({}^{t}Bu_2CN)_3H_2Sn_3Cl_5$, M.Pt. 70-71° (sealed tube).

(Found: C 34.1, H 5.9, N 5.2, Cl 21.0%

$C_{27}H_{56}N_{3}Sn_{3}Cl_{5}$ requires: C 33.9, H 5.9, N 4.4, Cl 18.6%)

ν_{max}(Nujol mull): 3245sh, 3156br.vs, 1671vs, 1653sh, 1632m, 1604vw, 1587w, 1578w, 1534m, 1400mw, 1365s, 1308vw, 1332w, 1311w, 1172m, 1152s, 970vw, 937sh, 903s, 842mw, 755vw, 738mw, 723w, 663sh, 645mw, 570s, 540sh, 494mw, 478mw, 460 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, $^{t}Bu_{2}CNH.SnCl_{4}$, m.pt. 210-12° 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%)

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

viii) Reaction of 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, $(^tBu_2CNH)_2.SnCl_4$, m.pt. 137-9° dec. (sealed tube).

(Found: C 39.4, H 7.4 , N 5.2, Cl 27.8% .
$C_{18}H_{38}N_2SnCl_4$ requires: C 40.5, H 7.0, N 5. 2, Cl 26.2%).

ν_{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 $(^{t}Bu_2CN)_2SnCl_2$ are not listed here, since their spectroscopic and structural properties will be discussed in Chapter 3.

TABLE 12

New Methyleneamino derivatives of Group IVB elements in oxidation state (iv).

$(Ph_2CN)_4Sn^{IV}$	yellow crystals
$[(Ph_2CN)_3Sn^{IV}Cl]_n$	yellow powder
$[(Ph_2CN)_2Sn^{IV}Cl_2]_n$	colourless crystals
$(Ph_2CN)_2GeCl_2$	colourless crystals
$Ph_2CNGeCl_3$ *	yellow oil
$Ph_2CNSiCl_3$ *	colourless crystals
$(^{t}Bu_2CN)_4Sn^{IV}$	colourless crystals
$(^{t}Bu_2CN)_3Sn^{IV}Cl$	yellow oil
$(^{t}Bu_2CN)_2Sn^{IV}Cl_2$	yellow oil
$(^{t}Bu_2CN)_6Sn_2$	colourless crystals
$^{t}Bu_2CNH.SnCl_4$	white powder
$(^{t}Bu_2CNH)_2.SnCl_4$	white powder

* : 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.[240-3,346,355,356] Their relative stabilities to hydrolysis are of interest; a comparative study of the compounds $Me_{4-n}M(NC(CF_3)_2)_n$ (M = Si, Ge, Sn; n = 1-4)[292] found that hydrolytic sensitivity increased $Si < Ge < Sn$ and $n = 1 < 2 < 3 < 4$. The latter result was also found for the series $(Ph_2CN)_nSiR_{4-n}$,[290] but the new compounds described here showed no such effect, possibly owing to the complicating presence of M-Cl bonds. Also, while $(Ph_2CN)_4Sn$ resembles the corresponding silicon compound[356] in its high sensitivity to atmospheric moisture, the germanium analogue is stable to air exposure for several hours.[346] Other imino-germanium derivatives are very moisture sensitive, so that this is probably a kinetic effect associated with the crystal packing (the three $(Ph_2CN)_4M$ compounds have quite different arrangements in the crystal[302]).

The new compounds are probably monomeric, with the exception of the diphenylmethyleneaminotin chlorides, $(Ph_2CN)_nSnCl_{4-n}$, n = 2,3, for which the infra-red data, together with the results of a preliminary Mössbauer study,[381] 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 (iv)) are monomeric,[329] the associated nature of the diphenylmethyleneaminotin chlorides being attributable to the greater Lewis acidity of tin(iv) halides. The di-t-butylmethyleneaminotin chlorides are, however, almost certainly monomeric, which may be due to the greater bulk of the t-butyl groups.

The observed molecular weight for $({}^{t}Bu_2CN)_6Sn_2$ 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 ${}^{t}Bu$ groups. However, even quite crowded hexaorganoditins (e.g. hexa-o-tolyl ditin) show no evidence

$$({}^{t}Bu_2CN)_3Sn\text{-}Sn(NC{}^{t}Bu_2)_3 \longrightarrow 2\ ({}^{t}Bu_2CN)_3Sn^{\bullet} \qquad 2.1$$

of dissociation in solution,[358] 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[358] (Eqns. 2.2 and 3), and is related to the procedure used for the majority of preparations in this

$$R_3SnX + R_3SnLi \longrightarrow R_3SnSnR_3 + LiX \qquad 2.2$$

$$({}^{t}Bu_2CN)_3SnCl + Li({}^{t}Bu_2CN)_3Sn \longrightarrow ({}^{t}Bu_2CN)_6Sn_2 + LiCl \qquad 2.3$$

$$MCl_4 + nR_2CNLi \longrightarrow Cl_{4-n}M(NCR_2)_n + nLiCl \qquad 2.4$$

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, $({}^{t}Bu_2CN)_4Sn$, in contrast to the germanium[346] and silicon systems,[355] for which the most highly substituted derivatives preparable were $({}^{t}Bu_2CN)_3GeCl$ and ${}^{t}Bu_2CNSiCl_3$ respectively. This may be explained in terms of the bulk of the ${}^{t}Bu$ 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[372]), 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 $Ph_2CNSiPh_3$ from Ph_2CNH and Ph_3SiCl.[356] Here it provides an alternative route to the known compound, $(Ph_2CN)_2SiCl_2$ (Eqn. 2.5).

$$\begin{tikzcd} Ph_2CNH + SiCl_4 + Et_3N \arrow[r, "\Delta"] & Et_3NH^+Cl^- + & \left[Ph_2CNSiCl_3\right] \arrow[d, "x\ 2"] \\ & & (Ph_2CN)_2SiCl_2 + SiCl_4 \end{tikzcd} \qquad 2.5$$

Interestingly, as in the earlier preparation via the imino-lithium,[355] 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[290,355] (Eqn. 2.6), although in the case of $Ph_2CNSiMe_2Cl$ the process is sufficiently slow to enable the monosubstituted compound to be isolated and characterised before

$$2Ph_2CNSiMe_nCl_{3-n} \xrightarrow[n\ =\ 0\text{-}2]{} (Ph_2CN)_2SiMe_nCl_{2-n} + Me_nSiCl_{4-n} \qquad 2.6$$

significant disproportionation occurs. The corresponding di-t-butyl compounds, in contrast, are quite stable, indeed the disubstituted materials cannot be prepared.[355]

It is therefore of particular interest to find that reaction of $(Ph_2CN)_2SiCl_2$ 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 $Ph_2CNSiCl_3$. The possibility of this material being an adduct (Fig. 2-8) is eliminated by consideration of the azomethine stretching frequency, which at 1650cm^{-1} is too high for a bridged imino-group. Other possible explanations, such as incorporation of non-bonded $SiCl_4$ into the $(Ph_2CN)_2SiCl_2$ lattice, do exist, however, and further work is necessary to elucidate this matter.

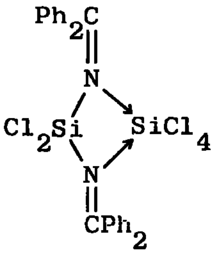
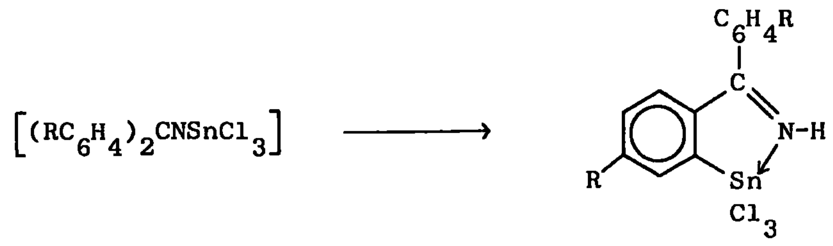


Figure 2-8

For germanium systems there is less evidence of disproportionation. Again the di-t-butylmethyleneamine derivatives show no tendency to disproportionate,[293,346] but attempts to prepare the di-p-tolylmethyleneaminogermanium halides were abandoned after preliminary experiments led to products of variable composition.[293] The present work suggests that disproportionation also occurs here, but less readily than for the silicon derivatives. Thus heating is necessary to decompose $Ph_2CNGeCl_3$ (Eqn. 2.7).

$$2Ph_2CNGeCl_3 \xrightarrow{\Delta} (Ph_2CN)_2GeCl_2 + GeCl_4\uparrow \qquad 2.7$$

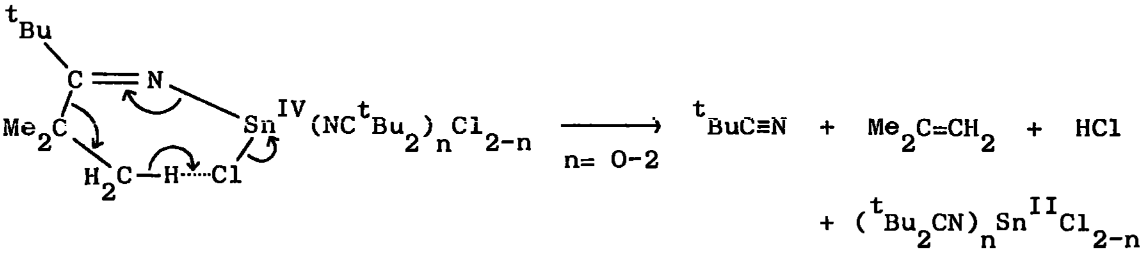
If the trend continues down the group, it might be expected that the corresponding tin derivatives would show even less tendency to disproportionate. However, this cannot be determined, because an alternative rearrangement is observed. The diarylmethyleneaminotin(iv) trichlorides cannot be isolated because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



2.8

on heating the other diarylmethyleneaminotin chlorides, $[(RC_6H_4)_2CN]_nSnCl_{4-n}$ (n = 2,3), (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 $-SnCl_3$ 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). ^{t}BuCN and $^tBu_2$CNH (from protolysis of imino-tin species by HCl) could be



2.9

identified in the reaction products. The reaction becomes slower with increasing n; $^{t}Bu_2CNSnCl_3$ (n = 0) is not preparable, and $(^{t}Bu_2CN)_2SnCl_2$ (n = 1) and $(^{t}Bu_2CN)_3SnCl$ (n = 2) decompose at room temperature over periods of several days and several months respectively. The order of stability is therefore:

$$(^{t}Bu_2CN)_4Sn \gg (^{t}Bu_2CN)_3SnCl > (^{t}Bu_2CN)_2SnCl_2 \gg {}^{t}Bu_2CNSnCl_3$$

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 $(^{t}Bu_2CN)_nHSn^{II}Cl_{3-n}$ (n = 1,2). However, from $(^{t}Bu_2CN)_2SnCl_2$, rather than the expected product $^{t}Bu_2CNH.SnCl_2$, a series of compounds of general formula $(^{t}Bu_2CNSnCl)_n.(n-1)HCl$ (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 $Sn^{II}\text{——}\overset{\|}{N}\rightarrow Sn^{II}$ bridge.

The formation of 1:1 and 2:1 adducts between $^{t}Bu_2CNH$ 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, $^{t}Bu_2CNH_2^{+}.{}^{t}Bu_2CNSnCl_4^{-}$, might be possible for the latter, but the spectroscopic evidence is not consistent with such a structure. It is probable that $^tBu_2CNH.SnCl_4$ and $(^tBu_2CNH)_2.SnCl_4$ 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 ~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 $(^tBu_2CN)_3SnCl$ showed any tin-containing fragments; a single peak, m/e 155, corresponding to $SnCl^+$ (intensity 2 relative to $^tBu_2CN^+$ 100). The sample of $(^tBu_2CN)_2SnCl_2$ 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 $(^tBu_2CN)_6Sn_2$ (Table 13a) or of any fragments of mass charge ratio greater than that of $(^tBu_2CN)_3Sn^+$, 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) $(^t\text{Bu}_2\text{CN})_6\text{Sn}_2$

m/e	Rel.Intensity	Assignment
540	4	$(^t\text{Bu}_2\text{CN})_3\text{Sn}^+$
457	26	$(^t\text{Bu}_2\text{CN})_2\text{Sn}^t\text{Bu}^+$
400	13	$(^t\text{Bu}_2\text{CN})_2\text{Sn}^+$
343	100	$^t\text{Bu}_2\text{CN}(^t\text{BuCN})\text{Sn}^+$
260	100	$^t\text{Bu}_2\text{CNSn}^+$
203	36	$^t\text{BuCNSn}^+$
140	2	$^t\text{Bu}_2\text{CN}^+$
120	8	Sn^+

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

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

m/e	Rel.Intensity	Assignment
649	0.1	$(\text{Ph}_2\text{CN})_3\text{GeCl}^+$
614	0.7	$(\text{Ph}_2\text{CN})_3\text{Ge}^+$
504	1.3	$(\text{Ph}_2\text{CN})_2\text{GeCl}_2^{\ +}$
469	1.3	$(\text{Ph}_2\text{CN})_2\text{GeCl}^+$
433	0.4	$\text{Ph}_2\text{CNGe}_2\text{Cl}_3^{\ +}$
427	0.5	$\text{Ph}_2\text{CN}(\text{PhCN})\text{-GeCl}_2^{\ +}$
401	0.6	$\text{Ph}_2\text{CN.PhGeCl}_2^{\ +}$
398	*	$\text{Ph}_2\text{CNGe}_2\text{Cl}_2^{\ +}$
359	19	$\text{Ph}_2\text{CNGeCl}_3^{\ +}$
324	10	$\text{Ph}_2\text{CNGeCl}_2^{\ +}$
282	55	$\text{PhCNGeCl}_3^{\ +}$
221	9	$\text{PhGeCl}_2^{\ +}$
180	100	Ph_2CN^+
179	*	$\text{GeCl}_3^{\ +}$
144	5	$\text{GeCl}_2^{\ +}$
109	25	GeCl^+

* overlapping neighbouring peak envelope.

off-scale.

c) $^{t}Bu_2CNH.SnCl_4$

m/e	Rel.Intensity	Assignment
260	10	$SnCl_4^+$
240	4	$MeSnCl_3^+$
225	85	$SnCl_3^+$
205	19	$MeSnCl_2^+$
190	39	$SnCl_2^+$
155	100	$SnCl^+$
142	45	$^{t}Bu_2CNH_2^+$
141	59	$^{t}Bu_2CNH^+$
120	38	Sn^+

d) $(^{t}Bu_2CNH)_2.SnCl_4$

m/e	Rel.Intensity	Assignment
260	4	$SnCl_4^+$
225	44	$SnCl_3^+$
190	44	$SnCl_2^+$
155	100	$SnCl^+$
142	39	$^{t}Bu_2CNH_2^+$
141	83	$^{t}Bu_2CNH^+$
120	32	Sn^+

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 $N \rightarrow M$ $(p \rightarrow p)$ π-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.

$$2\ (Ph_2CN)_2GeCl_2 \rightleftharpoons (Ph_2CN)_3GeCl + Ph_2CNGeCl_3 \qquad 2.10$$

ii) <u>Proton nuclear magnetic resonance spectra</u>

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-butylmethyleneamine derivatives, in the temperature range -100° to +45°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}

Compound	τ values p.p.m.^{a}	Effect of cooling
$(^tBu_2CN)_6Sn_2$	8.76s	- 100°C: No effect
$(^tBu_2CN)_4Sn$	8.83s	"
$(^tBu_2CN)_3SnCl$	8.72s	"
$(^tBu_2CN)_2SnCl_2$	8.75br.s (8.80sh,8.78sm,8.77sh)	"
$^tBu_2CNH.SnCl_4{}^b$	C-H : 8.00s (18) N-H : 1.26s (1)	- 70°C: Partially resolved doublet, separation 0.11 p.p.m
$(^tBu_2CNH)_2.SnCl_4{}^c$	C-H : 8.00s (18) N-H : -0.32s (1)	- 49°C: Partially resolved doublet, separation 0.09 p.p.m.

a: Relative to τ(TMS) = 10 p.p.m. (External reference)

All spectra run on solutions in d^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 ^{t}Bu resonance, at ambient temperatures except for that of $(^{t}Bu_2CN)_2SnCl_2$, 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 ^{t}Bu signals in the ^{1}H-NMR spectrum of $Li(^{t}Bu_2CN)_4Al$ ^{338} may be partially due to a similar effect, though involving C-H·······metal interactions, since two of the ^{t}Bu groups have been shown to be interacting with the lithium atom in the solid, and this may persist in solution.

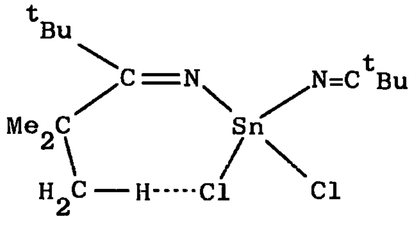


Figure 2-9

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 C=N⇌Sn unit, and since, in the light of infra-red and crystallographic evidence, it appears probable that there is little or no Sn-N π-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 ^{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 ^{t}Bu and $^{t}Bu'$ 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.

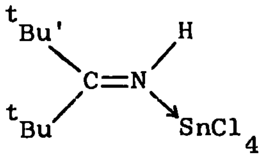


Figure 2-10

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. ^{117,119}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, ν(C=N), are listed in Tables 15 and 16, together with those of some related compounds.

Assignment of ν(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 ν(C=N) difficult. This is illustrated in Figure 2-11, which shows the absorptions in the region 1500-1700 cm^{-1} for the compounds $(Ph_2CN)_2MCl_2$ (M = Si, Ge, Sn) (Figure 2-11 a-c), and also for $(Ph_2CN)_3SnCl$(d). The shift of ν(C=N) to lower energy down the group can clearly be seen, as is also found in the series $(Ph_2CN)_4M$ and Ph_2CNMCl_3.

The large difference between silicon and germanium is probably indicative of a sharp change in properties; a significant amount of (p-d) π-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 ν(C=N) in the case of the silicon derivatives was considered to be too small to allow for complete linearity), with N→M dative π-bonding decreasing sharply down the group, little being apparent for tin and lead. A similar conclusion seems appropriate here.

For the compounds $(Ph_2CN)_2SnCl_2$ and $(Ph_2CN)_3SnCl$, 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 diphenylmethyleneamino derivatives of Group IVB

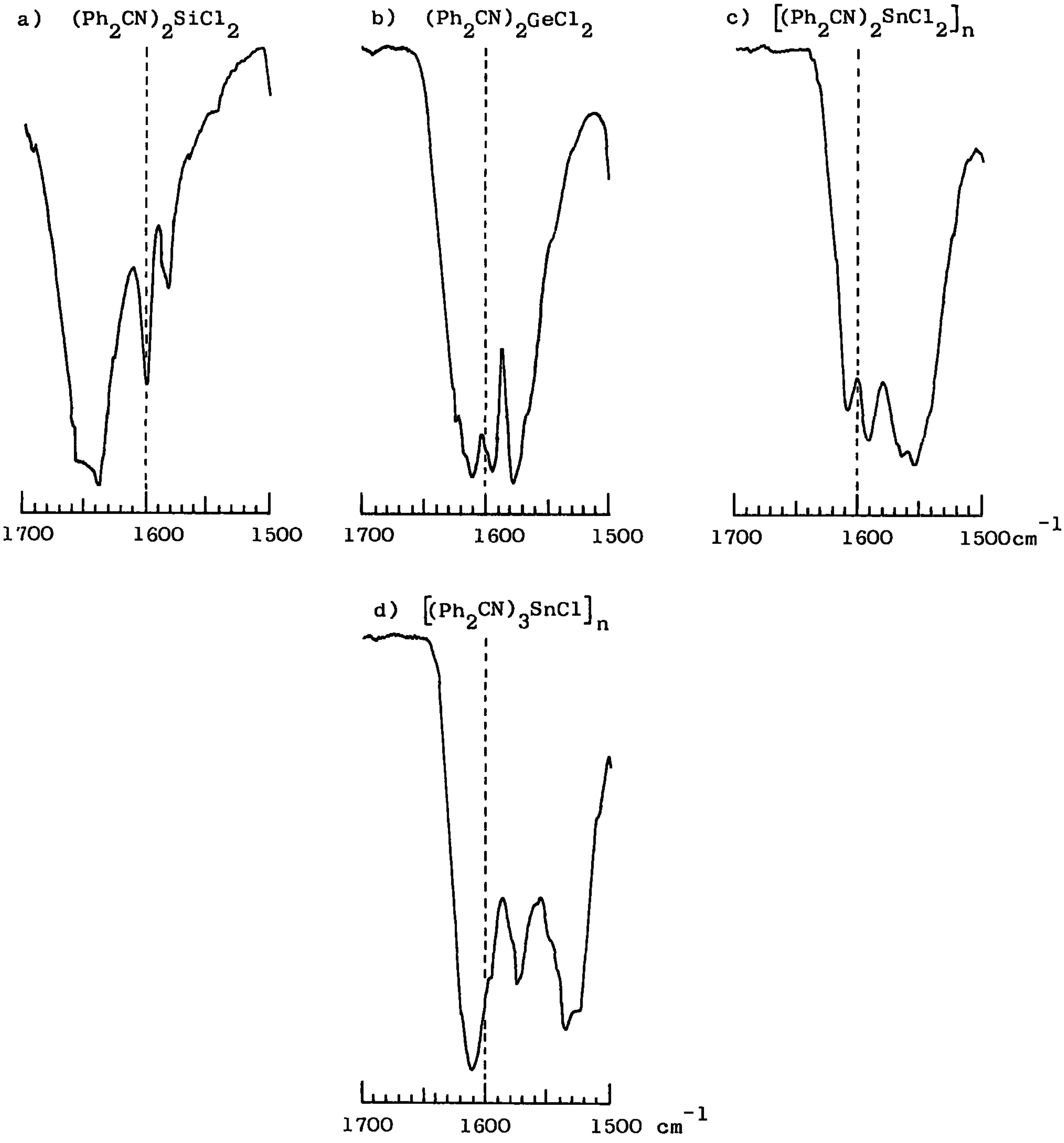
Compound	Phase	ν(C=N)cm^{-1}	Reference
$(Ph_2CN)_4Si$	Mull	1646	356
$(Ph_2CN)_4Ge$	"	1601	293
$(Ph_2CN)_4Sn^{IV}$	"	1590	a
$[(Ph_2CN)_3Sn^{IV}Cl]_n$	"	1612,[b] 1535[c]	a
$(Ph_2CN)_2SiCl_2$	"	1656	355
$(Ph_2CN)_2GeCl_2$	"	1610	a
$[(Ph_2CN)_2Sn^{IV}Cl_2]_n$	"	1607,[b] 1553[c]	a
$Ph_2CNSiCl_3$	"	1650	a
$Ph_2CNGeCl_3$	liquid film	1609	a
cf. Ph_2CNH	"	1603	335

a: This work

b: $\nu(C{=}N)_{terminal}$

c: $\nu(C{=}N)_{bridging}$

Infra-red spectra in the 1500-1700 cm^{-1} region for some diphenylmethyleneamino derivatives of Group IVB



a) $(Ph_2CN)_2SiCl_2$

b) $(Ph_2CN)_2GeCl_2$

c) $[(Ph_2CN)_2SnCl_2]_n$

d) $[(Ph_2CN)_3SnCl]_n$

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 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 $(Ph_2CN)_2SnCl_2$, since it would preclude the appearance of $\nu(C{=}N)_{terminal}$). $(Ph_2CN)_4Sn$, which has been proven by X-ray crystallography to be monomeric,[301,302] gives a single fairly sharp $\nu(C{=}N)$ absorption overlying one of the ring vibrations.

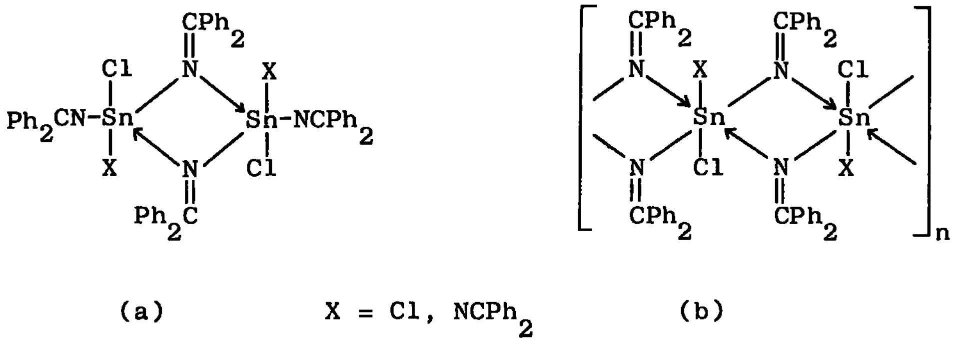


Figure 2-12.

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 $\nu(C{=}N)$ 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-butylmethyleneamino derivatives. Additionally, associated structures are supported by preliminary Mössbauer data,[381] which are inconsistent with a tetrahedral environment for tin in these two compounds.

The di-t-butylmethyleneamine 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, ${}^{t}Bu_2CNH_2{}^{+}\,.\,{}^{t}Bu_2CNSnCl_4{}^{-}$. 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-butylmethyleneamine derivatives of the Group IVB elements.

Compound	Phase	$\nu(C{=}N)cm^{-1}$	Reference
$(^tBu_2CN)_6Sn_2^{IV}$	Nujol mull	1631	a
$(^tBu_2CN)_4Sn^{IV}$	"	1627	a
$(^tBu_2CN)_3GeCl$	liquid film	1652	293
$(^tBu_2CN)_3Sn^{IV}Cl$	"	1627	a
$(^tBu_2CN)_2GeCl_2$	"	1645	293
$(^tBu_2CN)_2Sn^{IV}Cl_2$	"	1627	a
$^tBu_2CNSiCl_3$	"	1729	355
$^tBu_2CNH.SnCl_4$	Nujol mull	1641	a
$(^tBu_2CNH)_2.SnCl_4$	"	1662, 1583	a
cf. $^tBu_2CNH$	liquid film	1604	a

a: This work

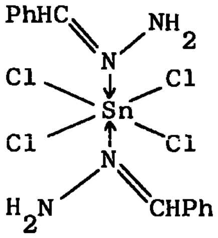


Figure 2-13

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 ν(C=N). Comparison with parallel silicon and germanium systems once again provides the order Si $\gg$ Ge $>$ Sn, but compared to the corresponding diarylmethyleneamino-derivatives, the shifts of ν(C=N) to higher energy relative to the parent imine are considerably larger, and have been interpreted in terms of appreciable N→M dative π-bonding for the silicon derivatives, with associated linearity of the C=N$\doteq$Si unit.[355] A lesser extent of (p→d) π-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 π-bonding than the germanium derivatives, although there is still a shift of ν(C=N) to higher frequency relative to the parent imine (albeit only 23 cm^{-1}).

The di-t-butylmethyleneaminotin chlorides show a single ν(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 $^{t}Bu_2$CN-derivatives of tin (ii) appear to be associated, possibly as a result of the larger covalent radius of Sn^{II} (1.63 Å compared to 1.40 Å 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, $[(CF_3)_2CN]_nMMe_{4-n}$, n = 1-4, M = Si,Ge,Sn[292] (Table 17). A similar picture emerges with respect to ν(C=N), i.e. Si$\gg$Ge$>$Sn, with a similar interpretation in terms of (p→d) π-bonding. If, however, the ν(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 N→M π-bonding ability of the imino-groups R_2CN- might be expected to decrease R = $^tBu > Ph > CF_3$. The observed order, in so far as this can be derived from ν(C=N) values for the Group IVB elements, is $^tBu > CF_3 > Ph$.

The reason for this is not immediately apparent, since $^tBu_2CNH$ and Ph_2CNH 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. Methyleneamino-derivatives of the lighter metals in particular show comparatively little difference in ν(C=N) frequency between $^tBu_2CN$- and Ph_2CN- derivatives, apart from those attributable to steric effects (consider, for example, the bis-imino derivatives of Be and Mg in Table 11). Since N→M π-bonding generally involves (p-p) π-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 M-N stretching frequencies presents a problem, due

TABLE 17

Azomethine stretching frequencies, $\nu(C{=}N)cm^{-1}$, for some Group IVB derivatives of $(CF_3)_2C{=}NH$.[292]

Compound	$\nu(C{=}N)cm^{-1}$		
	M = Si	Ge	Sn
$[(CF_3)_2CN]_4M$	1786	1730	1717
$[(CF_3)_2CN]_3MMe$	1774	1733	1717
$[(CF_3)_2CN]_2MMe_2$	1770	1730	1719
$(CF_3)_2CNMMe_3$	1765[a]	1730	1720
cf. $(CF_3)_2CNH$	1702[373]		

a: Other workers found 1780 cm^{-1}.[290]

TABLE 18

Frequency shifts, $\Delta\nu(C{=}N)cm^{-1}$, for Group IVB derivatives $(R_2C{=}N)_4M$ relative to the parent imine.

R	$\Delta\nu(C{=}N)cm^{-1}$		
	M = Si	Ge	Sn
^tBu	(125)[a]	(48)[b]	23
CF_3	84	28	15
Ph	43	- 2	-13

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

a: $^tBu_2CNSiCl_3$; b: $(^tBu_2CN)_3GeCl$. 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,[292] who, in their study of $(CF_3)_2CN$- derivatives of Si, Ge, and Sn, assigned ν(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,[388] 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 $(Ph_2CN)_2SnCl_2$ and $(Ph_2CN)_3SnCl$ would show ν(M-N) bands due to both terminal and bridged imino- groups. However, their spectra showed no significant differences from that of $(Ph_2CN)_4Sn$ in the region 300-600 cm^{-1}, and no even tentative assignments could be made for $\nu(M\text{-}N)_{bridged}$, 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) π-bonding.

It is interesting to note the generally higher ν(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 ν(C=N), and may indicate a greater extent of N-M π-bonding for the di-t-butylmethyleneamine derivatives.

TABLE 19

Possible assignments for ν(M-N) for some methyleneamino derivatives of the Group IVB elements

Compound	ν(M-N)cm^{-1}	Reference
$(Ph_2CN)_4Si$	866 (913)	a,(374)
$(Ph_2CN)_4Ge$	700^b (892)	a,293,(346)
$(Ph_2CN)_4Sn^{IV}$	654	a, 293
$[(Ph_2CN)_3Sn^{IV}Cl]_n$	667, 660, 650	a
$(Ph_2CN)_2SiCl_2$	894 (913)	a, (355)
$(Ph_2CN)_2GeCl_2$	700^b	a
$[(Ph_2CN)_2Sn^{IV}Cl_2]_n$	670, 661	a
$Ph_2CNSiCl_3$	875	a
$Ph_2CNGeCl_3$	700^b	a
$(^tBu_2CN)_6Sn_2{}^{IV}$	692	a
$(^tBu_2CN)_4Sn^{IV}$	693	a
$(^tBu_2CN)_3GeCl$	731(958)	a, (346)
$(^tBu_2CN)_3Sn^{IV}Cl$	698	a
$(^tBu_2CN)_2GeCl_2$	741 (959)	a, (346)
$(^tBu_2CN)_2Sn^{IV}Cl_2$	697	a

Previous assignments in parentheses.

a : This work

b : Obscured by phenyl absorption

iv) Basicity measurements on $(^{t}Bu_2CN)_nSnCl_{4-n}$, 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 ν(X-H····B) is concentration-dependant). It has proven convenient in practice to use deuterochloroform for infra-red studies, since ν(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).

$$Cl_3C\text{-}H \;+\; Base \;\rightleftharpoons\; Cl_3C\text{-}H\cdots Base \qquad 2.11$$

The observed frequency, ν_o, is intermediate between that of the hydrogen-bonded species, ν_H, and free chloroform, ν_F. ν_o is concentration-dependant, but the extrapolated shift at infinite dilution (of chloroform in solution) relative to free chloroform, ν_{∞} , has been used as a measure of the basicity of the solvent.[285]

When both methods were applied to iso-structural series of bases, good agreement was found, parallel variations in $\Delta\nu$(C-D) and ν_{∞} 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 ν_o is strongly affected by the equilibrium constant of Equation 2.11, which in turn is sensitive to steric effects.[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 $CDCl_3$ ($\sim$1 mole) in base ($\sim$5 moles). Comparison measurements were also made on $^tBu_2CNH$ and Ph_2CNH. 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 $CDCl_3$ (ν(C-D) = 2264 cm^{-1} [283]). Results are listed in Table 20. ν(C-D$\cdots$B) absorptions appeared as subsidiary peaks partially superimposed on the free $CDCl_3$ band. This may have been due to the comparatively high concentrations of $CDCl_3$ necessitated by the limited availability of the organometallics, but similar effects have been observed for other sterically crowded organometallic bases.[283] Only a single absorption was observed for the methyleneamines.

^{1}H-NMR studies were carried out over a range of concentrations, using neat $CHCl_3$ as external reference, but it was not possible to work at sufficiently low concentrations to obtain realistic extrapolations to infinite dilution. The curves of ν_o against concentration may, however, be used for qualitative comparisons, and data were also obtained for $^{t}Bu_2CNH$ 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 ν_o closer to ν_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)π-bonding might be expected). This may point to involvement of the nitrogen lone pairs in a certain amount of N→Sn dative π-bonding, or alternatively may be due to their inaccessibility for steric reasons.

It is interesting to note that, although the N-metallated derivatives of $^{t}Bu_2CNH$ and Ph_2CNH have differing properties in many cases, the parent imines have very similar basicities. They are, however, less basic than dialkylamines such as $^{t}BuNHEt$.

TABLE 20

$\Delta\nu$(C-D) for solutions of $CDCl_3$ in some organic and organometallic bases

Base	$\Delta\nu$(C-D)cm^{-1}	Reference
$(^t\mathrm{Bu_2CN})_3\mathrm{SnCl}$	25	a
$(^t\mathrm{Bu_2CN})_2\mathrm{SnCl_2}^b$	24	a
$^t\mathrm{Bu_2CNH}$	42	a
$\mathrm{Ph_2CNH}$	43	a
$\mathrm{Me_3CNHEt}$	89	283
$\mathrm{Me_3SiNEt_2}$	64	284
$\mathrm{Me_3SnNEt_2}$	90	284
$\mathrm{(Me_3Sn)_3N}$	106	284
liquid $CDCl_3$	12	283

$$\Delta\nu(\mathrm{C\text{-}D}) = \nu(\mathrm{C\text{-}D})_{\mathrm{gaseous\ CDCl_3}} - \nu(\mathrm{C\text{-}D})_{\mathrm{soln.}}$$

a: This work. b: freshly prepared.

TABLE 21

^{1}H Chemical shifts* for solutions of $CHCl_3$ in some organic and organometallic bases

Base	Mole Fraction $CHCl_3$	ν_o cps	Base	Mole Fraction $CHCl_3$	ν_o cps
$(^t\mathrm{Bu_2CN})_3\mathrm{SnCl}$	0.534	0.90	$(^t\mathrm{Bu_2CN})_2\mathrm{SnCl_2}$	0.495	-2.97
	0.696	1.34		0.658	-1.57
	0.821	1.78		0.746	-0.40
	0.873	1.73		0.797	0.70
	0.902	1.72		0.854	0.52
				0.883	0.65
$^t\mathrm{Bu_2CNH}$	0.286	-30.3			
	0.445	-27.7	Cyclohexane	0.286	22.9
	0.546	-24.9		0.546	15.2
	0.667	-18.5		0.667	11.7
	0.737	-12.2			

*: Upfield relative to neat $CHCl_3$

Uncorrected dilution curves for solutions of chloroform in $^{t}Bu_2CNH$, $(^{t}Bu_2CN)_nSnCl_{4-n}$ n = 2,3, and cyclohexane.

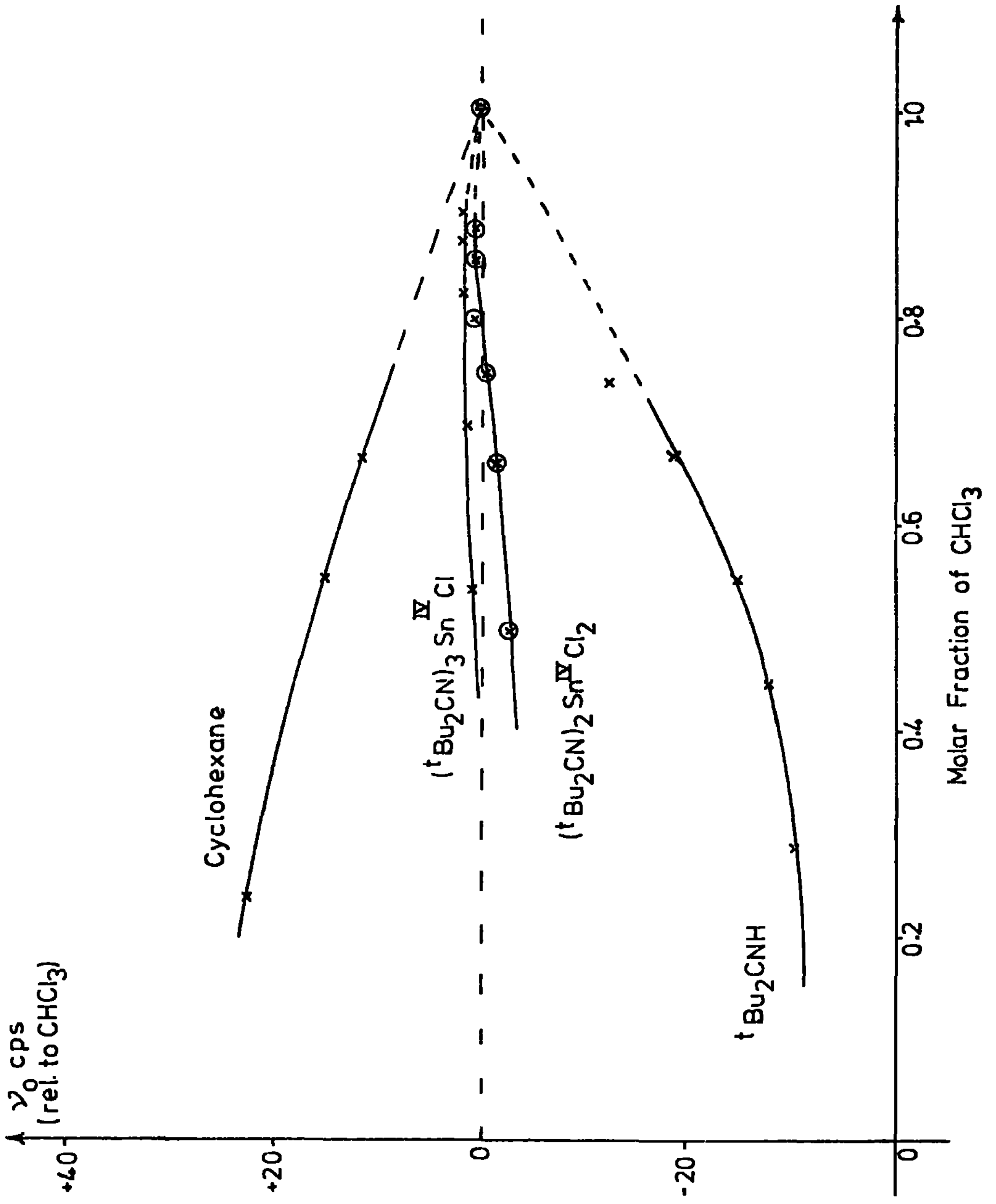


Figure 2-14

(v) Crystallographic studies.

N.W. Alcock and co-workers have determined the crystal and molecular structures of the tetrakis(diphenylmethyleneamino) derivatives, $(Ph_2CN)_4M$, M = Si, Ge, Sn.[301,302] 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 independant molecules (A and B) in the unit cell of the silicon compound.

The three compounds have similar general conformations, each containing an approximately tetrahedral N_4M unit. The lack of isomorphism is accounted for by the variation in the M-N=C bond angle (from 139.1^o and 134.5^o (averages) for silicon to 121.3^o 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 π-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 $N\longrightarrow M$ π-bonding. As a result, the bond angles at nitrogen are all less than 180^o, and can vary somewhat in order to accomodate 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 M-N π-bonding for germanium, and very little, if any, for tin. This interpretation is supported by the M-N

TABLE 22

Bond lengths and angles for the compounds $(Ph_2CN)_4M$, M = Si,Ge,Sn.[302]

M		M-N Å			M-N=C°		C=N Å [a]
		Obs. [a]	Calc.[c]	Δ[b]	Obs.	Av.	
Si	A	1.719(16)	1.879	0.160	136.2(1.3)	134.7	1.266(22)
					134.4(1.3)		
					139.5(1.3)		
					128.7(1.2)		
	B	1.716(16)	1.879	0.163	141.1(1.5)	139.5	1.274(24)
					138.6(1.3)		
					139.0(1.3)		
					139.1(1.4)		
Ge		1.872(5)	1.928	0.056	123.8(6)	127.0	1.266(6)
					130.1(6)		
Sn		2.06(4)	2.108	0.048	121.3(1.3)	121.3	1.33(4)

a : Mean values

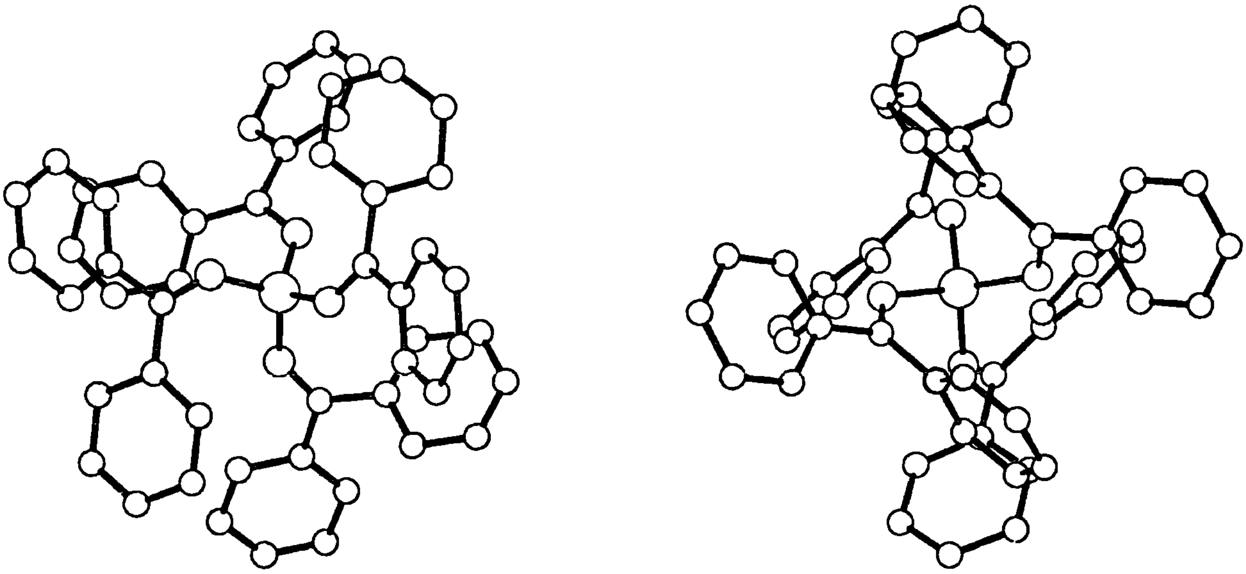
b : Δ = Calc. - Obs.

c : Derived by combining M-C, C-C (1.544Å), and C-N= (1.475 (Å)).[389]

Standard deviations in parentheses.

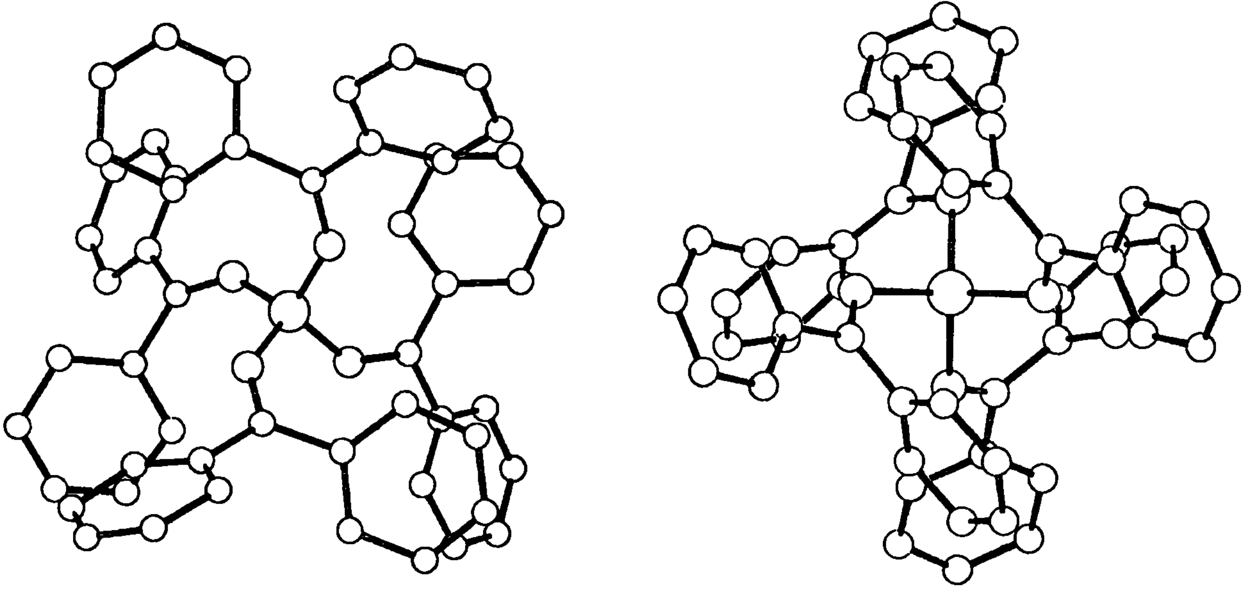
Molecular structures of the compounds $(Ph_2CN)_4M^{IV}$

M = Si, Ge, Sn.[301]



M = Si, molecule A.

M = Ge.



M = Si, molecule B.

M = 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.[389] The value for the tin compound (1.33Å) 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 SnN_4 unit, the tetrakis(dimethylamino) derivative, $(Me_2N)_4Sn$,[266] 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) π-bonding (electron diffraction study).

A preliminary crystallographic study has been carried out on $(^tBu_2CN)_4Sn$.[376a] 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, $(Ph_2CN)_2SnCl_2$ and $(Ph_2CN)_3SnCl$, which appear to be associated. The 1:1 and 2:1 adducts formed by $^tBu_2C{=}NH$ with $SnCl_4$ 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-butylmethyleneamine derivatives leaves room for a small amount of N→Sn π-donation.

It is clear that, for organonitrogen derivatives of the Group IVB elements in the tetravalent state, N→M (p→d) dative π-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 (σ-bond formation will be less sensitive than π-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 Sn^{II}-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 $\sim -20^oC$. Over a period of 3 days the solution deposited a mass of white solid, identified as the adduct diphenylmethyleneamine tin(II) dichloride, $Ph_2CNH.SnCl_2$, M.Pt. 132-3^oC (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%).

ν_{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^{o}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 $Ph_2CNH.SnCl_2$. (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^{o}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 ~-20°C, deposited a bright yellow crystalline solid, identified as diphenylmethyleneamine bis(diphenylmethyleneamino) ditin(II)-dichloride mono-toluene, $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8$, M.Pt. (sealed tube): Toluene lost at 121°C, turns orange and partially melts 175-185°C, completely melts ~245°C.

(Found: C 58.2; H 3.5; N 4.5; Cl 7.8%; M = 246

$C_{46}H_{39}N_3Sn_2Cl_2$ requires: C 58.6; H 4.1; N 4.5; Cl 7.5%; M = 941).

ν_{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, 954m, 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 diphenylmethyleneaminotin(II) chloride dimer, $(Ph_2CNSn^{II}Cl)_2$, M.Pt. 245-255°C (sealed tube).

(Found: C 46.4; H 3.3; N 4.2; Cl 11.1%; M = 546 slight dec.

$C_{26}H_{20}N_2Sn_2Cl_2$ requires: C 46.7; H 3.0; N 4.2; Cl 10.6%; M = 668).

ν_{max}(Nujol mull): 3100vw, 3070w, 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}.

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

A solution of 30 mmol. diphenylmethyleneaminolithium in ~35 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°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 ~95°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°C, when it deposited a bright red microcrystalline solid, bis(diphenylmethyleneamino)tin(II)dimer, $[(Ph_2CN)_2Sn^{II}]_2$ M.Pt. 133-4°C (Sealed Tube).

(Found: C 61.5; H 6.3; N 5.2; Cl 0%; M = 733 slight dec.
$C_{52}H_{20}N_4Sn_2$ requires: C 65.2; H 4.2; N 5.8; Cl 0%; M = 958).

ν_{max}(Nujol Mull): 3073vw, 3054w, 3020w, 1950vw, 1897vw, 1802vw, 1770vw, 1603s, 1595sh, 1588s, 1568s, 1560sh, 1542sh, 1485mw, 1444s, 1362s, 1307w, 1296vw, 1286vw, 1262w, 1251mw, 1245sh, 1192m, 1178mw, 1153w, 1072w, 1028mw, 1000vw, 972vw, 951vw, 946w, 937mw, 906w, 887m, 851vw, 843vw, 786m, 777m, 760mw, 721w, 707sh, 695vs, 661m, 648m, 623m, 572vw, 516mw, 501mw, 452mw, 426vw 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^oC. 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 1g. $(Ph_2CNSnCl)_2$ (1.495 mmol.) in 30 cm^3 dry THF at 0^oC. 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^oC, 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 $\nu(C{=}N)$ at 1604 cm^{-1} and a broad strong absorbtion at 766 cm^{-1} (typical of a π-complexed C_5H_5 group), consistent with the presence of $C_5H_5Sn^{II}N{=}CPh_2$.

vii) Attempted preparation of a diphenylmethyleneaminotin(II) chloride dimer - THF adduct.

0.6g. $(Ph_2CNSnCl)_2$ 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, $(Ph_2CNSnCl)_2$.

(Found: C 46.6%; $C_{26}H_{20}N_2Sn_2Cl_2$ requires C 46.7%).

It was concluded that no complex is formed with THF.

B. Di-t-butylmethyleneamine derivatives

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

A solution of 60 mmol. di-t-butylmethyleneaminolithium 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 bis(di-t-butylmethyleneamino)tin(II), $[({}^tBu_2CN)_2Sn^{II}]_n$, 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.

$C_{18}H_{36}N_2Sn$ requires: C 54.2; H 9.0; N 7.0; Cl 0;Li 0%; M = 399).

ν_{max}(Nujol mull): 1628s, 1604sh, 1560vs, 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 $(^tBu_2CN)_2Sn$ and $Li(^tBu_2CN)_3Sn$, tending towards the latter.

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

A solution of 45 mmol.di-t-butylmethyleneaminolithium 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^{o}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-butylmethyleneamino)tin (II), $Li(^tBu_2CN)_3Sn^{II}$, M.Pt. 170-180^{o}C dec. without melting (sealed tube).

(Found: C 58.9; H 9.6; N 7.7; Li 1.6%; M = 347 dec.

$C_{27}H_{54}N_3SnLi$ requires: C 59.4; H 9.9; N 7.7; Li 1.3%; M = 545).

ν_{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 $cm.^{-1}$

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 23

New tin(II) derivatives of methyleneamines

Group A:	
$(Ph_2CNSnCl)_2$	orange crystals
$[(Ph_2CN)_2Sn]_2$	red microcrystalline solid
$[({}^{t}Bu_2CN)_2Sn]_n$[a]	yellow crystalline solid
Group B:	
$Ph_2CNH.SnCl_2$	white solid
$Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$	yellow crystals
$({}^{t}Bu_2CN)_2HSn_2Cl_3$[b]	yellow crystalline solid
Group C:	
$({}^{t}Bu_2CN)_3H_2Sn_3Cl_5$[b]	colourless crystals
Group D:	
$Li({}^{t}Bu_2CN)_3Sn$	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 $(Ph_2CNSnCl)_2$, 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 $Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$ 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.[377] 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[290] (see Chapter 2, section 2.1) 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.

$$SnCl_2 + nLiN{=}CR_2 \longrightarrow (R_2CN)_nSnCl_{2-n} + nLiCl \qquad 3.1$$

$$Et_3N + Ph_2CNH.SnCl_2 \not\longrightarrow Ph_2CNSnCl + Et_3NH^+Cl^- \qquad 3.2$$

N-lithiated reagents have also been used in the preparation of bis(dimethylamino)tin(II)[105] and other bis(dialkylamino)tins;[103,104] 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 dialkylaminotin(II) cyclopentadienyls, $R_2NSn^{II}C_5H_5$,[103,104] prompted an attempt to prepare the corresponding diphenylmethyleneamino derivative, $Ph_2C{=}NSn^{II}C_5H_5$, which would be expected to contain a π-bonded C_5H_5 ring and a terminally bonded imino group. The spectrum of the product suggested that the reaction between $(Ph_2CNSnCl)_2$ and NaC_5H_5 (Eqn. 3.3) had produced the required compound,

$$(Ph_2CNSn^{II}Cl)_2 + 2NaC_5H_5 \longrightarrow 2Ph_2C{=}NSn^{II}C_5H_5 + 2\,NaCl \qquad 3.3$$

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 $Ph_2CNH.SnCl_2$, $[(Ph_2CN)_2Sn^{II}]_2$, and $(^tBu_2CN)_3H_2Sn_3Cl_5$, which generated no metal-containing fragments.

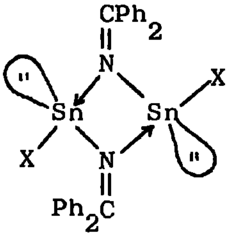
The ^1H-NMR spectra of the di-t-butylmethyleneamine derivatives (Table 28) were recorded as solutions in d^8-toluene or C_6D_6 at about 45°C and temperatures down to -100°C. The diphenylmethyleneamine derivatives, with the exception of the complex $(Ph_2CN)_3HSn_2Cl_2.C_7H_8$, were not investigated, 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 ν(C=N) for the diphenylmethyleneamino derivatives because of the obscuring aromatic absorptions, and some assignments are necessarily tentative.

S. Wallwork and M.M. Mahmoud[378] have determined the crystal and molecular structures of $(Ph_2CNSnCl)_2$ and its diphenylmethyleneamine adduct, $Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$, by X-ray diffraction. Their results are discussed in detail in the sections dealing with those compounds.

i) Group A. Compounds of the type $(R_2CNSnX)_n$, X = R_2CN,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 $(Ph_2CN)_2Sn$ 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 would be expected to minimise repulsion between the metal lone pairs.



X = Cl, N=CPh$_2$.

Figure 3-1

A crystallographic study[378] 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 $(^tBu_2CN)_2Sn$, 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 $[(^tBu_2CN)_2M]_2$ (M = Be, Zn, Mg), whose spectra all clearly differentiate between bridging and terminal methyleneamino groups even at room temperature[329,380] (for the beryllium and zinc compounds, the slightly bent terminal $C=N \rightleftharpoons M$ skeleton is also indicated by further splitting, a total of three signals being observed).[380] 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, $[(Me_2N)_2Sn]_2$,[105] which gives a single methyl signal at room temperature, but at -40°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_2N-groups. Cryoscopic studies indicated that $[(Me_2N)_2Sn]_2$ was dimeric in solution, and the ^1H-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 ^tBu-groups, there may be an equilibrium in solution between dimer and monomer.

The infra-red spectrum, however, shows two ν(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 t-butyl groups, but the corresponding beryllium compound, $[(^tBu_2CN)_2Be]_2$, 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.

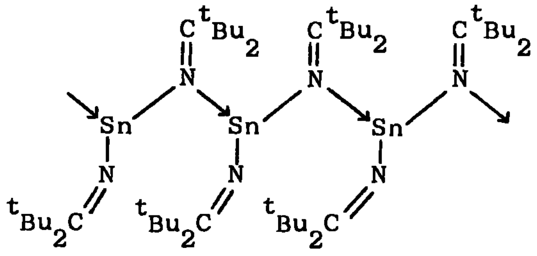


Figure 3-2

Such a structure might also explain the difficulty experienced in preparing $[(^tBu_2CN)_2Sn^{II}]_n$ free of lithium, in contrast to $[(Ph_2CN)_2Sn^{II}]_2$, 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).

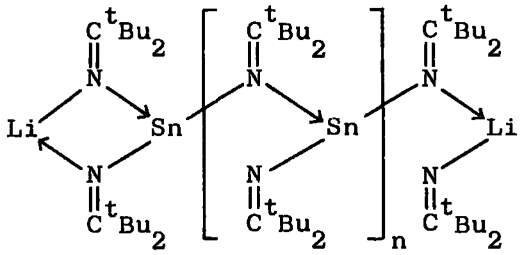


Figure 3-3

It is of interest that both $(^tBu_2CN)_2Be_2$[380] and $(^tBu_2CN)_3Al$[329] were similarly found to be difficult to prepare from the metal chloride and the iminolithium, due to formation of $Li(^tBu_2CN)_3Be$ and $Li(^tBu_2CN)_4Al$ respectively, whereas the related diphenylmethyleneamino derivatives $(Ph_2CN)_2Be$ and $(Ph_2CN)_3Al$ 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 $[(Ph_2CN)_2Sn]_2$ and $[(^tBu_2CN)_2Sn]_n$ 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 $(Ph_2CNSnCl)_2$.

The $\nu(C{=}N)$ values for terminally bonded methyleneamino 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 π-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] Å), might be expected to have a greater effect on ν(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}Bu$_2$CN)$_3$H$_2$Sn$_3$Cl$_5$). Generally, the absorptions vary little in position from that of the bridging imino-groups in $[(Ph_2CN)_2Sn^{IV}Cl_2]_n$ (1553 cm^{-1}; see Chapter 2).

The mass spectra of $[(^tBu_2CN)_2Sn]_n$ and $(Ph_2CNSnCl)_2$ 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 $(^tBu_2CN)_3Sn^+$ (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 $(^tBu_2CN)_2Sn^+$ and $^tBu_2CN^\bullet$), so that no firm support for an associated structure is provided. However, the spectrum of $(Ph_2CNSnCl)_2$ (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 $Ph_2CNSn_2Cl_2^+$ (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

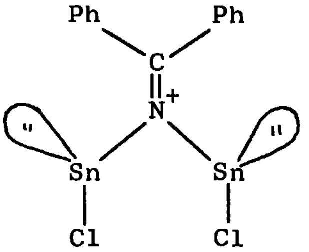


Figure 3-4

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 $(Ph_2CNSn^{II}Cl)_2$.

The crystal and molecular structures of diphenylmethyleneaminotin(II) chloride dimer, $(Ph_2CNSn^{II}Cl)_2$, have been determined by X-ray diffraction.[378] 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_2N_2 ring. The cross-ring Sn-Sn distance, 3.507Å, is considerably greater than the Sn-Sn bond distances reported for $(Ph_2Sn)_6$ (average 2.78 Å)[394] or crystalline $\{[(Me_3Si)_2CH]_2Sn\}_2$ (2.764 Å),[29] implying the absence of a metal-metal bond.

For $(Ph_2CNSnCl)_2$, 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).

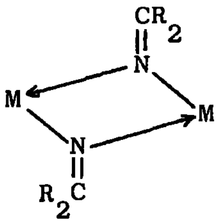


Figure 3-5

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_2N_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_2N_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 $(Ph_2CNSn^{II}Cl)_2$.[378]

Bond lengths.	Å	Bond angles	°
C(1)-N(1)	1.286 (7)	Sn(1)$\hat{N}$(1)Sn(2)	105.6 (2)
C(2)-N(2)	1.276 (8)	Sn(1)$\hat{N}$(2)Sn(2)	103.7 (2)
Sn(1)-N(1)	2.208 (5)	N(1)$\widehat{Sn}$(1)N(2)	75.0 (2)
Sn(1)-N(2)	2.230 (6)	N(1)$\widehat{Sn}$(2)N(2)	74.7 (2)
Sn(2)-N(1)	2.193 (5)	Cl(1)$\widehat{Sn}$(1)N(1)	84.6 (2)
Sn(2)-N(2)	2.228 (5)	Cl(1)$\widehat{Sn}$(1)N(2)	90.5 (2)
Sn(1)-Cl(1)	2.452 (2)	Cl(2)$\widehat{Sn}$(2)N(1)	84.8 (2)
Sn(2)-Cl(2)	2.472 (2)	Cl(2)$\widehat{Sn}$(2)N(2)	90.6 (2)

Non-bonded distances	Å
N(1)-N(2)	2.692 (7)
Sn(1)-Sn(2)	3.507 (1)

Calculated bond lengths.	Å	
Sn^{II}-Cl	2.62	From covalent radii.[372,397]
Sn^{II}-N	2.33	
C=N	1.265[389]	

Estimated standard deviations in parentheses

Molecular structure of $(Ph_2CNSn^{II}Cl)_2$.[378]

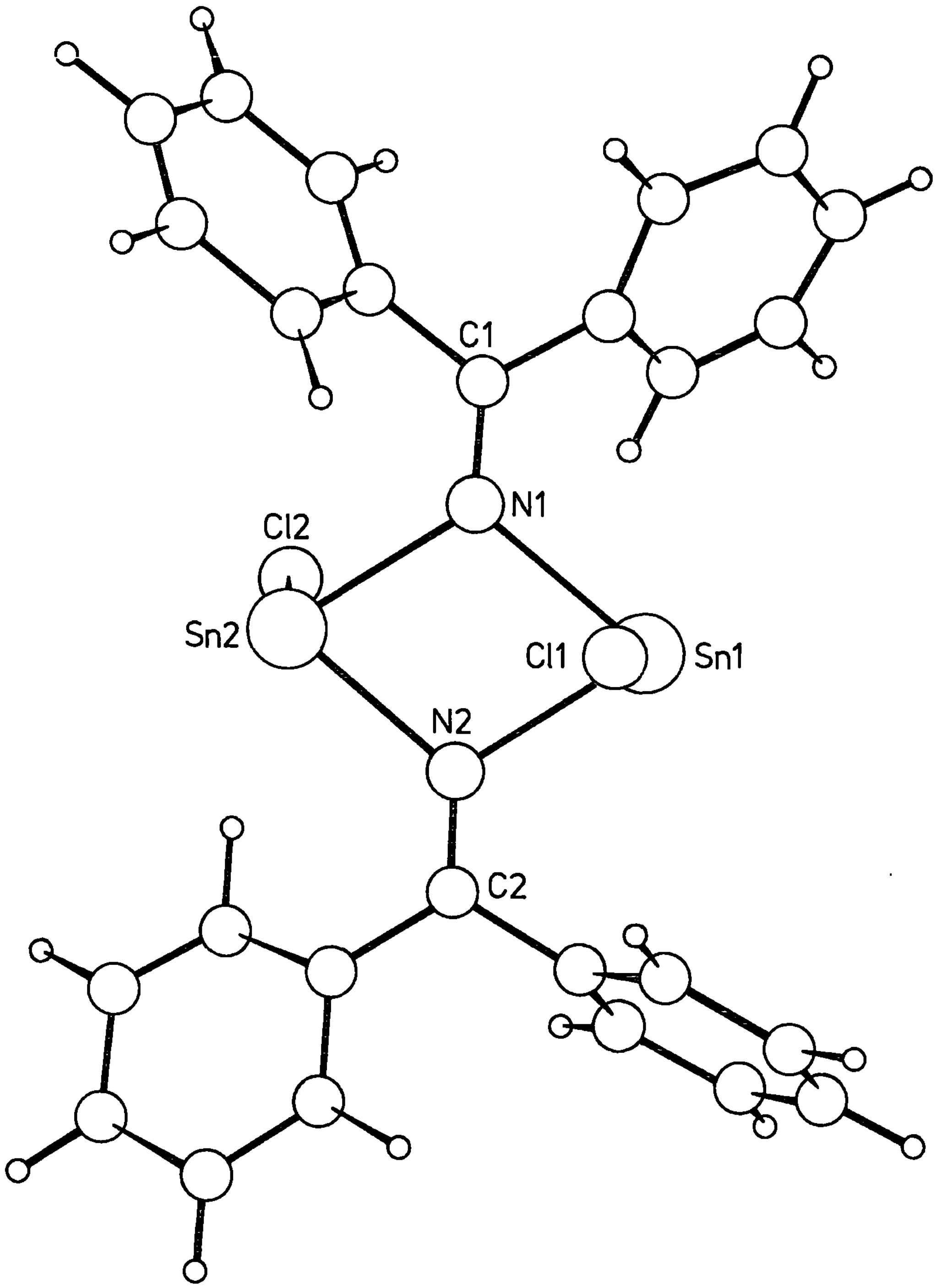


Figure 3-6

smaller than the tetrahedral angle, implying a large amount of p-character in the bonds, and the $N\hat{Sn}N$ 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 M_2N_2 ring a considerably smaller angle at nitrogen is tolerated in order to permit a wider angle at the metal (Table 25). The $Cl\hat{Sn}N$ angles are similar to the bond angles found in other pyramidal tin(II) species, such as the $SnCl_3^-$ ion.[395,396]

Table 25 lists the ring bond angles for those methyleneamino derivatives containing M_2N_2 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 Sn^{II}-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 Sn^{II}-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 ratdius 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 M_2N_2 ring system

Compound	$\hat{MNM}$ °	$\hat{NMN}$°	Ref.
$[(^tBu_2CN)_2Be]_2$	83.1 (7)	96.9 (7)	336
$(Ph_2CNMgBr.THF)_2$ THF	88.0 (2)	89.0 (2)	382
$(MeCH{=}NBMe_2)_2$	93.6 (3)	86.4 (3)	399
$(^tBu.MeC{=}NAlMe_2)_2$	94.6 (5)	85.4 (5)	399
$(p\text{-}BrC_6H_4.PhC{=}NAlPh_2)_2.2C_6H_6$	97.1	82.9	400
$(Ph_2CNSnCl)_2$	104.7 (2)^a	74.9 (2)^a	378
$Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$	101.5 (3)^a	77.1 (3)^a	378

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 $N\hat{M}N$ angle for the beryllium compound is about 12° greater than for the boron and aluminium compounds, which has been explained[336] 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 $N\hat{M}gN$ bond angle would be 120°.

The average Sn-Cl bond length for $(Ph_2CNSnCl)_2$, 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 2.67Å (crystalline $SnCl_2$[20]), 2.59 Å ($SnCl_2.2H_2O$[18]), 2.63 and 2.54 Å ($KSnCl_3$[395]) and 2.679 Å (C_5H_5SnCl[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(diphenylphosphino)ethane cobalt(II) trichlorostannate(II), $Cl(Ph_2PCH_2CH_2PPh_2)_2Co^{II}Sn^{II}Cl_3$[396] (2.431 Å). 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 $(Ph_2CNSnCl)_2$. Unassociated Sn^{IV}-Cl bonds are considerably shorter, e.g. 2.32 Å in $Ph_3Sn^{IV}Cl$.[398]

ii) Group B. The methyleneamine adducts, $R_2CNH.(R_2CN)_nSn_mCl_{(2m-n)}$.

The compounds discussed in this section are the related adducts $Ph_2CNH.SnCl_2$, $Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$, and ${}^tBu_2CNH.{}^tBu_2CNSn_2Cl_3$.

The diphenylmethyleneamine-tin dichloride adduct, $Ph_2CNH.SnCl_2$, is likely to be a monomeric, 3-coordinate species, although no evidence for its state of association could be obtained.

The other diphenylmethyleneamine adduct, $Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$, is derived from the dimer $(Ph_2CNSnCl)_2$, and a crystallographic study[378] (described in detail at the end of this section) has shown that the Sn_2N_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

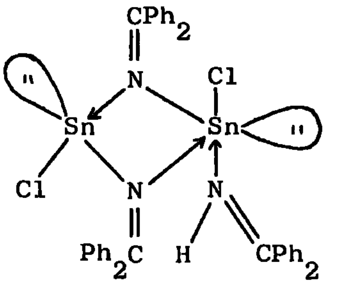


Figure 3-7

heating and the cryoscopic molecular weight (246) is sufficiently close to one third of the formula weight for $(Ph_2CN)_3HSn_2Cl_2.C_7H_8$ (313.8) to suggest complete dissociation in solution (Eqn. 3.4). Weaker bases, such as THF, do not form stable complexes.

$$(Ph_2CN)_3HSn_2Cl_2.C_7H_8 \longrightarrow Ph_2CNH + (Ph_2CNSnCl)_2 + C_7H_8 \qquad 3.4$$

Of the unusual complexes obtained from the thermal decomposition of the tin(IV) derivative $(^tBu_2CN)_2Sn^{IV}Cl_2$ (Chapter 2), $(^tBu_2CN)_2HSn_2Cl_3$ is probably related to the diphenylmethyleneamine derivative $(Ph_2CN)_3HSn_2Cl_2$, and the spectroscopic evidence is consistent with a related structure (Fig. 3-8).

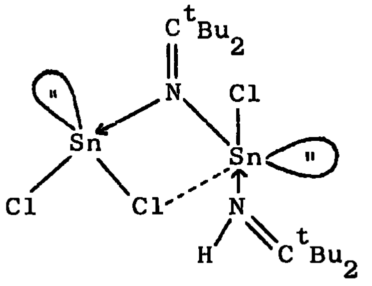


Figure 3-8

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 $Ph_2CNH.SnCl_2$, but like the methyleneamine attached to four-coordinate tin(II) in $Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$.

The dinuclear structure of $(^tBu_2CN)_2HSn_2Cl_3$ 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 $({}^{t}Bu_2CN)_2Sn_2Cl^+$ (m/e 555) is probably a result of recombination (from ${}^{t}Bu_2CNSnCl$ + ${}^{t}Bu_2CNSn$). The only detectable metal-containing fragment in the spectrum of $Ph_2CNH.-(Ph_2CNSnCl)_2.C_7H_8$ corresponds to the ion $Ph_2CNSn_2Cl_2^+$. (Table 27b).

Further evidence for the proposed structure of $({}^{t}Bu_2CN)_2HSn_2Cl_3$ is provided by its ${}^{1}H$-NMR spectrum (Table 28) which exhibits three singlet absorptions in the ${}^{t}Bu$ region, of which the upfield pair may be assigned to a ${}^{t}Bu_2CN$ ligand whose ${}^{t}Bu$ 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. $({}^{t}Bu_2CN)_2HSn_2Cl_3$, from its infra-red spectrum, contains a coordinated methyleneamine group, and the structure shown in Fig. 3-9 accounts for the observed ${}^{1}H$-NMR spectrum. Surprisingly, the signal due to the coordinated imine group could not be resolved as a doublet on cooling, unlike the ${}^{t}Bu_2CNH$-tin tetrachloride adducts (Chapter 2).

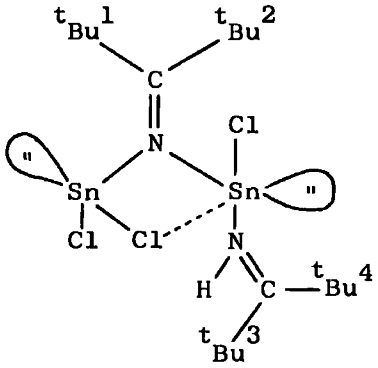


Figure 3-9

The spectrum of $(Ph_2CN)_3HSn_2Cl_2.C_7H_8$, 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 $(Ph_2CN)_3HSn_2Cl_2.2C_7H_8$ 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. $Ph_2CNH.SnCl_2$ has one band assignable to ν(C=N), while $(Ph_2CN)_3HSn_2Cl_2.C_7H_8$ and $(^tBu_2CN)_2HSn_2Cl_3$ have two, corresponding to the coordinated methyleneamine molecule and the bridging methyleneamino groups; the ν(C=N) frequencies for the latter differ little from those found for similarly bridging ligands in the compounds $[(Ph_2CN)_2Sn]_2$, $[(^tBu_2CN)_2Sn]_n$, and $(Ph_2CNSnCl)_2$, discussed as Group A.

It may be seen that ν(C=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 $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8$

The crystal and molecular structures of the imine adduct $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8$ have been determined by X-ray diffraction.[378]

Relevant bond lengths and angles for the imine adduct,

$Ph_2CNH.(Ph_2CNSnCl)_2.C_7H_8$, are listed in Table 26. The molecule is illustrated in Figure 3-10. The structure is essentially based upon that of $(Ph_2CNSnCl)_2$, with an additional molecule of diphenylmethyleneamine 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 Sn_2N_2 ring do not vary significantly from those of the parent compound $(Ph_2CNSnCl)_2$, 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 Sn_2N_2 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 $(Ph_2CNSnCl)_2$ (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 Ph_2CNH; 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 $\mathrm{Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8}$.[378]

Bond lengths. Å		Bond angles. °	
C(1)-N(1)	1.273 (13)	$\mathrm{Sn(1)\hat{N}(1)Sn(2)}$	101.6 (3)
C(2)-N(2)	1.284 (12)	$\mathrm{Sn(1)\hat{N}(2)Sn(2)}$	101.3 (3)
C(3)-N(3)	1.274 (12)	$\mathrm{N(1)\hat{Sn}(1)N(2)}$	77.3 (3)
		$\mathrm{N(1)\hat{Sn}(2)N(2)}$	76.9 (3)
Sn(1)-N(1)	2.198 (8)		
Sn(1)-N(2)	2.206 (8)	$\mathrm{Cl(1)\hat{Sn}(1)N(1)}$	72.8 (2)
Sn(1)-N(3)	2.474 (8)	$\mathrm{Cl(1)\hat{Sn}(1)N(2)}$	75.7 (2)
Sn(2)-N(1)	2.211 (8)	$\mathrm{Cl(1)\hat{Sn}(1)N(3)}$	143.8 (2)
Sn(2)-N(2)	2.211 (8)		
		$\mathrm{Cl(2)\hat{Sn}(2)N(1)}$	83.5 (2)
Sn(1)-Cl(1)	2.753 (8)	$\mathrm{Cl(2)\hat{Sn}(2)N(2)}$	93.5 (2)
Sn(2)-Cl(2)	2.550 (3)		
		$\mathrm{N(3)\hat{Sn}(1)N(1)}$	81.3 (3)
		$\mathrm{N(3)\hat{Sn}(1)N(2)}$	74.3 (3)
		$\mathrm{N(3)\hat{Sn}(1)C(3)}$	132.3 (6)

Non-bonded distances Å	
N(1)-N(2)	2.750 (11)
Sn(1)-Sn(2)	3.416 (1)

Estimated standard deviations in parentheses.

Molecular structure of $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8$.[378]

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

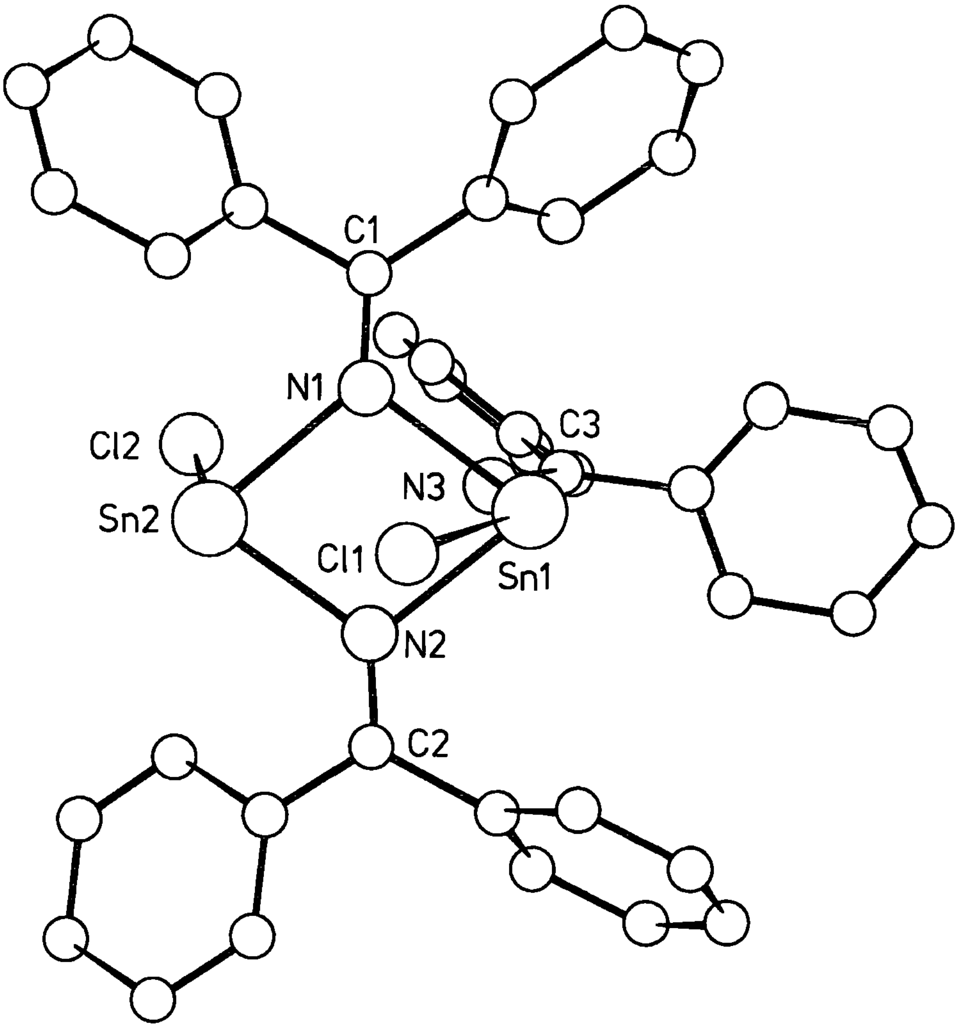


Figure 3-10

(the axial species are bent away from it; the N(3)$\hat{\text{Sn}}$(1)Cl(1) axial angle is only 143.8°) together with the constraint imposed by formation of the Sn_2N_2 ring. The latter accounts for the small angle between equatorial bonds (77.3°) when compared to the other two Sn^{II} compounds known to have structures based on the trigonal bipyramid, bis(benzylacetonato)tin(II)[39] and bis(N,N'-diethyldithiocarbamato)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'-diethyldithiocarbamato)tin(II) (139.6°).[38]

The axial Sn(1)-Cl(1) bond length (2.753 Å) is considerably longer than the majority of known Sn^{II}-Cl bonds. This is probably due to the higher coordination number of Sn(1), 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^{II}-Cl bond distance of 2.766 Å found in the pentagonal bipyramidal complex π-$C_6H_6Sn^{II}(AlCl_4)_2.C_6H_6$,[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(1)$\hat{\text{N}}$(3)C(3) bond angle of 132.3° is greater than the sp^2 hybrid angle of 120°, probably as a result of repulsion between the methyleneamine molecule and the Sn(1) lone pair. The Sn(1)-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).[40] It is, however, similar to the coordinate N→Sn bonds found in the EDTA complexes $Sn^{II}[Sn^{II}EDTA.H_2O].H_2O$ (2.45 and 2.46 Å)[21] and $Sn^{II}H_2EDTA$ (2.39 and 2.44 Å)[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^{II}-N bond distances may be compared to 2.06 Å found for $(Ph_2CN)_4Sn^{IV}$.[301,302] They are longer,as expected, consistent with the greater size of tin(II).

iii) Group C: $(^tBu_2CN)_3H_2Sn_3Cl_5$

The other material isolated from the decomposition products of $(^tBu_2CN)_2Sn^{IV}Cl_2$ is more complex. Several structures could be postulated for its formula, $(^tBu_2CN)_3H_2Sn_3Cl_5$, but the infra-red spectrum, which shows a high frequency for ν(C=N) and a broad, intense ν(N-H) absorption, is consistent with the presence of di-t-butylmethyleneaminium ions, $^tBu_2C{=}NH_2^+$.

The ^{1}H-NMR spectrum (Table 28 p. 178) consists of three singlet absorptions in the ^{t}Bu 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 $^tBu_2CNH_2^+$ 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 $^tBu^1$ and $^tBu^2$ in the diagram.

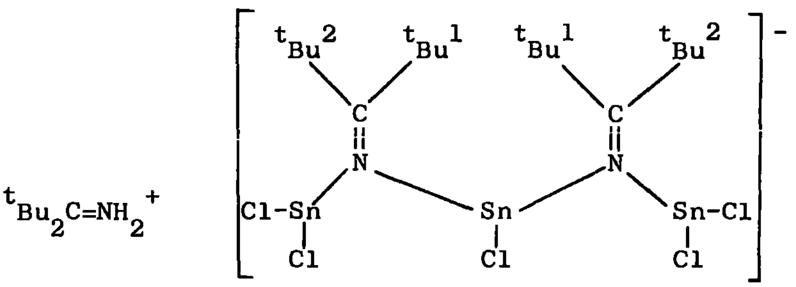
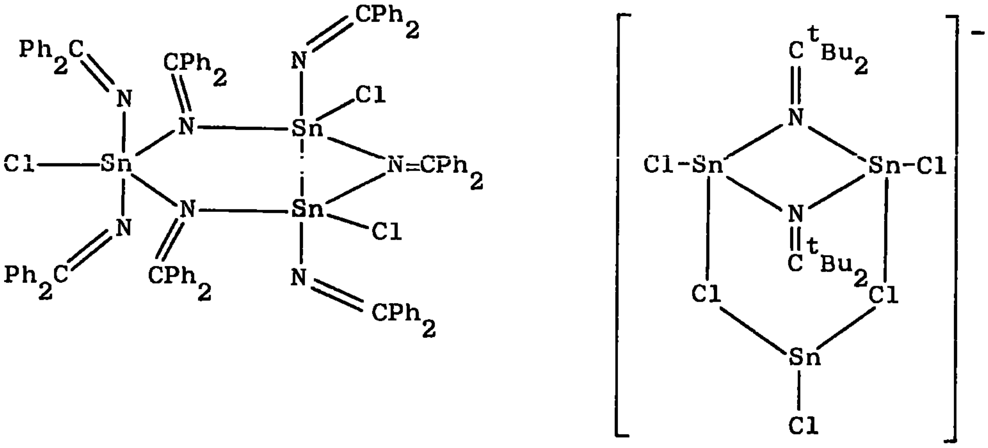


Figure 3-11

The infra-red spectrum of $(^tBu_2CN)_3H_2Sn_3Cl_5$ contains two bands assignable to $\nu(C=N)$ (Table 29; p. 179) the higher energy absorption corresponds quite closely to the value found for $^tBu_2CNH_2^+Cl^-$ (1670 cm^{-1}).[344] The lower energy absorption may be assigned to bridging $^tBu_2CN$ 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 $[(Ph_2CN)_2Sn^{IV}Cl_2]_n$ (1553 cm^{-1}; see Chapter 2). It is, however, closer to that of $[(Ph_2CN)_3Sn^{IV}Cl]_n$ (1535 cm^{-1}). It is probable that variations in $\nu(C=N)_{bridging}$ will arise from changes in the $Sn\hat{N}Sn$ bond angle, in accordance with which those compounds which probably contain 4-membered Sn_2N_2 rings all absorb at 1550-1560 cm^{-1}. This may support the suggestion of an Sn_2NCl ring for the compound $(^tBu_2CN)_2HSn_2Cl_3$, since this would similarly constrain the angle at nitrogen. The low frequencies for $(^tBu_2CN)_3H_3Sn^{II}{}_3Cl_5$ and $[(Ph_2CN)_3Sn^{IV}Cl]_n$ may therefore indicate a significant difference in structure, the absence of Sn_2N_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 $(^tBu_2CN)_2Sn_3Cl_5{}^-$, 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_2N_2 ring (e.g. Fig 3-12b).

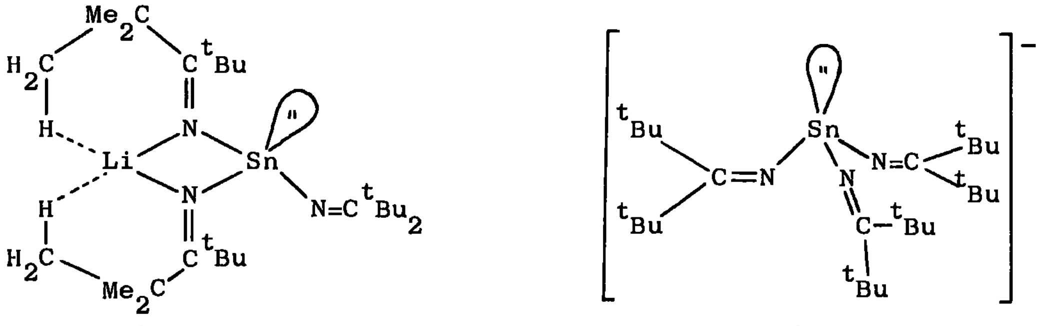


(a) Some imino-groups omitted for clarity (b)

Figure 3-12

iv) Group D: Li(^{t}Bu$_2$CN)$_3$Sn^{II}.

Lithium tris(di-t-butylmethyleneamino)tin(II), Li(^{t}Bu$_2$CN)$_3$Sn^{II}, 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.[381] The lithium triorganotins, R_3SnLi, are considered to be largely ionic,[14] but if the known structure of Li(^{t}Bu$_2$CN)$_4$Al[338] (Fig. 2-2d) is paralleled here, a structure involving an LiN$_2$Sn ring (Fig 3-13a) might be expected. This is, however, inconsistant 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



(a) (b)

Figure 3-13

chemical environments (only one resonance is observed in the ^{1}H-NMR spectrum). The only structure which could accomodate 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, $Li(^{t}Bu_2CN)_3Be$, which shows two ^{t}Bu resonances (split further on cooling),[380] 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 $Li(^{t}Bu_2CN)_3Sn^{II}$ 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.

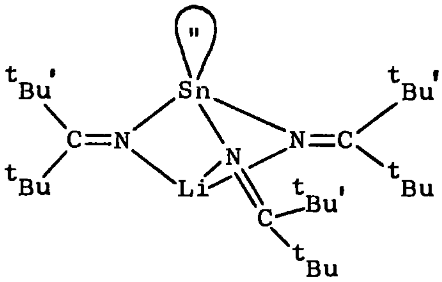


Figure 3-14

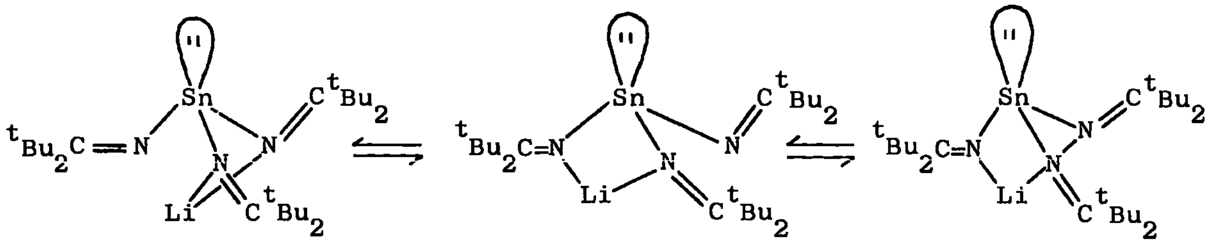


Figure 3-15

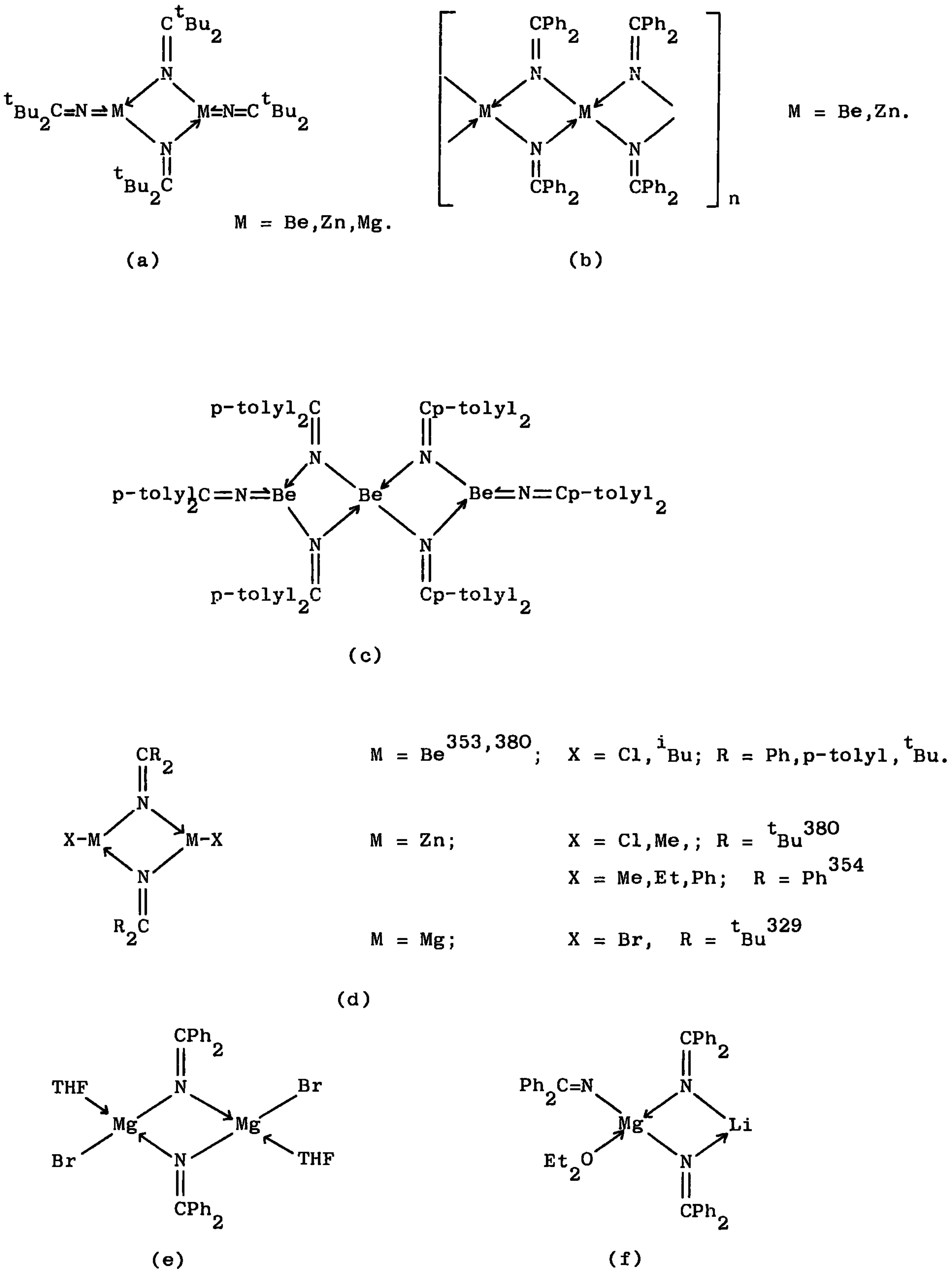
v) General considerations

The structural evidence for these compounds shows the apparent stability of the $Sn^{II}-N\rightarrow Sn^{II}$ 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 $[({}^tBu_2CN)_2Sn^{II}]_n$ 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 $[(Ph_2CN)_2Sn^{II}]_2$ and $(Ph_2CNSn^{II}Cl)_2$ are well-known; the di-t-butylmethyleneamino-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 π-bonding in the

Some Methyleneamino-derivatives of the Group II elements



M = Be^{353,380}; X = Cl, ^{i}Bu; R = Ph, p-tolyl, ^{t}Bu.

M = Zn; X = Cl, Me, ; R = ^{t}Bu^{380}

X = Me, Et, Ph; R = Ph^{354}

M = Mg; X = Br, R = ^{t}Bu^{329}

Figure 3-16

case of the bis-imino derivatives (Fig. 3-16a and d). The bis-diarylmethyleneamino-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 $(Ph_2CNMgBr)_2.3THF$ 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 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 $(Ph_2CNSn^{II}Cl)_2$[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.

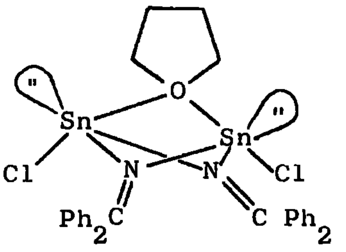


Figure 3-17

An additional matter of some interest concerns metal-nitrogen stretching frequencies. Comparison of the spectra of the di-t-butylmethyleneamino derivatives of tin(II) and tin(IV) allows the tentative assignment of $\nu(Sn^{II}-N)$ for $Li(^{t}Bu_2CN)_3Sn$ and $[(^{t}Bu_2CN)_2Sn]_n$ as 663 and 657 cm^{-1} respectively, showing the expected shift to lower energy relative to the derivatives of the more electronegative oxidation state ($\nu(Sn^{IV}-N) \sim 690-700\ cm^{-1}$). Assignments are few in the literature for Sn^{II}-N stretching frequencies; it has been suggested that for $\{[(Me_3Si)_2N]_2Sn^{II}\}_2$ and some related compounds,^{104} $\nu_{as}(Sn-N)$ 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 ($\nu_{as}(Cd-N) = 410\ cm^{-1}$, $\nu_s(Cd-N) = 385\ cm^{-1}$).^{393} Similarly $\nu_{as}(Sn^{II}-N)$ for $[(Me_2N)_2Sn^{II}]_2$ was assigned at 440 cm^{-1}.^{105} The spectra of $Li(^{t}Bu_2CN)_3Sn^{II}$ and $[(^{t}Bu_2CN)_2Sn^{II}]_n$ do in fact show well-defined absorptions (which are not seen for $^{t}Bu_2CNH$ or $^{t}Bu_2CN$-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 $[(Ph_2CN)_2Sn^{II}]_2$, or the spectra of any of the other imino-tin(II) derivatives, and attempts to assign $\nu(Sn^{II}-N)$ for $[(Ph_2CN)_2Sn^{II}]_2$ 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_2N_2 ring.

For the di-t-butylmethyleneamine derivative $[(^{t}Bu_2CN)_2Sn^{II}]_n$ 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 $[(Ph_2CN)_2Sn^{II}]_2$ 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 accomodated without cleavage of the Sn_2N_2 ring.

Where the compounds contain terminally-bonded imino-groups, there is little evidence for (p→d) $N \rightarrow Sn^{II}$ dative π-bonding with associated linearity of the $C{=}N{\rightleftharpoons}Sn$ skeleton. This behaviour is similar to that of Sn^{IV}, probably for similar reasons, one of the most important of which may be that the π-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) $(Ph_2CNSnCl)_2$

m/e	Relative Intensity	Assignment
670	1.5	$(Ph_2CN)_2Sn_2Cl_2{}^+$
635	1.0	$(Ph_2CN)_2Sn_2Cl^+$
534	0.4	?
525	0.4	$Ph_2CNSn_2Cl_3{}^+$
490	18	$Ph_2CNSn_2Cl_2{}^+$
335	2	$Ph_2CNSnCl^+$
300	7	Ph_2CNSn^+
258	2	$PhCNSnCl^+$
197	22	$PhSn^+$
190	4	$SnCl_2{}^+$
180	100 *	Ph_2CN^+
155	25	$SnCl^+$
120	5	Sn^+

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

b) $(Ph_2CN)_3HSn_2Cl_2.C_7H_8$

m/e	Relative Intensity	Assignment
490	0.01	$Ph_2CNSn_2Cl_2{}^+$
181	57	Ph_2CNH^+
180	100	Ph_2CN^+
91	100*	$C_7H_7{}^+$

c) $Li(^tBu_2CN)_3Sn$

m/e	Relative Intensity	Assignment
407	7	$Li(^tBu_2CN)_2Sn^+$
260	1	$^tBu_2CNSn^+$
204	0.4	$^tBuCHNSn^+$
203	0.8	$^tBuCNSn^+$
165	5	Me_3Sn^+
141	100	$^tBu_2CNH^+$
140	13	$^tBu_2CN^+$
135	4	$MeSn^+$

*: Off-scale

d) $[({}^{t}\mathrm{Bu_2CN})_2\mathrm{Sn}]_n$

m/e	Relative Intensity	Assignment
540	1.5	$({}^{t}\mathrm{Bu_2CN})_3\mathrm{Sn}^+$
483	0.2	$({}^{t}\mathrm{Bu_2CN})_2{}^{t}\mathrm{BuCNSn}^+$
457	4	$({}^{t}\mathrm{Bu_2CN})_2{}^{t}\mathrm{BuSn}^+$
400	2	$({}^{t}\mathrm{Bu_2CN})_2\mathrm{Sn}^+$
374	3	${}^{t}\mathrm{Bu_2CN}.{}^{t}\mathrm{Bu_2Sn}^+$
352	7	?
343	14	${}^{t}\mathrm{Bu_2CN}.{}^{t}\mathrm{BuCNSn}^+$
260	28	${}^{t}\mathrm{Bu_2CNSn}^+$
204	13	${}^{t}\mathrm{BuCHNSn}^+$
203	14	${}^{t}\mathrm{BuCNSn}^+$
141	100	${}^{t}\mathrm{Bu_2CNH}^+$
140	14	${}^{t}\mathrm{Bu_2CN}^+$

e) $({}^{t}\mathrm{Bu_2CN})_2\mathrm{HSn_2Cl_3}$

m/e	Relative Intensity	Assignment
555	0.2	$({}^{t}\mathrm{Bu_2CN})_2\mathrm{Sn_2Cl}^+$
450	0.4	${}^{t}\mathrm{Bu_2CNSn_2Cl_2}^+$
381	0.3	?
295	0.6	${}^{t}\mathrm{Bu_2CNSnCl}^+$
260	2	${}^{t}\mathrm{Bu_2CNSn}^+$
238	6	${}^{t}\mathrm{BuCNSnCl}^+$
190	87	$\mathrm{SnCl_2}^+$
155	100 *	SnCl^+
141	44	${}^{t}\mathrm{Bu_2CNH}^+$
140	14	${}^{t}\mathrm{Bu_2CN}^+$
120	42	Sn^+

*: Off-scale

TABLE 28

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

Compound	τ^a values. ppm.
$[(^tBu_2CN)_2Sn]_n$	$8.77s^b$
$Li(^tBu_2CN)_3Sn$	8.88s.
$(^tBu_2CN)_2HSn_2Cl_3$	C-H: 8.79s(2),9.06s(1),9.19s(1) N-H: not detected.
$(^tBu_2CN)_3H_2Sn_3Cl_5$	C-H: 8.35s(1),9.04s(1),9.18s(1) N-H: not detected.
$(Ph_2CN)_3HSn_2Cl_2.C_7H_8{}^c$	Ar-H: 2.54br.m,3.40s.(total 20) CH_3: 8.13s(3). $N-H^d$: 0.16br.s.

Relative intensities in parentheses

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

b: Partially resolved at -100°C as a doublet, separation 0.10ppm.

c: C_6D_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, $\nu(C=N)cm^{-1}$, for some new methyleneamino derivatives of tin(II)

Compound	$\nu(C=N)cm^{-1}$		
	Terminal	Bridging	Coordinated $R_2C=NH$
$Ph_2CNH.SnCl_2$			1594
$[(Ph_2CN)_2Sn]_2$	1603	1560 ?	
$(Ph_2CNSnCl)_2$		1564	
$(Ph_2CN)_3HSn_2Cl_2.C_7H_8$		1564 ?	1600
$[(^tBu_2CN)_2Sn]_n$	1628	1560	
$Li(^tBu_2CN)_3Sn$	1619		
$(^tBu_2CN)_2HSn_2Cl_3$		1552	1586
$(^tBu_2CN)_3H_2Sn_3Cl_5$		1534	1671 *

All spectra were recorded on nujol mulls.

cf. $\nu(C=N)$ for the parent imines:

Ph_2CNH	1603 cm^{-1}
$^tBu_2CNH$	1604 cm^{-1}

* : $^tBu_2CNH_2^+$

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;[403] arylmethyleneamines were known to undergo ortho-metallation with both palladium(II)[404,405]

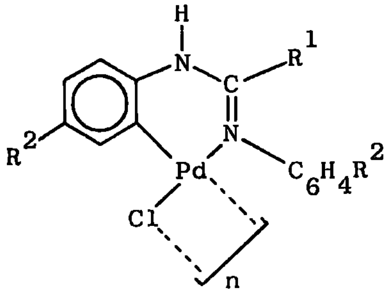


Figure 4-1

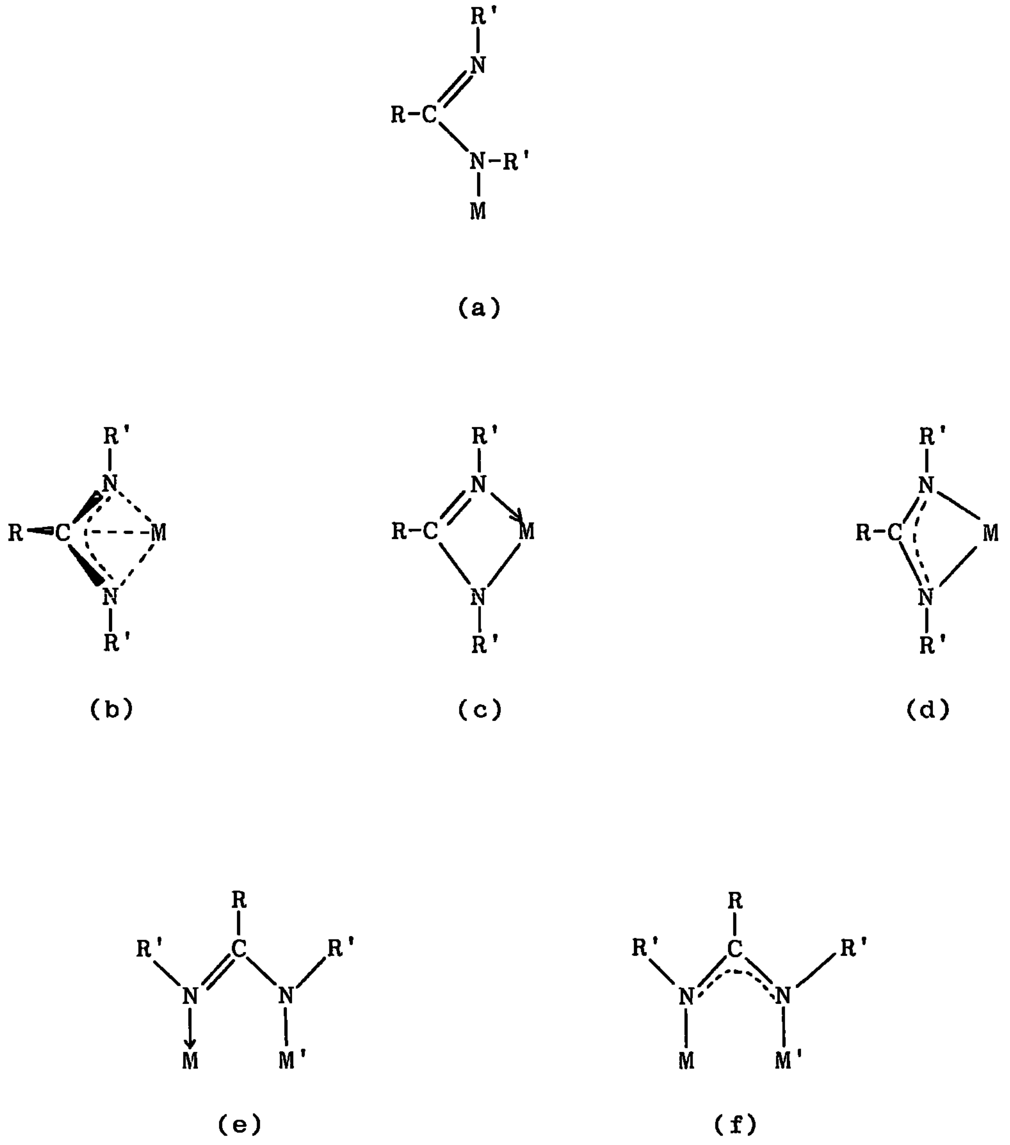
and tin(IV) chlorides (see Chapter 5).

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 CX_2 unit (X = O, NR)[406] (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)

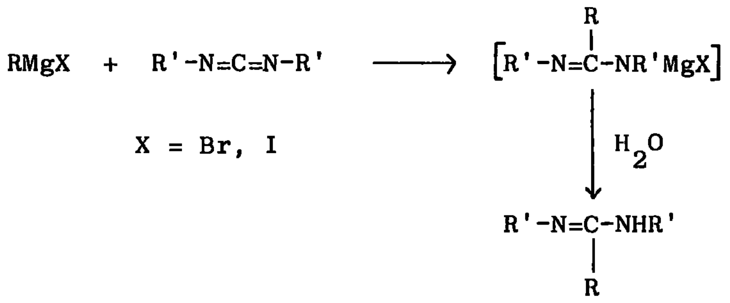
(b) (c) (d)

(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,[304] 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[407] (Eqn. 4.1).

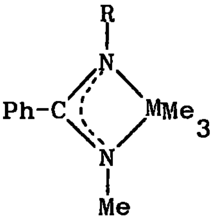


$$\mathrm{RMgX} + \mathrm{R'{-}N{=}C{=}N{-}R'} \longrightarrow \left[\mathrm{R'{-}N{=}\overset{\overset{\displaystyle R}{|}}{C}{-}NR'MgX}\right] \xrightarrow{\mathrm{H_2O}} \mathrm{R'{-}N{=}\underset{\underset{\displaystyle R}{|}}{C}{-}NHR'} \qquad X = \mathrm{Br, I} \qquad 4.1$$

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,[408,411] manganese,[409] iron and cobalt,[410] nickel,[411,414] molybdenum,[411,415] tungsten,[411] chromium,[415] rhenium,[416] tantalum and niobium,[412] and copper and silver.[413,414] The majority of these compounds appear to contain amidino groups which are bidentate to a single metal atom, although the nickel derivative $[\mathrm{C_5H_5Ni(PhN.CPhNPh)}]_n$ appears to be polymeric, probably via bridging amidino groups,[411] and the copper(I) derivative of N,N'-di(2-anthraquinonyl)formamidine was considered to be similarly bridged.[413] Molybdenum[415] and rhenium[416] 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 (MeN.CPh.NMe)MMe_3 (M = Si,Sn), and (Me_3SiN.CPh.NMe)MMe_3 (M = Si, Ge, Sn, Pb).[304] The compounds were generally considered to contain the delocalised bidentate skeleton illustrated in Figure 4-3,

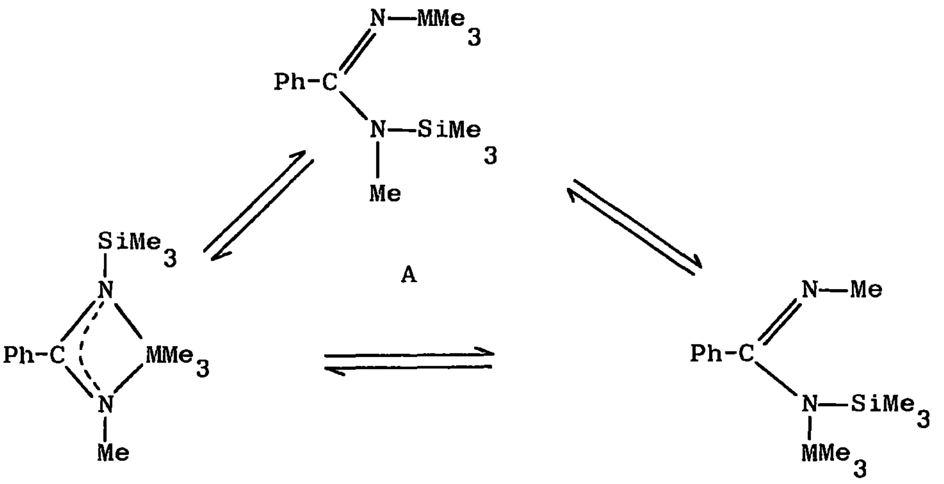


R = Me, M = Si,Sn;

R = $SiMe_3$, M = Si,Ge,Sn,Pb.

Figure 4-3

although for the latter series of compounds an equilibrium appeared to exist, giving rise to mixtures of isomers (Eqn. 4.2). The localised

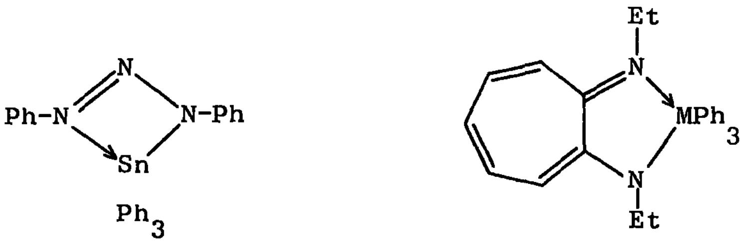


4.2

B M = Si,Ge,Sn, Pb. C

forms A and C appear to be preferred for M = 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 = Sn),[134] the aminophosphinimines (X = PPh$_2$, M = Sn)[415] and -arsinimines (X = AsPh$_2$, M = Sn)[416] and the aminotroponeimines (X = tropone, M = Si, Ge, Sn).[280] The triazenotins, which are monomeric, probably contain bidentate ligands (e.g. Fig. 4-4a).[134]



(a) (b)

Figure 4-4

No conclusion was reached for the compounds Ph$_3$SnNPh-MPh$_2$=NPh (M = P,As),[415,416] but the aminotroponeimates, on the basis of NMR evidence, were considered to contain five-coordinate metal atoms (Fig. 4-4b),[280] in agreement with the observed decrease in stability of the compounds in the order M = Sn > Ge > 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).

i) Reaction of N,N'-diphenylacetamidinolithium with silicon tetrachloride (Mole ratio 1:1)

A solution of 2.103g. N,N'-diphenylacetamidine (10 mmol.) in 60 cm^3 dry ether was cooled to -196°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°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°C for 2 days, deposited a white, microcrystalline solid, identified as bis(N,N'-diphenylacetamidino)dichlorosilane, $[CH_3C(NPh)_2]_2SiCl_2$.

(Found: C 66.8, H 3.9, N 10.1, Cl 13.3%; $C_{28}H_{26}N_4SiCl_2$ requires: C 65.0, H 5.0, N 10.8, Cl 13.7%).

ν_{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, $\left\{\left[CH_3C(NPh)_2\right]_2SiCl_2\right\}_2.C_7H_8$,^{c} M.Pt. (sealed tube) 94-6°C.

(Found: C 68.4, H 8.3, N 9.4, Cl 10.0%; M = 462.
$C_{63}H_{60}N_8Si_2Cl_4$ requires: C 67.2, H 5.3, N 10.0, Cl 12.6%; M = 563^a, 375^b)

a: Assuming formation of dimeric $(Am_2SiCl_2)_2$ in solution.

b: Assuming formation of monomeric Am_2SiCl_2 in solution.

c: Favoured by ^{1}H-NMR data.

ν_{max} (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, 496m, 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 $(Am_2SiCl_2)_2$.

ii) Reaction of N,N'-diphenylacetamidinolithium with germanium tetrachloride (Mole ratio 1:1)

A suspension of 10 mmol. N,N'-diphenylacetamidinolithium in about 65 cm^3 ether/hexane (prepared as in the previous reaction) was cooled to $-196^{o}C$ and 1.165 cm^3 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 cm^3 dry toluene. The mixture was then heated to $100^{o}C$ and filtered while hot, yielding a white precipitate (LiCl) and a pale greenish-yellow solution. The latter was concentrated under vacuum to 20 cm^3, and 10 cm^3 dry hexane were added. On cooling to $-20^{o}C$ for several days, the resulting solution deposited a white microcrystalline solid, identified as <u>bis(N,N'-diphenylacetamidino)germanium dichloride,</u> $\{[CH_3C(NPh)_2]_2GeCl_2\}_n$, M.Pt. (sealed tube): $166^{o}C$, phase transition-sample falls to powder. Melts, $184-6^{o}C$.

(Found: C 60.5, H 5.1, N 9.1, Cl 12.8%; M = 673 dec. $C_{28}H_{26}N_4GeCl_2$ requires: C 59.8, H 4.6, N 10.0, Cl 12.7%; M(monomer) = 561.5).

ν_{max}(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^oC 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 <u>N,N'-diphenylacetamidinotin(IV)trichloride</u>, $CH_3C(NPh)_2Sn^{IV}Cl_3$, M.Pt.: $166-8^oC$ (sealed tube).

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

$C_{14}H_{13}N_2SnCl_3$ requires: C 38.7, H 3.0, N 6.4, Cl 24.5%; M = 448).

ν_{max}(Nujol mull): 3078w, 3039w, 1956vw, 1881vw, 1810vw, 1750vw, 1645w, 1600m, 1590m, 1514sh, 1498vs, 1455vs, 1422vs, 1326mw, 1310m, 1291mw, 1214w, 1180vw, 1163vw, 1080m, 1034m, 1008mw, 978vw, 925mw, 917w, 852m, 770m, 759vs, 753s, 698vs, 678w, 628vw, 623vw, 590mw, 523m, 470vw, 446w, 425vw, 385vw, 363sh, 353 m cm.$^{-1}$

iv) Reaction between N,N'-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'-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, $CH_3C(NHPh)_2{}^+Cl^-$, with the 1:1 amidine-tin tetrachloride adduct, $CH_3C(=NPh)NHPh.SnCl_4$, in the approximate mole ratio 2:3.

(Found: C 42.6, H 3.0, N 7.3, Cl 28.8%.
$C_{14}H_{15}N_2Cl$ requires: C 68.1, H 6.1, N 11.4, Cl 14.4%;
$C_{14}H_{14}N_2SnCl_4$ requires: C 35.6, H 3.0, N 5.9, Cl 30.2%)

The yellow solution, on standing for several hours at -20°C, deposited a mass of bright yellow crystals, identified from their infra-red spectrum as <u>N,N'-diphenylacetamidinotin(IV)trichloride</u>, $CH_3C(NPh)_2Sn^{IV}Cl_3$.

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

A suspension of 16.8 mmol. N,N'-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, $[CH_3C(NPh)_2Sn^{II}Cl]_2$, M.Pt. 92-4°C (sealed tube).

(Found: C 46.9, H 2.7, N 7.7, Cl 9.9%; M = 551 dec.
$C_{14}H_{13}N_2SnCl$ requires: C 46.3, H 3.5, N 7.7, Cl 9.8%; M (monomer) = 363.5).

ν_{max}(Nujol mull): 3063w, 3023w, 1944vw, 1880vw, 1807vw, 1739vw, 1650vw, 1597s, 1580m, 1523vs, 1495vs, 1450s, 1416vs, 1382s, 1320mw, 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 $Sn^{II} > Si > Ge > Sn^{IV}$. Decomposition was indicated by the appearance in the infra-red spectrum of a band at ~ 1640 cm^{-1}, corresponding to $\nu(C{=}N)$ for the free imine, accompanied by a $\nu(N\text{-}H)$ 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 > Ge > 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.

TABLE 30

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

$\{[CH_3C(NPh)_2]_2SiCl_2\}_2.nC_7H_8$	n = 0,1	white solids
$\{[CH_3C(NPh)_2]_2GeCl_2\}_m$		white solid
$CH_3C(NPh)_2Sn^{IV}Cl_3$		yellow crystals
$[CH_3C(NPh)_2Sn^{II}Cl]_2$		white crystalline solid

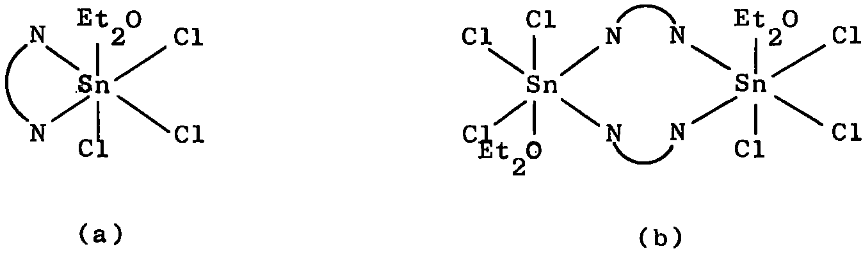
The most convenient preparative route to these compounds was the reaction of N,N'-diphenylactamidinolithium with the metal halide (Eqn. 4.3). This method has been previously used in the preparation of the compounds $PhC(NMe)_2MPh_3$ (M = Si,Sn),[304] and also extensively in the study of

$$\mathrm{nAmLi} + \mathrm{MCl}_m \longrightarrow \mathrm{nLiCl} + \mathrm{Am}_n\mathrm{MCl}_{m-n} \qquad 4.3$$

transition element systems.[408,409,411] 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 $\mathrm{AmSn^{IV}Cl_3}$ (Eqn. 4.4), but the reaction did not go to completion.

$$\begin{tikzcd}
\mathrm{AmH} + \mathrm{SnCl_4} \arrow[r] & \mathrm{AmH.SnCl_4} \arrow[d, "\Delta"', "\times 2"] & \\
& \mathrm{Am\overset{+}{H}_2\overset{-}{Cl}} + \mathrm{AmSnCl_3} + \mathrm{SnCl_4} & 4.4
\end{tikzcd}$$

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 $\overset{\frown}{\mathrm{N\ N}}$ to represent an amidino group). Even mild heating of this white intermediate led to yellowing and formation of $\mathrm{AmSn^{IV}Cl_3}$.



(a) (b)

Figure 4-5

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 diarylmethyleneamino derivatives (Chapter 2).

$$2AmMCl_3 \longrightarrow Am_2MCl_2 + MCl_4 \qquad 4.5$$

$M = Si, Ge.$

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,[378] which shows $AmSn^{IV}Cl_3$ to contain five-coordinate tin with a bidentate amidino group (Fig. 4-6).

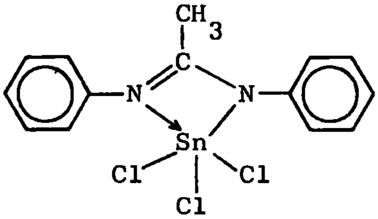
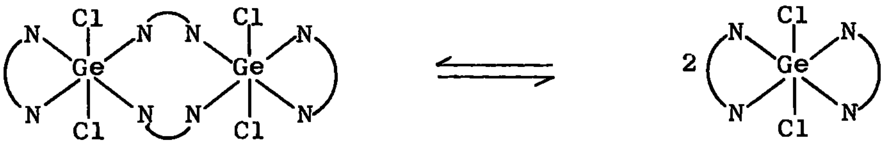


Figure 4-6

Interpretation of the observed molecular weight (462) of the silicon compound $Am_2SiCl_2.nC_7H_8$ 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 $(Am_2SiCl_2)_2.C_7H_8$. 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 Am_2GeCl_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



4.6

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 Am_2MCl_2 (M = 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 ν(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 $Me_2M(CN)_2$ (M = Si,Ge, Sn)^{188} would remain possible for the solid materials. Both show an absorption in the ν(C=N) region which is not found in the spectrum of $AmSn^{IV}Cl_3$ (although it is seen for $(AmSn^{II}Cl)_2$), suggesting a different mode of bonding for the

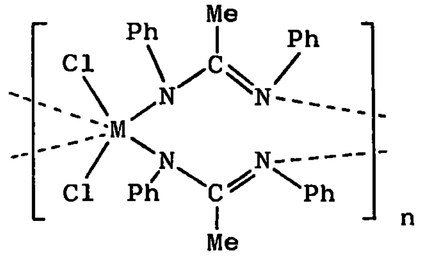
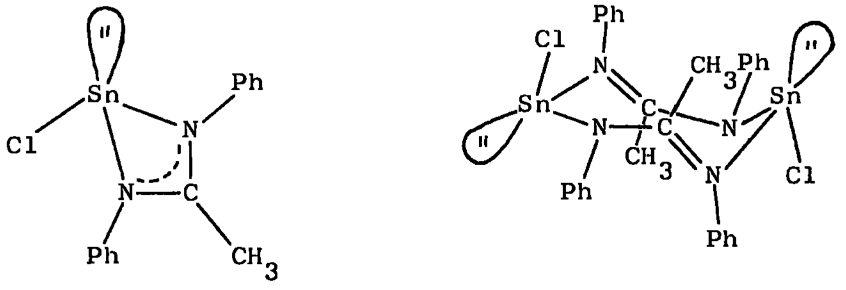


Figure 4-7

amidino groups.

The observed molecular weight of 551 for the tin(II) compound, $(\mathrm{AmSn^{II}Cl})_2$, 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 ^{1}H-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 accomodate 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 (N$\hat{\mathrm{S}}$nN is 61.1° in $\mathrm{AmSn^{IV}Cl_3}$ compared to 74.9° in the $\mathrm{Sn_2N_2}$ ring in $(\mathrm{Ph_2CNSn^{II}Cl})_2$[401]), 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 π-systems are therefore probably localised, since maintenance of a planar SnNCNSn skeleton, necessary for delocalisation



(a) (b)

Figure 4-8

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[415] and rhenium[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 $AmSn^{IV}Cl_3$, 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 $Ph^{\cdot}$ or $PhN^{\cdot}$; loss of the methyl group; elimination of the stable molecule acetonitrile, $CH_3C{\equiv}N$, leaving the fragment Ph_2N-. 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 $(AmSn^{II}Cl)_2$ is in contrast to the situation for the methyleneamino-bridged tin(II) derivatives, such as $(Ph_2CNSn^{II}Cl)_2$, where

TABLE 31

Important fragments in the mass spectra of some N,N'-diphenylacetamidino derivatives of the Group IVB elements

a) Am_2SiCl_2

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
683	3	-	275	11	-
602	7	-	271	3	$AmSiCl^+-H^{\cdot}$
567	14	-	258	2	$Am_2SiCl_2^{2+}$
516	72	$Am_2SiCl_2^+$	240.5	1	Am_2SiCl^{2+}
500	5	$Am_2SiCl_2^+-CH_3^{\cdot}-H^{\cdot}$	236	7	$AmSi^+-H^{\cdot}$
499	7	$Am_2SiCl_2^+-CH_3^{\cdot}-2H^{\cdot}$	230	7	$CH_3CN_2PhSiCl_2^+$
481	100*	Am_2SiCl^+	210	100	AmH^+
475	7	-	194	5	$PhNCNPh^+$
465	8	-	180	2	$PhNCPh^+$
400	15	-	169	12	Ph_2NH^+
393	100*	$AmSiCl_2Ph^+-H^{\cdot}$	167	8	$Ph_2N^+-H^{\cdot}$
377	39	-	154	2	Ph_2^+
364	18	$AmSiClNPh^++H^{\cdot}$	118	100*	$PhNCCH_3^+$
357	7	-	105	61	$PhN_2^+ PhNCH_2^+$
331	2	Ph_2NSiCl^+	92	100*	$PhNH^+$
307	100*	$AmSiCl_2^+$	91	100*	PhN^+
291	27	$C(NPh)_2SiCl_2^+-H^{\cdot}$	77	100*	Ph^+

* : Off-scale.

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

b) Am_2GeCl_2

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
597	0.2	$Am_2GeCl_3^+$	263.5	2	Am_2GeCl^{2+}
562	92	$Am_2GeCl_2^+$	260	10	$PhNCH_3GeCl_2^+$
546	0.7	$Am_2GeCl_2^+-CH_3^{\cdot}-H^{\cdot}$	209	100^*	Am^+
527	100	Am_2GeCl^+	194	31	$PhNCNPh^+$
501	0.5	? $AmGeCl^+ + Ph^{\cdot} + PhNCH_3^{\cdot}$	180	3	$PhNCPh^+$
445	0.4	$AmGeCl_2NPh^+ + H^{\cdot}$	167	75	$Ph_2N^+-H^{\cdot}$
410	3	$AmGeClNPh^+ + H^{\cdot}$	118	100^*	$PhNCCH_3^+$
397	1	-	105	9	PhN_2^+, $PhNCH_2^+$
388	0.5	$AmGeCl_3^+$	93	27	$PhNH_2^+$
374	0.4	$AmGeNPh^+$	91	17	PhN^+
353	100^*	$AmGeCl_2^+$	83.5	2	$Ph_2N^{2+}-H^{\cdot}$
337	1	?$AmGeCl_2^+-CH_3^{\cdot}-2H^{\cdot}$	77	100^*	Ph^+
318	25	$AmGeCl^+$			
283	5	$AmGe^+$			
277	11	$CH_3CN_2PhGeCl_2^+ + H^{\cdot}$			

c) $AmSn^{IV}Cl_3$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
643	0.2	$Am_2SnCl_3^+$	287	1	$CH_3CN_2PhSnCl^+$
608	13	$Am_2SnCl_2^+$	260	21	$SnCl_4^+$
573	3	Am_2SnCl^+	247	1	$PhNSnCl^+ + H^\cdot$
525	0.1	$AmSnCl_3.NPh^+$	225	100	$SnCl_3^+$
490	0.2	$AmSnCl_2.NPh^+$	209	100^*	Am^+
477	0.6	$CH_3CN.AmSnCl_3^+ + 2H^\cdot$	199.5	1	$AmSnCl_2^{2+}$
455	0.1	$AmSnCl.NPh^+$	194	14	$PhNCNPh^+$
434	26	$AmSnCl_3^{\cdot+}$	190	26	$SnCl_2^+$
399	29	$AmSnCl_2^+$	180	32	$PhNCPh^+$
364	37	$AmSnCl^+$	168	36	Ph_2N^+
352	1	-	155	74	$SnCl^+$
342	1	-	118	100^*	$PhNCCH_3^+$
329	7	$AmSn^+$	104	21	$PhNCH^+$
323	8	Ph_2NSnCl^+	91	57	PhN^+
304	1	-	77	100	Ph^+

d) $(AmSn^{II}Cl)_2$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
608	0.1	$Am_2SnCl_2^+$	231	8	$PhSnCl^+-H^\cdot$
573	0.1	Am_2SnCl^+	224	6	$PhNCSn^++H^\cdot$
538	1	Am_2Sn^+	209	100^*	Am^+
537	1	$Am_2Sn^+-H^\cdot$	194	67	$PhNCNPh^+$
			190	4	$SnCl_2^+$
456	2	$(Ph_2N)_2Sn^+$	185	8	$C_5H_5Sn^+$
441	7	$AmSnClPh^+$	180	7	$PhNCPh^+$
408	21	-	168	100^*	Ph_2N^+
364	100^*	$AmSnCl^+$	164.5	7	$AmSn^{2+}$
349	4	$C(NPh)_2SnCl^+$	155	100^*	$SnCl^+$
347	6	$C(NPh)_2SnCl^+-2H^\cdot$	118	100^*	$PhNCCH_3^+$
329	100^*	$AmSn^+$	105	100	PhN_2^+, $PhNCH_2^+$
309	3	Ph_2SnCl^+	91	100^*	PhN^+
287	30	$CH_3CN_2PhSnCl^+$	77	100^*	Ph^+
272	3	$PhNCNSnCl^+$			
247	15	$PhNSnCl^++H^\cdot$			

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 C_6D_6 solutions at approximately 42°C, and on d^8-toluene solutions of $(Am_2SiCl_2)_2.C_7H_8$ and $(AmSn^{II}Cl)_2$ 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 $(Am_2SiCl_2)_2.C_7H_8$, 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 tin(II) and then to tin(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 monsubstituted 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

Compound	Chemical shifts τ ppm.^{a}		
	Ar-H	CH_3	N-H
$(Am_2SiCl_2)_2.C_7H_8$	2.92s (~40)	8.01s^b(3)	-
	2.99s^b(~5)	8.74s^c(6)	
		8.87s (6)	
$(Am_2GeCl_2)_n$	3.10s (10)	8.98s (3)	-
$AmSn^{IV}Cl_3$	3.08,3.12d(10)	8.85s(3)	-
$(AmSn^{II}Cl)_2^e$	3.08s (~2.5)		
	3.17,3.23d(~6)	8.75s(3)	-
	3.30,3.36m(~1.5)		
AmH	2.82s(~2)		
	2.88s (~5)	8.66s(3)	4.17s(1)
	3.03,3.11,3.18m(~3)		

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_6D_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 π-system (Fig. 4-9) allows assignment of the strong singlet

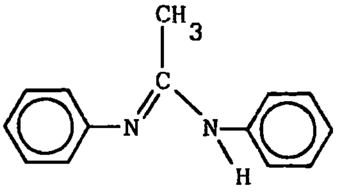


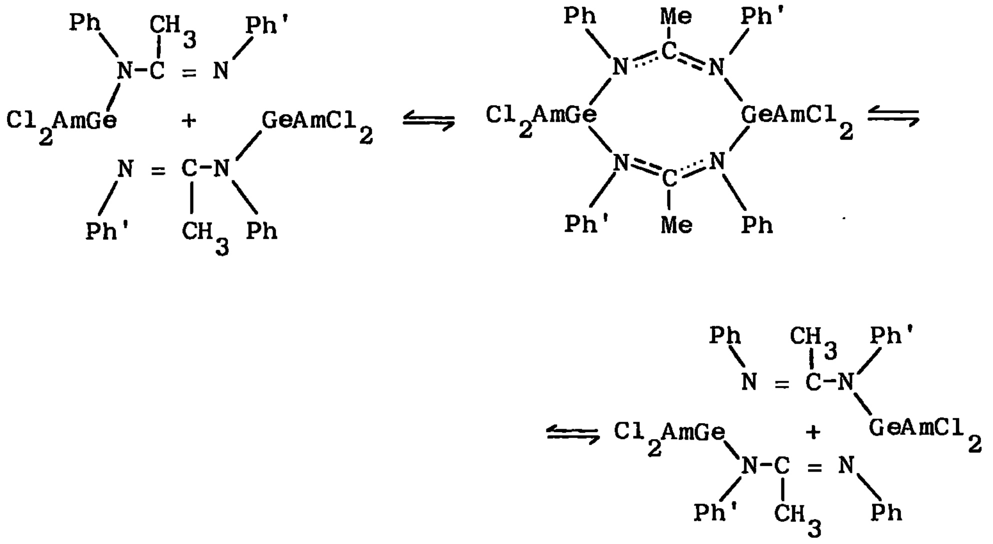
Figure 4-9

at 2.88τ to the imino-bonded phenyl group (PhN=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 $(AmSn^{II}Cl)_2$ 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 π-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 $\text{Sn}\hat{\text{N}}\text{C}$ angle ($\sim 94^\circ$ compared to 120° 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, Am_2MCl_2 (M = 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



4.7

etc.

the silicon compound Am_2SiCl_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_2SiCl_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 $(AmSn^{II}Cl)_2$, which contains only bridging amidino groups, it seems likely that for $(Am_2SiCl_2)_2$ 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.

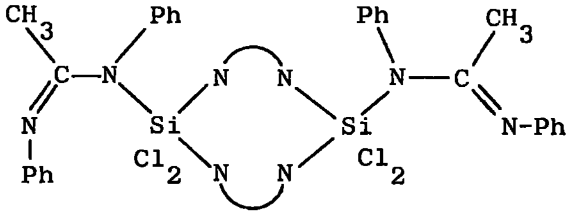


Figure 4-10

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.[406] For several tantalum or niobium chloride derivatives of a number of bidentate N,N'-disubstituted acetamidines, ν(NCN) was assigned to a weak band at ~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 ~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 33

ν(NCN) for some N,N'-diphenylacetamidino derivatives of the Group IVB elements

Compound	ν(NCN) cm^{-1}
$(Am_2SiCl_2)_2$	1566vs, 1332m
$(Am_2SiCl_2)_2.C_7H_8$	1566vs, 1336m
$(Am_2GeCl_2)_n$	1554vs, 1324w
$(AmSn^{II}Cl)_2$	1523vs, 1382s
$AmSn^{IV}Cl_3$	?
AmH	1633vs,1535vs,1338s

If the higher energy absorption (1520-1570 cm^{-1}) is assigned to ν_{as}(NCN), then a decrease is observed Si > Ge > Sn^{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 π-system.

For the compounds Am_2MCl_2 (M = 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. 4-11a). In this case separate ν(NCN) absorptions would be expected for the two types of ligand. However, $AmSn^{IV}Cl_3$, which contains only bidentate chelating amidino groups, shows no absorptions in this region apart from the aromatic ring bands at ~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 ^1H-NMR evidence for the silicon derivative Am_2SiCl_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 ν(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. 4-11b). The similarity of the spectrum of the corresponding germanium compound may indicate a similar structure in the solid.

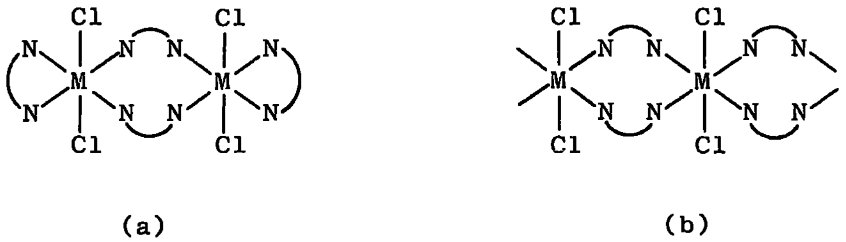


Figure 4-11

Some N,N'-diphenylacetamidino derivatives of molybdenum and tungsten have been found to show a medium absorption at ~1630 cm^{-1}, attributed to ν_{as}(NCN).[411] 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 $AmSn^{IV}Cl_3$ cannot be disregarded as a possible candidate for ν_{as}(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 $(Am_2SiCl_2)_2$ where a band at 566 cm^{-1} does not appear in the spectra of the other compounds. This is in the appropriate region for ν_s(NSiN),[418] 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

ν(M-Cl) for some N,N'-diphenylacetamidino derivatives of the Group IVB elements

Compound	ν(M-Cl) cm^{-1}	
	ν_{as}	ν_s
$(Am_2SiCl_2)_2$	492	436,412
$(Am_2SiCl_2)_2.C_7H_8$	496	436,400
$(Am_2GeCl_2)_n$	360	340,324
$(AmSn^{II}Cl)_2$	?	325
$AmSn^{IV}Cl_3$	353	-

the two asymmetric and one symmetric stretching vibrations of the $SnCl_3$ group,[452] would be expected for $AmSn^{IV}Cl_3$. The observed band is probably one of the former; ν_s is probably outside the range studied.

The presence of absorptions corresponding to ν_s(ClMCl) 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;[418] this may be indicative of a higher coordination number in these compounds. Generally the expected trend in frequencies is followed, i.e. $Si > Ge > Sn^{IV} > Sn^{II}$.

iv) Crystallographic studies.

The crystal and molecular structure of $AmSn^{IV}Cl_3$ has been determined by X-ray diffraction.[401] 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_2Sn ring is planar, and the skeleton is also planar at carbon and both nitrogens, suggesting the possibility of a delocalised π-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.[401] 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,[372] suggesting that partial

TABLE 35

Bond lengths and angles from the crystal structure of $CH_3C(NPh)_2Sn^{IV}Cl_3$ 401

Bond lengths	Å	Bond angles	°
Sn-N(1)	2.180(20)	$N(1)\hat{C}(1)N(2)$	109.5(9)
Sn-N(2)	2.087(23)	$C(1)\hat{N}(1)Sn$	93.7(1.6)
		$C(1)\hat{N}(2)Sn$	95.6(1.7)
C(1)-N(1)	1.29 (4)	$N(1)\hat{Sn}N(2)$	61.1(3)
C(1)-N(2)	1.37 (4)		
		$Cl(1)\hat{Sn}Cl(2)$	106.9(5)
Sn-Cl(1)	2.315(3)	$Cl(2)\hat{Sn}Cl(3)$	95.6(1)
Sn-Cl(2)	2.335(10)	$Cl(3)\hat{Sn}Cl(1)$	100.7(5)
Sn-Cl(3)	2.317(9)		

Non-bonded interactions. Å	
Sn-C(1)	2.60(1)

Estimated standard deviations in parentheses.

Molecular structure of $CH_3C(NPh)_2Sn^{IV}Cl_3$.[401]

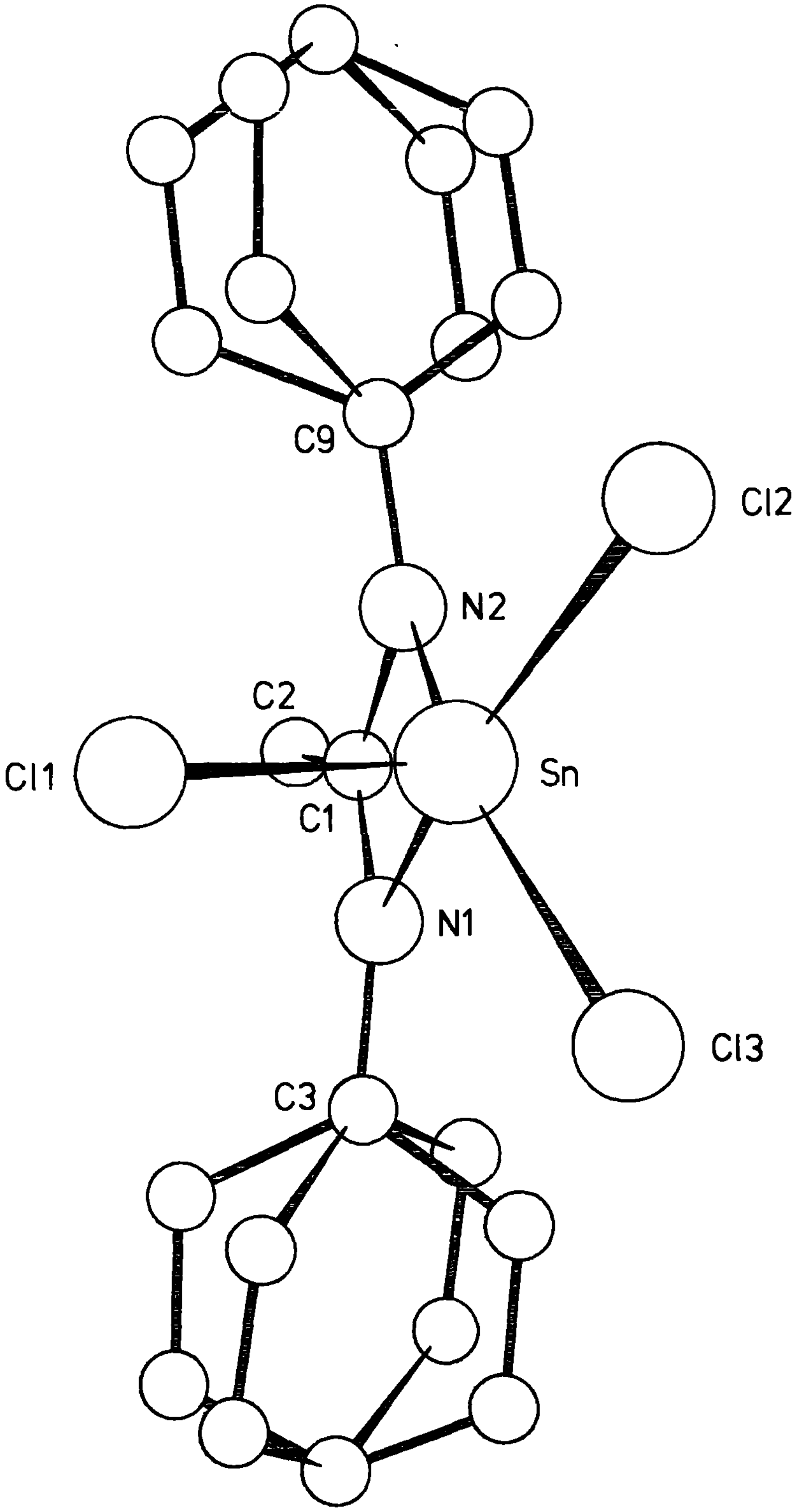


Figure 4-12

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,[401] and for the tantalum derivative $(^iPrNCCH_3N^iPr)_2$-$TaCl_3$, it is 1.35(3) Å.[419] The latter contains two symmetric amidino groups, but the related compound $(C_6H_{11}NCCH_3NC_6H_{11})_2TaMeCl_2$ contains one symmetric and one asymmetric ligand;[420] 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 N$\hat{\text{Sn}}$N 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 N$\hat{\text{Sn}}$N angle than the symmetric form with the ligand occupying two equatorial positions. A similar effect is seen in the structure of $(C_6H_{11}NCCH_3NC_6H_{11})_2TaMeCl_2$,[420] which is based on a severely distorted pentagonal bipyramid; the symmetrically bonded amidino group occupies two equatorial sites, and the asymmetrically

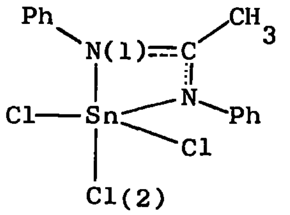


Figure 4-13

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] tetranitrates, $M^{IV}(NO_3)_4$ (M = 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.

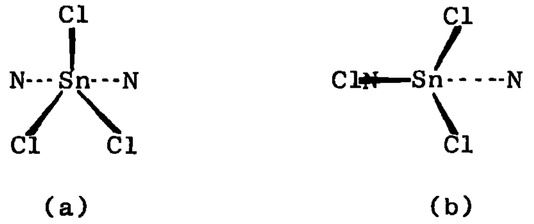


Figure 4-14

The shorter Sn-N bond length, 2.087(23) Å, is slightly longer than those observed in the four-coordinate compounds $\text{Sn}^{\text{IV}}(\text{NCPh}_2)_4$[301,302] and $\text{Sn}^{\text{IV}}(\text{NMe}_2)_4$[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_3SnNCS,[191] but is generally shorter than most $\text{N}\leftarrow\text{Sn}^{\text{IV}}$ dative bonds,[12] e.g. 2.260(5) Å in the ortho-metallated compound $2\text{-SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tolyl)=NH}$[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 $\text{Me}_2\text{SnCl}_3^-$,[61] 2.316(2) Å average for $2\text{-SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tolyl)=NH}$[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 $\text{Me}_2\text{SnCl}_3^-$,[61] 2.416(2) Å for $2\text{-SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tolyl)=NH}$[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_3SnCl (2.318(15) Å)[422] and Ph_2SnCl_2 (2.336(2) and 2.355(2) Å).[423]

C. Summary

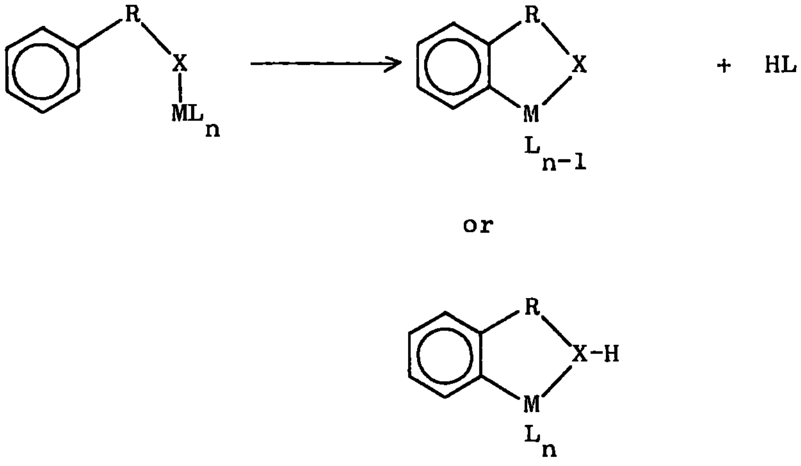
Several new N,N'-diphenylacetamidino derivatives of silicon, germanium, and tin have been prepared. The mono-amidinotin(IV) trichloride is stable, but the silicon and germanium analogues are unstable to disproportionation to the bis-amidino metal dichlorides and cannot be isolated. The mono-amidinotin(II) chloride may also be obtained, as a dimeric species probably containing an eight-membered $\text{Sn}_2\text{N}_4\text{C}_2$ ring involving three-coordinate tin(II). $\text{AmSn}^{\text{IV}}\text{Cl}_3$ 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 Am_2GeCl_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 DIARYLMETHYLENEAMINOTIN(IV) TRICHLORIDES

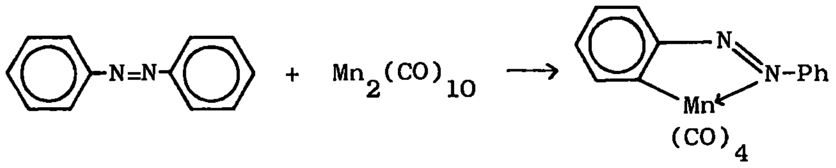
5.1 Introduction

The generalised intramolecular aromatic metallative rearrangement of metal complexes may be written as in Equation 5.1. An aryl

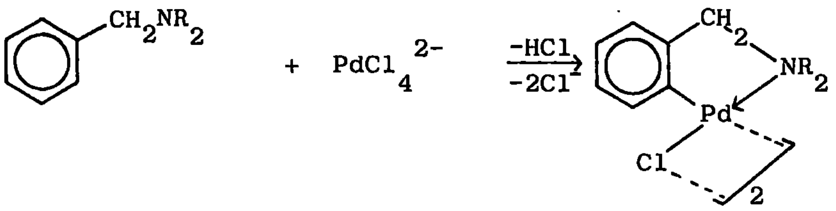


5.1

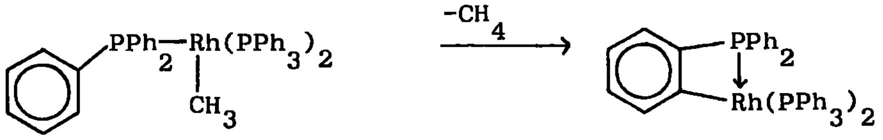
C-H bond of the ligand, PhRX (X is an electronegative element, e.g. O,N,P,) reacts with the central metal M to form a metal-carbon bond. The hydrogen atom so displaced may be eliminated from the molecule or may be transferred to the group X. Owing to the steric restrictions, such reactions occur in the 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.



(426) 5.2.



(427) 5.3



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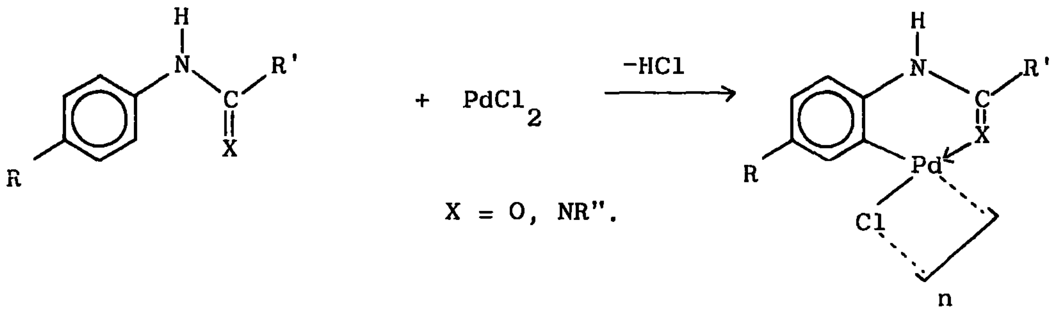
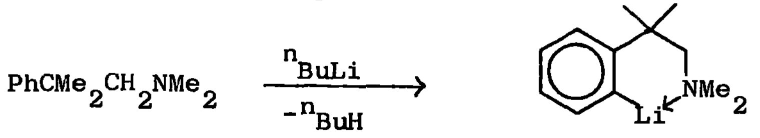


(403) 5.5

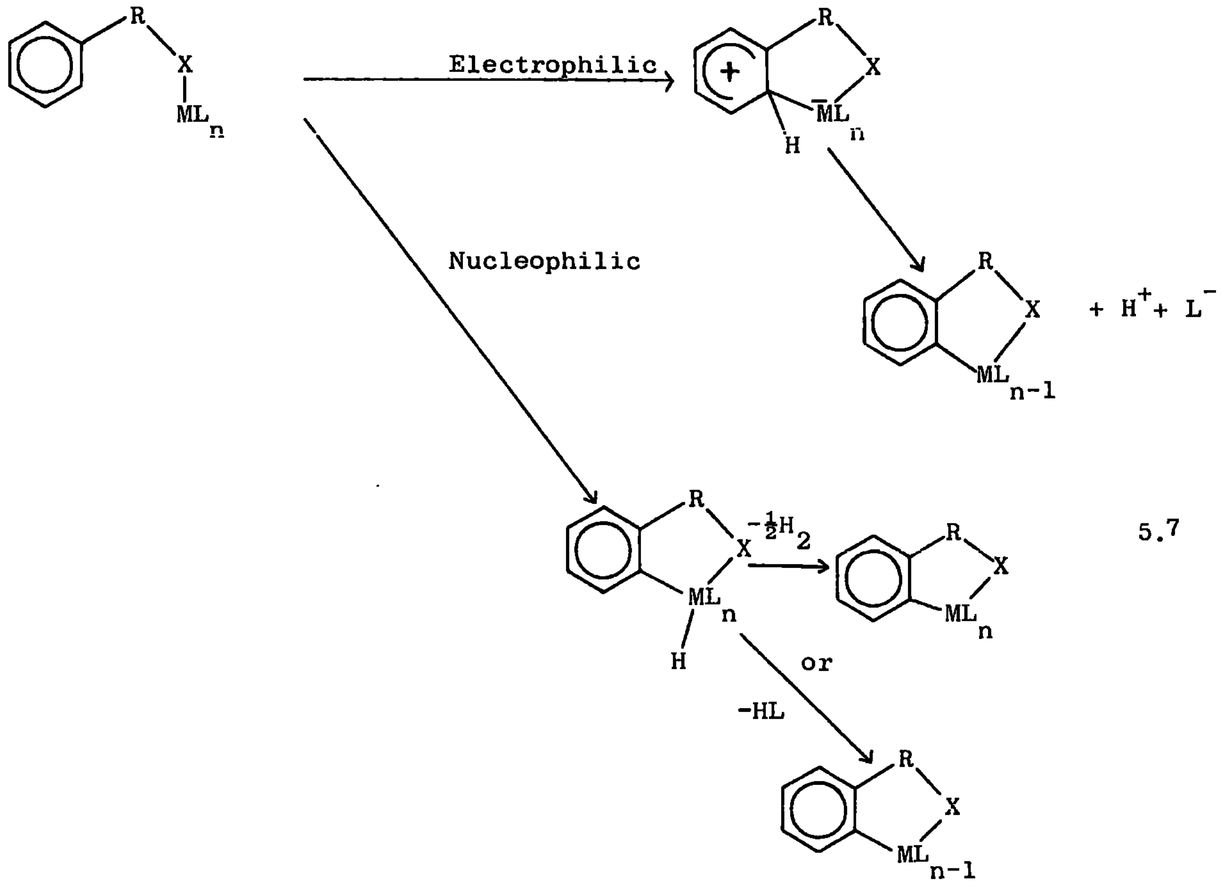
Such reactions in the main result in the formation of 5-membered heterocycles, although phosphine ligands in particular often rearrange to give 4-membered rings (Eqn. 5.4). Few reports exist to date of the formation of 6-membered metallocycles by such a process (e.g. Eqn. 5.5).[403]

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,[437,438] arylmethyleneamines,[404,405] 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[426] 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[429] (e.g. Eqn. 5.6).



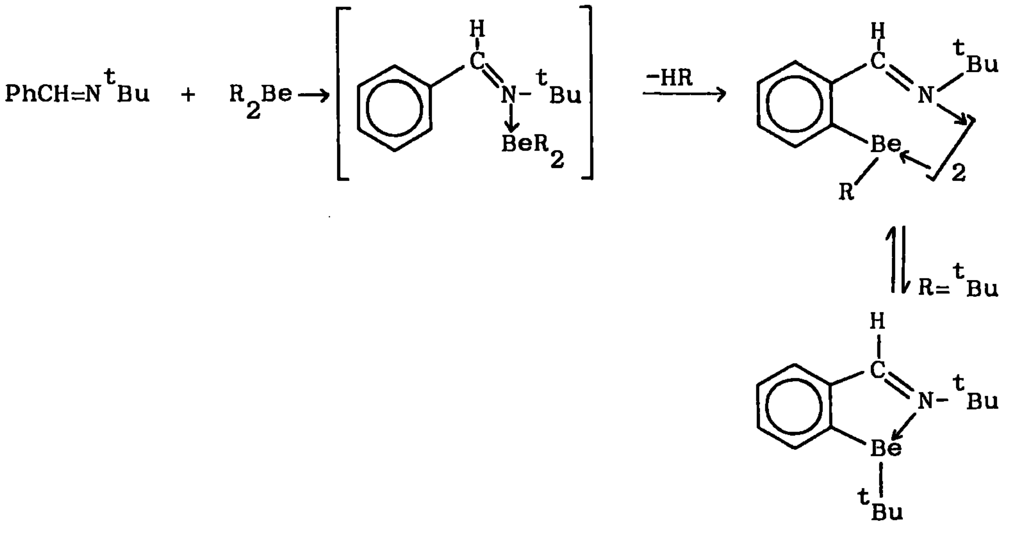
(430) 5.6



5.7

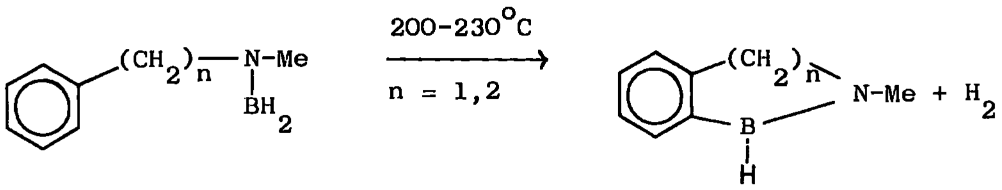
It might be expected that similar direction of metallation could occur in mercuration and thallation reactions, but this does not appear to have been reported.

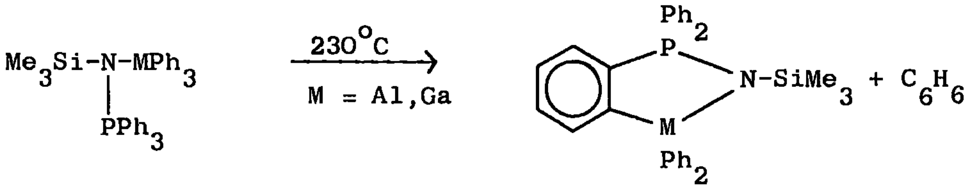
Alkyl or aryl derivatives of the Group IIA and IIIB elements similarly undergo directed metallations with elimination of the displaced proton as a hydrocarbon; some examples are given in Equations 5.8-10.



(431)

5.8

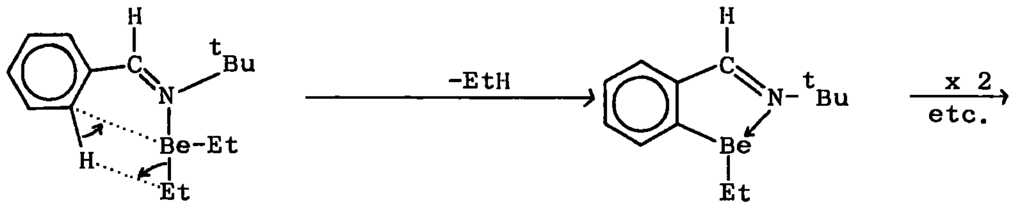

(432) 5.9


(433) 5.10

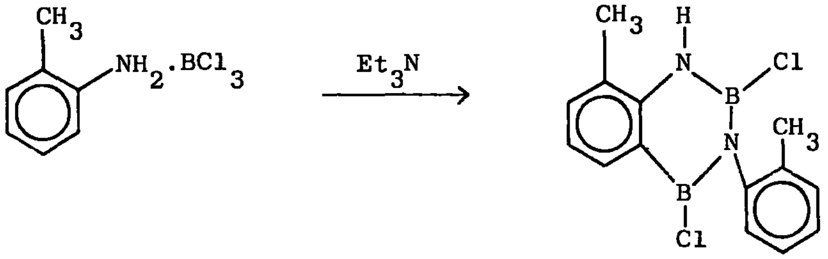
The beryllium system is particularly interesting in that the ortho-metallated products are dimeric, containing a ten-membered heterocycle. If the system is sterically hindered, e.g. for the t-butyl beryllium derivative, an equilibrium exists in solution between the dimer and the monomeric 5-membered ring.[431]

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.

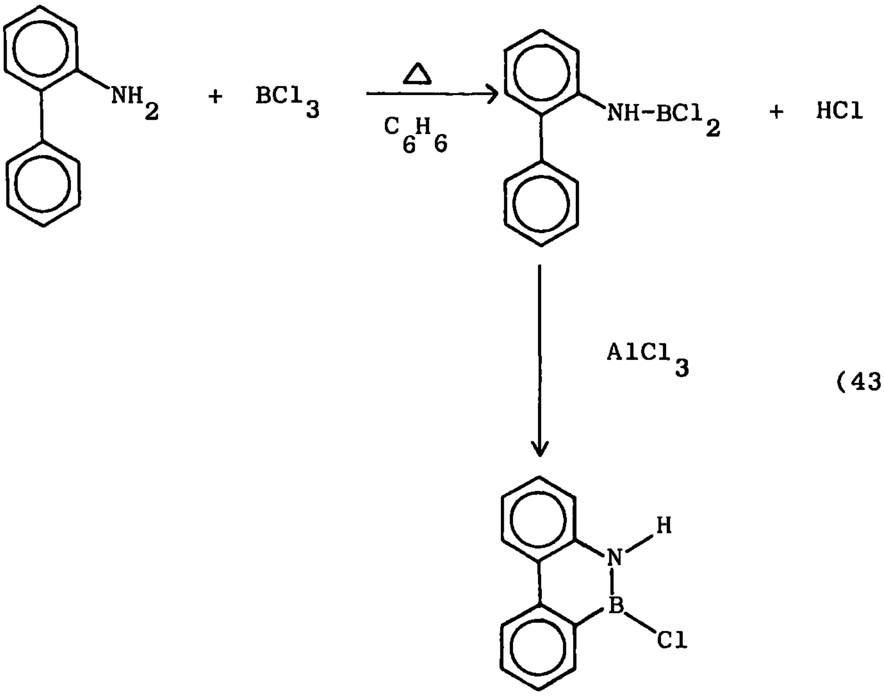
Like the lithium system, the beryllium reaction goes under mild conditions, but the Group III derivatives require much higher temperatures. It may be seen that all these reactions involve elimination of hydrocarbon, but the reaction mechanism is probably not identical to the nucleophilic process suggested 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).


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, $-SnCl_3$, 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.



(434) 5.12



(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 $-196^{o}C$ 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 ν(N-H) region (3100-3400 cm^{-1}) and a band corresponding to ν(C=N) at 1555 cm^{-1}. A band assignable to coordinated diethyl ether was also visible at 1062 cm^{-1} (ν_{as}(C-O-C)).

40 cm^3 dry toluene were then added to the residue, and the mixture was heated to about $100^{o}C$ 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, $\underline{o\text{-}Cl_3\overset{\downarrow}{Sn}C_6H_4C(Ph) = \overset{|}{N}H.C_7H_8}$, M.Pt.: $270\text{-}310^{o}C$ (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%)

ν_{max}(Nujol mull): 3332vs, 3102vw, 3080sh, 3057w, 3024w, 1990vw, 1967vw, 1953vw, 1914vw, 1888vw, 1848vw, 1821vw, 1598vs, 1587s,* 1572s, 1548vs, 1523sh, 1495m*, 1492m, 1444vs, 1417vw, 1365sh, 1354vs, 1314m, 1298sh, 1288vs, 1277s, 1263mw, 1254sh, 1200s, 1187sh, 1157s, 1122sh, 1119m, 1082w*, 1045w, 1030mw*, 1003mw, 999mw, 994sh, 977vw, 960s, 939vw, 923mw, 915w, 908mw, 892w, 856w, 848w, 837s, 797vs, 775s, 763m, 748m, 734vs*, 724vs, 711vs, 700vs, 697sh*, 680m, 672sh, 659w, 645s, 617vw, 608vw, 582w, 561mw, 496vw, 479w, 471mw*, 458mw, 443w, 421mw, 405w, 372m, 362m, 348w cm.$^{-1}$

A sample of the product was heated under vacuum to 150°C for 30 mins., and the volatile material evolved was collected in a trap at -196°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-$\overline{\mathrm{SnCl_3C_6H_4C(Ph)=N}}$H prepared from $\mathrm{Ph_2CNSiMe_3}$(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 ~70°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, Me_3SiCl, 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-$SnCl_3C_6H_4C(Ph){=}NH$.

ν_{max}(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 $cm.^{-1}$

Recrystallisation of the crude product from 20 cm^3 dry THF yielded a white microcrystalline solid, identified as o-trichlorostannyldiphenylmethyleneamine mono-THF, o-$SnCl_3C_6H_4C(Ph){=}NH.THF$, M.Pt.: 177-9°C (sealed tube).

(Found: C 40.4, H 3.6, N 3.0, Cl 22.2%;

$C_{17}H_{18}NOSnCl_3$ requires: C 42.8, H 3.8, N 2.9, Cl 22.3%).

ν_{max}(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, 1161s, 1128s, 1086vw, 1038m, 1017s, 1006sh, 980vw, 964mw, 936mw, 918m, 895mw, 863sh, 847vs, 802vs, 766m, 764sh, 742mw, 728vs, 702vs, 681w, 677sh, 665m, 652m, 623vw, 588w, 501vw, 488w, 453w, 429mw, 412w, 365vw, 354m. $cm.^{-1}$

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 ν(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 ~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, $2\text{-}Cl_3\overleftarrow{Sn\text{-}4\text{-}ClC_6H_3C(p\text{-}ClC_6H_4)\text{=}N}H$, M.Pt.: 252-7°C dec. (sealed tube).

(Found: C 30.2, H 2.1, N 2.5, Cl 37.9%;

$C_{13}H_8NSnCl_5$ requires: C 32.9, H 1.7, N 3.0, Cl 37.4%).

ν_{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, 773sh, 759s, 736w, 718vw, 700vw, 674vw, 663mw, 637w, 624vw, 617w, 572m, 532mw, 503mw, 484w, 442mw, 416w, 371m, 364m, 342vw cm.$^{-1}$

iv) Reaction of di-p-tolylmethyleneaminolithium with tin tetrachloride (Mole ratio 1:1)

A solution of 20 mmol. di-p-tolylmethyleneaminolithium in 50 cm^3 ether/hexane was cooled to -196°C and 2.34 cm^3 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 cm^3 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, $2\text{-}Cl_3Sn\text{-}4\text{-}MeC_6H_3C(p\text{-}MeC_6H_4)=NH$, M.Pt. : 230-240°C (sealed tube).

(Found: C 41.4, H 4.3, N 3.3, Cl 24.3%;
$C_{15}H_{14}NSnCl_3$ 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, 1022mw, 1002vw, 970vw, 958mw, 925s, 856s, 844sh, 837vs, 820vs, 793m, 757vs, 723w, 700vw, 682w, 673sh, 665m, 638w, 611m, 567w, 517vw, 481mw, 457vw, 443m, 409mw, 402mw, 371s, 363 sh. cm.$^{-1}$

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 d^8-toluene, heated briefly, and sealed in an NMR tube. Its ^{1}H-NMR spectrum was then recorded, listed as follows: (All values τ ppm, integrations in parentheses).

Ar-$\underline{H}$:	2.48 2.60 3.02 3.13	Multiplet (8)	CH_3-$C\underline{H}_2$-O :	6.47 6.57 6.69 6.82	Quartet (4)
Ar-$C\underline{H}_3$:	7.97	singlet (6)	$C\underline{H}_3$-CH_2-O:	8.86 8.97 9.09	Triplet (6)

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 τ, 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 cm^3 dry N,N,N',N'-tetramethylethylenediamine (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.$SnCl_4$ on the basis of its infra-red spectrum and analysis.

(Found: C 20.7, H 4.2, N 6.9, Cl 35.8%.
$C_6H_{16}N_2SnCl_4$ 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°C for several hours, deposited a colourless, semi-crystalline solid, analysing as an approximately 1:1 mixture of the complex bis-THF. tin tetrachloride, $(C_4H_8O)_2.SnCl_4$, with the mono-THF adduct of di-p-tolylmethyleneaminotin trichloride, 2-$SnCl_3$-4-MeC_6H_3C(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%;
$C_{15}H_{14}NSnCl_3.C_4H_8O$ requires: C 45.1, H 4.4, N 2.8, Cl 21.1%;
$(C_4H_8O)_2.SnCl_4$ 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, $2\text{-}\overset{\downarrow}{\mathrm{Sn}}\mathrm{Cl_3}\text{-}4\text{-}\mathrm{MeC_6H_3C}(p\text{-}\mathrm{MeC_6H_4})=\mathrm{NH.2THF}$, 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%;

$C_{23}H_{30}NO_2SnCl_3$ requires: C 47.8, H 5.2, N 2.4, Cl 18.4%)

ν_{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, 666m, 638w, 611m, 570w, 527vw, 483mw, 460vw, 445w, 436mw, 413w, 406w, 374mw, 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 ν(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. $2\text{-}SnCl_2N{=}C(p\text{-}tolyl)_2\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl){=}NH$.

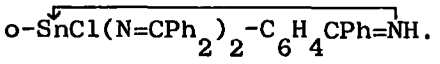
(Found: C 58.0, H 5.7, N 4.0, Cl 16.4%;

$C_{30}H_{28}N_2SnCl_2$ requires: C 59.5, H 4.6, N 4.6, Cl 11.7%)

ν_{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, 962w, 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 $Cl_3SnC_6H_4CPh{=}NH^+$ (m/e 405), $Cl_2SnC_6H_4CPh{=}NH^+$ (m/e 370), and $ClSnC_6H_4CPh{=}NH^+$ (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.



$\text{o-}\overset{\downarrow}{\text{Sn}}\text{Cl(N=CPh}_2)_2\text{-C}_6\text{H}_4\text{CPh=}\overset{|}{\text{N}}\text{H}$.

(Found: C 56.5, H 3.4, N 4.8, Cl 7.2%;

$C_{39}H_{30}N_3SnCl$ requires: C 67.4, H 4.3, N 6.1, Cl 5.1%)

ν_{max}(Nujol mull): 3332m, 3085w, 3060m, 3028sh, 1960vw, 1830vw, 1609vs, 1599vs, 1576vs, 1557s, 1543vs, 1492m, 1447s, 1404m, 1369s, 1361s, 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 2.57g. 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 3.94g. 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%; $C_{12}H_{10}N_2$ requires: C 79.2, N 15.4%).

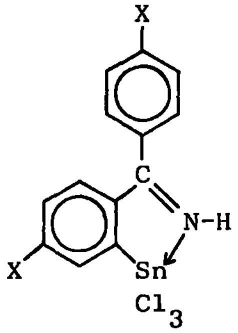
5.3 Discussion

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

New ortho-metallated derivatives of tin(IV)



I:	$o\text{-}SnCl_3\text{-}C_6H_4CPh{=}NH.C_7H_8$	Colourless crystalline solid
II:	$2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl){=}NH$	Pale yellow crystals
III:	$2\text{-}SnCl_3\text{-}4\text{-}ClC_6H_3C(p\text{-}ClC_6H_4){=}NH$	Pale brown microcrystalline solid
Ia:	$o\text{-}SnCl_3\text{-}C_6H_4CPh{=}NH.THF$	Colourless microcrystalline solid
IIa:	$2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl){=}NH.2THF$	Colourless crystals

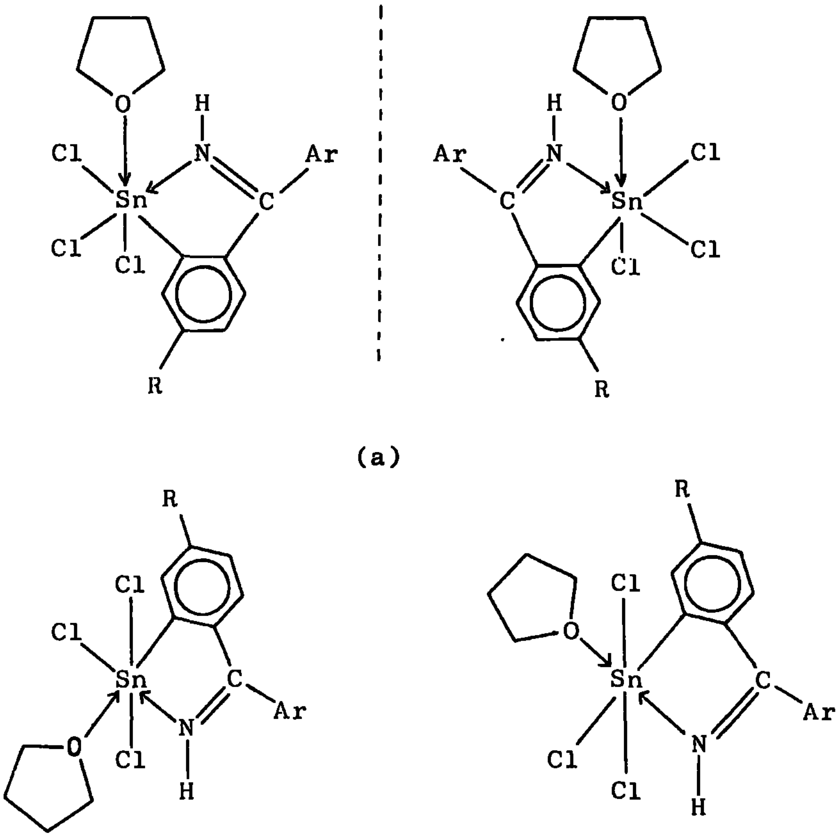
on exposure to air, although both I and III absorb atmospheric moisture which may be removed under vacuum. The di-p-tolylmethyleneamine derivative II and the THF adduct of the diphenylmethyleneamine derivative, Ia, appear to be completely stable to air, although the THF adduct of the di-p-tolylmethyleneamine 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; $2\text{-}\overline{\text{SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-CH}_3\text{C}_6\text{H}_4\text{)=N}}\text{H}$ (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,[436] 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.[381] 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.[431]

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.



(a)

(b)

(c)

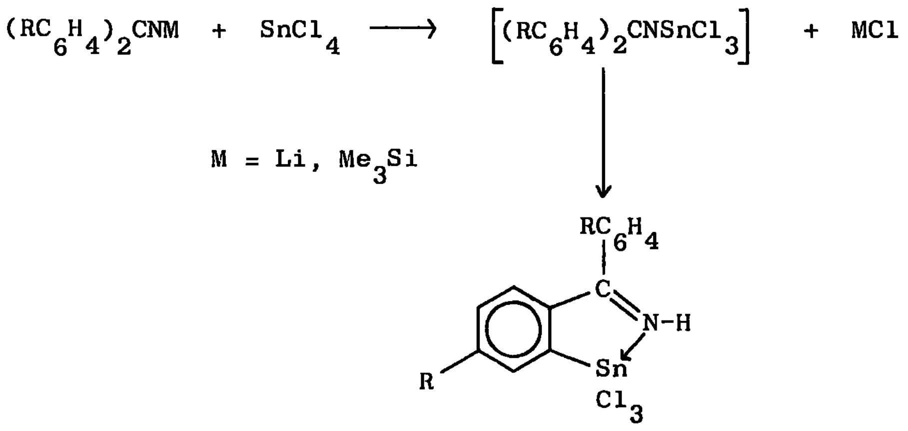
Figure 5-1

In the enantiomeric forms (a), the $SnCl_3$ 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 $SnCl_3$ 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-tolylmethyleneamine derivative IIa, the infra-red spectrum of which does not show the strong $\nu_{as}(SnCl_3)$ absorption at $\sim 365\ cm^{-1}$. 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,[12] 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



$$(RC_6H_4)_2CNM + SnCl_4 \longrightarrow \left[(RC_6H_4)_2CNSnCl_3\right] + MCl$$

M = Li, Me_3Si

5.14

to involve formation of the unrearranged diarylmethyleneaminotin(IV) trichloride, $Ar_2CNSnCl_3$, 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. $PhCH_2NHMe$.[429] 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).

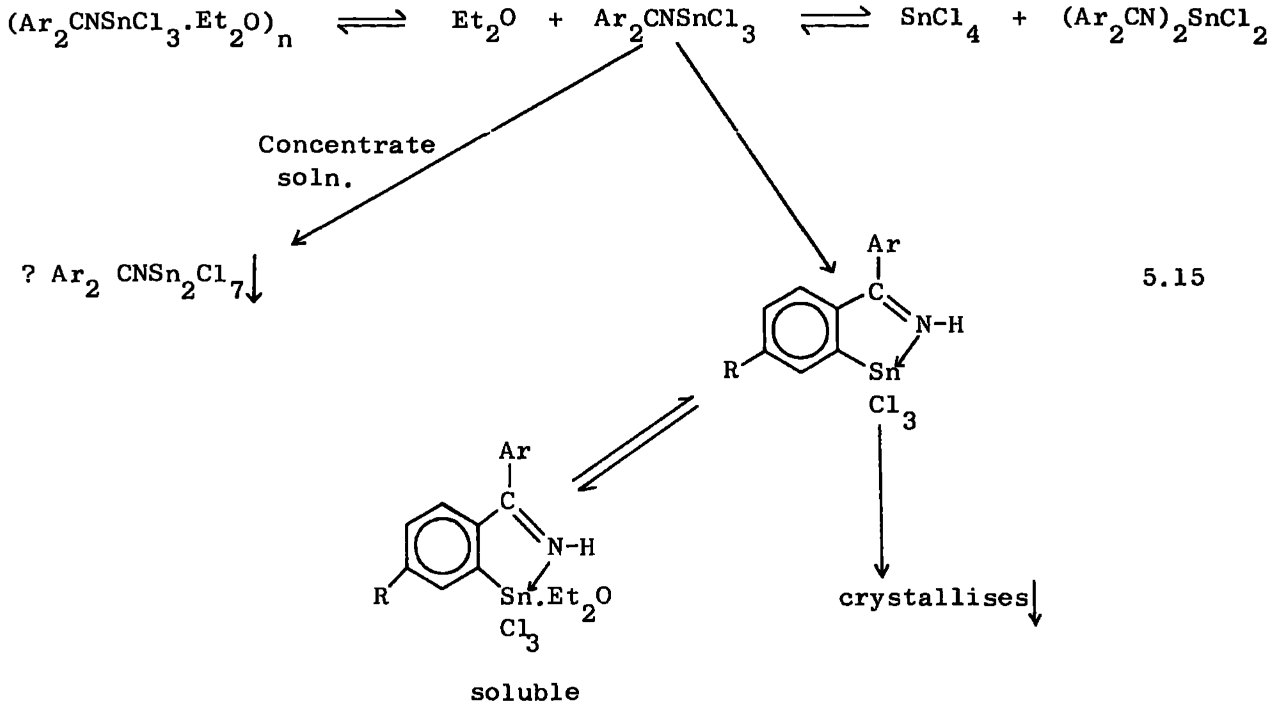
In the synthesis via imino-lithium, however, the initial stage of the reaction was carried out in diethyl ether at low temperatures, and the intermediates could be observed spectroscopically as ether complexes. The infra-red spectra of these materials, obtained as mixtures with lithium chloride, show 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 $(Ar_2CNSnCl_3.Et_2O)_n$.

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-chlorophenylmethyleneamino 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 $(Ar_2CNSnCl_3)_n$, and it seems likely that a complex with tin tetrachloride of the type $Ar_2CNSn_2Cl_7$ is formed, presumably from the disproportionation of $Ar_2CNSnCl_3$ 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 metallation process, since it enhances disproportionation of the mono-iminotin trichloride to tin tetrachloride, with which it forms a complex. Some metallation occurs, however, but if a stronger base such as N,N,N',N'-tetramethylethylenediamine is added

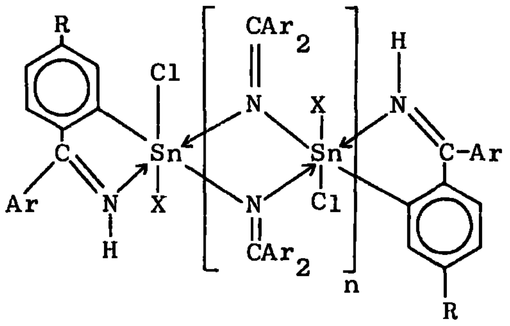


5.15

the metallation is blocked completely and the TMED.$SnCl_4$ adduct is precipitated. Such disproportionation reactions occur for the monodiarylmethyleneaminosilicon 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 metallation and the relative Lewis acidities of the Group IVB tetrachlorides.

Similar rearrangements appeared to occur for more highly substituted diarylmethyleneaminotin(IV) chlorides $(Ar_2CN)_nSnCl_{4-n}$, n = 2,3, but although there was spectroscopic evidence (mainly infra-red - the appearance of sharp ν(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.

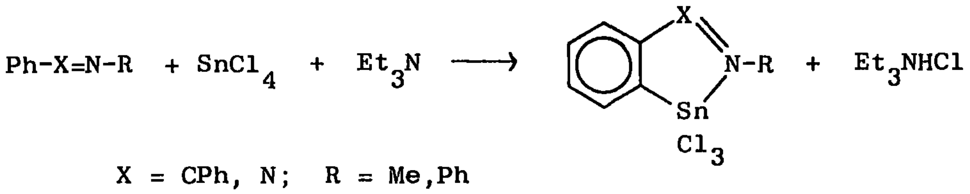
In view of the ease of formation of 6-coordinate adducts from the ortho-metallated trichlorides, it might be expected that cyclised forms of the higher iminotin chlorides might have dimeric or polymeric structures (Fig. 5-2).



X = Cl, N$=$CAr$_2$

Figure 5-2

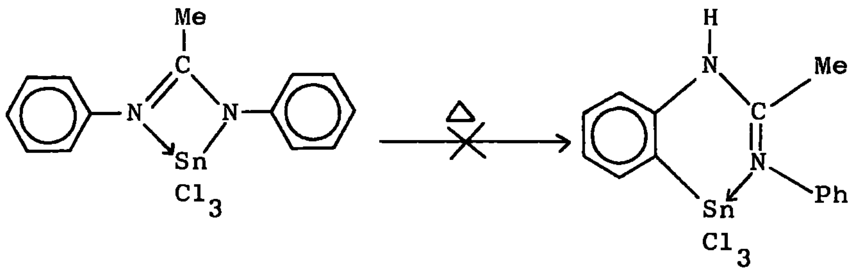
As has been stated, this ortho-metallation reaction may be related to the cyclopalladation of arylmethyleneamines.[404,405] Palladium also forms cyclic derivatives with a wide range of other aromatic ligands, but all attempts to form similar tin compounds failed. The ligands studied were N-methyl- and N-phenyldiphenylmethyleneamine, 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



5.16

X = CPh, N; R = Me,Ph

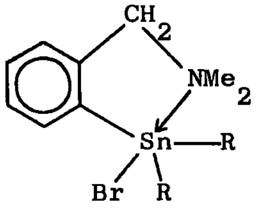
obtained were intractable tars and unreacted starting material. It is possible that the presence of a blocking substituent on the tin-bonded nitrogen atom may be important, since it prevents the formation of a 4-coordinate N-SnCl$_3$ group, which will be more electrophilic than tin in a higher coordination 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).



5.17

This is in contrast to the palladium system, where ortho-metallation of N-arylamidines is facile.[403] There is, however, some evidence that at high temperatures the 2:1 adduct of N-methyldiphenylmethyleneamine with tin tetrachloride rearranges by cyclometallation.[439]

Such 5-membered rings involving dative bonds to tin(IV) are not unknown. The analogous saturated species shown in Figure 5-3 have been

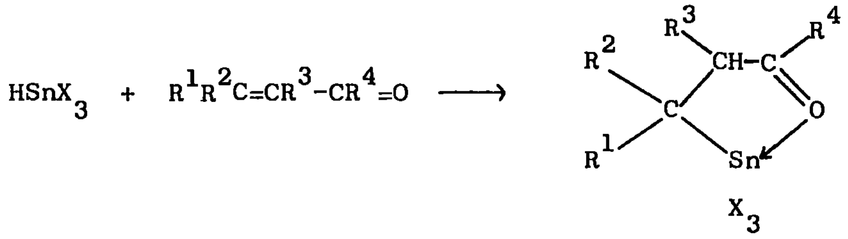


R = Me, Ph.

Figure 5-3

prepared by the reaction of diorganotin dibromides with an appropriately substituted aryllithium or arylcopper(I),[440] and an X-ray crystal structure has been reported for the compound where R = Ph.[447]

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).[441]



5.18

However, the unique nature of the new reactions reported here lies in the directed electrophilic substitution of an aromatic ring by an $Sn^{IV}Cl_3$ 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

i) Mass spectra

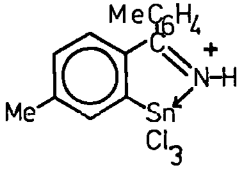
The mass spectra of the three ortho-metallated diarylmethyleneamino-tin(IV) trichlorides were recorded, but their THF adducts were not investigated by this method. The results obtained are listed in Table 37a-c, consisting of the major metal-containing fragments, together with the major identifiable 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

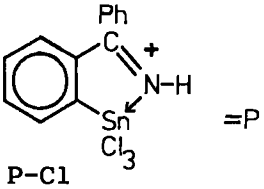
Mass spectra of the new ortho-metallated diarylmethyleneamino tin (IV) trichlorides

a) $2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl)=NH$

m/e	Relative Intensity	Assignment
489	0.7	P-Cl + C_7H_7
433	13	 =P
418	0.6	P-CH_3
398	70	P-Cl
383	0.5	P-Cl-CH_3
363	5	P-2Cl
348	1	P-2Cl-CH_3
342	0.5	P-C_7H_7
328	3	P-3Cl
312	1.5	P-3Cl-CH_3-H
307	2	P-Cl-C_7H_7
272	0.8	P-2Cl-C_7H_7
271	0.8	P-2Cl-C_7H_7-H
243	11	$(C_7H_7)_2CNCl^+$
236	3	$C_7H_7CNSn^+$-H
228	16	C_7H_7CNCl
225	0.5	$SnCl_3^+$
208	100	$(C_7H_7)_2CN^+$ or $CH_3C_6H_3.C_7H_7CNH^+$
199	3.5	$(P-Cl)^{2+}$
193	12	$C_6H_4.C_7H_7CN^+$
178	6	$(C_6H_4)_2CN^+$
165	14	?
155	17	$SnCl^+$
120	3.5	Sn^+
118	15	$C_7H_7CNH^+$
91	25	$C_7H_7^+$

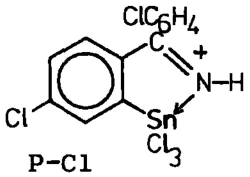
m/e values refer to the fragment containing the most abundant isotopes (i.e ^{35}Cl and ^{120}Sn).

b) $o\text{-}SnCl_3\text{-}C_6H_4C(Ph)=NH.C_7H_8$

m/e	Relative Intensity	Assignment
461	0.2	$P-Cl + C_7H_7$
405	4	
370	32	P-Cl
335	5	P-2Cl
300	2.5	P-3Cl
294	1.5	P-Cl-Ph + H
260	2	$SnCl_4^+$
258	*	P-2Cl-Ph
225	10	$SnCl_3^+$
190	6	$SnCl_2^+$
180	100	Ph_2CN^+ or $Ph.C_6H_4CNH^+$
155	24	$SnCl^+$
120	9	Sn^+
104	27	$PhCHN^+$
91	12	$C_7H_7^+$
77	49	Ph^+

* : Overlapping adjoining peak envelope.

c) $2\text{-}\overset{\downarrow}{Sn}Cl_3\text{-}4\text{-}ClC_6H_3C(p\text{-}ClC_6H_4)=NH$

m/e	Relative Intensity	Assignment
484	3	?
373	8	 =P
438	88	P-Cl
403	10	P-2Cl
384	0.4	?
368	2	P-3Cl
330	1.5	?
326	2	$P\text{-}Cl\text{-}ClC_6H_4\text{-}H$
283	8	$(ClC_6H_4)_2CNCl^+$
248	100	$(ClC_6H_4)_2CN^+$ or $ClC_6H_3.ClC_6H_4CNH^+$
225	7	$SnCl_3^+$
219	5	$(P\text{-}Cl)^{2+}$
214	15	$(ClC_6H_4)_2CN^+\text{-}Cl + H$
177	30	$C_6H_3.C_6H_4CN^+$
155	23	$SnCl^+$
138	15	$ClC_6H_4CNH^+$
120	2.5	Sn^+
111	14	$ClC_6H_4^+$
91	37	$C_7H_7^+$

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. $2\text{-}\overline{\text{SnCl}_2\text{-4-XC}_6\text{H}_3\text{C(p-XC}_6\text{H}_4\text{)=N}}\text{H}^+$. The relatively high stability of this ion is probably due to extensive delocalisation of the positive charge over the aromatic π-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.

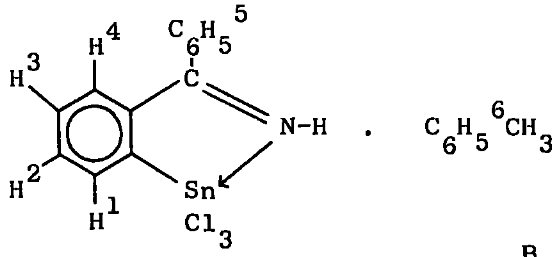
The spectra were recorded on solutions in d^6-DMSO, THF, d^6-acetone, or $CDCl_3$. The THF adduct of the di-p-tolylmethyleneamine derivative IIa was sufficiently soluble in aromatic hydrocarbons for a spectrum to be obtained in C_6D_6. The spectra are listed in Table 38, and those of the 5-coordinate tin derivatives, I-III, in the range 1-3.5 τ (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 ^{1}H-N-^{117,119}Sn coupling is observed (^{117}Sn and ^{119}Sn splitting could not be resolved). The coupling constants J(^{1}H-^{117,119}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

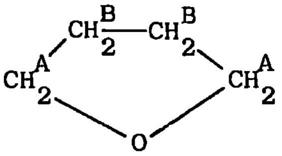
TABLE 38

^{1}H-NMR spectra for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides and their THF adducts

I:

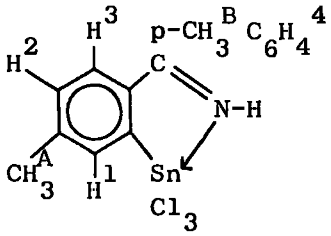


Ia: " .

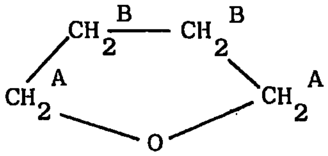


	Solvent	τ ppm^a							
		N-H	H^1	H^2	H^3	H^4	H^5	H^6	CH$_3$
I	d^6-acetone^b	2.00s	2.22s	2.43s				2.94s	7.87s
	d^6-DMSO^c	-2.15s (1)	1.76sh, 1.83s, 1.97sh, 2.09s (9)					2.51s (5)	7.44s (3)
		N-H	H^1	H^2	H^3	H^4	H^5	CH$_2$^{A}	CH$_2$^{B}
Ia	d^6-DMSO	-2.26s (1)	1.73s (1)	1.89s, 2.03s (8)				6.12m (4)	8.00m (4)

II:

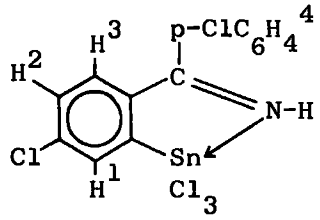


IIa: " .2



	Solvent	τ ppm^a								
		N-H	H^1	H^2	H^3	H^4	CH_3^A	CH_3^B	CH_2^A	CH_2^B
II	$CDCl_3$^{b}	1.58s	1.99s	2.19s			7.16s	7.19s	-	-
	d^6-DMSO^c	-2.01s (1)	2.00s (1)	2.23s, 2.34sh,2.5m (6)			7.27s (6)		-	-
	THF	-0.94s (1)	1.84s (1)	2.12s,2.27s,2.37sh, 2.5m (6)			7.33s (6)		-	-
IIa	d^6-DMSO	-1.85s. br (1)	2.01s (1)	2.25s (6)			7.31s (6)		6.13m (8)	8.00m (8)
	C_6D_6	2.02s (1)	2.94s (1)	3.22s (6)			7.08s (3)	7.20s (3)	6.62m (8)	8.77m (8)

III:



	Solvent	τ ppm^a				
		N-H	H^1	H^2	H^3	H^4
III	THF	-1.44s (1)	1.74s (1)	2.07s,2.18sh (6)		

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

b: Noise to signal ratio too high for integration.

c: Run at 21°C. All other spectra run at ~45°C.

s: singlet sh: shoulder m: multiplet br: broad.

TABLE 39

Coupling constants, $J(^{1}H\text{-}N\text{-}^{117,119}Sn)$, for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides

Compound	Solvent	$J(^{1}H\text{-}N\text{-}^{117,119}Sn)$cps.
I	d^{6}-DMSO	38
II	d^{6}-DMSO	37
II	THF	31
III	THF	32.5
Ia	d^{6}-DMSO	36.5
IIa	d^{6}-DMSO	35.5

in solution (on standing, the d^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.[442] 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 $J(^1H\text{-}C\text{-}^{117,119}Sn)$ and $J(^1H\text{-}C\text{-}N\text{-}^{117,119}Sn)$ for the dialkylaminomethylstannanes, $Me_nSn(NR_2)_{4-n}$.[272]

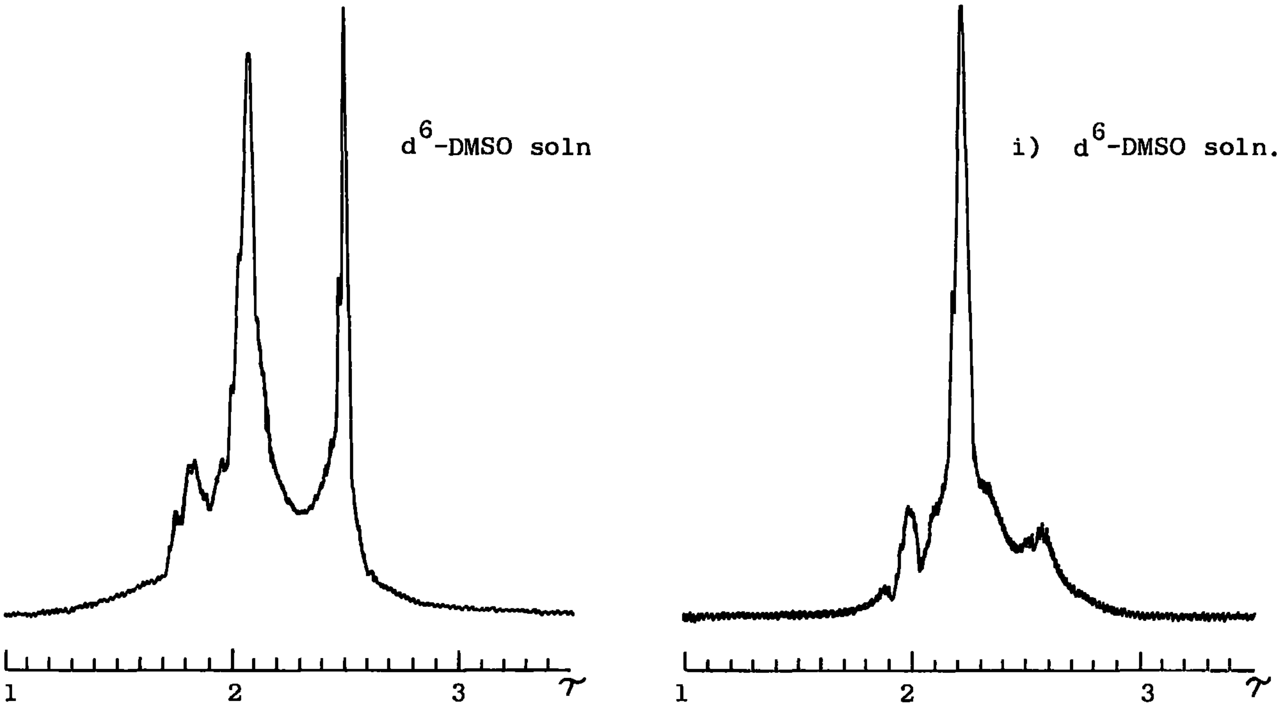
Unexpectedly the chemically inequivalent methyl groups of the di-p-tolylmethyleneamine derivatives gave a single signal in both of the polar solvents used. However, in $CDCl_3$ solution slight splitting of the methyl signal was observed (0.03 ppm), and in a non-polar solvent, C_6D_6, the two methyl groups 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[426] and benzylideneaniline (N-phenylphenylmethyleneamine).[443]

Aromatic proton resonances in the ^1H-NMR spectra of some ortho-metallated diarylmethyleneaminotin(IV) trichlorides.

a) $o\text{-}SnCl_3C_6H_4C(Ph)=NH.C_7H_8$ (I)

b) $2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl)=NH$ (II)



c) $2\text{-}SnCl_3\text{-}4\text{-}ClC_6H_3C(p\text{-}ClC_6H_4)=NH$ (III)

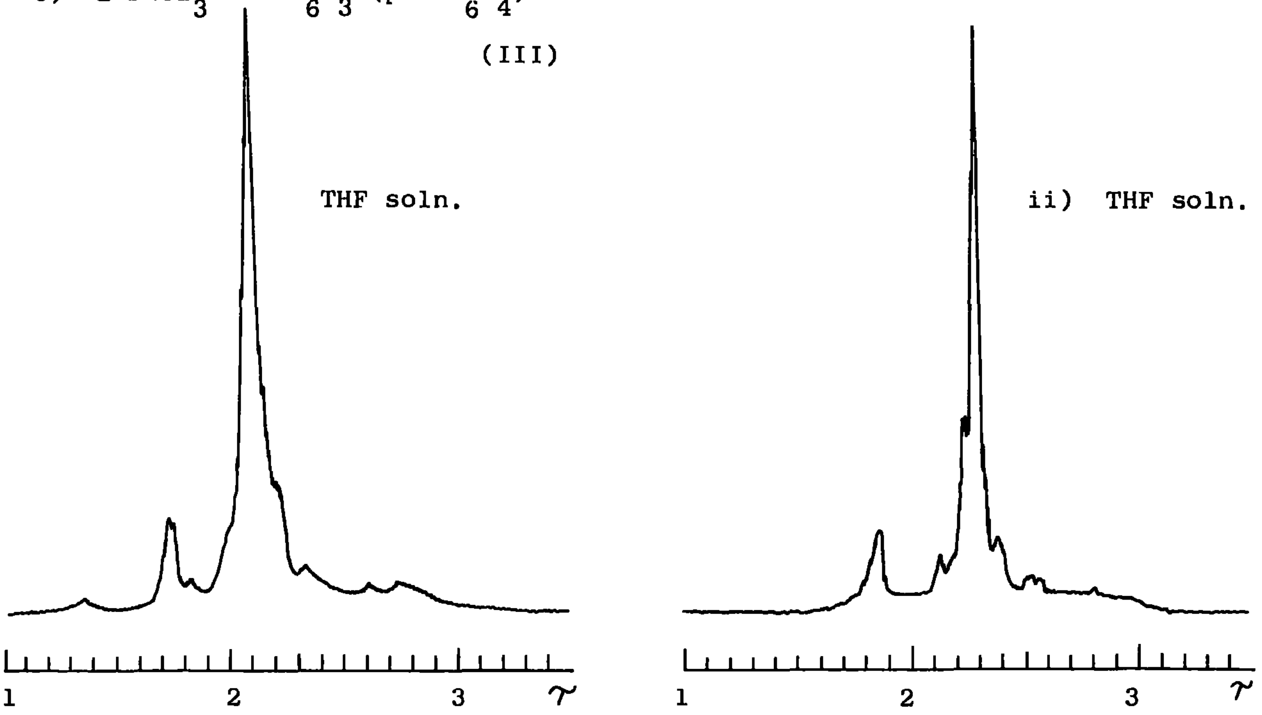


Figure 5-4

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)

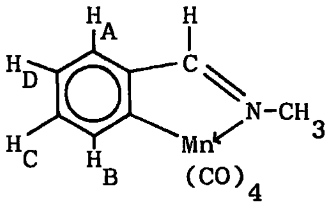
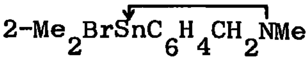


Figure 5-5

H_A; H_B; H_C 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 $SnCl_3$ group is considerably more electrophilic than the $Mn(CO)_4$ group, a different order might be expected anyway.

The spectrum of the related compound  $2\text{-}Me_2BrSnC_6H_4CH_2NMe_2$ (Fig. 5-6) has also been assigned with the proton adjacent to the

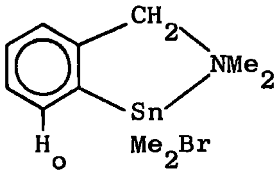


Figure 5-6

metallation site (H_o) giving rise to the aromatic signal at lowest field;[440] here, as in the manganese compound referred to above, the aromatic proton signals are much better separated than those of the ortho-metallated trichlorostannyldiarylmethyleneamines.

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 ν(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, ν(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 ν(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,[405] where a shift of ν(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 ν(C=C) and ν(C=N) region for some ortho-metallated diarylmethyleneaminotin(IV) trichlorides

Compound	ν (C=C, C=N) cm^{-1}
I	1598,1572, 1548 (1605,1578, 1557*)
II	1599, 1582, 1545
III	1600, 1569, 1545
Ia	1599, 1579, 1551
IIa	1604, 1587, 1551

* : Crude sample, without toluene of crystallisation, from reaction $Ph_2CNSiMe_3/SnCl_4$.

is also a little low for an aromatic ν (C=C) vibration, may be identified as ν (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 ν(C=N) to higher energy is found.[344] 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) <u>Other vibrations</u>

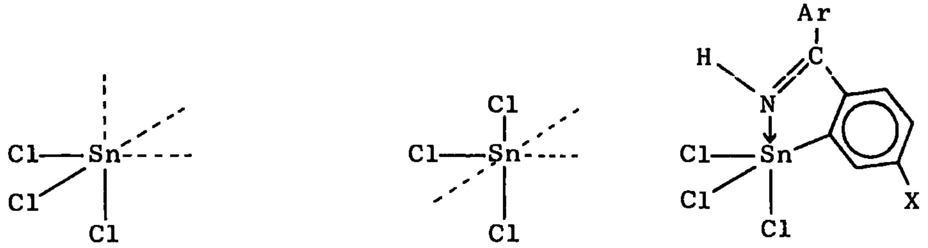
The most obvious sign of ortho-metallation for these compounds is the appearance in the infra-red spectrum of the ν(N-H) absorption in the region 3275-3335 cm^{-1}. In all cases, this is strong and sharp, although for the THF adduct $2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl)\text{=}NH.2THF$ (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,[417] so that this does not provide a reliable indication of ortho-metallation for the di-p-chlorophenyl- and di-p-tolylmethyleneamine derivatives. For the ortho-metallated diphenylmethyleneamine derivatives, however, a strong absorption at ~ 730 cm^{-1} which does not appear in the spectra of non-cyclised N-metallated derivatives may be assigned to δ(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 ν(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.[452] The two ν_{as}(Sn-Cl) absorptions for $PhSnCl_3$ lie at 439 and 377 cm^{-1};[452] 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-tolylmethyleneamine derivative IIa.

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 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 diphenylmethyleneamine derivative, Ia, which does show a band corresponding to $\nu_{as}(SnCl_3)$ in its spectrum. The alternative trans-arrangement (Fig. 5-7b) therefore seems likely for the THF adduct of the di-p-tolylmethyleneamine derivative, IIa. A far infra-red spectral study on these compounds should further elucidate this.



(a) (b) (c)

Figure 5-7

The THF adducts both show bands corresponding to the C-O-C stretching vibrations of their THF molecules. These are listed in Table 41, together with the frequencies for free THF. The absorptions shift to lower energy on adduct formation, as might be expected since some weakening

TABLE 41

ν (COC) for some THF adducts of ortho-metallated diarylmethyleneamino tin(IV) trichlorides

Compound	ν_{as} cm^{-1}	ν_s cm^{-1}
Ia: o-$SnCl_3C_6H_4CPh{=}NH$.THF	1017	847
IIa: 2-$SnCl_3$-4-MeC_6H_3C(p-tol)$=NH$.2THF	1054, 1023	862, 838
THF (liq. film)	1076	917

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 ν(COC) absorptions; one THF molecule appears to be more strongly bonded than the other, and its ν (COC) frequencies are quite close to those of the diphenyl analogue, Ia. This is preaumably 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 ν(N-H) absorption.

iv) Crystallographic data

The crystal and molecular structure of the di-p-tolylmethyleneamine derivative $2\text{-}\overline{\mathrm{SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tolyl)=N}}\mathrm{H}$, II, has been determined in an X-ray diffraction study by G. Whitehead and H.M.M. Shearer.[436] 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 $o\text{-}\overline{\mathrm{Mn(CO)_4C_6H_4CH=N}}\mathrm{Ph}$,[445] but in this compound the metallocycle makes an angle of 3° with the metallated phenyl ring. The C=N bond distance (1.285 (10) Å), however, is similar to that found here (1.280 (7) Å), and both may be compared to that of the coordinated diphenylmethyleneamine molecule in the tin(II) compound $\mathrm{Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8}$ (1.274 (12) Å; ref. 378 and Chapter 3).

TABLE 42

Selected bond lengths and angles from the crystal structure of

$2\text{-}SnCl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}MeC_6H_4)=NH.^{436}$

Bond lengths. Å		Bond angles.°	
C(1)-C(2)	1.474(8)	$Sn\hat{N}C(1)$	114.2(4)
		$N\widehat{C(1)}C(9)$	117.0(5)
C(1)-N	1.280(7)	$C(1)\widehat{C(9)}C(14)$	117.2(5)
C(1)-C(9)	1.487(8)	$C(9)\widehat{C(14)}Sn$	114.6(4)
C(9)-C(14)	1.391(7)	$C(14)\widehat{Sn}N$	76.5(2)
Sn-C(14)	2.116(5)		
Sn-N	2.260(5)	$N\widehat{Sn}Cl(2)$	88.1(1)
		$N\widehat{Sn}Cl(3)$	90.4(1)
Sn-Cl(1)	2.416(2)		
Sn-Cl(2)	2.315(2)	$C(14)\widehat{Sn}Cl(2)$	123.2(2)
Sn-Cl(3)	2.318(2)	$C(14)\widehat{Sn}Cl(3)$	126.6(2)
		$Cl(2)\widehat{Sn}Cl(3)$	101.7(1)
		$Cl(1)\widehat{Sn}C(14)$	96.7(1)
		$Cl(1)\widehat{Sn}Cl(2)$	94.1(1)
		$Cl(1)\widehat{Sn}Cl(3)$	94.7(1)
		$Cl(1)\widehat{Sn}N$	173.1(1)

Estimated standard deviations in parentheses.

Molecular structure of 2-$\overline{\text{SnCl}_3\text{-4-MeC}_6\text{H}_3\text{C(p-tolyl)=N}}$H.[436]

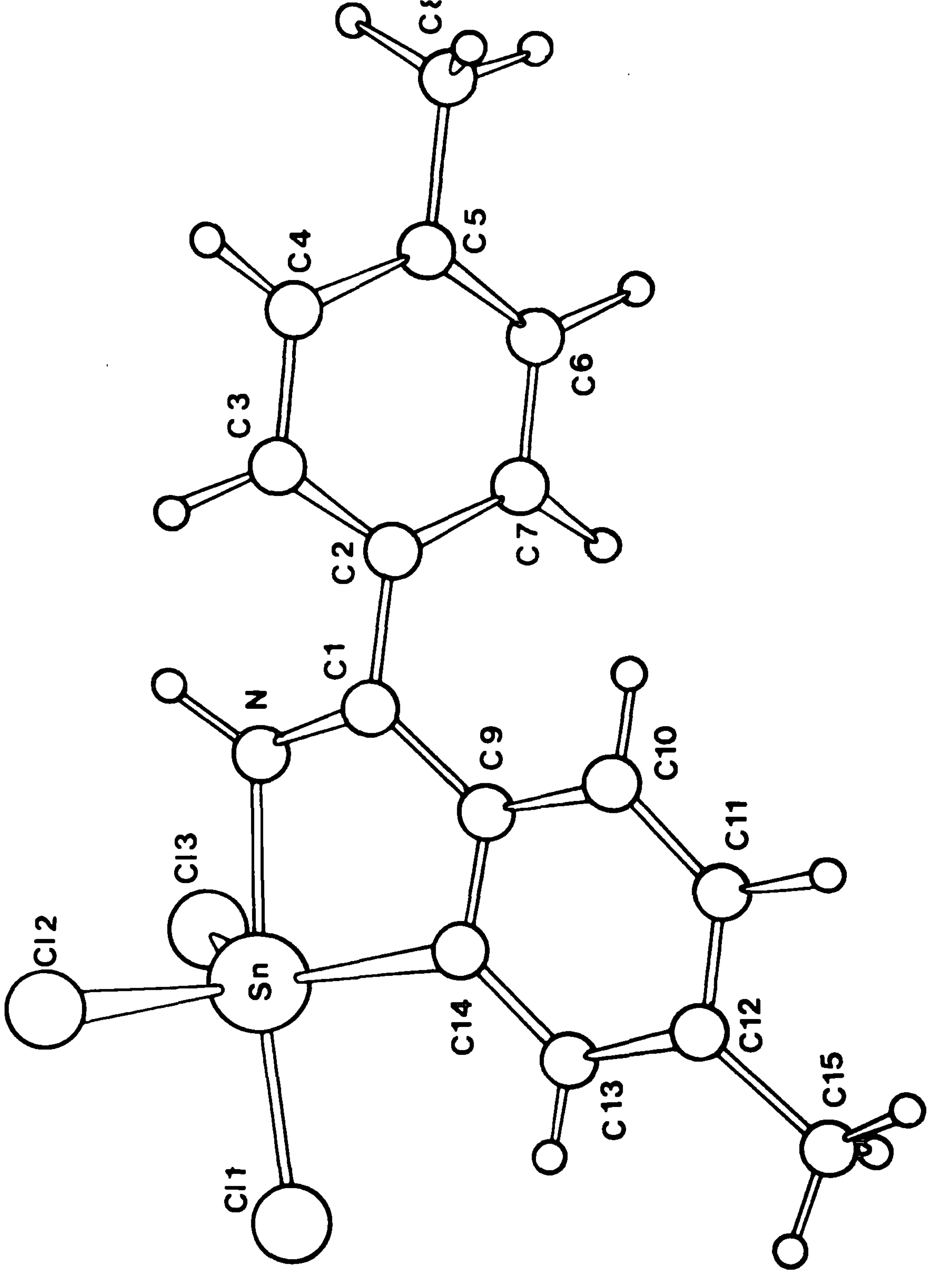


Figure 5-8

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 b 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 $C\hat{M}N$ 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 $o\text{-}\mathrm{Ph_2\overline{Sn^{IV}BrC_6H_4CH_2N}Me_2}$[447] (Fig. 5-3).

M	a	b	c	d	e
Sn^{IV}	1.391(7)	1.487(8)	1.280(7)	2.260(5)	2.116(5)
Mn^{I}	1.418(11)	1.443(10)	1.285(10)	2.070(7)	2.060(8)

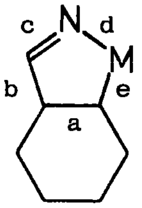


Figure 5-9 All distances in Å.

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,[12] 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 accomodate the small $Sn\hat{N}C$ 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 $o\text{-}Ph_2SnBr.C_6H_4CH_2NMe_2$; the angle between axial bonds in this structure is 171.0(1)°.[447]

The $Sn^{IV}\leftarrow N$ distance, 2.260(5)Å, is considerably shorter than the dative $Sn^{II}\leftarrow N$ distance in the diphenylmethyleneamine complex $Ph_2CNH.(Ph_2CNSn^{II}Cl)_2.C_7H_8$ (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 $Sn^{IV}\leftarrow N$ dative bond; for example the bonds in the bipyridyl complex $bipy.Ph_2SnCl_2$ (2.344(6) and 2.375(6)Å)[73] and the nitrile complex $cis\text{-}(MeCN)_2SnCl_4$ (average 2.311 (24) Å).[74] It is also considerably shorter than the $Sn^{IV}\leftarrow N$ bond in the corresponding saturated metallocycle in the compound $o\text{-}Ph_2SnBr.C_6H_4CH_2NMe_2$ (2.511(12) Å).[447] It is, however, longer than the non-dative Sn^{IV}—N bonds in the 4-coordinate compounds $(Me_2N)_4Sn^{IV}$ (2.045 Å)[266] and $(Ph_2CN)_4Sn^{IV}$ (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 (Ph_3SnNCS)[100] and 2.111(5) Å (Ph_2SnCl_2),[423] but it is still shorter than the corresponding bond in $o\text{-}Ph_2SnBr\ C_6H_4CH_2NMe_2$ (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 $Sn\overset{IV}{—}Cl$ distances in trigonal bipyramidal complexes, e.g. 2.321(1) Å for the anion $Me_2SnCl_3^-$,[61] and 2.316 (6) Å (average) for $AmSn^{IV}Cl_3$ (ref. 401 and previous chapter). It is also close to 2.318 (15) Å found in the 4-coordinate species Ph_3SnCl.[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 $Sn\overset{IV}{—}Cl$ distances; 2.54 (2) Å for $Me_2SnCl_3^-$,[61] 2.42 (4) Å for $py.Me_3SnCl$[63a,b] and 2.335(10) Å for $AmSnCl_3$.[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 $SnCl_3$ 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 $Ph_2CNH.SnCl_2$ and $Li(^tBu_2CN)_3Sn$ clearly label them as tin(II) derivatives; the quadrupole splitting (ΔE) for the latter is significantly greater than for most other tin(II) compounds,[451] a feature paralleled by the recently-prepared tin(II) amines.[104,105]

The two tetrakis(methyleneamino)tins, $(^tBu_2CN)_4Sn^{IV}$ and $(Ph_2CN)_4Sn^{IV}$, 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,[451] but in this case the tetrahedral geometry has been proven for $(Ph_2CN)_4Sn^{IV}$ 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 ΔE 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)

Compound	ΔE mm.s.$^{-1}$	δ mm.s.$^{-1}$
$Li(^tBu_2CN)_3Sn^{II}$	2.27	3.44[b]
$Ph_2CNH.Sn^{II}Cl_2$	1.51	3.52[b]
$(^tBu_2CN)_4Sn^{IV}$	0	1.16[b]
$(Ph_2CN)_4Sn^{IV}$	0	0.805[b]
$[(Ph_2CN)_2Sn^{IV}Cl_2]_n$	0.88	0.98[b]
$[(Ph_2CN)_3Sn^{IV}Cl]_n$	1.47	1.08[b]
$2\text{-}Sn^{IV}Cl_3\text{-}4\text{-}MeC_6H_3C(p\text{-}tol){=}NH$	1.58	1.66[b]
"	1.588	0.874[c]
$o\text{-}Sn^{IV}Cl_3C_6H_4CPh{=}NH$	1.730	0.716[c]
$2\text{-}Sn^{IV}Cl_3\text{-}4\text{-}ClC_6H_3C(p\text{-}ClC_6H_4){=}NH$	1.440	0.764[c]

a: ΔE is the quadrupole splitting, δ is the chemical isomer shift.

b: Relative to a $BaSnO_3$ absorber.

c: Relative to a $CaSnO_3$ 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 strcture determination[436] (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.[436]

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 P_2O_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 P_2O_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 alkyl lithiums were standardised against a 0.1M solution of sec-butanol in xylene using 1,10-phenanthroline as indicator.[448]

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.[449,450] 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) ^{1}H-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° 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 $HClO_4$, 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.

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Dr Samuel Johnson, Lexicographer, wit, and amateur chemist.

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