Studies in the organic and coordination chemistry of tin

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UNIVERSITY OF DURHAM

A THESIS

entitled

STUDIES IN THE ORGANIC AND COORDINATION CHEMISTRY OF TIN

Submitted by

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(Van Mildert College)

A candidate for the degree of Doctor of Philosophy

1985

TO MY PARENTS AND BRIAN

"The stumbling way in which even the ablest of the scientists in every generation have had to fight through thickets of erroneous observations, misleading generalisations, inadequate formulations and unconscious prejudice, is rarely appreciated by those who obtain their scientific knowledge from text books."

J.B.Conant.

ACKNOWLEDGEMENTS

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I am grateful to Dr. K.B.Dillon for his help in the n.q.r. studies.

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Finally, I would like to express my thanks to my husband and our parents for their continual help and encouragement.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1981 and October 1984. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

ABSTRACT

Hydrometallation reactions of Group IV metal hydrides are reviewed in the first chapter.

The reaction of tin IV chloride with aryl methylene amines, ArylCR$=$NR', has led to two new orthometallated compounds; ortho-trichlorostannyl (N-methyl) diphenyl methyleneamine, $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NMe$, of which the crystal structure has been determined, and ortho- trichlorostannyl (N-phenyl) diphenyl methyleneamine, $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NPh$.

Studies on the complex equilibrium mixture between HCl, $SnCl_2$ and Et_2O, which include ^{119}Sn n.m.r. spectroscopy and the reaction with proton sponge, suggest that it consists largely of the ionic species ethereal trichlorostannane, $Et_2OH^+ \; SnCl_3^-$. Its reaction with Schiffs' bases yields trichlorostannate salts of which the crystal structure has been determined for (N-methyl) diphenyl methyleneammonium trichlorostannate, $Ph_2C{=}NHMe^+ \; SnCl_3^-$.

2-Cyanoethyltin trichloride, $Cl_3SnCH_2CH_2C{\equiv}N$, is formed in the hydrostannation of acrylonitrile ($CH_2{=}CHCN$) by ethereal trichlorostannane and is an int- -molecular coordination polymer which easily breaks down to form adducts with Lewis bases. Analogous hydrostannation products, $Cl_3SnCHRCHRCN$ (R = H,Me) and $Cl_3Sn(CH_2)_3CN$, have been prepared from crotonitrile ($MeCH{=}CHCN$), methacrylonitrile ($CH_2{=}C(Me)CN$) and allyl cyanide ($CH_2{=}CHCH_2CN$). They also yield products where the nitrile bond has been converted to an azomethine bond. Similar conversion of the nitrile group occurs for saturated nitriles, RCN (R = Me,Et,Bu^t,Cl_3C,$ClCH_2CH_2$,Ph, $PhCH_2$).

The attempted addition of ethereal trichlorostannane to carbonyl compounds (PhCHO, $PhCH_2CHO$, Ph_2CO, PhCOCl, PhNCO) yielded mainly unreacted starting materials, with the exception of benzaldehyde where a low molecular weight polymer was obtained.

N.q.r. spectra have been recorded for a series of ammonium and phosphonium tribromo and trichloro- stannates ($R_4N^+ SnX_3^-$ and $R_4P^+ SnX_3^-$) and also for the alkylideneammonium salt, $Ph_2C{=}NHMe^+ SnCl_3^-$, and are related to crystallographic data. Temperature dependence studies on $CsSnBr_3$ reveal a first order phase transition between 13 and 17°C.

ABBREVIATIONS

N.M.R.	Nuclear Magnetic Resonance
N.Q.R.	Nuclear Quadrupole Resonance
G.L.C.	Gas Liquid Chromatograph
e.f.g.	electric field gradient

Compounds

DMSO	Dimethyl Sulphoxide
THF	Tetrahydrofuran
TMS	Tetra methyl silane
CETTB	2 - Cyanoethyltin tribromide
CETTC	2 - Cyanoethyltin trichloride
TMEDA	Tetramethyl ethylene diamine
bipy	2,2′ - bipyridine
phen	or~~o~~tho-phenanthroline
hal	halogen

For the Compound data tables

Infra-red (I.R.) spectra

s	strong
m/s	medium to strong
m	medium
w/m	weak to medium
w	weak
vw	very weak
shl	shoulder
b	broad
sh	sharp

N.M.R. Spectra

δ	chemical shift
Mult	multiplicity
J	splitting constant
Int	relative intensity
Assign	assignment
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
b	broad

Mass spectra

I	relative intensity
m.pt	melting point (°C) ; d- with decomposition

CONTENTS

Chapter 3 INVESTIGATIONS OF ROUTES TO ORTHOMETALLATED TIN COMPOUNDS

Chapter 4 THE REACTION OF SATURATED NITRILES WITH ETHEREAL TRICHLOROSTANNANE

Chapter 5 2-CYANOETHYLTIN TRICHLORIDE (CETTC)

Chapter 6 HYDROSTANNATION OF UNSATURATED NITRILES

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Chapter 8 NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPIC STUDIES

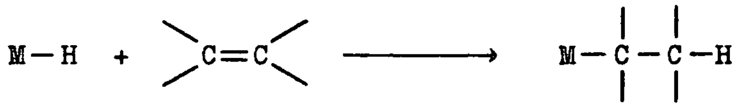
CHAPTER 1

HYDROMETALLATION REACTIONS OF GROUP IV METAL HYDRIDES

1.1 Introduction

Hydrometallation is the addition of the metal-hydrogen (M-H) bond of a metal hydride across an unsaturated bond.

e.g.



(1.1)

This is an excellent route to functionally substituted organometallic compounds provided that the functional groups attached to the alkene bond are themselves of a type that are unaffected.

This chapter is a review of hydrometallation by the group IV metals involving both organo and halogeno metal hydrides. Hydrostannation is discussed in greater detail so that the work of the following chapters may be put into perspective.

An important factor to consider when comparing the reactivity of the metal hydrides towards hydrometallation is the relevant bond energy terms as summarised in table 1.1 [1].

Table 1.1

Bond Energy Terms Relevant to Group IV Hydrometallation Reactions [1].

Bond Energy Term* KJ/mol A	A − H	A − C
C	413	$C-C = 347$; $C=C = 611$; $C\equiv C = 837$
Si	318	305
Ge	285	247
Sn	251	209

* see overpage

* The bond energy term is the quantity assigned to each of the bonds in a molecule such that the sum over all bonds is equal to the enthalpy change associated with the conversion of the molecule into separate atoms (1 atmosphere, 300K, ideal gas state).

Table 1.1 shows that hydrometallation reactions, in which a C = C and M - H bond are replaced by a C - C, C - H and M - C bond, are favourable energetically. They all result in an overall increase in the total bond energy term.

e.g.

$$\underset{251}{Sn-H} + \underset{611}{C=C} \longrightarrow \underset{209}{Sn-C} + \underset{347}{C-C} + \underset{413}{C-H} \qquad (1.1a)$$

$$\Delta_{\text{(bond energy terms)}} = +\ 107\ \text{KJ/mol.}$$

1.2 HYDROSILATION

Hydrosilation reactions are used to synthesise organosilicon monomers and polymers, to cross-link silicone polymers and to copolymerise silicone and organic polymer blocks. A number of major reviews have been written on the subject [2-5]. Chlorosilanes are the most reactive and are the most widely used.

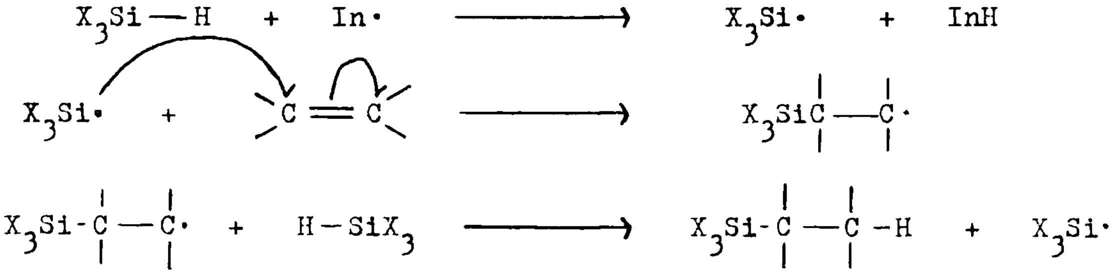
The reaction may occur simply by heating the components together under pressure but often results in oligomers of the alkene [6].

$$H_2C = CH_2 \quad + \quad MeSiHCl_2 \quad \xrightarrow[100\text{-}500\ \text{atm.}]{250\text{-}300\ ^{\circ}C} \quad MeCl_2Si(CH_2CH_2)_nH \qquad (1.2)$$

However, the majority of hydrosilations are catalysed, and oligomerisation is not a series problem. Free radical initiators, tertiary amines and transition metal complexes are commonly used as catalysts.

(i) Free Radical Reactions.

In the presence of ultra violet or gamma irradiation or with initiators such as peroxides or azobisisobutyronitrile (AIBN) free radical reactions occur. The weak Si-H bond is attacked to give a silyl radical which may then take part in a simple chain reaction according to Scheme 1.1 [7].



In = initiator , X = (see below)

Scheme 1.1

The reactivity of the silane in peroxide initiated reactions follows the series;

$$X = Cl_3SiH > Cl_2RSiH > ClR_2SiH > R_3SiH$$

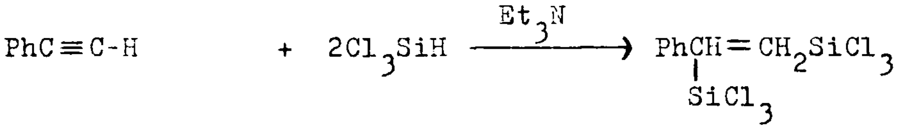
and the reactivity of alkenes towards trichlorosilane is as below.

As expected unsymmetrical alkenes undergo terminal addition via the most stable radical [8] .

(ii) Base Catalysed Reactions.

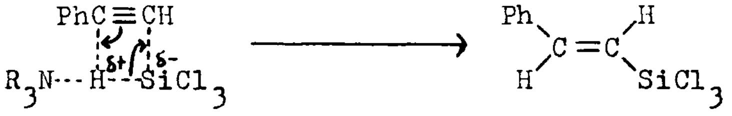
Tertiary amines catalyse reactions believed to occur via addition of the trichlorosilane nucleophile to the unsaturated bond, as exemplified below [9-11] .

$$CH_2{=}CHC{\equiv}N \quad + \quad Cl_3SiH \xrightarrow{Et_3N} Cl_3SiCH_2CH_2C{\equiv}N \qquad (1.3)$$



$$PhC{\equiv}C\text{-}H \quad + \quad 2Cl_3SiH \xrightarrow{Et_3N} \underset{\displaystyle SiCl_3}{PhCH}{=}CH_2SiCl_3 \qquad (1.4)$$

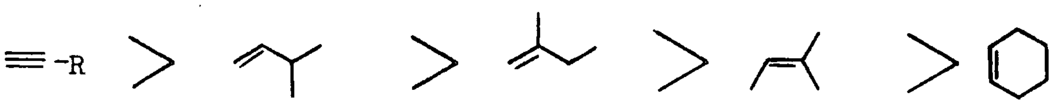
Benkeser considers the reaction to proceed in terms of a solvated four membered transition state [10] , (equation 1.5).



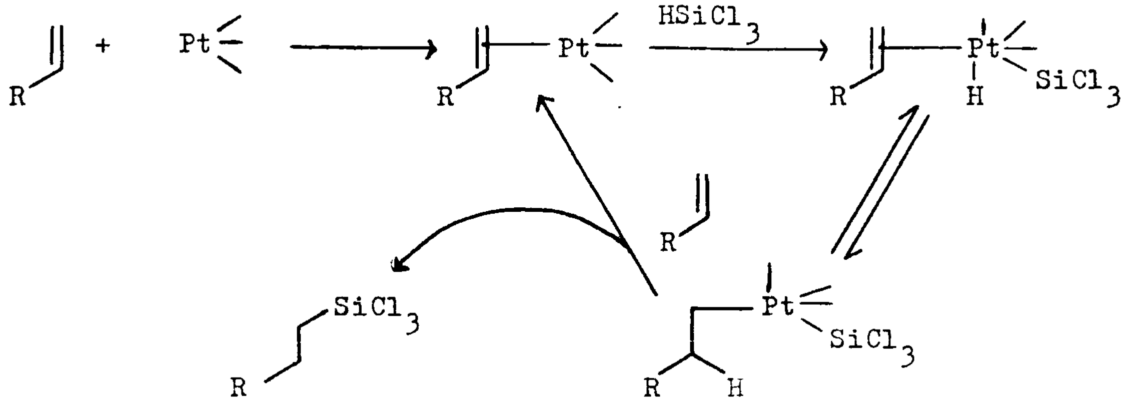
(1.5)

(iii) Transition Metal Catalysed Reactions.

The majority of hydrosilation reactions are catalysed by transition metal complexes, chiefly those of Pt, Ni, Rh, Co, Pd and Fe. In contrast to free radical hydrosilation, the activity of alkenes and alkynes decreases with alkyl group substitution according to the series:

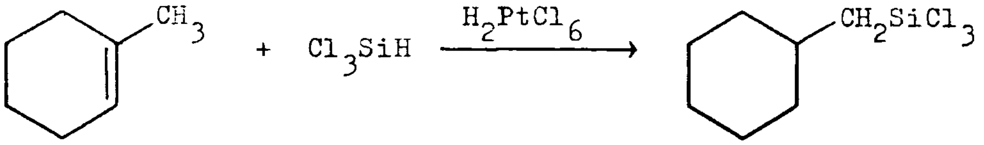


The most common platinum complex, and one of the most reactive catalysts, is chloroplatinic acid ($H_2PtCl_6.6H_2O$) or Speier's catalyst [5] . Other complexes used include $[Pt(C_2H_4)_2Cl_2]$, $[Pt(PPh_3)_2Cl_2]$, [12-14] and $[Pt(PPh_3)_4]$ [14,15] . The general mechanism is represented schematically below (Scheme 1.2) [16] but it is not clear whether the active species is Pt(II) [16,17] or Pt(0) [5,18] although Speier favours the latter [5,19] .



Scheme 1.2

There is a strong preference for terminal addition, even with non-terminal alkenes, due to the reversible step in Scheme 1.2 . This allows isomerisation of the alkene and double bond migration [20,21] as illustrated below.



(1.6)

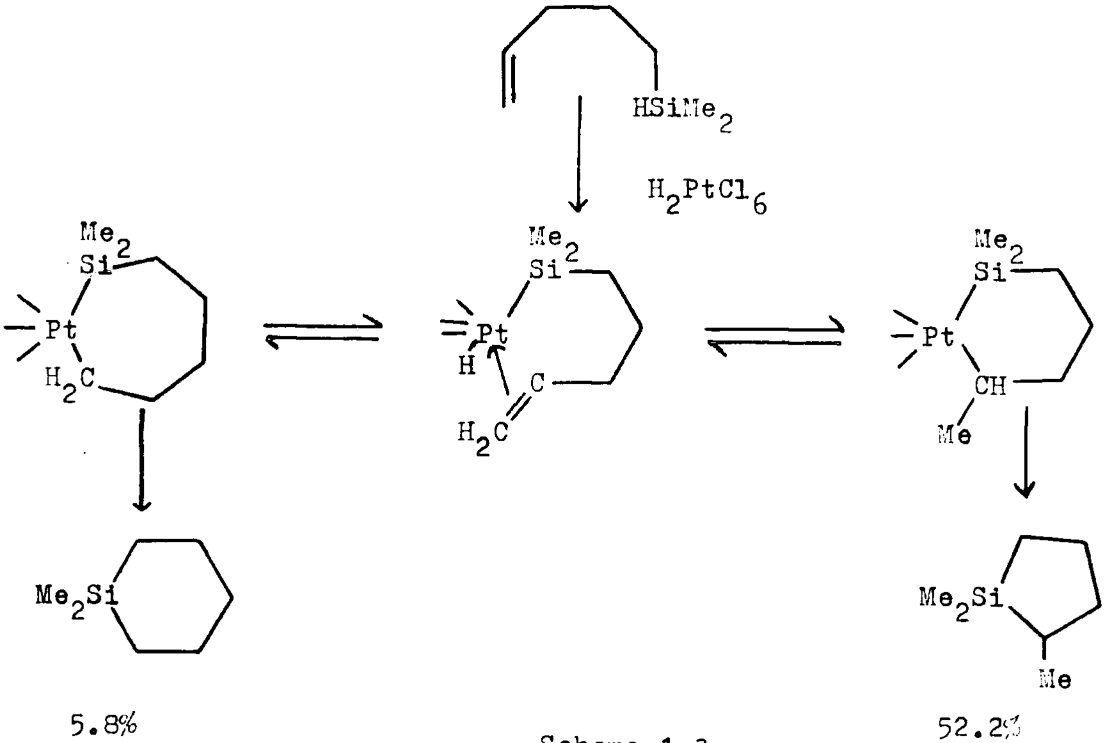
Tertiary phosphine platinum complexes are less reactive than chloroplatinic acid but give rise to a chiral centre in the catalyst and subsequently to asymmetric hydrosilation.

The catalysts $[Pt\{SiR_3\}H(PCy_3)]_2$ [15, 22] and $[Pt\{Si(OEt)_3\}H(PMeBu^t{}_2)]_2$ [14] have been prepared by oxidative addition reactions involving the silane as exemplified below.

$$[Pt(PCy_3)(C_2H_4)_2] + R_3SiH \longrightarrow [Pt\{SiR_3\}H(PCy_3)]_2. \qquad (1.7)$$

These catalysts give a similar yield to chloroplatinic acid but do not cause hydrosilation of internal **alkenes** nor do they cause isomerison of terminal alkenes .

Intra-molecular hydrosilation of 4-pentasilanes leads to silacycloalkanes, five membered rings being formed preferentially [23, 24] (scheme 1.3)

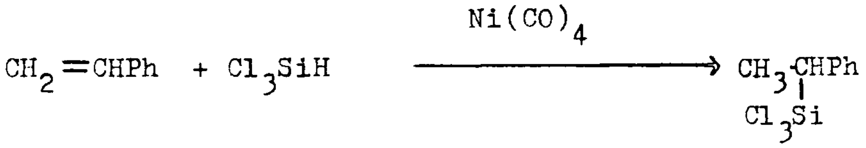


Scheme 1.3

Oligomers are not formed, even in the case of styrene [25]

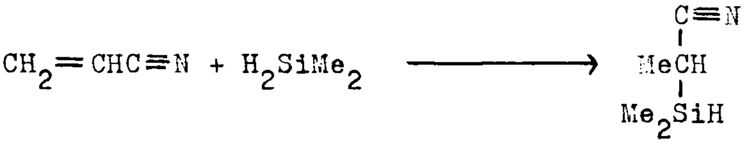
$$CH_2{=}CHPh + Cl_3SiH \xrightarrow{H_2PtCl_6} Cl_3SiCH_2CH_2Ph \qquad (1.8)$$

By comparison, whilst chloroplatinic acid leads to terminal addition in the above reaction, $Ni(CO)_4$ leads mainly to the α product [26]



$$CH_2{=}CHPh + Cl_3SiH \xrightarrow{Ni(CO)_4} CH_3\underset{\displaystyle Cl_3Si}{CH}Ph \qquad (1.9)$$

Nickel catalysed hydrosilation reactions take place in the presence of reducing agents, often the silane itself, and are limited to terminal and cyclic alkenes [27]. The reaction mechanism is again one of oxidative addition of the silane to the zero valent metal [27, 28] . The direction of addition depends on both the ligand attached to the nickel [29, 30] and on the substituent on the alkene. Equations 1.10 and 1.11 demonstrate the effect of electron withdrawing and donating substituents respectively on the alkene [31].



$$CH_2{=}CHC{\equiv}N + H_2SiMe_2 \longrightarrow \underset{\displaystyle Me_2SiH}{\overset{\displaystyle C{\equiv}N}{MeCH}} \qquad (1.10)$$

$$CH_2{=}C\begin{matrix}\diagup Me\\ \diagdown Et\end{matrix} + HSiMeCl_2 \longrightarrow Cl_2MeSiCH_2\underset{\displaystyle Et}{\overset{\displaystyle Me}{CH}} \qquad (1.11)$$

Catalysts include $[Ni(cod)_2]$, $[Ni(PPh_3)_4]$ and $[Ni(CO)_2(PPh_3)_2]$ [32-36] or $[Ni(acac)_2]$ reduced by an aluminium alkyl, hydride or the silane itself [32,33,35,37] .

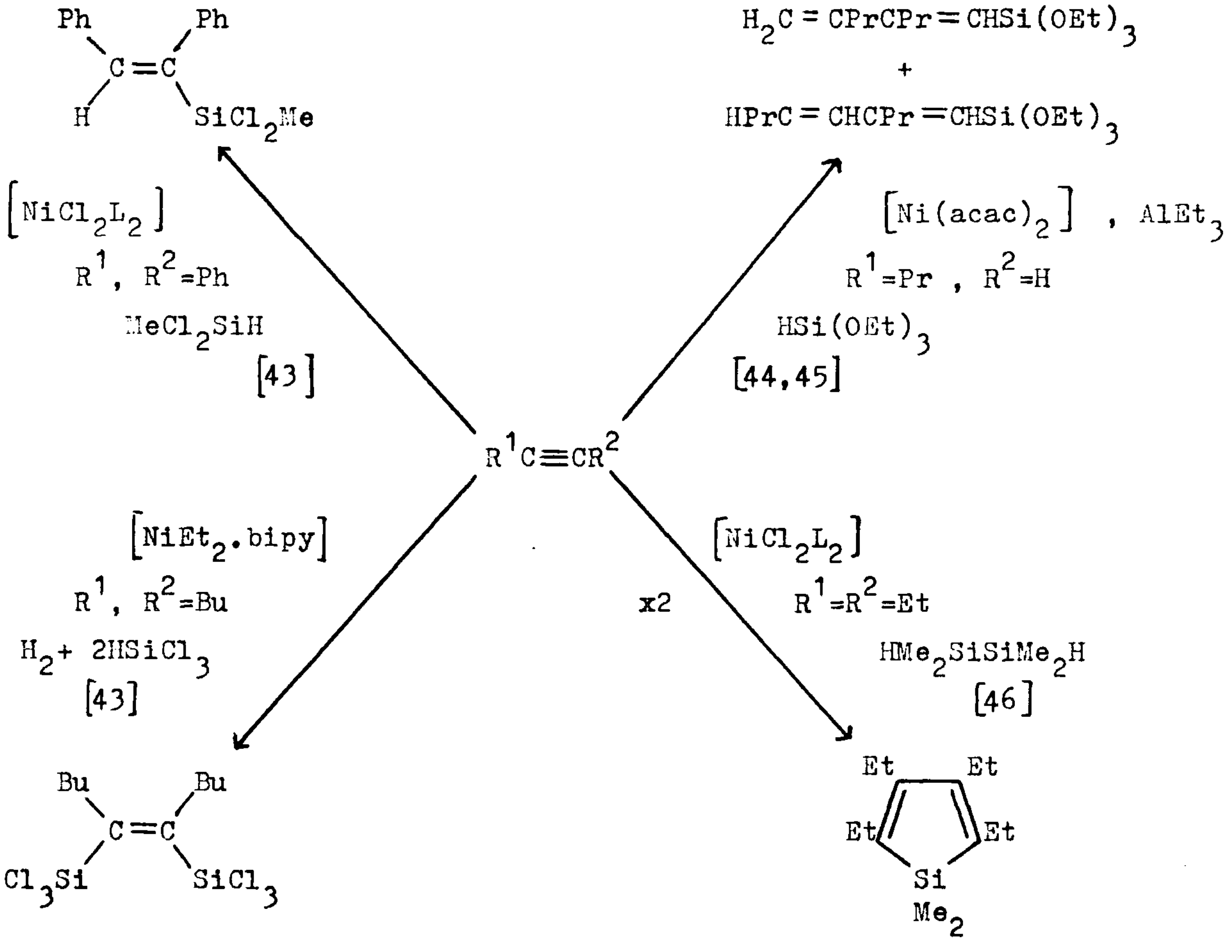
A useful summary of the hydrosilation of alkenes including dienes has been compiled by P.W.Jolly [31a] . As an example, the reaction with butadiene is given below, with the cis isomer predominating [32,38].

$$CH_2{=}CHCH{=}CH_2 + Cl_3SiH \longrightarrow CH_3CH{=}CHCH_2SiCl_3 \qquad (1.12)$$

1,4 addition , cis and trans isomers

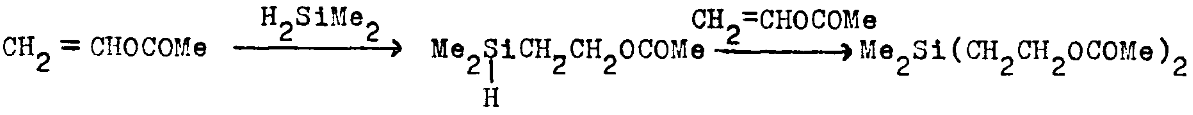
$$\left.\begin{array}{l} + CH_2{=}CHCH_2CH_2SiCl_3 \\ + Cl_3SiCH_2CH{=}CHCH_2SiCl_3 \end{array}\right\} \text{(traces)}$$

The hydrosilation of alkynes proceeds according to Scheme 1,4



Scheme 1.4

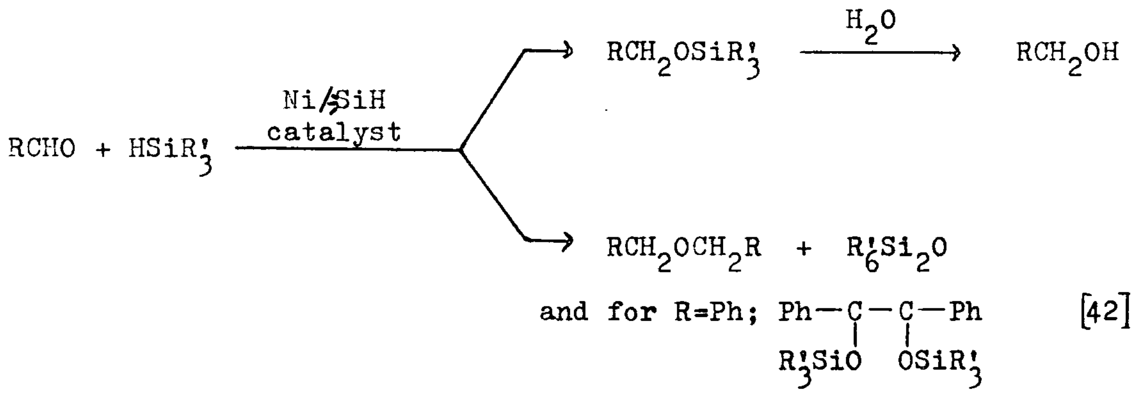
Stepwise addition of the dihydride is also possible, though not common [39].



$$CH_2{=}CHOCOMe \xrightarrow{H_2SiMe_2} \underset{\displaystyle H}{Me_2SiCH_2CH_2OCOMe} \xrightarrow{CH_2=CHOCOMe} Me_2Si(CH_2CH_2OCOMe)_2$$

(1.13)

Nickel catalysts, prepared by treating $NiCl_2$ with the silane, are used to hydrosilate carbonyl compounds according to Scheme 1.5 [40-42].

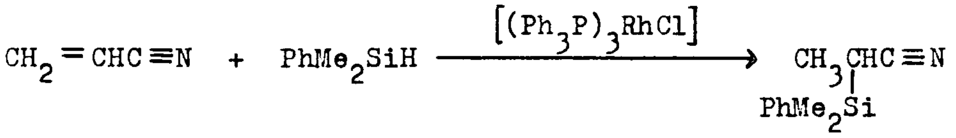


Scheme 1.5

The hydrosilation of ketones is reviewed in references 43 and 44. Conjugated ketones give saturated ketones or alcohols as a result of 1,4 or 1,2 addition respectively.

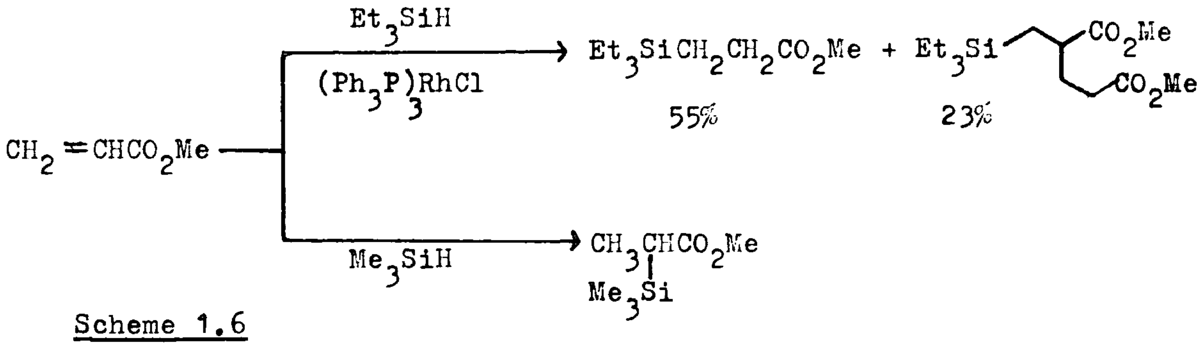
Similarily, the hydrosilation of an imine is possible and upon hydrolysis gives the amine [45-47].

Rhodium catalysts, such as $[(Ph_3P)_3RhCl]$ or Wilkinsons catalyst, are also widely used as this metal has one of the highest catalytic activities towards hydrosilation. The oxidative addition of the silane to the metal complex is a fast, reversible reaction which results in retention of configuration on the silicon atom. [43,44]. Rhodium catalysed hydrosilations follow a similar course to nickel, rather than platinum, catalysis and result in formation of the α adduct [48].



$$CH_2{=}CHC{\equiv}N \;+\; PhMe_2SiH \xrightarrow{[(Ph_3P)_3RhCl]} \underset{PhMe_2Si}{CH_3\overset{}{C}HC{\equiv}N} \qquad (1.14)$$

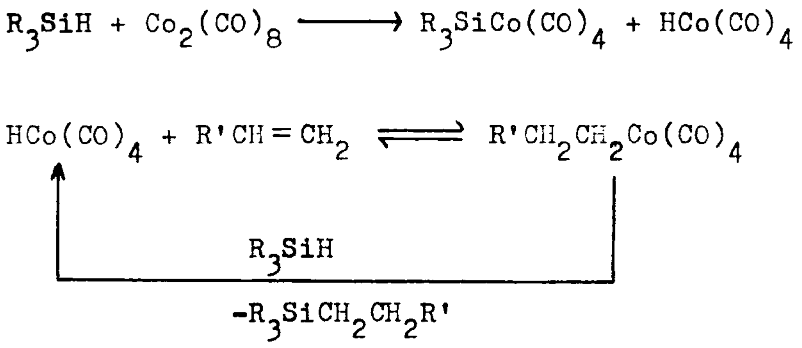
The hydrosilation of methyl acrylate, catalysed by Wilkinsons catalyst , results in β silation with some oligomerisation compared to α silation for the chloroplatinic acid catalysed reaction (Scheme 1.6) [49] .



Scheme 1.6

A comprehensive listing of rhodium and iridium complexes which catalyse hydrosilation reactions has recently been published [50].

Higher selectivity is achieved using chromium hexacarbonyl rather than chloroplatinic acid as a catalyst [51,52]. Dicobalt octacarbonyl is also a valuable catalyst. The reaction postulated is one of addition of Si-H across the Co-Co bond followed by oxidative addition. Although a compound containing both metals is formed, the actual catalyst is $HCo(CO)_4$. The reaction is represented schematically below [53-55].

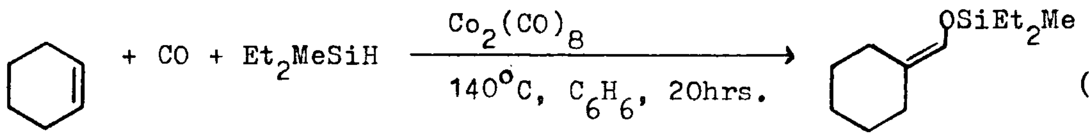


$$R_3SiH + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4$$

$$HCo(CO)_4 + R'CH{=}CH_2 \rightleftharpoons R'CH_2CH_2Co(CO)_4 \xrightarrow[-R_3SiCH_2CH_2R']{R_3SiH} HCo(CO)_4$$

Scheme 1.7

Metal carbonyls also catalyse carbonylative hydrosilation reactions according to equation 1.15 [56,57].

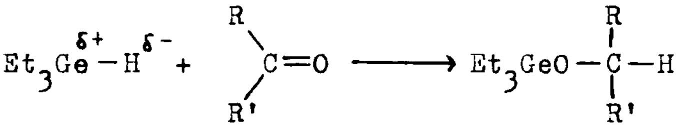


(1.15)

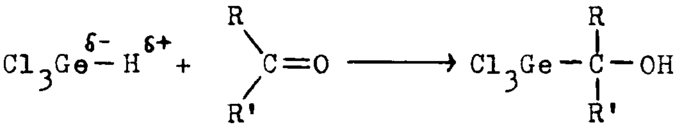
Iron pentacarbonyl catalysed hydrosilation has been reported [58] and also polymer supported transition metal catalysis [59,60].

1.3 HYDROGERMYLATION

The course of reaction in hydrogermylation appears to reflect the polarity of the germanium-hydrogen bond. It is believed that as the electronegativities of germanium and hydrogen are very similar on the Pauling scale (2.01 and 2.20 respectively [61,62]) then substituents on the germanium have an important effect. Organic substituents cause polarity of the germanium-hydrogen bond $(\overset{\delta-}{C}-\overset{\delta+}{Ge})$ and the effect is often strong enough to reverse the polarity of the metal hydrogen bond [63-66] compared to that of other metal hydrides. This is borne out in the examples below [63,67] .



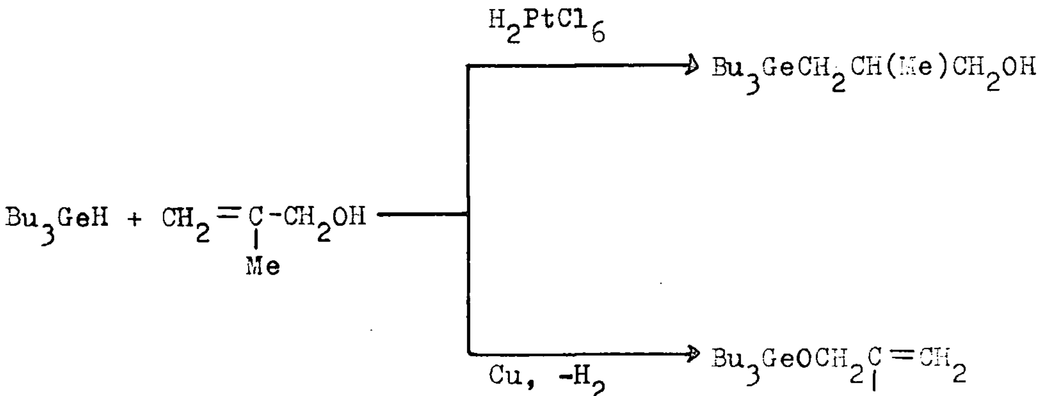
$$\mathrm{Et_3}\overset{\delta+}{\mathrm{Ge}}-\overset{\delta-}{\mathrm{H}} + \mathrm{RR'C{=}O} \longrightarrow \mathrm{Et_3GeO}-\mathrm{CRR'}-\mathrm{H} \qquad (1.16)$$



$$\mathrm{Cl_3}\overset{\delta-}{\mathrm{Ge}}-\overset{\delta+}{\mathrm{H}} + \mathrm{RR'C{=}O} \longrightarrow \mathrm{Cl_3Ge}-\mathrm{CRR'}-\mathrm{OH} \qquad (1.17)$$

An alternative explanation for the direction of addition in equations 1.16 and 1.17 may be that the former is proceeding by a polar mechanism and the latter by a free radical one.

As with hydrosilation reactions, both free radical and polar mechanisms operate. The free radical chain mechanism is similar to that for the silicon hydrides and results in retention of configuration at the germanium atom[63-68]. Transition metal catalysts, mainly $H_2PtCl_6 . H_2O$ [19] and $[(Ph_3P)_3RhCl]$ [69] , give rise to a similar oxidative addition process [70] to that for hydrosilation. The resultant anti-Markownikov addition gives linear adducts, again with retention of configuration at the metal atom [71,72]. The catalyst may also change the course, as well as the rate, of reaction as exemplified below [70] by replacing chloroplatinic acid by copper (scheme 1.8).

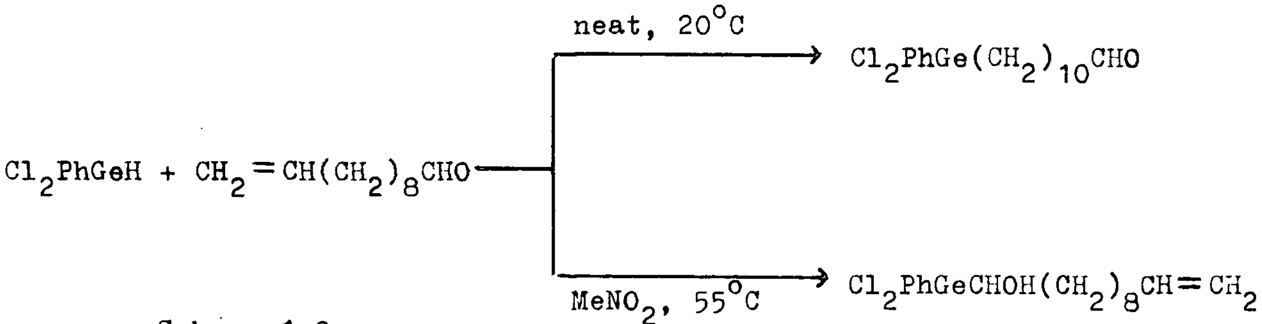


$$Bu_3GeH + CH_2{=}C(Me){-}CH_2OH \xrightarrow{H_2PtCl_6} Bu_3GeCH_2CH(Me)CH_2OH$$

$$Bu_3GeH + CH_2{=}C(Me){-}CH_2OH \xrightarrow[Cu,\ -H_2]{} Bu_3GeOCH_2C(Me){=}CH_2$$

Scheme 1.8

The above catalysts do not work well with triaryl and diaryl halogermanes [73]. The majority of hydrogermylation reactions are performed in the absence of solvent. However, when nucleophilic or polar solvents are employed they may give rise to a change in the course of reaction [74-77] and also increase the yield.



$$Cl_2PhGeH + CH_2{=}CH(CH_2)_8CHO \xrightarrow{neat,\ 20^\circ C} Cl_2PhGe(CH_2)_{10}CHO$$

$$Cl_2PhGeH + CH_2{=}CH(CH_2)_8CHO \xrightarrow[MeNO_2,\ 55^\circ C]{} Cl_2PhGeCHOH(CH_2)_8CH{=}CH_2$$

Scheme 1.9

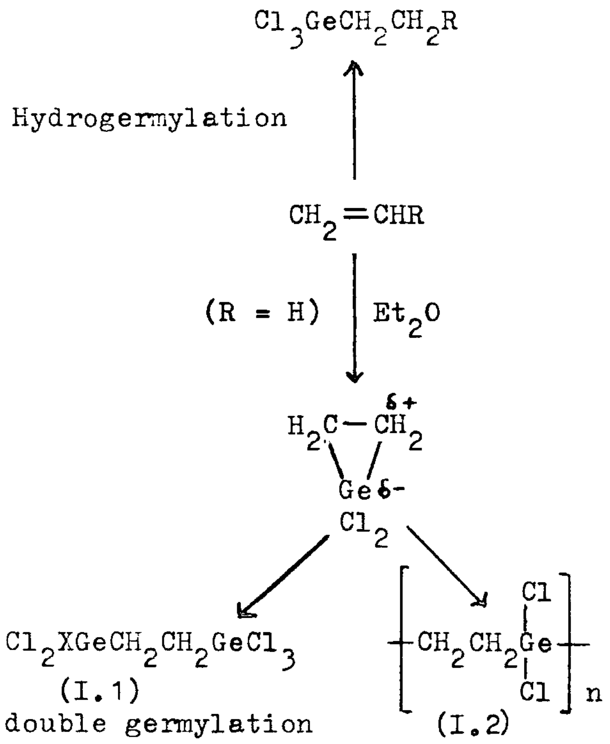
It has been suggested that strong nucleophiles are able to abstract the hydrogen atom from the germanium hydride to give the stable germyl anion (R_3Ge^-) which may then take part in the reaction [78].

Apart from their reactions with alkenes and alkynes [2,74,79,80] hydrogermylation studies have been conducted on enynes [81], ketones [82-84], nitrones [85], quinones [84,86] and ketenes [87-91].

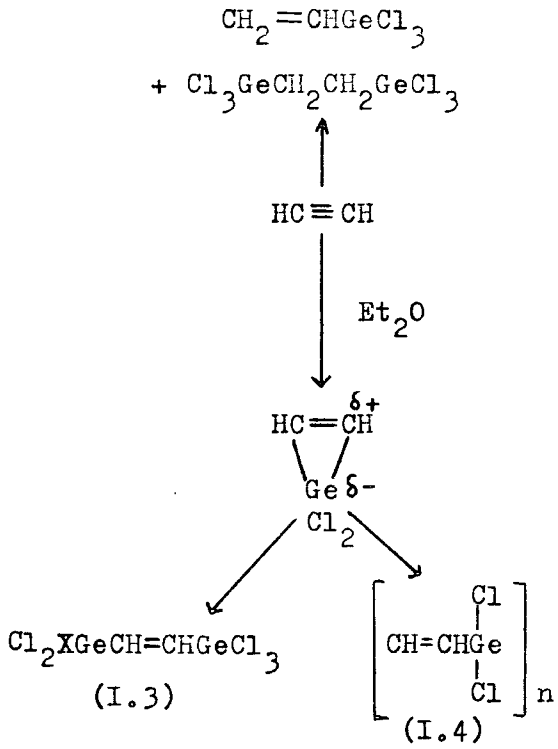
The chemistry of trichlorogermane has also been reviewed [67]. It reacts as if it were an equilibrium mixture (equation 1.18).

$$HGeCl_3 \rightleftharpoons H^+GeCl_3^- \rightleftharpoons GeCl_2 + HCl \tag{1.18}$$

The presence of ether causes the equilibrium to be shifted to the right hand side by formation of complexes ($R_2OH^+ \; GeCl_3^-$) which can act as a source of the nucleophile $GeCl_3^-$ or the ene $GeCl_2$. Reactions involving the latter proceed via a three membered heterocyclic intermediate which may either be opened by the hydrogen halide to give compounds I.1 and I.3 or be polymerised to give compounds I.2 and I.4. The reactions of trichlorogermane with alkenes and alkynes are represented schematically below (schemes 1.10 and 1.11 respectively).



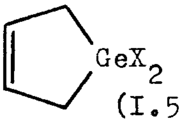
Scheme 1.10



Scheme 1.11

X = Cl,H

The proposed carbene mechanism is supported by the formation of a heterocyclic product from both trichloro- and tribromo- germane with butadiene but not by the reaction with piperylene [67,76].

$CH_2{=}CH{-}CH{=}CH_2 + HGeX_3 \longrightarrow$  $+ \ CH_3CH{=}CHCH_2GeX_3$ (1.19)

(I.5)

X=Cl 9 : 1

Br 1 : 2

$$MeCH{=}CH{-}CH{=}CH_2 + HGeCl_3 \longrightarrow EtCH{=}CHCH_2GeCl_3 \quad (1.20)$$

Mirinov et al [67] have also prepared the germacyclopentene (I.5) from preformed $GeBr_2$ and butadiene. An alternative route to this compound may be a 1,4 addition of the germanium dihalide to the conjugated diene or 1,2 addition followed by rearrangement [67]. A free radical mechanism for the double germylation reaction in the absence of ether is ruled out on the grounds that these products are formed more readily in the presence of ether, in which the etherate has been shown to be ionic from the proton n.m.r. spectrum [67]. Similar conclusions were drawn by Nefedov et al [92-96] for the above systems.

1.4 HYDROSTANNATION

Unsaturated species undergo hydrostannation by both organo and halogeno tin hydrides. Reactions involving the former are discussed in this section and those of the latter in chapter 2.

Hydrostannation by Organotin Hydrides

Organotin hydrides of general formula $R_{4-x}SnH_x$ (R =alkyl, aryl; x = 1-3) can react in hydrostannation reactions but as x increases the hydrides become thermally less stable. This limits the use of certain hydrides to reactions not requiring long heating periods. Several review articles have been published [97,98] since the first record of hydrostannation [99].

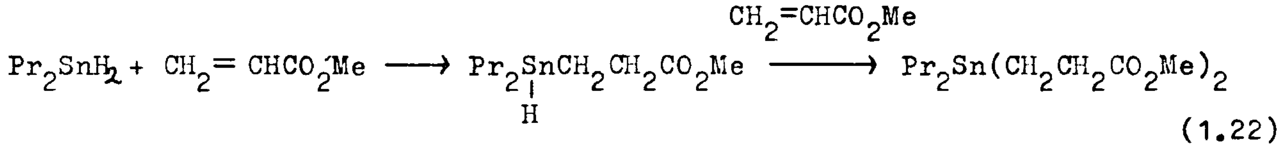
Hydrostannation reactions across alkenes give good yields at moderate temperatures (60-80°C) [100] and in many cases in the absence of a catalyst [101]. Terminal alkenes and those activated by electron-withdrawing substituents are the most reactive. The role of the functional group in facilitating addition is demonstrated by the difficulty of hydrostannation in their absence.

$$Me_3SnH + CH_2{=}CHR \longrightarrow \underset{2\%}{Me_3SnCH_2CH_2R} \qquad (1.21)$$

R = alkyl

The hydrostannation of non-terminal alkenes results in the organotin group becoming attached to the least sterically crowded carbon atom [99,100]. Strained internal alkenes, such as norbornadiene [102] undergo hydrostannation [103] contrary to early reports [97,104].

Aryl tin hydrides are more reactive than the alkyl analogues. Also mono-hydrides are more reactive than dihydrides as illustrated below where the intermediate monohydride reacts more readily than the dihydride [97].



$$Pr_2SnH_2 + CH_2{=}CHCO_2Me \longrightarrow \underset{\displaystyle H}{Pr_2\underset{|}{Sn}}CH_2CH_2CO_2Me \xrightarrow{CH_2{=}CHCO_2Me} Pr_2Sn(CH_2CH_2CO_2Me)_2 \qquad (1.22)$$

In spite of their low thermal stability, the trihydrides Bu^nSnH_3 and Bu^tSnH_3 will give hydrostannation reactions [101,104].

$$Bu^tSnH_3 + 3CH_2{=}CHCO_2Me \longrightarrow Bu^tSn(CH_2CH_2CO_2Me)_3 \qquad (1.23)$$

It is possible that in the above reactions the reactivity of the hydride is affected by coordination of the carbonyl oxygen to the tin atom.

It was originally believed that hydrostannation occurs by a polar mechanism [99,101,105,106] because of the effect of solvent polarity on the reaction rate and because radical initiators and scavengers appeared to be ineffective, until in 1961 Neumann proved otherwise [107,108]. In fact almost any alkene will react when catalysed by radical sources. The radical chain mechanism is similar to that for hydrosilation [97,98,107,109-111] (scheme 1.1). The site of attack is governed by the relative stability of the possible radicals thus formed, tertiary radicals being most stable, as illustrated in table 1.2.

Table 1.2

Hydrostannation of Selected Internal Alkenes and Terminal Disubstituted Alkenes by Me_3SnH to Illustrate the Preferred Site of Attack [110].

Alkene	Radical	Product (% Yield)
$EtCH{=}CMe_2$	$Me_3SnCH(Et)\dot{C}Me_2$	$Me_3SnCH(Et)CHMe_2$ (51)
$H_2C{=}CEt_2$	$Me_3SnCH_2\dot{C}Et_2$	$Me_3SnCH_2CH(Et)_2$ (91)
$H_2C{=}C(Me)CHMe_2$	$Me_3SnCH_2\dot{C}(Me)CHMe_2$	$Me_3SnCH_2CH(Me)CHMe_2$ (98)

Hydrostannation reactions may be catalysed by free radical initiators, ultra-violet light, trialkyl aluminiums and by choice of solvent.

(a) Catalysis by free radical initiators

The hydrostannation of alkenes can be catalysed by azobisisobutyronitrile (AIBN) and the corresponding esters, benzyl hyponitrite, phenyl azoisobutyronitrile and other free radical sources. This reduces the time and temperature(30-80°C) of the reaction, as illustrated in table 1.3. Also the hydrostannation of non-activated alkenes, which otherwise do not react, [104,107] is now possible.

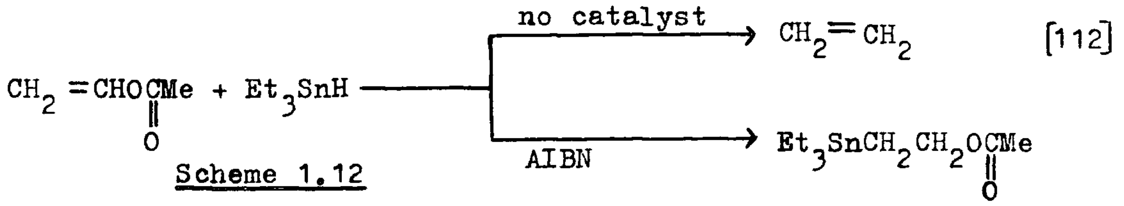
Table 1.3

Some Hydrostannation Reactions of Et_3SnH assisted by Free Radical Initiators

Alkene	Catalyst	Conditions	% Yield	Ref.
$CH_2=CH(CH_2)_8CO_2Et$	a	40-50°C, 50hrs	78	[108]
$CH_2=CHCO_2Me$	b	40°C, 2.5hrs	93	[97,104] [108]
$CH_2=CHC\equiv N$	a	60°C,	86	[97,104]
	c	40-50°C, 1.5hrs	79	[108]
$CH_2=CH(CH_2)_5Me$	d	80-90°C, 78hrs	98	[108]

a = AIBN; b = diethyl azo-bis-isobtyrate; c = benzyl hyponitrite;
d = phenyl azo triphenylmethane

Also reactions that are catalysed by AIBN are not catalysed by chloroplatinic acid or platinised carbon [97,106]. The catalyst may also alter the course of reaction, as demonstrated in scheme 1.12 [108].



$$CH_2{=}CHO\overset{\displaystyle O}{\overset{\|}{C}}Me + Et_3SnH \xrightarrow{\text{no catalyst}} CH_2{=}CH_2 \quad [112]$$

$$CH_2{=}CHO\overset{\displaystyle O}{\overset{\|}{C}}Me + Et_3SnH \xrightarrow{\text{AIBN}} Et_3SnCH_2CH_2O\overset{\displaystyle O}{\overset{\|}{C}}Me$$

Scheme 1.12

(b) Catalysis by ultra-violet light

Both tin-carbon and tin-hydrogen bonds are cleaved by u.v. light of wavelength;

$$\lambda \ll 400\text{nm}, \quad \text{i.e. energy} \gg 293\text{KJ mol}^{-1} \qquad [113]$$

It can therefore initiate such reactions [114-118]. For disubstituted terminal alkenes where no reaction occurs in the absence of a catalyst, and even with AIBN the reaction is unsatisfactory, u.v. irradiation catalysed reactions proceed more smoothly and with good yields. Due to the efficient catalytic effect of u.v. irradiation the hydrostannation of simple hydrocarbon and fluorocarbon alkenes has been studied. As a result the first fluorocarbon organometallic compound from a fluoroalkene and a metal hydride was synthesised [119].

$$Bu_2SnH_2 + 2\ CF_2{=}CF_2 \xrightarrow[\text{u.v. light}]{90^{\circ}C,\ 4hrs} Bu_2Sn(CF_2CF_2H)_2 \qquad (1.24)$$

By comparison, the mono adduct only was obtained by Clark et al [116].

In certain cases diorganotin dihydrides will react with simple alkenes in the dark at a reasonable rate [116,117] but u.v. irradiation always accelerates the reaction. Thermal assistance gives further acceleration. As a result both mono- and di- adducts are formed.

$$CF_2{=}CF_2 + Me_2SnH_2 \xrightarrow[50hrs,\ 25^{\circ}C]{\text{u.v. light}} \underset{22.4\%}{Me_2Sn(H)CF_2CF_2H} + \underset{40\%}{Me_2Sn(CF_2CF_2H)_2} \qquad (1.25)$$

The proportion of mono and di- adducts produced depends on the molar ratio of starting materials but the total yield is unaffected [116,117].

Stepwise addition of the tin dihydride occurs as shown schematically for tetrafluoro ethylene (scheme 1.13).

$$Me_2SnH_2 + CF_2{=}CF_2 \longrightarrow Me_2Sn(H)CF_2CF_2H$$

$$2\ Me_2Sn(H)CF_2CF_2H \longrightarrow Me_2Sn(CF_2CF_2H)_2 + Me_2SnH_2$$

or

$$Me_2Sn(H)CF_2CF_2H + CF_2{=}CF_2 \longrightarrow Me_2Sn(CF_2CF_2H)_2$$

Scheme 1.13

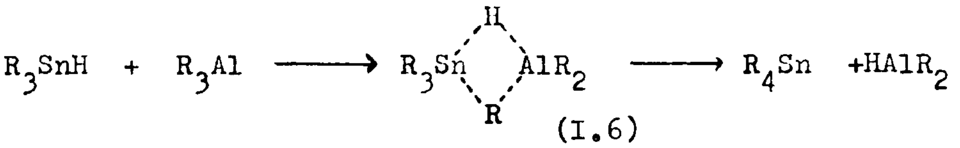
In cases where only the diadduct is formed there is good evidence for the transient existence of the mono adduct [116,117]. For simple alkenes the mono-adduct is less stable than the di-adduct. The organotin fluoroalkanes are very unstable and consequently decompose to the stable inert fluorides [116].

$$\begin{tikzcd}
Me_2SnH(C_2F_2H_3) \arrow[r] & Me_2SnHF \arrow[d, "x2"] + CH_2{=}CHF \\
 & Me_2SnH_2 + Me_2SnF_2
\end{tikzcd} \qquad (1.26)$$

The reaction mechanism for the hydrostannation of fluoroalkenes appears to be free radical, although a four center transition complex has not been excluded.

(c) Catalysis by trialkyl al~~l~~uminium compounds

A hydrogen atom of an organotin hydride and an alkyl residue from a trialkyl aluminium catalyst are exchanged via a transition state (I.6) [120] which takes advantage of the electron deficiency of the aluminium.



$$R_3SnH + R_3Al \longrightarrow R_3Sn\overset{H}{\underset{R}{\diamond}}AlR_2 \longrightarrow R_4Sn + HAlR_2 \qquad (1.27)$$

(I.6)

The first hydrogen atom of the di- and tri- hydrides reacts most readily and only one alkyl group per aluminium compound can be replaced by hydrogen [121, 122]. The alkyl groups attached to the two metals should correspond to the alkene otherwise preferential displacement of unwanted groups may occur. Upon addition of an α alkene to I.6 the original trialkyl aluminium compound is regenerated, the net result being hydrostannation of the alkene.

$$R'CH{=}CH_2 + HAl(CH_2CH_2R')_2 \longrightarrow (R'CH_2CH_2)_3Al \xrightarrow{R'CH=CH_2} (R'CH_2CH_2)_4Sn \qquad (1.28)$$

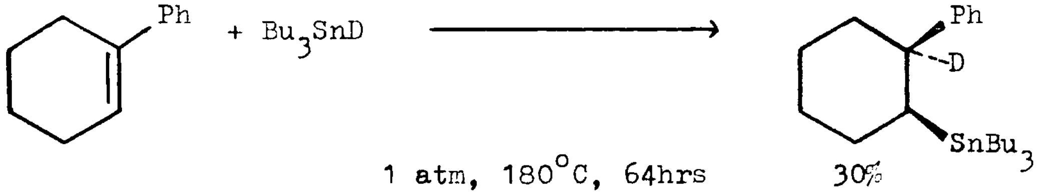
Dialkyl aluminium hydrides, lithium aluminium hydride and ether free aluminium trihydrides [123, 124] may also be used.

(d) The effect of solvent

The polarity of the solvent affects ionic, but not free radical reactions [97, 100, 101] as expected.

(e) Reactions under pressure

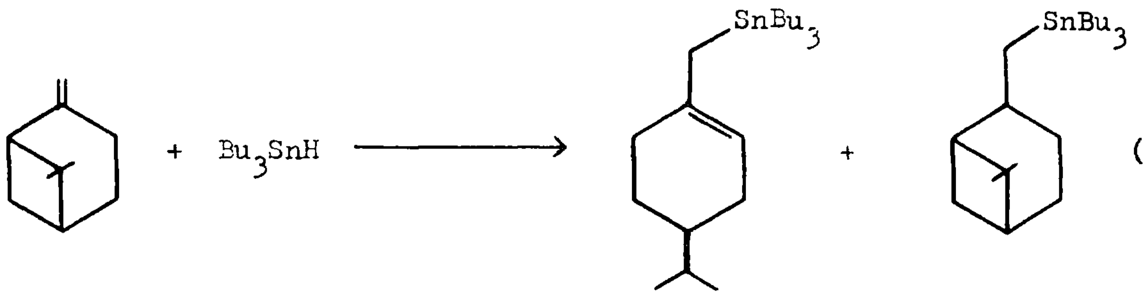
The hydrostannation of alkenes has also been performed under high pressure [125] and occurs by anti-addition. The result may be a higher yield of product (equation 1.29) [125, 126] or a change in the course of reaction (equation 1.30) [125, 127].



(1.29)

1 atm, 180°C, 64hrs 30%

10 Kbars, 50°C, 64hrs 90%



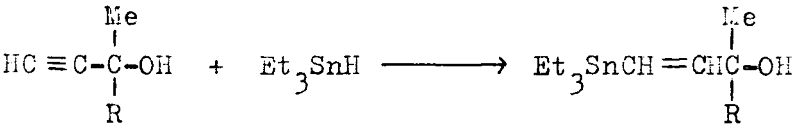
(1.30)

1 atm, AIBN, 24hrs, 70-200°C	100%	-
14 Kbar, 24hrs, 55°C	3%	97%

Organotin hydrides are more reactive towards alkynes rather than alkenes. The reaction can therefore be controlled to stop either at the vinyl organotin compound (I.7) or after further hydrostannation, at the diadduct (I.8).

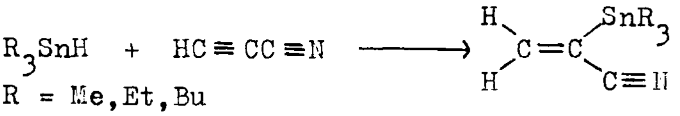
$$R_3SnH + HC{\equiv}CR' \longrightarrow \underset{(I.7)}{R_3SnCH{=}CHR'} \xrightarrow{R_3SnH} \underset{(I.8)}{R_3SnCH_2CHR'SnR_3} \qquad (1.31)$$

It was originally suggested that for mono substituted alkynes 1,2 terminal addition occurs [100,104,112,128].



$$HC{\equiv}C-\underset{R}{\overset{Me}{C}}-OH + Et_3SnH \longrightarrow Et_3SnCH{=}CH\underset{R}{\overset{Me}{C}}-OH \qquad (1.32)$$

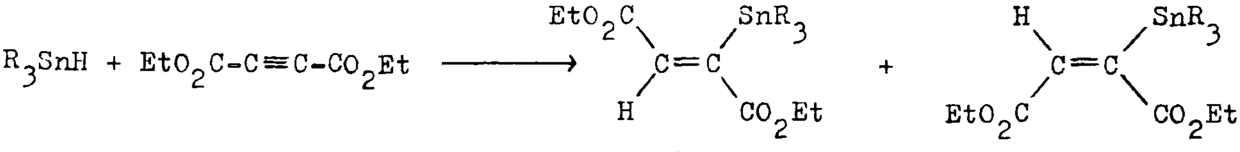
However, Leusink et al [129] proved otherwise for cyanoethylene;



R = Me,Et,Bu

(1.33)

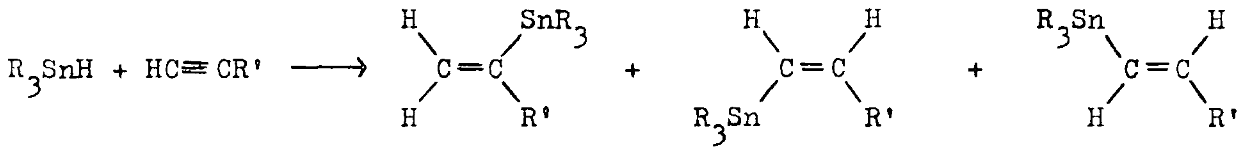
Addition to di-substituted alkynes yields mainly the trans adduct [130].



9 : 1

(1.34)

The general equation below applies to mono-substituted alkynes;



(1.35)

α adduct (I.9) cis- β adduct (I.10) trans- β adduct (I.11)

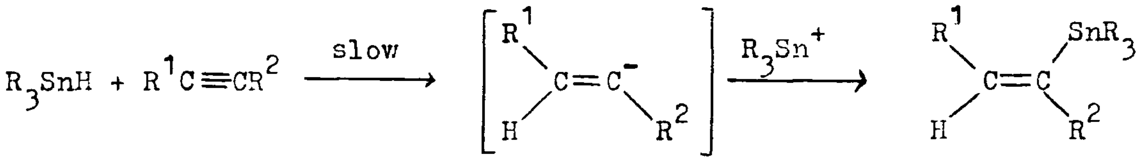
Strongly electron withdrawing substituents (CO_2R, CN) favour the formation of the non-terminal α adduct (I.9). Conversely, electron releasing substituents (Br, OEt) and weakly electron withdrawing substituents (CH_2OH, Ph) yield mainly cis- and trans- β adducts (I.10 and I.11) [130]. The latter case also applies to disubstituted alkynes with both an electron withdrawing and releasing substituent [131]. These trends are tabulated below (table 1.4)

Table 1.4

The hydrostannation of selected monosubstituted alkynes to show the effect of substituent (R') on the alkyne on the ratio of isomers, α: cis β : trans β [130] (equation 1.35).

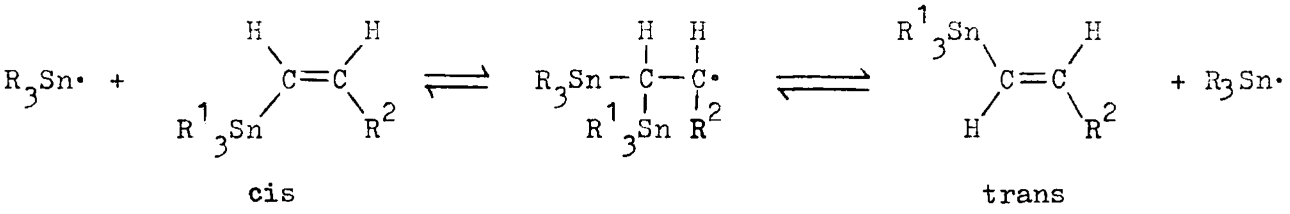
R'C≡CH; R' =	R_3SnH; R =	Ratio
CO_2Et	Me	67 : 25 : 8
C≡N	Me	100 : 0 : 0
Bu	Ph	0 : 85 : 15
OEt	Ph	0 : 97 : 3
CH_2OH	Ph	5 : 45 : 50
Ph	Et Ph	0 : 70 : 30 0 : 28 : 72

The α adduct is believed to be formed mainly by an ionic mechanism [132]. A radical mechanism leads to the cis β adduct [133], isomerism of which results in the trans β adduct [134].
The polar mechanism Scheme 1.14 [132] consists of the nucleophilic attack of the hydride hydrogen on the alkyne to generate an organotin cation and a vinyl carbanion which add together in a trans manner rather than proceeding via a four centre transition state in which bond making and breaking occur simultaneously.



Scheme 1.14

Conversely the free radical mechanism proceeds via an organotin vinyl radical to give the cis β adduct which is converted to the trans β adduct by a trialkyl stannyl radical induced reaction.



Scheme 1.15

It is also possible to saturate the vinyl tin products by further hydrostannation resulting in a di-adduct. A β,α adduct would be expected for minimal steric hindrance [97, 135, 136].

$$HC\equiv CR' \xrightarrow{R_3SnH} \underset{\beta\text{ adduct}}{R_3SnCH{=}CHR'} \xrightarrow{R_3SnH} \underset{\beta,\alpha\text{ adduct}}{R_3SnCH_2CHR'SnR_3} \qquad (1.36)$$

However, it is also possible for $\beta\beta$, $\beta\alpha$ and $\alpha\beta$ adducts to be formed [136, 137] and it is claimed that $\beta\beta$ adducts predominate [135].

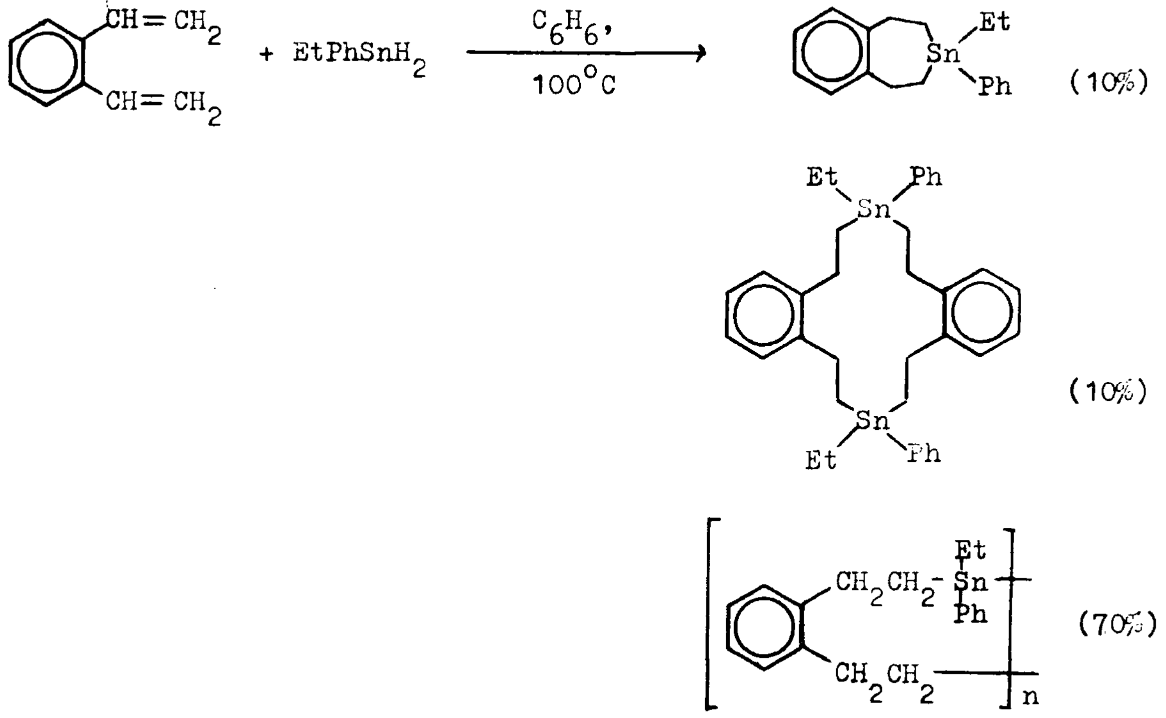
Alkynyl derivatives of tin and other metals undergo hydrostannation to yield compounds containing two metal atoms joined through a vinyl group [138, 139].

$$Bu_3SnH + HC{\equiv}CMBu_3 \longrightarrow Bu_3SnCH{=}CHMBu_3 \qquad (1.37)$$

M = Sn,Ge.

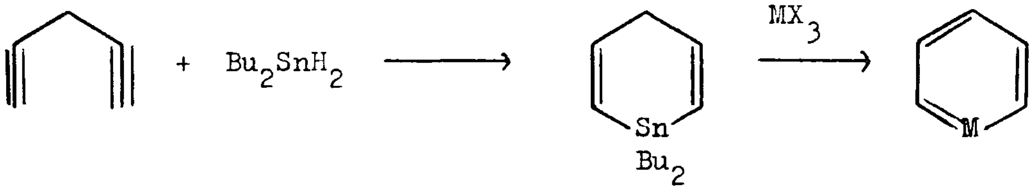
Products with a bridge of carbon atoms between two R_3Sn groups [101, 106] are formed by the hydrostannation of dienes. By comparison conjugated dienes yield 1,4 and 1,2 mono adducts, of which the former predominate. This again is rationalised in terms of a free radical mechanism which will obviously proceed via the most stable intermediate radical [138]. Similarily the hydrostannation of allenes has also been studied [139, 140]

Sterically favoured terminal dienes such as o-divinyl- and o-diethynylbenzene lead to metallocycles and polymers [141-143].



(1.38)

1-Stanna cyclohexa 2,5 diene is a useful intermediate in the preparation of certain benzene heterocycles [144-146].


(1.39)

The preparation of linear hetero polymers by the hydrostannation of α,ω dienes, ethynes and α,ω diynes by diorganotin dihydrides is a useful route to organometallic polymers with molecular weights ranging from 45,000 to 100,000 (equations 1.40 to 1.42) [106,147-149] .

$$R_2SnH_2 + \underset{I.12}{H_2C{=}CHXCH{=}CH_2} \longrightarrow \left[Sn(R_2)CH_2CH_2XCH_2CH_2\right]_n \qquad (1.40)$$

$X = C_6H_4, OCOCH_2CH_2OCO, R'_2Sn, R'_2Ge, R'_2Si$ [149]

$$Pr_2SnH_2 + HC{\equiv}CPh \longrightarrow \left[Sn(Pr_2)CH_2CH(Ph)\right]_n \quad [150] \qquad (1.41)$$

$$R_2SnH_2 + \underset{I.13}{HC{\equiv}CXC{\equiv}CH} \longrightarrow \left[Sn(R_2)CH{=}CHXCH{=}CH\right]_n \quad [112,\ 150] \qquad (1.42)$$

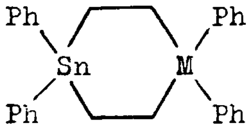
The substituents R on the tin atoms have a marked effect on the properties of the polymer. The polymer from 1,5 hexadiene and diphenyltin dihydride is a rubber like elastic solid whereas those from alkyl tin dihydrides with 1,5 hexadiene are viscous liquids [150] which upon heating become more rubbery. The paraphenylene link in the polymer derived from paraphenylene bis-(dimethyltin hydride) and diphenyl-tin dihydride causes enhanced rigidity of the polymer backbone [149].

Polymerisation also occurs in the trialkyl aluminium catalysed hydrostannation of poly-unsaturated species by dialkyltin dihydrides [120].

$$n\ H_2C=CH(CH_2)_4CH=CH_2 + n\ Bu_2SnH_2 \xrightarrow{AlR_3} \left[(CH_2)_8Sn(Bu_2)\right]_n \qquad (1.43)$$

Partially or fully cross-linked polymers are obtained from trihydrides such as the isobutyl derivative [104,107,108,120]. Polymerism can be seriously impeded by cyclisation reactions which are minimised by careful choice of group 'X' in I.12 and I.13. Consequently, high molecular weight polymers are formed when 'X' is C_6H_4 and  [148,149]. The products of cyclisation are chiefly bimetallocyclohexanes [135,148,151].

$$Ph_2SnH_2 + Ph_2M(CH=CH_2)_2 \longrightarrow \qquad (1.44)$$

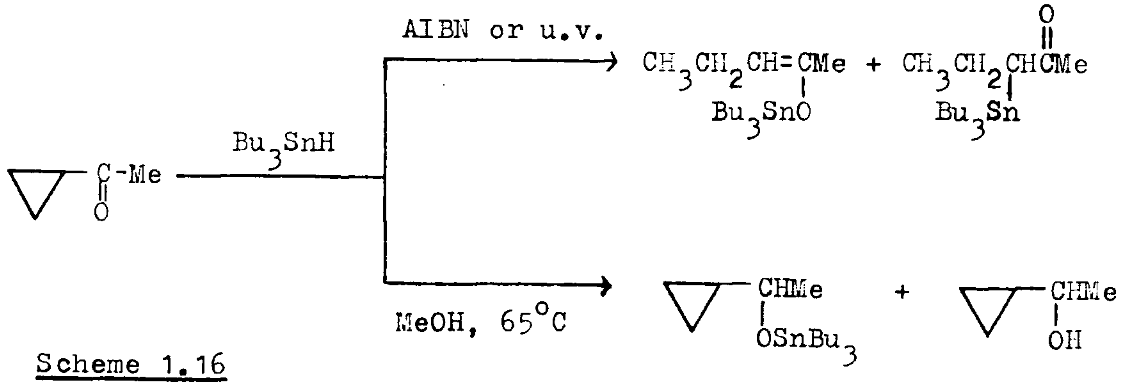


(I.14)

Ph_2M = X in equation 1.40
M = Ge,Si .

The hydrostannation of vinyl germanes and silanes almost exclusively yields the cyclic product, very little polymeric product being obtained, contrary to expectation. 1,4 distannacyclohexane cannot be synthesised by this method. Attempts to prepare the lead analogue of I.14 gave only metallic lead [151].

The hydrostannation of cyclopropanes and butanes in free radical conditions is a means of ring opening. However, the ring remains intact in polar conditions. This is illustrated in scheme 1.16 [125,152-157].

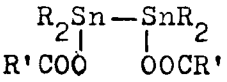
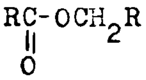
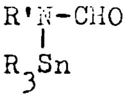


Scheme 1.16

The reactions of tin hydrides with carbonyl compounds are summarised in table 1.5.

Table 1.5

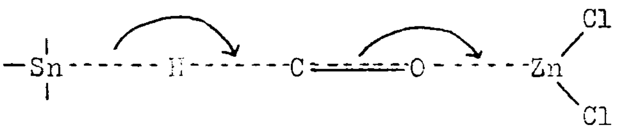
Reactions of Tin Hydrides with Carbonyl Compounds

Carbonyl Compound	$R_{4-x}SnH_x$	Product(s)	Ref.
$R^1R^2C=O$ R^1 may be H	R_3SnH	$R_3SnOCHR^1R^2$ * or R_3SnSnR_3 + $HOCHR^1R^2$	[97,114] [155, 158-172]
	R_2SnH_2	$R_2Sn(H)OCHR^1R^2$ * or R_2Sn + $HOCHR^1R^2$	
2 $R'CO_2H$	R_2SnH_2 2 R_2SnH_2	$R_2Sn(OCOR')_2$ + 2 H_2  $\underset{R'COO}{\underset{\mid}{R_2Sn}}-\underset{OOCR'}{\underset{\mid}{SnR_2}}$	[173-176]
R'COX	R_3SnH	RCHO or  $\underset{O}{\underset{\parallel}{RC}}-OCH_2R$	[97,100, 176-181]
$R'N=C=O$	R_3SnH	 $\underset{R_3Sn}{\underset{\mid}{R'N}}-CHO$ *	[182-186]
$R'N=C=S$	R_3SnH	$R'-N=CH-S-SnR_3$ *	[182-186]

* hydrostannation reactions

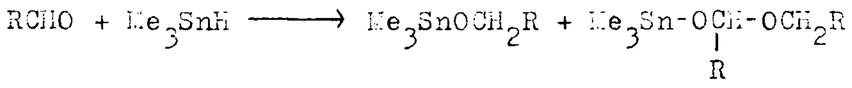
The hydrostannation of aldehydes and ketones lead to an alkoxide or a carbinol and exclusive conversion occurs in the absence of a catalyst [97, 158 - 160, 172]. The reduction of a carbonyl compound may be catalysed by a small amount of a dialkyltin dihalide, [170, 172], by radical initiators (AIBN [155, 161, 167] , u.v. irradiation [114, 166]) and by $ZnCl_2$ [155,161,167] . Mechanistic studies show that the reaction may follow a radical [163,166,167] or polar [97,168] mechanism. The catalytic role of the Lewis acid $ZnCl_2$ and weak acids such as methanol and phenol [167] is probably to increase the electrophilic character of the carbonyl carbon atom and make it more susceptible to nucleophilic attack as illustrated below (I.15 and I.16).

$$R_2C=O.\ \ ZnCl_2 \longleftrightarrow R_2C^{+}\text{——}O^{-}.\ \ ZnCl_2 \qquad \text{I.15} \quad [167]$$



I.16 [169]

Strongly electrophilic carbonyl compounds give both mono- and diadducts [169].



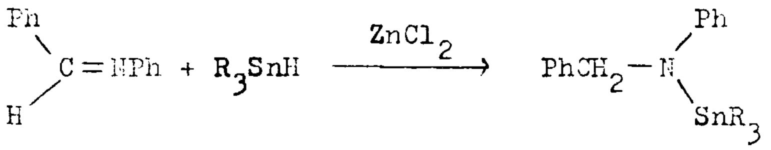
$$RCHO + Me_3SnH \longrightarrow Me_3SnOCH_2R + Me_3Sn\text{-}O\underset{\substack{|\\R}}{CH}\text{-}OCH_2R \qquad (1.45)$$

R = Cl_3C	30%	70%
C_6F_5	70%	25%

The alkene bond in $\alpha\beta$ unsaturated carbonyl compounds is usually unaffected [158].

The hydrostannation of acid halides proceeds via a free radical mechanism whilst the reactions involving isocyanates and isothiocyanates follows a polar mechanism. A tin-sulphur bond is formed in the reaction with isothiocyanates but no analogous tin-oxygen bond from isocyanates. This arises because of the capacity of sulphur only to facilitate back donation of electrons from the tin atom into a low energy 'd' orbital [186] and thus form a stronger bond.

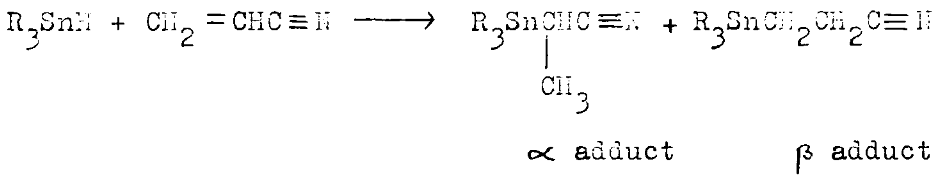
Azomethines, (including isocyanates) undergo hydrostannation [107,108,161,187] in the presence of Zinc chloride to give products with a tin-nitrogen bond whilst hydrogenation occurs in the absence of the catalyst [161].



$$\text{PhCH}{=}\text{NPh} + R_3SnH \xrightarrow{ZnCl_2} PhCH_2-N(Ph)SnR_3 \qquad (1.46)$$

R = Et, Ph

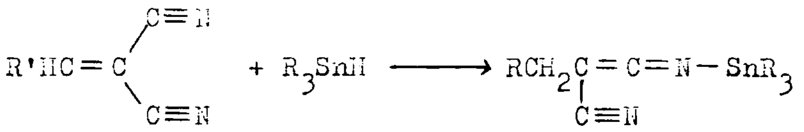
In the hydrostannation of cyanoethyne [129] dicyanoethyne [130] and acrylonitrile [9,104,108,188] the nitrile group is unaffected. Both α and β adducts are formed from acrylonitrile by polar and free radical mechanisms respectively.



$$R_3SnH + CH_2{=}CHC{\equiv}N \longrightarrow R_3SnCH(CH_3)C{\equiv}N + R_3SnCH_2CH_2C{\equiv}N \qquad (1.47)$$

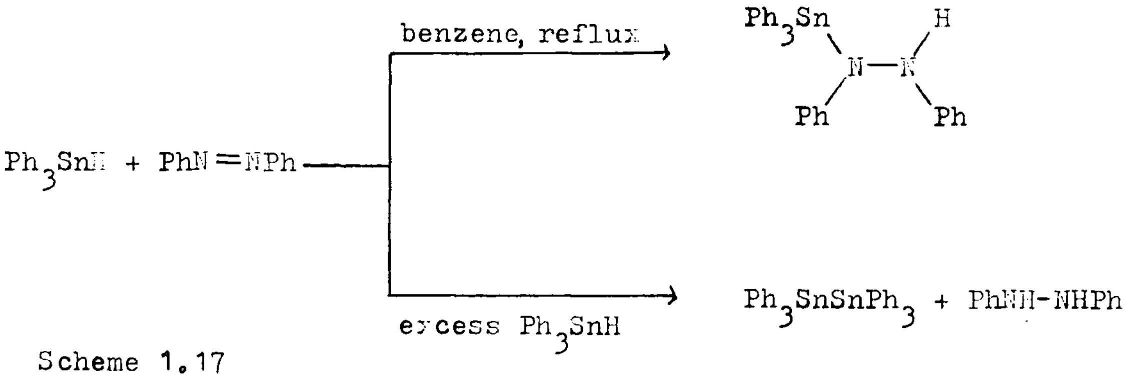
α adduct β adduct

However, the hydrostannation of conjugated nitriles where the alkene bond is sufficiently polarised, such as alkylidene malononitriles, results in addition across the cyanide group to form N-stannyl ketenimines [189].



$$R'HC{=}C(C{\equiv}N)_2 + R_3SnH \longrightarrow RCH_2C(C{\equiv}N){=}C{=}N-SnR_3 \qquad (1.48)$$

Also triorganotin hydrides are extremely reactive towards an azo bond to give derivatives of hydrazine [190]. In the presence of excess hydride hydrostanolysis occurs (scheme 1.17).



Scheme 1.17

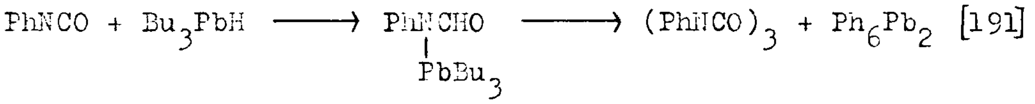
The nitrogen-nitrogen double bond in azo-bis isobutyronitrile (AIBN) and phenyl azo-bis isobutyronitrile are not affected by triethyltin hydride [107].

1.5 HYDROPLUMBYLATION

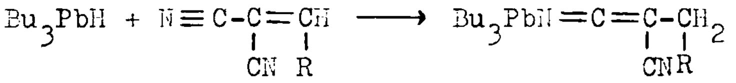
The low thermal stability of the lead hydrides particularly those with small alkyl groups, makes them more difficult to handle, but also affords hydroplumbylation reactions at low temperature and without the aid of a catalyst. The scope of hydroplumbylation reactions is represented below (equations 1.48 to 1.51)

$Bu_3PbH + CH_2{=}CHR \longrightarrow Bu_3PbCH_2CH_2R.$ [191] (1.48)

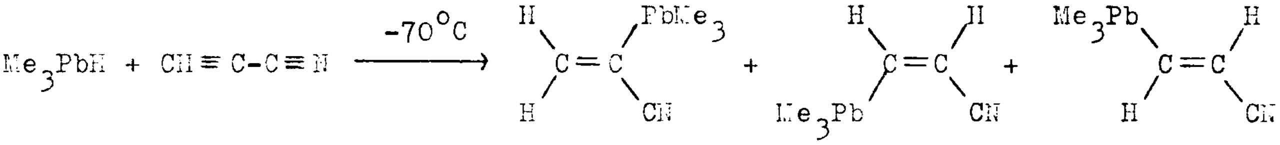
$R = Ph, CN, CO_2Me$



$$PhNCO + Bu_3PbH \longrightarrow \underset{PbBu_3}{PhNCHO} \longrightarrow (PhNCO)_3 + Ph_6Pb_2$$ [191] (1.49)



$$Bu_3PbH + N{\equiv}C{-}\underset{CN}{C}{=}\underset{R}{CH} \longrightarrow Bu_3PbN{=}C{=}\underset{CN}{C}{-}\underset{R}{CH_2}$$ [192] (1.50)



α cis-β trans-β

[193,194] (1.51)

The reaction with cyanoethylene leads to the α and (cis- and trans-) β adducts by both polar and free radical mechanisms, which occur separately but simultaneously in a similar manner to that discussed in the previous section for the hydrostannation of alkynes.

CHAPTER 2

THE REACTION BETWEEN TIN (II) CHLORIDE AND HYDROGEN CHLORIDE IN DIETHYL ETHER AND ITS USE IN ORGANOMETALLIC SYNTHESIS.

2.1 Introduction

Species that behave as "$HSnX_3$", though really $LH^+SnX_3^-$ (where L is a Lewis base) may be employed for hydrostannation reactions and are prepared from L (typically Et_2O), HX and SnX_2 [1,2] . Likewise species that behave as "H_2SnX_2" can be used and are prepared from Sn and HX in Et_2O [3]. Halostannane complexes may also be prepared by reducing the tin (II) halide by lithium aluminium hydride in ether or in an amine [4,5] . The former methods are the subject of discussion in this section, followed by a short review of their subsequent reactions which are represented generally in equations 2.1 to 2.3.

$$HCl + SnCl_2 + R^1R^2C{=}CR^3R^4 \xrightarrow{Et_2O} Cl_3SnCR^1R^2CHR^3R^4 \quad (2.1)$$

$$2HCl + Sn + 2R^1R^2C{=}CR^3R^4 \xrightarrow{Et_2O} Cl_2Sn(CR^1R^2CHR^3R^4)_2 \quad (2.2)$$

$$3HCl + Sn + R^1R^2C{=}CR^3R^4 \xrightarrow[-H_2]{Et_2O} Cl_3SnCR^1R^2CHR^3R^4 \quad (2.3)$$

R^1, R^2, R^3 = H or Me

$R^4 = \underset{\displaystyle O}{\overset{\|}{C}}{-}R^5$ (see table 2.1)

In the reactions discussed in chapters 3 to 7 hydrostannation is performed by the product of reactions between tin (II) chloride and hydrogen chloride in diethyl ether. It is therefore appropriate to consider the nature of this product, hereafter referred to, for simplicity, as "ethereal trichlorostannane", $HSnCl_3$. Its true nature is complex because several equilibria between solvent and solute species are involved as shown in scheme 2.1.

$$\begin{array}{lcll}
Et_2O + HCl & \rightleftharpoons & Et_2OH^+\ Cl^- & \\
SnCl_2 + HCl & \rightleftharpoons & HSnCl_3 & \\
SnCl_2 + Cl^- & \rightleftharpoons & SnCl_3^- & \\
HSnCl_3 + Et_2O & \rightleftharpoons & Et_2OH^+\ \ SnCl_3^- & \mathrm{II\ .\ 1} \\
SnCl_3^- + Cl^- & \rightleftharpoons & SnCl_4^{2-} & \\
SnCl_4^{2-} + 2Et_2OH^+ & \rightleftharpoons & [Et_2OH]^+_2\ \ SnCl_4^{2-} & \mathrm{II\ .\ 2}
\end{array}$$

Scheme 2. 1

This may be summarised in equation 2.4 [1], where II.3 is a combination of II.1 and II.2.

$$nHCl + SnCl_2 + mEt_2O \rightleftharpoons H_nSnCl_{2+n}.mEt_2O \qquad \mathrm{II\ .\ 3} \qquad (2.4)$$

The reaction (equation 2.4) is a thermodynamically controlled equilibrium [1]. The reverse reaction occurs upon :

(i) addition of excess ether,

(ii) addition of inert apolar substances, or

(iii) evaporation of hydrogen chloride and/or ether, and the intermediate (II.3) is reformed upon addition of more hydrogen chloride.

The earliest record of a solvated trichlorostannane complex dates back to 1839 [6] when a substance believed to be $HSnCl_3.3H_2O$

was prepared by cooling an aqueous solution of tin dichloride saturated with hydrogen chloride down to -40°C, at a time when analytical techniques were somewhat in their infancy. Since then physical [7,8] and, more recently, spectroscopic [1] aspects have been studied. Nefedov et al [9, 10] claim to have prepared $HSnCl_3 . 2Et_2O$ by dissolving tin (II) chloride in a mixture of concentrated hydrochloric acid and ether, on the grounds of evidence in the proton n.m.r. spectrum of a peak at 11.8 ppm [9] or 12.8 ppm [10] attributed to the acidic proton. Similar spectra were obtained by Bulten [1]. The ionic character (II. 1 and II. 2) is reflected by a down-field shift of the methylene and methyl protons of the protonated ether as is indeed the case, although to a lesser extent, for ethereal hydrogen chloride [9]. The integration values lead to an m/n value (II.3) ranging from 1.1 to 1.5. The non-integral value is a result of the equilibria present. The stability of the intermediate was monitored by proton n.m.r. studies and after fifty days it had decomposed to a small extent to ethyl tin trichloride and ethanol. The analogous germanium system acts similarily [10].

$$Et_2OH^+ \; GeCl_3^- \longrightarrow EtGeCl_3 \; + \; EtOH \qquad (2.5)$$

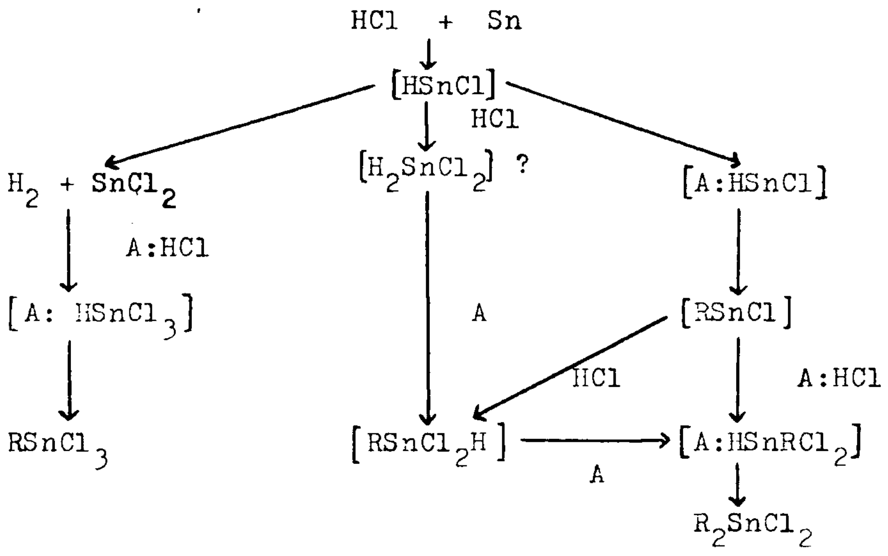
The dearth of evidence for a tin-hydrogen bond in the n.m.r. spectra is supported by the infra-red spectrum as there is no peak between 2200 and 1700 cm^{-1} assignable to v(Sn - H).

The elemental analysis of the species (II.3) revealed a Cl:Sn ratio ranging from 3.3 to 4.3. Again difficulties arose due to the equilibria. However, Bulten [1] claims that m is equal to n in II. 3. Also the degree of dissociation increases with the amount of co-ordinating ether, i.e. with the value of m [1].

Finally, the Mössbauer spectrum [1] which consists of a peak at 3.46mm sec^{-1} (relative to SnO_2), with a quadrupole splitting of 1.30mm sec^{-1}, implies that the tin atom is in oxidation state two. The isomer shift is comparable to those of known trichlorostannates.

The Dutch workers therefore conclude [1] that the product is mainly strongly ionised dihydrogen tetrachlorostannate (II) dietherate, $H_2SnCl_4 . 2Et_2O$, $[(Et_2OH^+)_2\ SnCl_4{}^{2-}]$. Attempts to characterise the species further are discussed below.

It is difficult to explain the formation of the dialkyl tin dichloride from tin powder via trichlorostannane (equation 2.3). Instead the intermediate may be [HSnCl] or $[H_2SnCl_2]$ [11, 12]. The germanium analogues do exist [13 - 16] but there is limited evidence for the tin species [17]. Amberger [18] suggests that the intermediate may be dichlorostannane $[H_2SnCl_2]$ from the decomposition of chlorostannane $[H_3SnCl]$ but there is little evidence to support this. Dichlorobutyl tin hydride, although very unstable, has been isolated [19]. Accordingly scheme 2.2 has been proposed [3,20].



Scheme 2.2

Key on following page

A = alkene, $R^1R^2C{=}CR^3R^4$,

R = AH,

R^1,R^2,R^3,R^4 as for equations 2.2 and 2.3 ,

Cl may be replaced by Br or I [20] .

Both the rate of addition of hydrogen chloride and the temperature affect the proportions of each product,

e.g.

$$\begin{array}{llll} Sn + HCl + CH_2{=}CHCO_2Me & \longrightarrow Cl_2Sn(CH_2CH_2CO_2Me)_2 & + Cl_3SnCH_2CH_2CO_2Me & \\ \%\ \text{yields at:} \quad 40^\circ C & \quad 90 & \quad 10 & (2.6) \\ \qquad\qquad\quad -10^\circ C & \quad 5 & \quad 95 & \end{array}$$

An alternative scheme involves formation of the dialkyl tin dichloride via the monoalkyl tin trichloride, (scheme 2.3) [3] .

$$HCl + Sn \longrightarrow [HSnCl] \xrightarrow{HCl} H_2 + SnCl_2$$

$$CH_2{=}CHCO_2R{:}HCl + SnCl_2 \longrightarrow [CH_2{=}CHCO_2R{:}HSnCl_3] \longrightarrow Cl_3SnCH_2CH_2CO_2R$$

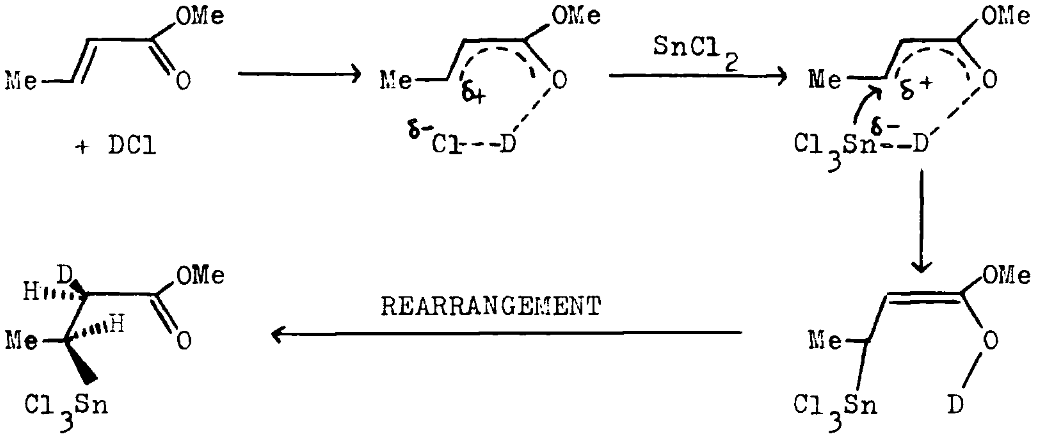
$$Cl_3SnCH_2CH_2CO_2R + HSnCl \longrightarrow Cl_2Sn(H)CH_2CH_2CO_2R + SnCl_2$$

$$Cl_2Sn(H)CH_2CH_2CO_2R + CH_2{=}CHCO_2R \longrightarrow Cl_2Sn(CH_2CH_2CO_2R)_2$$

Scheme 2.3

In a monitored reaction between tin powder, ether and hydrogen chloride (added quickly) the mono adduct is formed rapidly but subsequently disappears whilst the percentage of dialkyl tin product continues to rise. Formation of the alkyl tin trichloride from reactions starting with tin powder is minimised by adding the hydrogen chloride gas slowly and thus preventing the formation of tin (II) chloride which facilitates the side reaction. This is reflected later in table 2.1 by comparing the figures in the two time columns.

Finally, a mechanism has been postulated for hydrostannation in non-protonating solvents, such as the alkene itself, as a result of deutereostannation experiments (scheme 2.4) [2].



Scheme 2.4

It is believed that the hydrostannation occurs by cis-addition via a concerted mechanism in contrast to the trans addition for the organo-tin hydrides, (chapter 1). (Isophorone, which has a trans configuration, is unreactive).

The first report of hydrostannation involving trichlorostannane appeared in a German patent [21].

$$HSnCl_3 + H_2C{=}CHR \longrightarrow Cl_3SnCH_2CH_2R \qquad (2.7)$$

R = alkyl,H.

However, Hutton and Oakes [22] found α-alkenes to be unreactive towards hydrostannation. Monomers which undergo preferential polymerisation (e.g. styrene) or hydrochlorination cannot be used [22]. The reaction has been well established for α,β unsaturated carbonyl compounds and results in β substitution. Nevertheless, hydrostannation of acrylonitrile has been achieved [3,23].

Hydrostannation of an acetylenic bond has also been reported [2] and results in vinyl tin products. The scope of the reaction is illustrated in table 2.1. More ster~~r~~ically hindered alkenes and alkynes will react but more slowly.

Table 2.1

HYDROSTANNATION REACTIONS FROM HYDROGEN CHLORIDE AND TIN POWDER OR TIN DICHLORIDE IN ETHER

UNSATURATED COMPOUND (A)	REACTION WITH $SnCl_2$ + HCl in Et_2O [2]^a		REACTION WITH Sn + HCl in Et_2O [3]^a		
	TIME (hrs)	YIELD^b OF $Cl_3Sn(AH)$	TIME (hrs)	YIELD^b OF $Cl_2Sn(AH)_2$	YIELD^b OF $Cl_3Sn(AH)$
$CH_2{=}CHCO_2R$					
R = Me	3.5	98	14	94	3.5
Et	1	79	25	60	1.5
Bu	2	92	20	c	9.5
Ph	5	89	10	d	6
$CH_2{=}CMeCO_2Me$	3.5	62	13	25	$\simeq$50
$MeCH{=}CHCO_2Me$	4	30	17	5.5	<3 e
$Me_2C{=}CHCO_2Me$	2	80	10	46	22
$CH_2{=}CHCO_2H$	4 1	99 75 [22]	6.5 15	70 50 f [22]	<3 c
$CH_2{=}CMeCO_2H$	g	g	h	h	h
$MeCH{=}CHCO_2H$	5	40	h	h	h
$CH_2{=}CHCOCl$	3	90	20	low [22]	
$CH_2{=}CHCOMe$	2.5	70	14	i	47
$Me_2C{=}CHCOMe$	2	80	10	46	22
$(Me_2C{=}CH)_2C{=}O$	4	<20 [22]	g	g	g
$CH_2{=}CHCONH_2$	10	<20	23	79	<3 e
$CH_2{=}CHCN$	48 23		15	14	<3 e
$CH{\equiv}CCO_2H$	2	$\simeq$60	12	80 [22]	j
$CH{\equiv}CCO_2Me$	6	60	h	h	h

Key on the following page

(a) Unless otherwise stated.

(b) Detected by ^{1}H n.m.r. spectroscopy.

(c) Isolation pure not proved possible.

(d) Not isolated.

(e) Not detected by ^{1}H n.m.r

(f) Total yield, mainly mono.

(g) Has been reported but no data given [22]

(h) Has not been reported.

(i) Pure difficult to isolate.

(j) Total yield, amount mono not determined.

Any solvent which does not react with hydrogen chloride may be employed. Hydrocarbons, halocarbons, ethers (THF), esters, (ethyl acetate), alcohols (methanol, dimethoxymethane) and even water [20] and aqueous hydrochloric acid [22] have been used. Hydrolysis and hydrochlorination of the alkene lower the organotin yield in the aqueous reactions [22]. Preparation of trichlorostannane is unsuccessful in hydrocarbon solvents such as n-hexane, toluene and benzene, and dibutyl ether due to the insolubility of tin dichloride. However they can be used when the alkene is present in solution during the addition of hydrogen chloride. (Scheme 2.4.).

The substituted monoalkyl tin trichlorides may react with tin to give the dialkyl tin dichloride and a relatively stable organotin species containing a tin-tin bond [3].

2.2 Experimental

2.2.1 Preparation of Ethereal Trichlorostannane

Etheral trichlorostannane was prepared in a dry nitrogen atmosphere according to a modified method of Hutton [2].

Hydrogen chloride (calcium chloride dried) was bubbled through a suspension of anhydrous tin (II) chloride (15.0g, 79mmoles) in anhydrous diethyl ether (90 mls) at 0°C until, after 10 to 15 minutes, all of the tin dichloride had dissolved and the characteristic yellow oil and colourless ethereal phase appeared in two layers. (If a homogenous colourless liquid is formed instead, the oily layer separates upon addition of ether). The upper ethereal layer was removed by syringe. Any etherealtrichlorostannane disolved in the ether discarded may account for a lower yield of the final product, so for this reason it was not always removed. If any tin (II) chloride precipitated then hydrogen chloride was added until the clear yellow oil reappeared. This was used immediately.

In the following chapters ethereal trichlorostannane is prepared by this method and the quantity quoted (in moles) corresponds to the amount of tin (II) chloride used.

2.2.2 Addition of Proton Sponge, [1,8-bis(dimethyl amino) naphthalene], to Ethereal Trichlorostannane.

[1,8-bis(dimethyl amino) naphthalene] (2.953 g, 13.8mmoles) dissolved in a minimal amount of ether (12 mls) was added to ethereal trichlórostannane (14.7mmoles) under nitrogen to form an immediate white precipitate. This was stirred in ether (150mls) overnight, filtered, washed and dried in vacuo. Elemental analyses and the mass spectrum of the product (compound 2.1) (4.57g) are recorded in tables 2.2 and 2.3. The reaction was done in duplicate to check the authenticity of the results and gave product 2.2.

Table 2.2

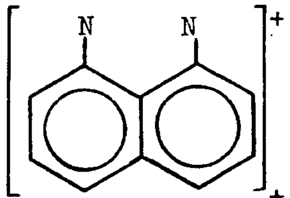
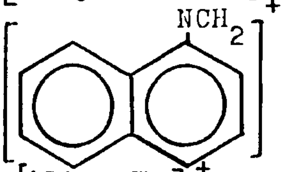
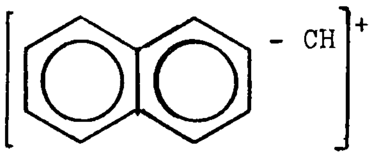
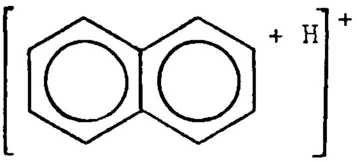
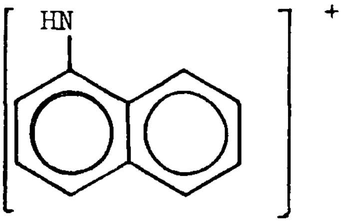
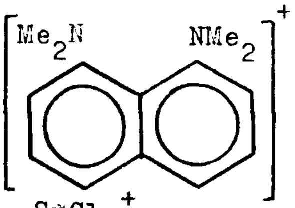
Elemental Analysis for products 2.1 and 2.2

	COMPOUND 2.1		COMPOUND 2.2		II.4*	II.5*
	Run 1	Run 2	Run 1	Run 2	(calc.)	(calc.)
C	40.5	38.7	38.9	38.8	38.2	48.7
H	4.5	4.6	4.2	4.3	4.3	5.5
N	6.0	6.7	6.0	6.2	6.4	8.1
Sn	24.5	24.0	26.0	24.6	27.0	17.2
Cl	24.1	24.3	24.4	25.2	24.2	20.5
Cl:Sn	3.3	3.4	3.3	3.4	3.0	4.0

* section 2.3
All figures, except in row six, are percentages.

Table 2.3

Mass Spectrum of Compound 2.1

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	154	 or 	31
77	Ph^+	40			
91	$PhCH_2^+$				
115		20			
120	Sn^+	3.0	168	$[154 + CH_2]^+$	98
127		50	183	$[168 + Me]^+$	99
			190	$SnCl_2^+$	2.0
			199	$[183 + MeH]^+$	57
141		18	214		95
			225	$SnCl_3^+$	1.5

2.2.3 ^{119}Sn N.m.r. Studies of Ethereal Trichlorostannane.

Ethereal trichlorostannane (5.5 mmoles) was prepared in the n.m.r. tube (without removal of the ethereal layer) which was then sealed off. ^{119}Sn n.m.r. spectra were recorded over a period of three months and the singlet at -62.84ppm did not shift within experimental error.

2.2.4 Mass Spectroscopic Studies.

Ethereal trichlorostannane (3μl) was syringed into the mass spectrometer and the spectrum recorded. It contained peaks attributable to ether, tin dichloride and hydrogen chloride, the yellow oil (II.3) decomposing possibly before entering the mass spectrometer, even though several attempts were made to improve the result.

2.2.5 ^{35}Cl N.q.r. Studies.

Approximately 2 mls of ethereal trichlorostannane was transferred by syringe to a septum sealed sample bottle and placed inside the n.q.r. spectrometer coil. As the sample must be solid (and preferentially crystalline) it was cooled to -77°C and -196°C but unfortunately it froze to a glass and no results were obtained.

The n.q.r. spectrum was run for the proton sponge product, compound 2.1, but no peaks were observed.

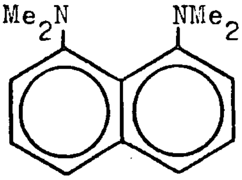
2.3 Discussion of Results

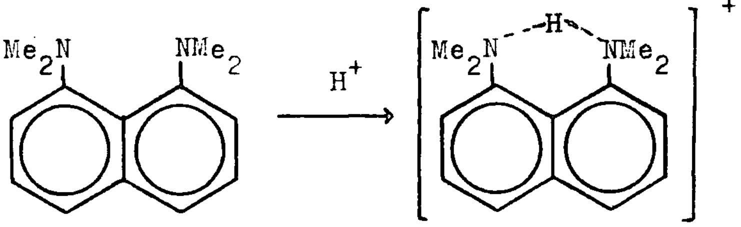
Proton sponge, as the name suggests is a strong proton acceptor. Its strength as a base ($pK_a = 12.34$) [24] results from steric strain in the free base which is overcome by protonation and from the fact that the site available for protonation is ideally suited to intramolecular hydrogen bonding.

It was added to ethereal trichlorostannane in the hope of forming either the tri- or tetra- chlorostannate according to equation 2.8.

$$B + H_nSnCl_{2+n}\cdot mEt_2O \longrightarrow \underset{\text{II.4}}{[BH]^+ SnCl_3^-} \text{ +/or } \underset{\text{II.5}}{[BH]_2^+ SnCl_4^{2-}} + mEt_2O + [BH]^+ Cl^- \qquad (2.8)$$

B =





(2.9)

Some hydrochloride $[BH]^+ Cl^-$ was also expected due to the excess hydrogen chloride in the media. The Cl:Sn ratio of the products ranges from 3.3 to 3.4 suggesting a mixture of the expected products due to the equilibria present. However, due to the limitations of the tin analysis (see Appendix 1) misleading conclusions could be drawn. C,H and N micro analyses were therefore performed and strongly support the trichlorostannate, II.4. (table 2.2). Also, the mass spectrum contains mainly peaks for [1,8 bis-(dimethyl amino) naphthalene] and its break down. Peaks for tin containing fragments up to $SnCl_3^+$ are also present but there is no evidence for a fourth chlorine atom.

The ^{119}Sn n.m.r. spectrum consists of a singlet which is in the correct region for a trichlorostannate salt by comparison with the spectra of known compounds (table 2.4).

Table 2.4

^{119}Sn N.m.r. Chemical Shifts of Known Compounds for Comparison with that of $H_nSnCl_{2+n}.mEt_2O$

COMPOUND (Solvent)	SHIFT, ppm	Ref.
$H_nSnCl_{2+n}.mEt_2O$ (Et_2O)	-62.8	a
$SnCl_4$ (neat)	-150	25
$SnCl_2$ (THF)	-236	25
$SnCl_2.2H_2O$ (12.17N HCl)	+341.2	26
$MeSnCl_3$ (neat, 74 C)	+6.3	25
$PhSnCl_3$	-63.0	25
$Ph_2C{=}NHMe^+\ SnCl_3^-$ (CH_2Cl_2)	-71.8	b

(a) This work, (b) see chapter 3.

However one must also consider the solvating power of the ether. When a tin atom has one or more electronegative substituents then electron donating species, which could easily include Et_2OH^+, may cause reversible association or auto association. Upon increasing the co-ordination number of tin from four to five or six the shielding of the tin nucleus is decreased resulting in the n.m.r. peak being shifted several hundred ppm as illustrated in table 2.5.

Table 2.5

The effect of co-ordination on the Chemical Shift (δ) in ^{119}Sn N.m.r. Spectroscopy [25].

COMPOUND	δ, ppm
Me_3SnCl	+154 to +166
Me_3SnCl.DMSO (in DMSO)	+ 3
Me_3SnCl.py (in $CHCl_3$)	+25.4

There is no ^{119}Sn n.m.r data in the literature for tetrachlorostannates for comparison. Even if the results did suggest a higher co-ordination number then one would still not be able to distinguish whether this is due to extra chlorine or ether being attached to the tin atom.

The spectrum was re-run periodically to monitor any decomposition to ethyl tin trichloride (δ at 20 ppm [25]) as in the proton n.m.r studies [1] but there was no evidence for such decomposition over three months.

The ^{35}Cl N.Q.R. studies were unfruitful as mentioned earlier. The technique reflects the electric field gradient within the quadrupolar nucleus (Chapter 8) so should be capable of distinguishing the nature of the proton sponge product and hence indirectly that of the ethereal species (II.3).

2.4. Conclusion

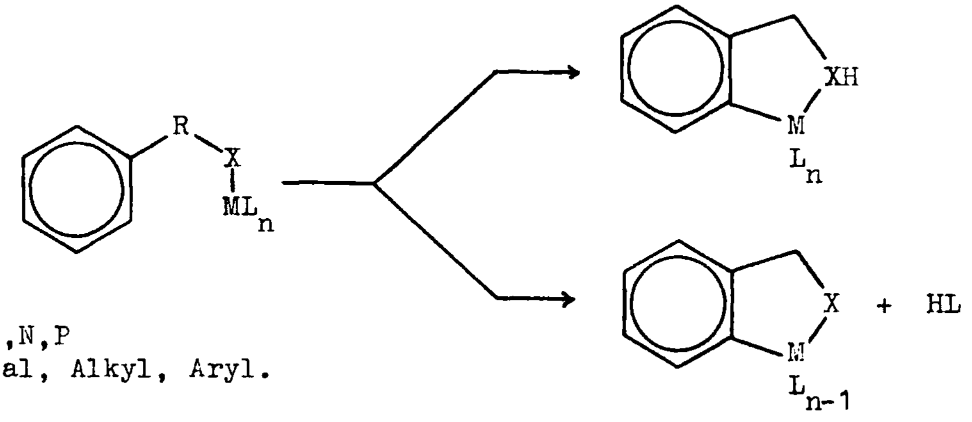
It is apparant that the product from the reaction between tin (II) chloride and hydrogen chloride in diethyl ether is very complex due to the equilibria attained. However the predominant component seems to be ethereal trichlorostannane, $HSnCl_3.Et_2O$, i.e. $Et_2OH^+SnCl_3^-$ contrary to the conclusion of Bulten [1] .

CHAPTER 3

INVESTIGATIONS OF ROUTES TO ORTHOMETALLATED TIN COMPOUNDS.

3.1 Introduction

Orthometallation is the intra-molecular rearrangement of metal complexes to give a metallacycle according to scheme 3.1



X = O,N,P
L = Hal, Alkyl, Aryl.

Scheme 3.1

In this rearrangement a metal-carbon bond is formed and the hydrogen atom originally on the aromatic ring is transferred to the electronegative group X or eliminated as HL.

Orthometallation is well established in transition metal chemistry but less so for main group metals and is the subject of a number of reviews [1-6]. A selection of main group orthometallated compounds is listed in tables 3.1 to put the experimental work discussed in this chapter into perspective.

Table 3.1

Orthometallated Compounds of Main Group Metals.

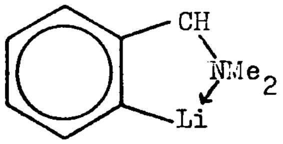
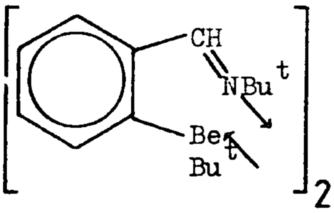
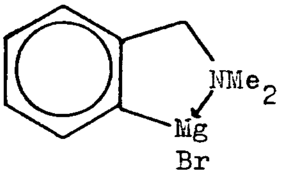
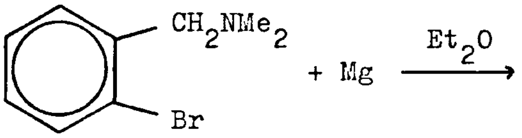
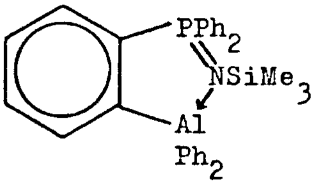
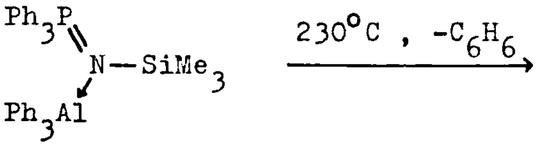
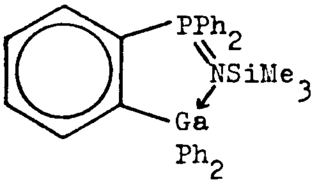
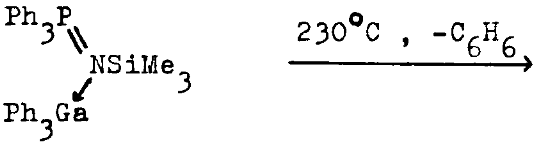
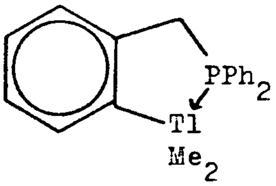
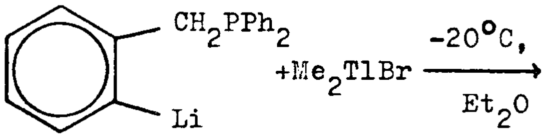
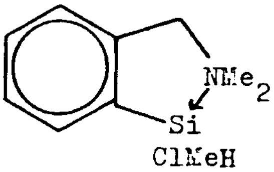
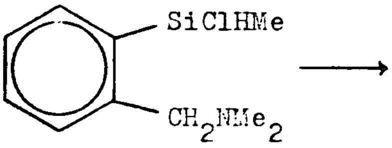
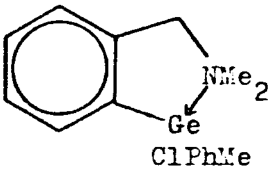
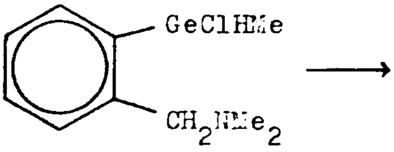
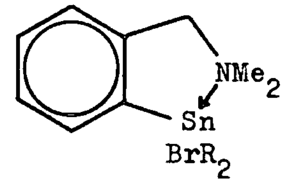
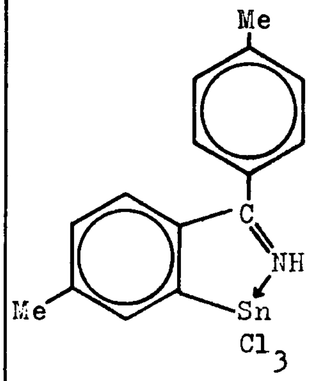
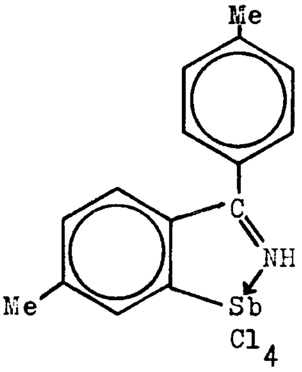
Compound	Origin	Ref.
	$PhCH_2NMe_2 + LiBu \xrightarrow{Et_2O}$	[7]
	$PhCH{=}NBu^t + Bu^t{}_2Be \longrightarrow$	[8]
		[9]
		[10]
		[10]
		[11]
		[12]
		[12]

Table 3.1 - continued

Compound	Origin	Ref.
	R'Cu + R_2SnBr_2 (R'=$PhCH_2NMe_2$; R=Me,Ph) or R'Li + Me_2SnBr_2	[13-15]
	$R_2C{=}NLi$ + $SnCl_4$ or $R_2C{=}NSiMe_3$ + $SnCl_4$	[16,17] [17]
	(p-tolyl)$_2C{=}NLi$ + $SbCl_5$	[6]

It is useful, at this stage, to be aware of the research involving orthometallation already performed in this laboratory, [17,18]. The results are summarised in Tables 3.2 and 3.3 .

Table 3.2

Routes to Orthometallated Material. [17,18]

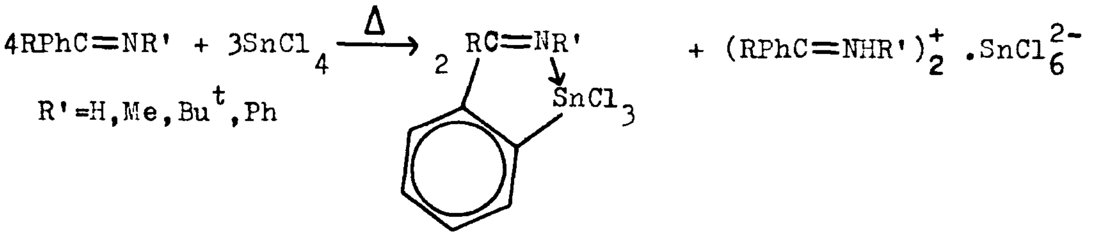
Experimental Method	Product
$R^1R^2C{=}NLi + SnCl_4$	
R^1=p-tolyl ; R^2=Bu^t	$2\text{-}Cl_3Sn\text{-}4\text{-}Me\text{-}C_6H_3C(Bu^t){=}NH$
=p-tolyl =Pr^i	$2\text{-}Cl_3Sn\text{-}4\text{-}Me\text{-}C_6H_3C(Pr^i){=}NH$
=4-$MeOC_6H_4$ =p-tolyl	$2\text{-}Cl_3Sn\text{-}4\text{-}MeO\text{-}C_6H_3C(p\text{-}tolyl){=}NH$
=4-F-C_6H_4 =4-F-C_6H_4	$2\text{-}Cl_3Sn\text{-}4\text{-}F\text{-}C_6H_3C(4\text{-}F\text{-}C_6H_4){=}NH$
$(p\text{-}tolyl)_2C{=}NCl + SnCl_2$	$2\text{-}Cl_3Sn\text{-}4\text{-}Me\text{-}C_6H_3C(p\text{-}tolyl){=}NH$
$Ph_2C{=}NSiMe_3 + SnBr_4$	$2\text{-}Br_3Sn\text{-}C_6H_4C(Ph){=}NH$
$2,6\text{-}Me_2\text{-}C_6H_3C(Ph){=}NSiMe_3 + SnCl_4$	$2\text{-}Cl_3SnC_6H_4C(2,6\text{-}Me_2\text{-}C_6H_3){=}NH$
$PhCH{=}NSiMe_3 + SnCl_4$	$(2\text{-}Cl_3SnC_6H_4CH{=}NH)_n$
$Ph_2C{=}NSiMe_3 + Me_2SnCl_2$	No reaction
$Ph_2C{=}NSiMe_3 + TiCl_4$ $Ph_2C{=}NLi + TiCl_4$	$(Ph_2C{=}NTiCl_3)_n$

Table 3.3

Reactions of 2-Cl_3Sn-4-Me-C_6H_3C(p-tolyl)=NH [18]

Reagent	Product
MeLi (1:3)	2-$SnCl_xMe_{3-x}$-4-Me-C_6H_3C(p-tolyl)=NH
NaOMe (1:3)	2-$SnCl(OMe)_2$-4-Me-C_6H_3C(p-tolyl)=NH
MeOH	2-$SnCl_2$MeO-4-Me-C_6H_3C(p-tolyl)=NH
EtOH	2-$SnCl_2$EtO-4-Me-C_6H_3C(p-tolyl)=NH
py	2-$SnCl_3$.py-4-Me-C_6H_3C(p-tolyl)=NH
TMEDA	2-$SnCl_3$.TMEDA-4-Me-C_6H_3C(p-tolyl)=NH
PhC≡CPh	No reaction
hv	No reaction

This chapter reports a new route to orthometallated tin compounds according to equation 3.1.



$$4RPhC{=}NR' + 3SnCl_4 \xrightarrow{\Delta} 2\ \overset{RC=NR'}{\ } \quad SnCl_3 + (RPhC{=}NHR')_2^+ .SnCl_6^{2-} \qquad (3.1)$$

R'=H,Me,Bu^t,Ph

This method for direct formation of metal-carbon bonds does not involve a second organometallic compound such as RLi or RCu which is an obvious advantage. An alkyl or aryl group may be attached to the nitrogen atom whereas the route via imino-lithium derivatives $R^1C_6H_4CR^2{=}NSnX_3$, [16,17] gives rise only to compounds with a protonated nitrogen atom. New orthometallated tin compounds have been prepared and the crystal structure has been determined for ortho-trichlorostannyl N-methyl diphenyl methylene amine, $2\text{-}Cl_3Sn\text{-}C_6H_4\text{—}C(Ph){=}NMe$. The crystal structure of (N methyl) diphenyl methyleneammonium trichlorostannate, $[Ph_2C{=}NHMe]^+SnCl_3^-$, is also reported with this work.

This chapter is divided into four sections :-

(i) The hydrostannation of Schiff's bases, $R^1R^2C{=}NR^3$.

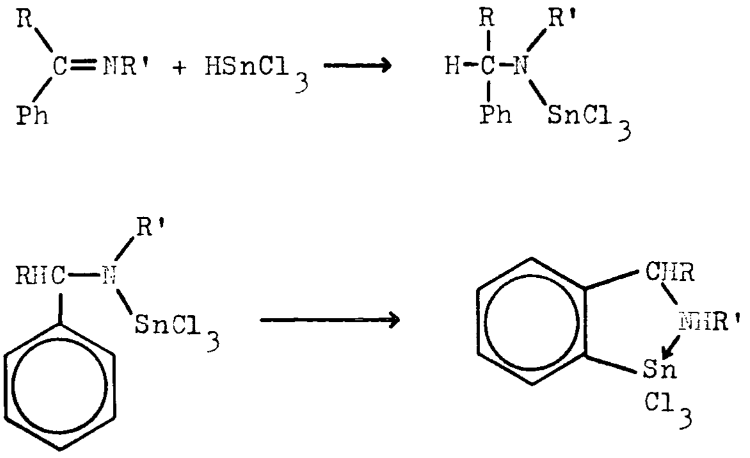
(ii) Development of the orthometallation reaction between tin (IV) chloride and N-methyl diphenyl methylene amine.

(iii) Extension of section (ii) to a range of Schiff's bases.

(iv) Investigation of alternative routes to orthometallated compounds.

3. 2. Hydrostannation of Schiff's Bases.

3.2.1 It is possible that the hydrostannation of a methyleneamine (ketimine) could lead to a orthometallated species according to scheme 3.2.



Scheme 3.2

However, one would expect the reaction to proceed according to equation 3.2 and this was indeed found to be the case.

$$\underset{}{PhRC{=}NR'} + HSnCl_3 \longrightarrow \underset{III.1}{PhRC{=}NHR'}\ {}^{+}.SnCl_3^{-} \qquad (3.2)$$

III.1	R	R'
3.1	Ph	Me
3.2	Ph	Ph
3.3	H	Ph
3.4	Ph	H

3.2.2. Experimental

3.2.2.1. Hydrostannation of N-methyl diphenyl methyleneamine

N-Methyl diphenyl methyleneamine (8.7 mls, 47.0 mmoles) was added by syringe to ethereal trichlorostannane (47.1 mmoles) after removal of the excess ether, to give an immediate yellow precipitate which was stirred overnight in dichloromethane (50 mls). Upon filtering crystals grew in the filtrate and after isolation were identified as (N-Methyl) diphenyl methylene ammonium trichlorostannate, $Ph_2C{=}NHMe^{+}SnCl_3^{-}$ (compound 3.1) , 6.428g. 32.5%, with 1.39g. of crude material not crystallised.

In addition to the data tabulated overpage, the following data have been obtained; ^{13}C and ^{119}Sn n.m.r. (see text), ^{35}Cl n.q.r. (chapter 8.) ^{119}Sn Mossbauer (see text) and F.A.B. mass spectra (pages 57 to 61).

3.2.2.2 The experimental procedure was repeated, exactly as in section 3.2.2.1, for (N-phenyl)diphenylmethyleneamine ($Ph_2C{=}NPh$) , (N-phenyl)phenylmethyleneamine ($PhCH{=}NPh$) and diphenylmethyleneamine ($Ph_2C{=}NH$), to give their trichlorostannates; compounds 3.2 (crystalline), 3.3 (powder) and 3.4 (powder) respectively, the data of which are given on pages 53 to 56 .

Compound No. 3.1	**Origin** $HSnCl_3/Et_2O + Ph_2C=NMe$

Name & Structure

$Ph_2C=NHMe^+ \ SnCl_3^-$

(N-methyl) diphenyl methyleneammonium trichlorostannate

m.pt. 113-4

Elemental Analysis

C	39.4	(39.9)
H	3.7	(3.4)
N	3.1	(3.3)
Sn	28.4	(28.2)
Cl	25.2	(25.2)

Empirical Formula $C_{14}H_{14}NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc (fig.3.4)

3130m,b, 3040m/s, 1634m/s, 1590m, 1460w, 1439m, 1389w, 1299m/s, 1168m, 988m, 930w/m, 910w/m, 848m/s, 777s, 764s, 715m, 689s, 640w/m, 558m, 457w/m, 387w/m, 280m/s, 230s.

¹H N.M.R. $CDCl_3$; Int. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.71	s	-	3	Me
7.56 7.60 7.67 7.80 7.83	m	-	10	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	54	225	$SnCl_3^+$	5.9
77	Ph^+	99	260	$SnCl_4^+$	2.6
91	$PhCH^+$	44	351	$[155 + 196]^+$	3.8
105	$PhCNH_2^+$	16	468	$[Ph_2CN + Ph_2CH_2Sn]^+$	4.2
118	$PhCNMe^+$	100		or $[(2 \times 196) + 76]^+$	
120	Sn^+	6.0			
155	$SnCl^+$	51			
166	Ph_2C^+	37			
181	Ph_2CNH^+	26			
190	$SnCl_2^+$	32			
196	Ph_2CNMeH^+	100			

Other Information ^{13}C and ^{119}Sn N.M.R., ^{119}Sn Mossbauer, ^{35}Cl N.Q.R. and F.A.B. mass spectra, crystal structure - see text.

Compound No. 3.2

Origin $HSnCl_3/Et_2O + Ph_2C{=}NPh$

Name & Structure

$$Ph_2C{=}NHPh^+ \; SnCl_3^-$$

(N-phenyl) diphenyl methyleneammonium trichlorostannate

m.pt. 210

Elemental Analysis

C	46.9	(47.2)
H	3.3	(3.3)
N	2.8	(2.9)
Sn	24.4	(24.6)
Cl	21.8	(22.0)

Empirical Formula $C_{19}H_{16}NCl_3Sn$

Infra-red, ν cm^{-1} KBr disc (fig.3.4)

3190m,b, 3050m,b, 1605m, 1590m, 1555 m/s, 1482m, 1450m/s, 1443m,shl, 1435 m,shl, 1335m/s, 1324m,shl, 1270m/s, 1208w/m, 1188w/m,shl, 1182m, 1167w, 1147m, 1105w, 1079w, 1021m, 997m/s, 960m, 935w, 926w,913m, 842m/s, 820 m/s, 781s, 767s, 728m/s, 699s, 687s, 616w, 610w, 598w, 581m/s, 547m/s, 509w, 498m/s, 450w/m, 394m, 289m/s, 255s, 235s.

^{1}H N.M.R. $CDCl_3$; Int. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.23 7.30 7.38 7.43 7.50 7.70 7.75 7.78 7.83	m	-	-	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	83			
77	Ph^+	100			
105	$PhCNH_2^+$	25			
120	Sn^+	8.2			
128m	?	24			
155	$SnCl^+$	37			
166	Ph_2C^+	100			
180	Ph_2CN^+	100			
190	$SnCl_2^+$	18			
225	$SnCl_3^+$	2.8			
258	Ph_2CNPhH^+	100			

Other Information ^{119}Sn Mossbauer (table 3.9), ^{119}Sn N.M.R (table 3.8) and F.A.B. mass spectra (table 3.6, fig. 3.2.)

Compound No. 3.3

Origin $HSnCl_3/Et_2O + PhCH=NPh$

Name & Structure

$PhCH=NHPh^{+}\ SnCl_3^{-}$

(N-phenyl) phenyl methyleneammonium trichlorostannate

m.pt. d 146-8

Elemental Analysis

C	41.2	(38.3)
H	2.7	(3.0)
N	2.9	(3.4)
Sn	22.9	(29.1)
Cl	25.5	(26.1)

Empirical Formula $C_{13}H_{12}NCl_3Sn$

Infra-red, ν cm^{-1} KBr disc (fig.3.4)

3160m, 3050m, 1639m/s, 1610m/s, 1580s, 1480m, 1470m, 1449m, 1408m, 1372m, 1330m, 1315m, 1280m, 1240m, 1205m, 1188m/s, 1163m, 1100w, 1069m, 1016m/s, 1000m, 970m, 920m, 875m, 839m, 828m/s, 784m, 766s, 730m, 715m,shl, 699m/s,shl, 680s, 616w, 569m, 530m/s, 520s, 490m, 464m, 320s, 288s, 250m/s.

^{1}H N.M.R. $CDCl_3$; Int. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.20 to 7.60	m,b	-	-	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
28	$CHNH^{+}$	100	225	$SnCl_3^{+}$	100
36	HCl^{+}	100	260	$SnCl_4^{+}$	17
51	$C_4H_3^{+}$	100			
77	Ph^{+}	100			
90	$PhCH^{+}$	61			
91	PhN^{+}	64			
104	$PhCNH^{+}$	100			
120	Sn^{+}	39			
155	$SnCl^{+}$	100			
182	$PhCNH_2Ph^{+}$	100			
190	$SnCl_2^{+}$	76			

Other Information

Compound No. 3.4

Origin $HSnCl_3/Et_2O + Ph_2C=NH$

Name & Structure

$Ph_2C=NH_2^+ \ SnCl_3^-$

diphenyl methyleneammonium trichlorostannate

m.pt. 140-1

Elemental Analysis

C	36.9	(38.3)
H	3.2	(3.0)
N	3.4	(3.4)
Sn		(29.1)
Cl	28.0	(26.1)

Empirical Formula $C_{13}H_{12}NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc (fig.3.4)

3230w,shl, 3040m,b, 2910m,shl, 2830m,b, 1640m/s, 1588m/s, 1495w, 1484w, 1440m, 1369m/s, 1296m, 1280m, 1189m, 1160m/s, 1141m/s, 1073w, 1029w/m, 1000m, 931m, 871m,shl, 849m, 829m,shl, 800m/s, 782m/s,shl, 762m, 725m/s, 702s, 698s, 612m, 605m, 561m/s, 445m, 434m, 404w/m, 383w/m, 361w/m, 286m, 235m/s.

^1H N.M.R $CDCl_3$; Int. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.27				
7.57				
7.70	m	-	-	Ph
7.91				
8.03				NH ?

Mass Spectrum

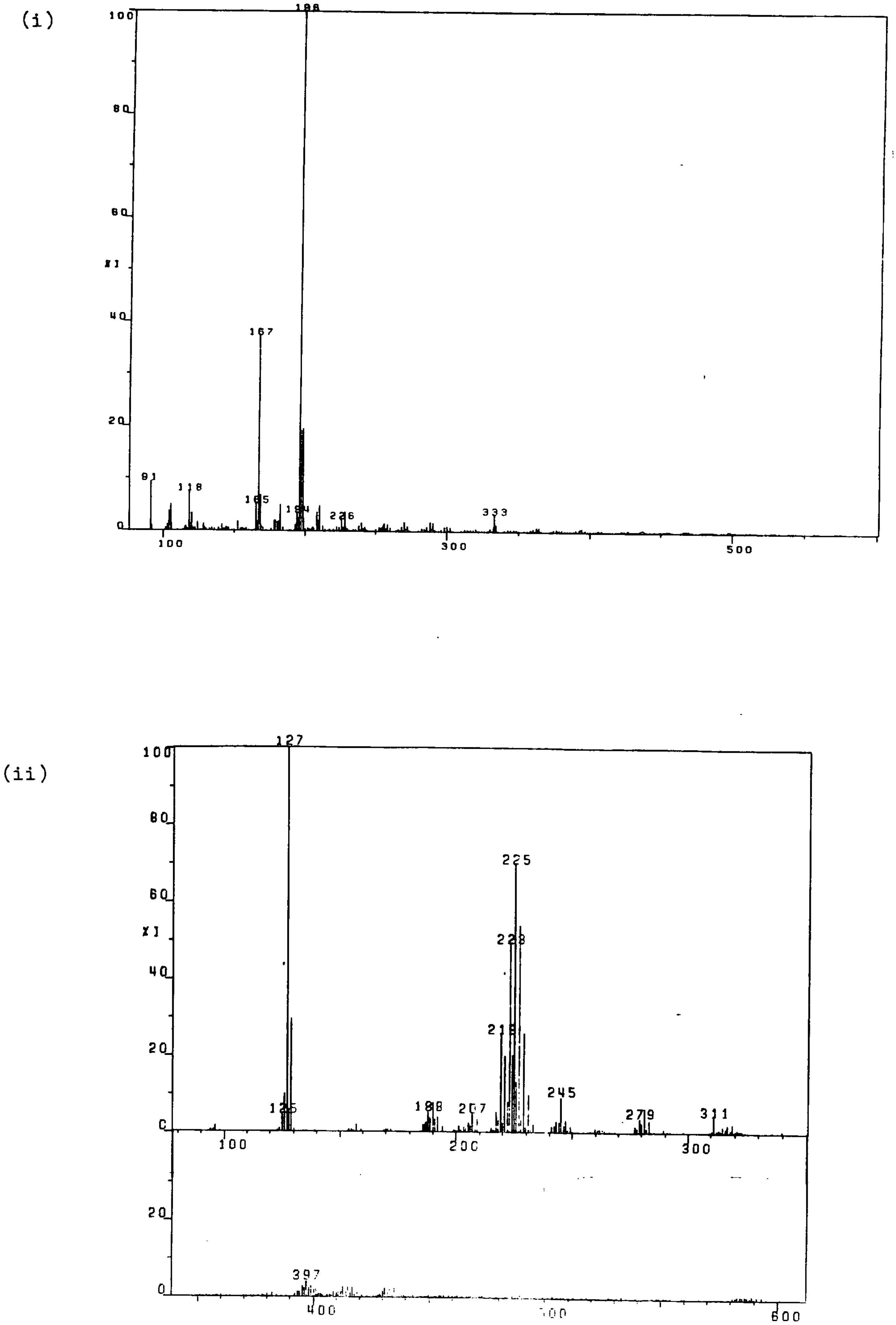
m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	24			
77	Ph^+	50			
90	$PhCH^+$ or Ph_2CN^+	4.8			
104	$PhCNH^+$	72			
120	Sn^+	2.3			
155	$SnCl^+$	14			
165	$[Ph_2C-H]^+$	3.5			
180	Ph_2CN	100			
190	$SnCl_2^+$	7.8			
225	$SnCl_3^+$	1.7			

Other Information F.A.B. mass spectrum(table 3.7, fig.3.3)

Table 3.4

F.A.B. Positive Mass Spectrum of $Ph_2C=NHMe^+.SnCl_3^-$ (see Fig 3.1)

m/e	Fragment Ion	I	m/e	Fragment Ion	I
91	$PhCH_2^+$	9.3	362	$[2(Ph_2CNH)]^+$	0.8
105	$PhCNH_2^+$	5.0		or $[Ph_2C+Ph_2CNMeH]^+$	
118	$PhCNMe^+$	7.4	376	$[Ph_2CN + Ph_2CNMeH]^+$	0.4
120	Sn^+	3.4		or $[300 + Ph - H]^+$	
167	Ph_2CH^+	37	394	$[2(Ph_2CNMeH_2)]^+$	0.6
182	$Ph_2CNH_2^+$	5.1	406	$[210 + 196]^+$	0.4
196	Ph_2CNMeH^+	100		or $[180 + 226]^+$	
210	$[Ph_2CNMe + Me]^+$	4.8	437	$[196 + 240 + H]^+$	0.5
	or $[2(PhCNH_2)]^+$		454	$[166 + 288]^+$	0.3
226	$[SnCl_3 + H]^+$	2.2	466	$[166 + 300]^+$	0.4
240	$MeSnCl_3^+$	1.7	468	$[180 + 288]^+$	0.4
256	$[Me_2SnCl_3 + H]^+$	1.5		or $[(2 \times 196)+(Ph - H)]^+$	
	or $[MeSnCl_3+NH_2]^+$		480	$[180 + 300]^+$	0.2
270	$Me_3SnCl_3^+$	1.8	486	$[196 + 288 + 2H]^+$	0.2
288	$Ph_2CH_2Sn^+$	1.8	497	$[196 + 300 + H]^+$	0.4
			512	$[(2 \times 196) + 120]^+$	0.1
300	Ph_2CNSn^+	1.0	527	$[(2 \times 196)+120+(Me\ or\ NH)]^+$	0.2
316	$Ph_2CNMeHSn^+$	0.4	528	$[195 + 333]^+$	0.2
			542	$[196 + 346]^+$	0.1
333	$[2(Ph_2C) + H]^+$	3.3	558	$[196 + 362]^+$	0.1
346	$[Ph_2C + Ph_2CN]^+$	0.4	572	$[196 + 376]^+$	0.1



<u>Fig. 3.1</u> F.A.B. Mass Spectra ; (i) positive and (ii) negative, of $Ph_2C=NHMe.SnCl_3$

Table 3.5

F.A.B. Negative Mass Spectrum of $Ph_2C=NHMe^+.SnCl_3^-$ (see Fig 3.1)

m/e	Fragment Ion	I	m/e	Fragment Ion	I
127	PhClMe	100	311	?	4.0
	or PhClNH		319	$[Cl_3Sn + 94]$	2.4
157	[SnCl + 2H]	1.8		or $[Cl_2Sn + 127 + 2H]$	
190	$SnCl_2$	7.7	397	[319 + PhH]	3.9
207	[SnCl + Me + 2H]	4.6	415	$[SnCl_3 + SnCl_2]$	2.5
	or SnClOH (if hydrolysed)		433	$[SnCl_3 + 207 + H]$	2.0
225	$SnCl_3$	69	456	[196 + 260]	0.5
245	ClSnPhCH	8.9	470	[225 + 245]	0.6
260	$SnCl_4$	1.0	489	[225 + 264]	0.7
281	$Cl_2SnPhCH_2$	6.3	589	[190 + 397 + 2H]	1.1

Table 3.6

F.A.B. Positive Mass Spectrum of $Ph_2C=NHPh^+.SnCl_3^-$ (see Fig 3.2)

m/e	Fragment Ion	I	m/e	Fragment Ion	I
91	$PhCH_2^+$, PhN^+	12	272	$[258 + 14(CH_2 \text{ or } N)]^+$	2.4
94	?	18	290	?	7.1
105	$PhCNH_2^+$	12	300	Ph_2CNSn^+	0.6
115	?	3.1	318	$[225 + 93]^+$?	1.2
120	Sn^+	0.7	333	$[2(Ph_2C) + H]^+$	1.0
155	$SnCl^+$	0.8	348	$[258 + 90]^+$	1.3
167	Ph_2CH^+	20		or $[Ph_2CH + PhCNH]^+$	
180	$PhCNPh^+$	18	362	$[104 + 258]^+$	0.7
190	$SnCl_2^+$	0.5	376	$[300 + Ph - H]^+$	0.4
197	$SnPh^+$	28		or $[104 + 272]^+$	
225	$SnCl_3^+$	0.3	382	$[347 + Cl]^+$?	0.5
258	Ph_2CNPhH^+	100	424	$[166 + 258]^+$	1.1
			515	$[(2 \times 258)-1]^+$	0.5

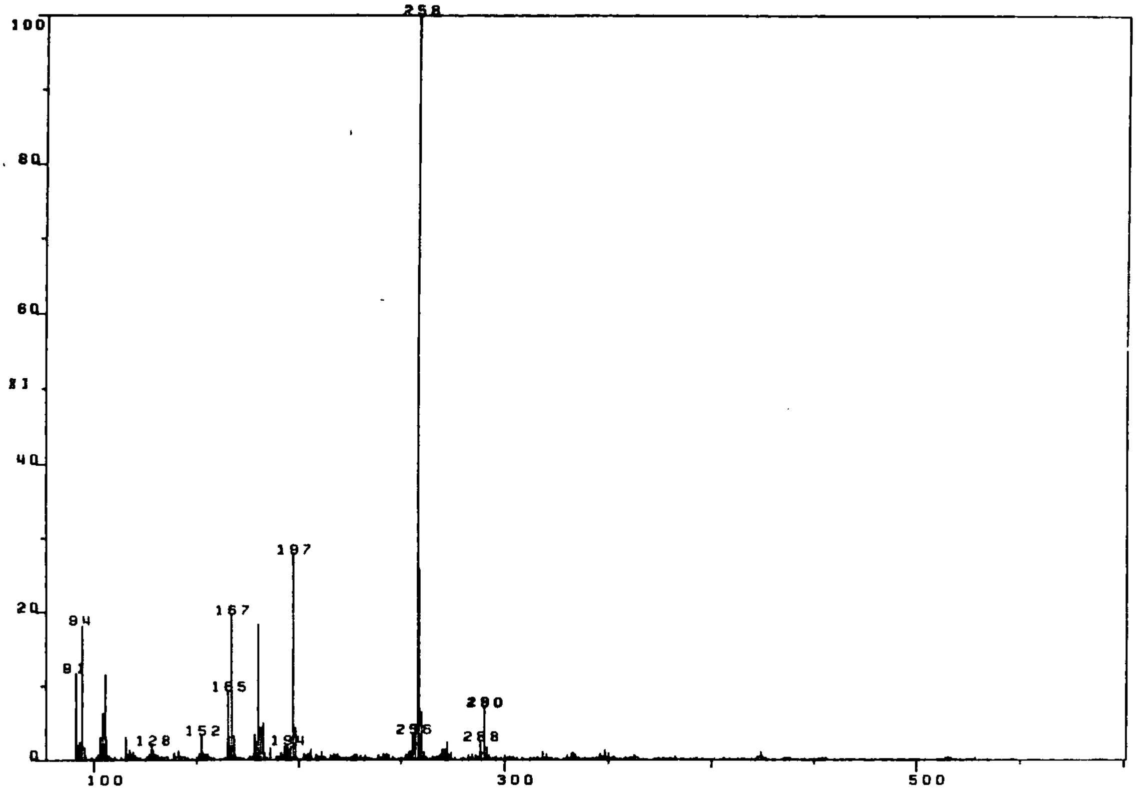


Fig. 3.2 F.A.B. Mass Spectrum (positive) of $Ph_2C=NHPh^+.SnCl_3^-$

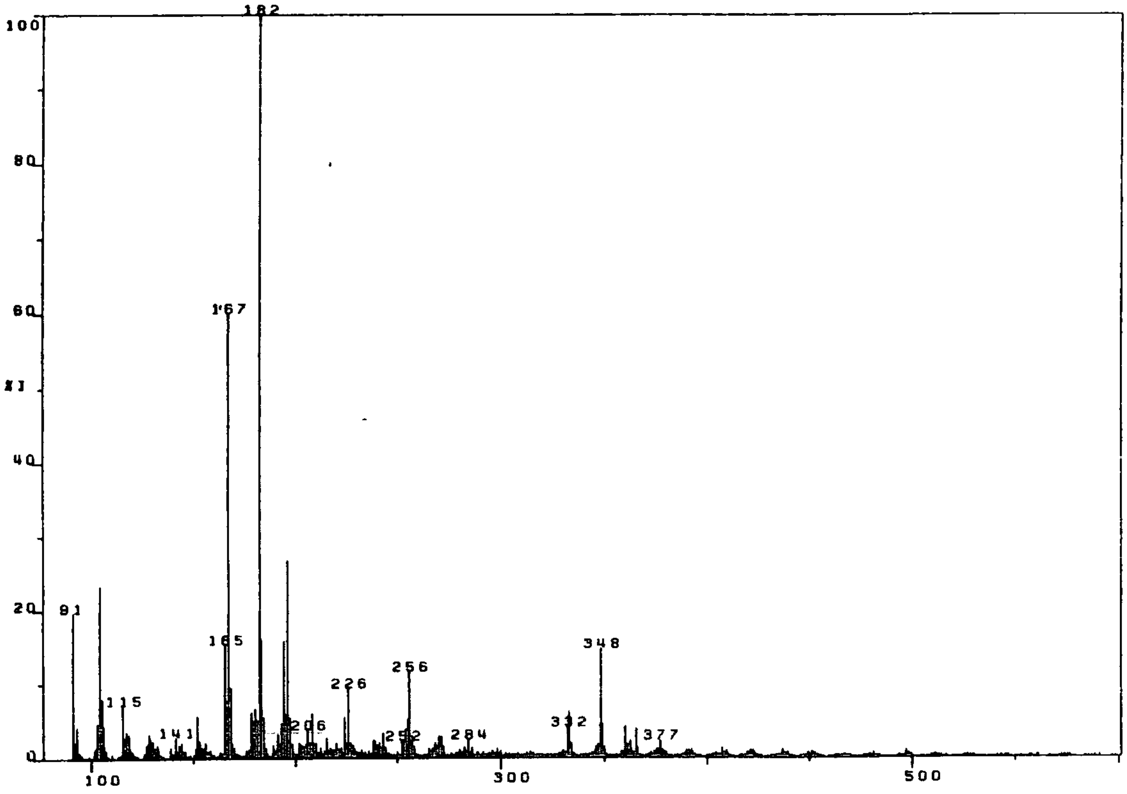


Fig. 3.3 F.A.B. Mass Spectrum (positive) of $Ph_2C=NH_2^+.SnCl_3^-$

Table 3.7

F.A.B. Positive Mass Spectrum of $Ph_2C=NH_2^+.SnCl_3^-$ (see Fig 3.3)

m/e	Fragment Ion	I
91	$PhCH_2^+$	20
104	$PhCNH^+$	23
115	?	7.0
120	Sn^+	1.0
128	?	3.3
141	?	2.7
151	?	5.7
155	$SnCl^+$	1.4
167	Ph_2CH^+	60
182	$Ph_2CNH_2^+$	100
190	$SnCl_2^+$	1.8
196	$[182 + 14(N,CH_2)]^+$	27
208	$[182 + 26(CN)]^+$	5.9
226	$HSnCl_3^+$	9.3
238	?	2.4
243	$[Ph + Ph_2C]^+$	3.4
256	$[PhCH + Ph_2C]^+$	12
271	$[256 + 15(NH)]^+$	2.9
284	$[Ph_2C + Sn - 2H]^+$ or $[271+13(CH)]^+$ or $[Ph_2CN+PhCNH]^+$	2.4

m/e	Fragment Ion	I
296	$[Ph_2CNH + 115]^+$	1.0
298	$[Ph_2CNH_2 + 115 + H]^+$ or $[284 + 14(N, CH_2)]^+$ or $[271 + 27(CN)]^+$	1.2
333	$[2(Ph_2C) + H]^+$	6.2
348	$[Ph_2CH + PhCNH]^+$ or $[Ph_2CNH + PhCH]^+$	15
365	$[(2 x 182) + H]^+$	3.9
377	$[298 + Ph + 2H]^+$ or $[181 + 196]^+$	2.2
390	$[182 + 208]^+$	1.0
409	$[182 + 227]^+$ or $[2(Ph_2C) + Ph]^+$	1.0
422	$[256 + 166]^+$	1.0
437	$[181 + 256]^+$	1.1
451	$[437 + 14(N,CH_2)]^+$ or $[167 + 284]^+$	0.8
497	$[(3 x 166) - H]^+$	0.9

3.2.3 Discussion of Results

3.2.3.1. Infra-red Data

The most characteristic absorption in the infra-red spectra of these compounds is the iminium bond stretching frequency v(C=N) which characteristically appears between 1700 and 1640 cm^{-1} [19]. Each spectrum (fig 3.4) contains either two or three peaks between 1650 and 1550 cm^{-1} which represent v(C=N) and also the aromatic skeletal vibrations within the ring v(C⚌C). By comparison with the starting materials v(C=N) has been shifted to a lower frequency in each case ($\Delta v \simeq 20$ cm^{-1}). The spectra may also be complicated in this region by N-H scissoring but as these peaks are characteristically much weaker than v(c=N) and v(C⚌C) they will probably be hidden.

N-H stretching peaks are observed between 3200 and 3000 cm^{-1} in each case. Crystallographic studies on $Ph_2C{=}NHMe^+ SnCl_3^-$ showed that weak hydrogen bonding occurs between the cation and anion [N-H·······Cl] and this causes a lowering of v(N-H). This seems to hold for the other spectra in this series.

All of the compounds exhibit two peaks below 300 cm^{-1} as expected for a pyramidal $SnCl_3^-$ ion representing tin chlorine stretching. Compound 3.2 has a third peak below 300 cm^{-1} whilst compound 3.3 has an additional peak at 320 cm^{-1}.

3.2.3.2. N.M.R. Data.

The ^1H n.m.r. peaks are as assigned in the data tables and the ^{13}C n.m.r. spectra are discussed in section 3.3.2 for comparison with that of the orthometallated material, $2SnCl_3C_6H_4(Ph)C{=}NMe$.

The ^{119}Sn n.m.r and Mössbauer results are as tabulated over page and are as expected for trichlorostannate salts.

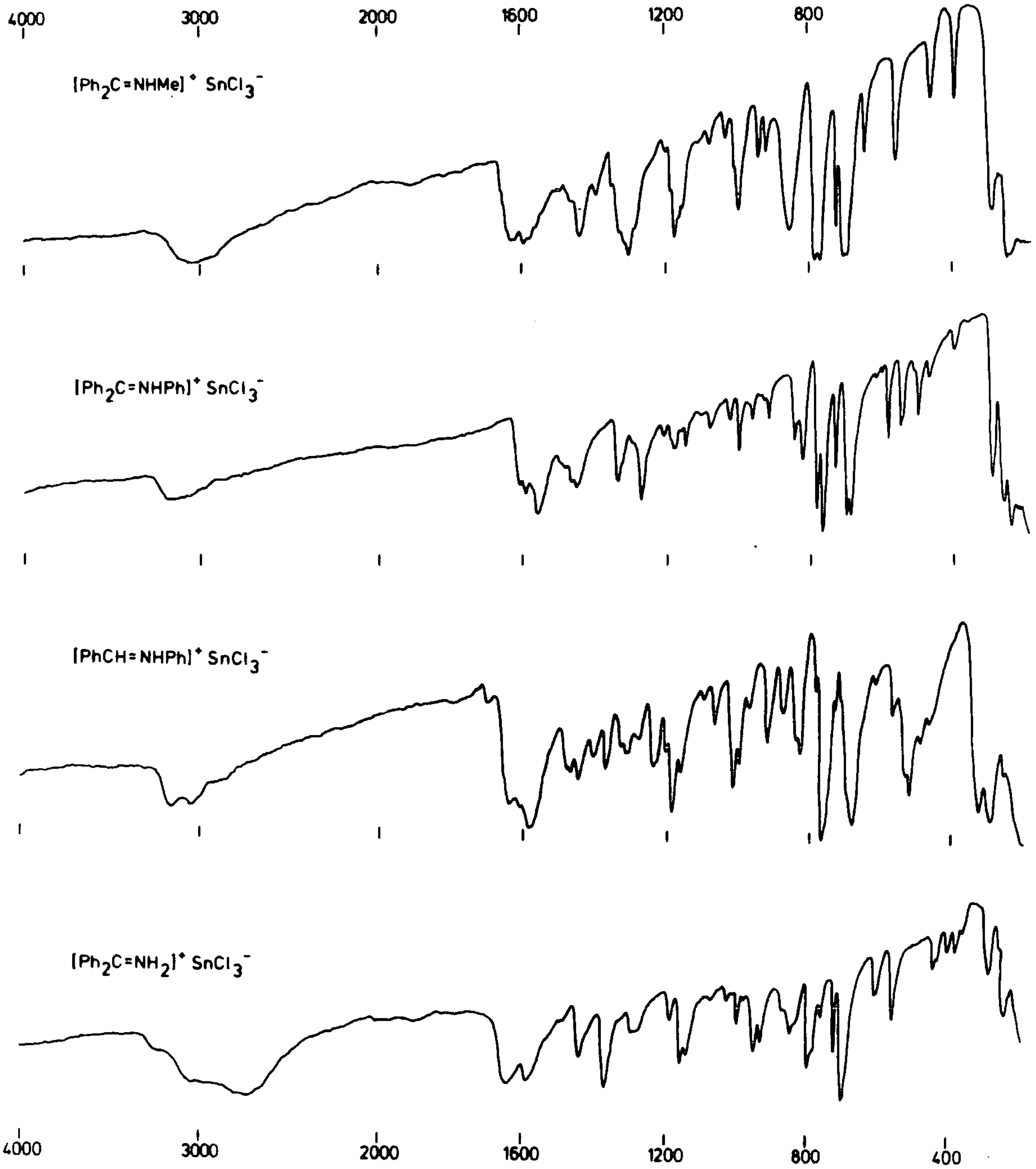


Fig. 3.4 Infra-red Spectra of Methyleneammonium Trichlorostannates

Table 3.8

^{119}Sn N.M.R. Spectra of **Trihalostannates.**

Compound[a]	Chemical Shift, ppm
$Ph_2C{=}NHMe^+\ SnCl_3^-$	-71.87
$Ph_2C{=}NHPh^+\ SnCl_3^-$	-69.82
$PhCH{=}NHPh^+\ SnCl_3^-$	b
$Ph_2C{=}NH_2^+\ SnCl_3^-$	b
$Et_4N^+\ SnBr_3^-$	-130.93
$Pr_4N^+\ SnBr_3^-$	c

a = CH_2Cl_2 solution

b = No peak observed, solubility problems

c = **No peak observed**

Table 3.9

^{119}Sn Mössbauer Spectra of Methyleneammonium trichlorostannates

Compound	Isomer Shift mm sec^{-1}	Quadrupole Splitting mm sec^{-1}
$Ph_2C{=}NHMe^+\ SnCl_3^-$	3.396	1.208
$Ph_2C{=}NHPh^+\ SnCl_3^-$	3.247	1.345

The isomer shifts are typical of Sn^{2+} and the quadrupole splitting is comparable to that of 1.37 mm sec^{-1} for $Bu^n{}_4N^+\ SnCl_3^-$ [20].

3.2.3.3. Mass Spectra

The mass spectra are as tabulated in the data tables. They each contain the expected peaks for the two ions and their respective breakdown.

Fast Atom Bombardment (F.A.B.) mass spectroscopy is a relatively new technique, the first report appearing in the literature in 1981 [21].

In conventional mass spectrometry the sample is vapourised, before bombarding with electrons, so the spectrum obtained may be that of the products of thermal decomposition. F.A.B. mass spectra may be run at room temperature which is an obvious advantage for thermally unstable or involatile samples. The sample is dissolved in a high boiling point solvent such as glycerol and bombarded with neutral atoms (from a Xenon source). Both positive and negative ions are emitted and these are detected to give their respective spectra.

The positive spectra for $Ph_2C{=}NHR.SnCl_3$ (R = H,Me,Ph) contain similar peaks to those of the conventional mass spectra but also contain high mass peaks attributed to ion recombination within the mass spectrometer, as assigned in tables 3.4 to 3.7. The negative spectrum of $Ph_2C{=}NHMe^+SnCl_3^-$ is quite different from its positive spectrum and reveals mainly the tin halide fragments.

3.2.3.4. Crystal Structure of $Ph_2C{=}NHMe^+ SnCl_3^-$

The crystal structure of (N-methyl) diphenyl methyleneammonium trichlorostannate has been determined (table 3.10) and is illustrated in figures 3.5 to 3.7

$[Ph_2C{=}NHMe]^+ SnCl_3^-$

$C_{14}H_{14}NCl_3Sn$, $M = 421.3$, triclinic, $a = 9.067(1)$, $b = 12.563(1)$ $c = 21.925(2)$ Å, $U = 2470.3$ Å^3, $Z = 6$, $D_c = 1.4136$ gcm^{-3}, $F(000) = 1032$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 1.70$ mm^{-1}, Stoe Sieness AED Diffractometer, graphite monochromator, Patterson synthesis.

There are three independant ion pairs in the structure resulting in six per unit cell. Hydrogen bonding gives rise to weak N-H------Cl bonds which link the anions and cations, as illustrated in fig. 3.7.

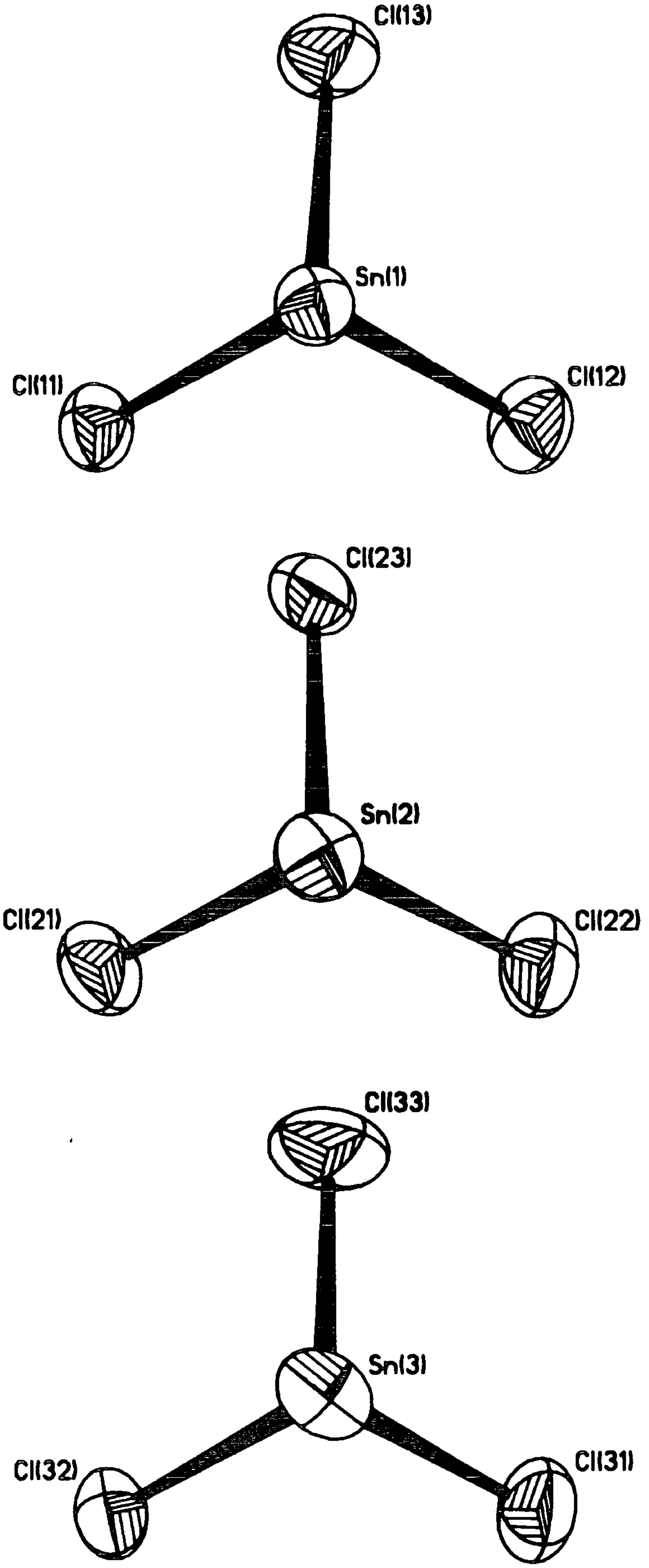


Fig. 3.5 Crystal Structure of the Anion of $(Ph_2C = NHMe)^+$ $SnCl_3^-$.

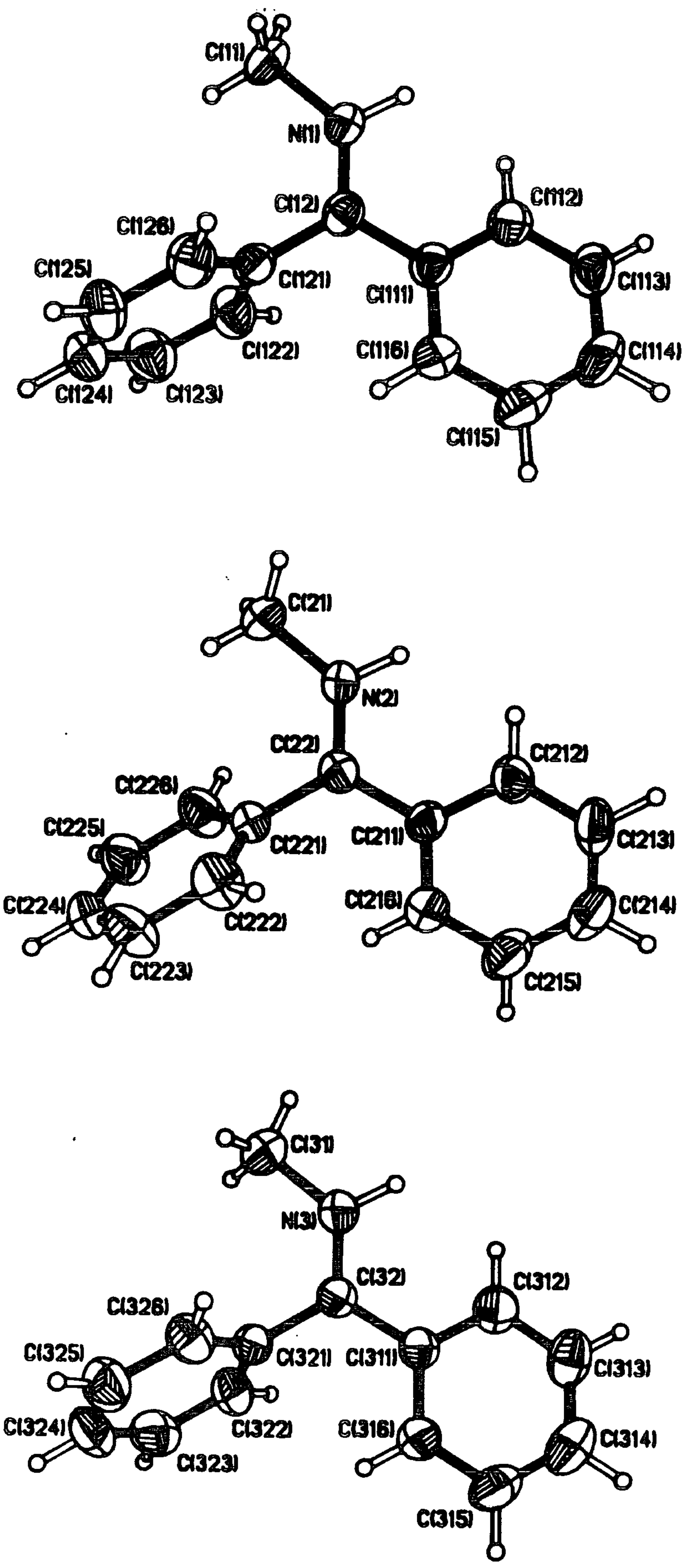


Fig. 3.6 Crystal Structure of the Cation of $[Ph_2C=NHMe]^+ SnCl_3^-$

Fig. 3.7 Unit Cell of $Ph_2C=NHMe^+.SnCl_3^-$

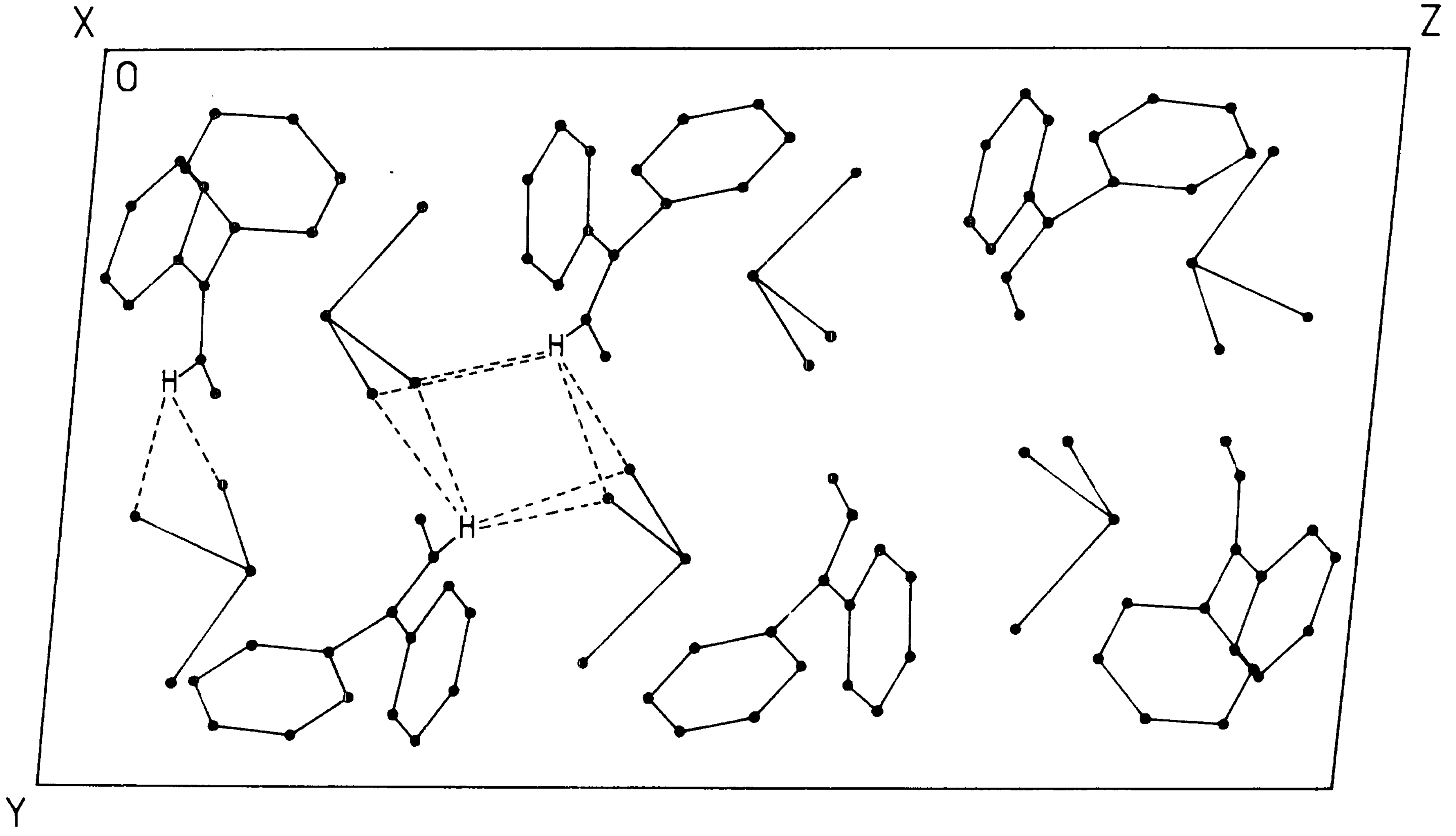


Table 3.10 Crystal Structure Data of $Ph_2C=NHMe^+SnCl_3^-$.

Bond lengths (Å)

Sn(1)-Cl(11)	2.533(1)	Sn(1)-Cl(12)	2.513(1)
Sn(1)-Cl(13)	2.479(2)	Sn(2)-Cl(21)	2.472(1)
Sn(2)-Cl(22)	2.473(1)	Sn(2)-Cl(23)	2.514(1)
Sn(3)-Cl(31)	2.502(2)	Sn(3)-Cl(32)	2.511(1)
Sn(3)-Cl(33)	2.455(2)	N(1)-C(11)	1.470(5)
N(1)-C(12)	1.287(5)	C(12)-C(111)	1.477(5)
C(12)-C(121)	1.488(5)	C(111)-C(112)	1.412(5)
C(111)-C(116)	1.377(6)	C(112)-C(113)	1.383(6)
C(113)-C(114)	1.376(7)	C(114)-C(115)	1.381(7)
C(115)-C(116)	1.378(6)	C(121)-C(122)	1.368(5)
C(121)-C(126)	1.381(5)	C(122)-C(123)	1.388(6)
C(123)-C(124)	1.371(6)	C(124)-C(125)	1.367(7)
C(125)-C(126)	1.379(7)	N(2)-C(21)	1.460(6)
N(2)-C(22)	1.290(5)	C(22)-C(211)	1.466(5)
C(22)-C(221)	1.482(5)	C(211)-C(212)	1.411(5)
C(211)-C(216)	1.383(6)	C(212)-C(213)	1.378(6)
C(213)-C(214)	1.375(7)	C(214)-C(215)	1.383(7)
C(215)-C(216)	1.383(6)	C(221)-C(222)	1.371(5)
C(221)-C(226)	1.388(5)	C(222)-C(223)	1.398(7)
C(223)-C(224)	1.372(6)	C(224)-C(225)	1.343(7)
C(225)-C(226)	1.384(6)	N(3)-C(31)	1.467(6)
N(3)-C(32)	1.287(5)	C(32)-C(311)	1.473(5)
C(32)-C(321)	1.476(5)	C(311)-C(312)	1.395(6)
C(311)-C(316)	1.389(6)	C(312)-C(313)	1.377(6)
C(313)-C(314)	1.385(8)	C(314)-C(315)	1.370(7)
C(315)-C(316)	1.379(6)	C(321)-C(322)	1.390(5)
C(321)-C(326)	1.382(6)	C(322)-C(323)	1.385(6)
C(323)-C(324)	1.383(7)	C(324)-C(325)	1.362(6)
C(325)-C(326)	1.376(6)		

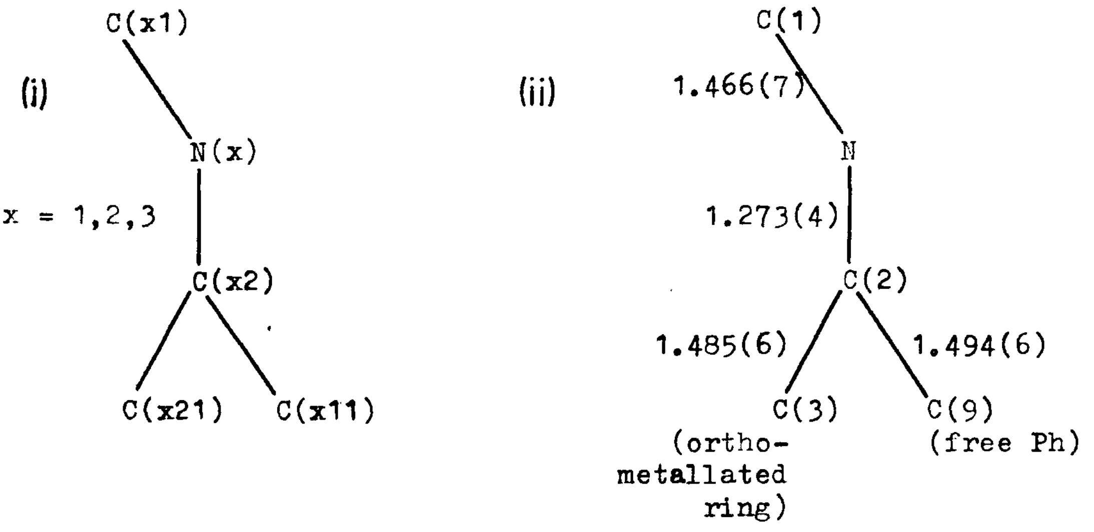
Bond angles (°)

Cl(11)-Sn(1)-Cl(12)	93.5(1)	Cl(11)-Sn(1)-Cl(13)	96.1(1)
Cl(12)-Sn(1)-Cl(13)	91.7(1)	Cl(21)-Sn(2)-Cl(22)	94.4(1)
Cl(21)-Sn(2)-Cl(23)	91.2(1)	Cl(22)-Sn(2)-Cl(23)	92.6(1)
Cl(31)-Sn(3)-Cl(32)	93.0(1)	Cl(31)-Sn(3)-Cl(33)	92.4(1)
Cl(32)-Sn(3)-Cl(33)	94.1(1)	C(11)-N(1)-C(12)	127.6(4)
N(1)-C(12)-C(111)	119.5(3)	N(1)-C(12)-C(121)	120.2(3)
C(111)-C(12)-C(121)	120.2(3)	C(12)-C(111)-C(112)	120.2(4)
C(12)-C(111)-C(116)	119.9(3)	C(112)-C(111)-C(116)	119.8(4)
C(111)-C(112)-C(113)	119.1(4)	C(112)-C(113)-C(114)	120.1(4)
C(113)-C(114)-C(115)	120.8(4)	C(114)-C(115)-C(116)	119.8(5)
C(111)-C(116)-C(115)	120.3(4)	C(12)-C(121)-C(122)	120.3(3)
C(12)-C(121)-C(126)	119.4(3)	C(122)-C(121)-C(126)	120.4(4)
C(121)-C(122)-C(123)	119.3(4)	C(122)-C(123)-C(124)	120.2(4)
C(123)-C(124)-C(125)	120.2(4)	C(124)-C(125)-C(126)	120.0(4)
C(121)-C(126)-C(125)	119.8(4)	C(21)-N(2)-C(22)	128.2(4)
N(2)-C(22)-C(211)	119.0(3)	N(2)-C(22)-C(221)	120.2(3)
C(211)-C(22)-C(221)	120.6(3)	C(22)-C(211)-C(212)	121.2(4)
C(22)-C(211)-C(216)	119.7(3)	C(212)-C(211)-C(216)	119.0(4)
C(211)-C(212)-C(213)	119.3(4)	C(212)-C(213)-C(214)	121.1(4)
C(213)-C(214)-C(215)	119.8(4)	C(214)-C(215)-C(216)	120.0(5)
C(211)-C(216)-C(215)	120.7(4)	C(22)-C(221)-C(222)	121.5(3)
C(22)-C(221)-C(226)	118.8(3)	C(222)-C(221)-C(226)	119.7(4)
C(221)-C(222)-C(223)	119.5(4)	C(222)-C(223)-C(224)	119.8(4)
C(223)-C(224)-C(225)	120.7(4)	C(224)-C(225)-C(226)	120.5(4)
C(221)-C(226)-C(225)	119.7(4)	C(31)-N(3)-C(32)	127.3(3)
N(3)-C(32)-C(311)	120.9(3)	N(3)-C(32)-C(321)	119.5(3)
C(311)-C(32)-C(321)	119.6(3)	C(32)-C(311)-C(312)	121.6(4)
C(32)-C(311)-C(316)	119.1(3)	C(312)-C(311)-C(316)	119.3(4)
C(311)-C(312)-C(313)	119.9(4)	C(312)-C(313)-C(314)	120.2(4)
C(313)-C(314)-C(315)	120.1(4)	C(314)-C(315)-C(316)	120.3(5)
C(311)-C(316)-C(315)	120.2(4)	C(32)-C(321)-C(322)	120.2(3)
C(32)-C(321)-C(326)	119.8(3)	C(322)-C(321)-C(326)	120.1(4)
C(321)-C(322)-C(323)	119.2(4)	C(322)-C(323)-C(324)	120.1(4)
C(323)-C(324)-C(325)	120.1(4)	C(324)-C(325)-C(326)	120.7(4)
C(321)-C(326)-C(325)	119.7(4)		

The anions are pyramidal, with Cl-Sn-Cl of 91.2 - 96.1° as shown in fig. 3.5 and table 3.10. The tin chlorine bond lengths range from 2.455 Å to 2.533Å (table 3.10). Each ion consists of two tin-chlorine bonds of similar lengths with the third one being either fractionally longer or shorter.

By comparision caesium trichlorostannate for example, has three inequivalent chlorine sites in the pyramidal $SnCl_3^-$ ions [22] . Also the bond lengths of the orthometallated material ortho-trichlorostannyl (N-methyl) diphenyl methyleneamine, 2-$Cl_3SnC_6H_4C(Ph){=}NMe$, are 2.355, 2.323 (equatorial) and 2.401 Å (axial) (fig 3.14 and table 6.17.)

The aromatic rings of the cation are not coplanar. The bond lengths of the back bone in fig 3.3 and table 3.4 are compared to those of 2-$Cl_3SnC_6H_4C(Ph){=}NMe$.



The atom numbers correspond to those in fig.3.14.

Fig. 3.8 Element nomenclature for (i) $Ph_2C{=}NHMe^+$ and (ii) the orthometallated derivative, including relevant bond lengths for comparison.

Table 3.10

Bond lengths* in $Ph_2C{=}NMeH^+SnCl_3^-$

x Bond	1	2	3
C(x1)-N(x)	1.470(5)	1.460(6)	1.467(6)
N(x)-C(x2)	1.287(5)	1.290(5)	1.287(5)
C(x2)-C(x11)	1.477(5)	1.466(5)	1.473(5)
C(x2)-C(x21)	1.488(5)	1.482(5)	1.476(5)

* All lengths are in Å, figures in parenthesis are the standard deviations.

The distances between the methyleneamine carbon atom (C(x2)) and the two adjacent phenyl carbon atoms (C(x11) and C(x21)) in each cation differ by over 0.1Å for x=1 and x=2 but are identical within experimental error for x=3. The bonds between C(x2) and C(x11) and C(x21) are shorter than the bond between the imine carbon atom and the free phenyl ring (C(2)-C(9)) of the orthometallated compound but are comparable to the C(2)-C(3) bond length of the metallocycle. The imine bond N(x)-C(x2) is approximately constant for the three cations and is longer than the corresponding bond in the metallocycle where orthometallation has caused shortening. The methyl carbon to nitrogen bond distance (C(x1)-N(x)) is hardly affected by orthometallation. Fig. 3.9 shows that the bond angles do not vary significantly for the three cations but that they are affected upon orthometallation.

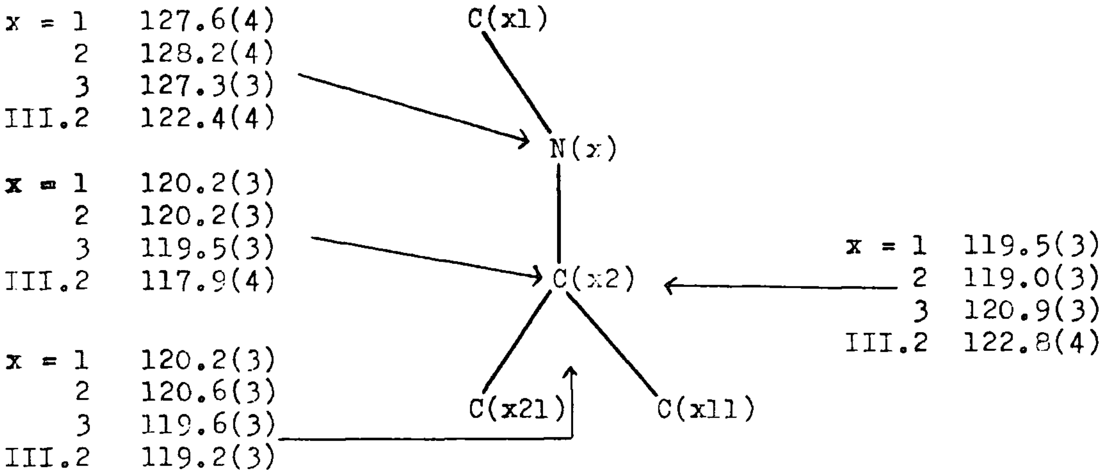


Fig. 3.9. Bond Angles* for $(Ph_2C{=}NHMe)^+ SnCl_3^-$ and $2\text{-}Cl_3SnC_6H_4C(Ph){=}NMe$ (III.2) (* = °)

C(x11) corresponds to C(9) of the orthometallated material
C(x1) corresponds to C(3) of the orthometallated material.

3.3 Development of Reaction conditions most conducive to orthometallation from tin (IV) Chloride and Schiff's Bases

3.3.1 Experimental

3.3.1.1. Reaction between N-methyl diphenyl methyleneamine ($Ph_2C{=}NMe$) and tin (IV) Chloride in a 1:1 molar ratio in toluene at room temperature, 20°C.

Tin (IV) chloride(12.9 mls, 24.85 mmoles) dissolved in toluene (15 mls) was added dropwise to N-methyl, diphenyl methyleneamine (4.6 mls, 24.85 mmoles) in toluene (25 mls) in a nitrogen purged Schlenk tube to give a white precipitate after 30 minutes and was stirred overnight. This was isolated by filtration and washing with cold toluene (compound 3.5) and identified as N-methyl diphenyl methyleneammonium hexachlorostannate $(Ph_2C{=}NHMe)_2^+ SnCl_6^{2-}$ (7.67g) The filtrate was placed in the fridge to induce crystallisation and over a few days a further small amount of $(Ph_2C{=}NHMe)_2^+SnCl_6^{2-}$ crystallised out.

Characterisation of $(Ph_2C=NHMe)_2{}^{+}SnCl_6{}^{2-}$ is given on its data sheet at the end of this experimental section.

3.3.1.2. The reaction between N-methyl diphenyl methyleneamine and Tin (IV) chloride in a 2:1 molar ratio in toluene at room temperature.

The experimental procedure was exactly as in section 3.3.1.1. but using 9.2 mls (49.7 mmoles) of $Ph_2C=NMe$ with $SnCl_4$ (2.9 mls, 24.9 mmoles) to give a white precipitate which was isolated and identified as N-methyl diphenyl methyleneammonium hexachlorostannate $(Ph_2C=NHMe)_2^{+}$ $SnCl_6{}^{2-}$ (compound 3.6, 7.59g, 42%).

A small amount of the crystalline adduct $2(Ph_2C=NMe)SnCl_4$ separated subsequently from the filtrate (compound 3.7, 0.31g, 2%).

3.3.1.3 The reaction between N-methyl diphenyl methyleneamine and Tin (IV) chloride in a 1:1 molar ratio in toluene with heating.

The experimental procedure was exactly as in section 3.3.1.1. but the reaction mixture was refluxed for 5 hours. The mixture separated to a lower dark brown liquid and a lighter brown upper layer. Each layer was syringed whilst hot to a separate flask and upon cooling they each yielded crystalline material which was isolated by filtration and in each case identified as bis (N-methyl diphenyl methyleneammonium hexachlorostannate (compounds 3.8 and 3.9 respectively total yield 2.64g, 60%).

The filtrates were placed in the fridge and after a week each gave crystals which upon isolation were both identified as $2\text{-}Cl_3\overleftarrow{Sn\text{-}C_6H_4C(PH)=N}Me$ (Compounds 3.10 and 3.11, total yield 1.54g, 60%.)

3.3.1.4 The Reaction between N-methyl diphenyl methyleneamine and Tin (IV) chloride in a 2:1 Molar ratio in toluene with heating.

The experimental procedure was exactly as in section 3.3.1.2. but the mixture was refluxed for 14 hours and filtered whilst hot to give a white solid identified as bis (N-methyl diphenyl methyleneammonium) hexachlorostannate $((Ph_2C{=}NHMe)_2^+\ SnCl_6^{2-}$, Compound 3.12, 3.03g, 69%). The filtrate was placed in the fridge and after two days colourless flat square crystals appeared and upon isolation were identified as ortho-trichlorostannyl (N-methyl) diphenyl methyleneamine (compound 3.13, 4.07g, 80%), the data for which are tabulated at the end of this section.

3.3.1.5 Reaction between N-Methyl diphenyl methyleneamine and tin (IV) chloride in a 4:3 molar ratio in toluene with heating.

The reaction procedure was repeated exactly as in section 3.3.1.4. but the molar ratio was as above. Again bis (N-methyl diphenyl methylene ammonium) hexachlorostannate (2.65g 92%, compound 3.14) and orthotrichlorostannyl (N-methyl) diphenyl methyleneamine (1.52g, 46%) compound 3.15) were isolated.

3.3.1.6. Reaction between N-methyl diphenyl methyleneamine and tin (IV) chloride in a 2:1 molar ratio in toluene in the presence of triphenyl amine at room temperature.

The reaction procedure was exactly as in section 3.3.1.2 using $Ph_2C{=}NMe$ (1.5 mls, 8.1 mmoles) and $SnCl_4$ (0.5 mls 4.3 mmoles) to give an immediate white precipitate. Ph_3N (0.89g, 3.6 mmoles) dissolved in toluene (5 mls) was added to give a deep yellow precipitate which, after stirring for 24 hours, was isolated by filtration and identified as bis (N-methyl diphenyl methyleneammonium) hexachlorostannate $(Ph_2C{=}NHMe)_2^+\ SnCl_6^{2-}$, contaminated with salts of protonated triphenyl-amine, either the hydrochloride or a chlorostannate (compound 3.16, 1.43g).

The filtrate was placed in the fridge upon which crystals grew over a week and were isolated and identified as orthotrichlorostannyl (N-methyl) diphenyl methyleneamine. (Compound 3.17, 0.50g, 29 %).

3.3.1.7 Reaction between N-methyl diphenyl methyleneamine and Tin (IV) chloride in a 1:1 molar ratio in ether at room temperature

$Ph_2C{=}NMe$ (4.6 mls, 24.9 mmoles) dissolved in diethyl ether (5 mls) was added to $SnCl_4$ (2.9 mls, 24.9 mmoles) in a nitrogen purged Schlenk tube at 77K and allowed to heat up slowly and gave a white solid. It was dissolved in ether (50 mls) and placed in the fridge to give a crystalline product which upon isolation was identified as a mixture of bis-(N-methyl diphenyl methylene ammonium) hexachlorostannate or N-methyl diphenyl methylene ammonium pentachlorostannate with $2\text{-}Cl_3\overset{\downarrow}{Sn}\text{-}C_6H_4C(Ph){=}NMe$, (Compound 3.18, 3.64g), from the infra-red spectrum.

3.3.1.8. Reaction between N-methyl diphenyl methyleneamine and Tin (IV) Chloride in a 2:1 molar ratio in the absence of a solvent

$Ph_2C{=}NMe$ (9.2 mls, 49.7 mmoles) and $SnCl_4$ (2.9 mls, 24.9 mmoles) were placed in a nitrogen purged Schlenk tube at 77K and allowed to heat up slowly. Dense fumes of hydrogen chloride were observed and an off white solid was formed. It was stirred in dichloromethane (50 mls), isolated by filtration and identified as bis (N-methyl) diphenyl methylene-ammonium hexachlorostannate. (compound 3.19, 6.215g, 69%)
Crystals of orthotrichlorostannyl (N-methyl) diphenyl methyleneamine (compound 3.20, 2.22g, 22%) were obtained from the filtrate after a week.

The following experiments were also conducted to help identify the above products.

3.3.1.9 Reaction between N-methyl diphenyl methyleneamine and hydrogen chloride

Hydrogen chloride gas was bubbled into diethyl ether for 90 minutes at 0°C and N-methyl diphenyl methyleneamine (10mls, 54.0 mmoles) was added by syringe to give a sticky white solid which was recrystallised from chloroform to give N-methyl diphenyl methyleneammonium chloride, $(Ph_2C{=}NHMe)^+Cl^-$, (compound 3.21, 3.56g, 30%).

3.3.1.10 Reaction between N-methyl diphenyl methyleneammonium chloride and tin (IV) chloride in a 1:1 molar ratio

$SnCl_4$(0.3mls, 2.6 mmoles) in CH_2Cl_2 (10mls) was added to $(Ph_2C{=}NHMe)^+Cl^-$ (0.579g, 2.5 mmoles) in CH_2Cl_2 (30mls) to give an immediate white precipitate which dissolved after 10 minutes. Upon placing in the fridge crystals grew over a week and, after isolation, were identified as N-methyl diphenyl methyleneammonium pentachlorostannate, $(Ph_2C{=}NHMe)^+SnCl_5^-$ (compound 3.22, 0.67g, 55%).

3.3.1.11 Reaction between N-methyl diphenyl methyleneammonium chloride and tin (IV) chloride in a 2:1 molar ratio

The reaction procedure was initially exactly as in section 3.3.1.10 but 1.15g (5.0 mmoles) of $(Ph_2C{=}NHMe)^+Cl^-$ were used with the $SnCl_4$ (0.3mls, 2·6mmol). An immediate white precipitate was formed and did not dissolve in the reaction mixture. Upon isolation by filtration it was identified as N-methyl diphenyl methyleneammonium pentachlorostannate, $(Ph_2C{=}NHMe)^+SnCl_5^-$. A small amount of crystals grew in the filtrate, also N-methyl diphenyl methyleneammonium pentachlorostannate, (compound 3.23, 1.3g, 53%).

Compound No.	**Origin** n $Ph_2C=NMe + SnCl_4 \xrightarrow{\Delta}$ n = 1,2 other methods - see text

Name & Structure

$$[Ph_2C=NHMe]^+_2\ SnCl_6^{2-}$$

(N-methyl) diphenyl methyleneammonium hexachlorostannate

m.pt. 105

Elemental Analysis

C	45.1	(46.5)
H	4.5	(3.9)
N	3.6	(3.9)
Sn	15.9	(16.4)
Cl	29.6	(29.4)

Empirical Formula $C_{28}H_{28}N_2Cl_6Sn$

Infra-red, ν cm⁻¹ KBr disc (fig.3.14)

3160m,b, 3045m,b, 2930w/m,b, 1640s, 1590m/s, 1580m/s,shl, 1500w,shl, 1489 w,shl, 1458m,shl, 1433m/s, 1400m, 1326 m,shl, 1310m,shl , 1299m/s, 1280m,shl, 1185w,shl, 1164m/s, 1070w, 1030w, 999 m/s,sh, 992m/s,shl 936m, 912w/m, 824 m/s, 777m/s, 762s, 719m/s, 707s, 690m, shl, 680m, shl, 641m, 533m, 459w/m, 386w/m, 290s.

¹H N.M.R. $CDCl_3$;Int. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.27	s	-	3	Me
7.55	s	-	10	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	100	225	$SnCl_3^+$	100
91	$PhCH_2^+$	100	260	$SnCl_4^+$	12
104	$PhCNH^+$	38	294	$[SnCl_5 - 1]^+$	2.0
118	$PhCNMe^+$	100	315	?	1.5
119	$PhCNMeH^+$	99			
120	Sn^+	26			
155	$SnCl^+$	58			
165	$[Ph_2C - H]^+$	75			
180	Ph_2CN^+	45			
190	$SnCl_2^+$	25			
195	Ph_2CNMe^+	100			

Other Information ^{119}Sn Mossbauer spectrum (table 3.16)

Compound No. 3.7

Origin 2 $Ph_2C=NMe + SnCl_4$

Name & Structure

$2[Ph_2C=NMe].SnCl_4$

bis (N-methyl) diphenyl methyleneamine tin (IV) chloride

m.pt. 161

Elemental Analysis

C	50.4	(51.7)
H	3.4	(4.0)
N	4.1	(4.3)
Sn	18.4	(18.2)
Cl	21.6	(21.8)

Empirical Formula $C_{28}H_{26}N_2Cl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3440w,b, 3220m,b, 3180m,b,shl, 3050w/m, 1735m,b, 1618m/s, 1594m/s, 1523m, 1556 m, 1540m, 1470m, 1439m/s, 1401m, 1331m, 1300m/s, 1281m/s, 1186m, 1174m, 1152m, 1118w/m, 1088w, 1075w, 1039w, 1017m/s, 1000w/m, 941w/m, 922w, 853w, 828m, 788 m/s, 784m/s, 772m, 758m/s, 733m/s, 724 m, 707s, 698m/s, 687m,shl, 666m, 647m, 549w/m, 490w/m, 483m, 456w, 448w, 420m, 402w, 388w, 354m, 323m/s, 288m/s, 276s.

¹H N.M.R d_6DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.28	s	-	1	Me
3.34	s	-		
7.66	s	-	3	Ph

Mass Spectrum

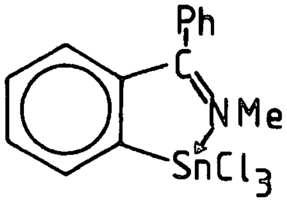
m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	195	Ph_2CNMe^+	100
51	$C_4H_3^+$	38	225	$SnCl_3^+$	24
77	Ph^+	100	260	$SnCl_4^+$	2.3
91	$PhCH_2$	48			
103	$PhCN^+$	13			
118	$PhCNMe^+$	100			
120	Sn^+	4.2			
155	$SnCl^+$	9.1			
166	Ph_2C^+	21			
181	Ph_2CNH^+ or $PhCMe^+$	14			
190	$SnCl_2^+$	3.8			

Other Information

Compound No.

Origin n $Ph_2C=NMe + SnCl_4 \xrightarrow{\Delta}$
n = 1,2; other methods - see text

Name & Structure



ortho-trichlorostannyl (N-methyl) diphenyl methyleneamine

m.pt. 178

Elemental Analysis

C	40.0	(40.1)
H	3.0	(2.9)
N	4.0	(3.3)
Sn	30.4	(28.3)
Cl	25.2	(25.4)

Empirical Formula $C_{14}H_{12}NSnCl_3$

Infra-red, ν cm^{-1} KBr disc (fig.3.14)

3045w, 2920w, 2780vw, 1622m/s, 1570m, 1560m, 1490w/m, 1438m, 1400w/m, 1311s, 1304s, 1183m, 1160m, 1120m, 1100w/m, 1075w/m, 1036m, 1017m/s, 998w/m,shl, 990w/m,shl 971w, 957w, 940m, 914w/m, 879m, 852vw, 783m/s, 770s, 728s, 708s, 681m, 669m, 658m, 480m, 428m, 419m, 395w, 355s, 300s, 250m/s.

^{1}H N.M.R. $CDCl_3$; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.33	s	-	1	Me
7.29	m	-	3	Ph
7.55				
7.64				
7.81				
8.23				

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	67	314	$[194 + Sn]^+$	5.9
92	$PhCH_2^+$	66	349	$[194 + 155]^+$	7.3
104	$PhCNH^+$	7.5	384	$[194 + SnCl_2]^+$	74
118	$PhCNMe^+$	100	419	$[194 + 225]^+$	0.7
120	Sn^+	7.7	426	?	1.7
155	$SnCl^+$	23	544	?	6.1
165	$PhC_6H_4C^+$	51			
179	$PhC_6H_4CN^+$	10			
194	$PhC_6H_4CNMe^+$	67			
225	$SnCl_3^+$	1.0			
270	$[194 + C_6H_4]^+$	31			

Other Information ^{13}C and ^{119}Sn N.M.R. and F.A.B. mass spectra, crystal structure - see text

Compound No.

Origin $Ph_2C=NMe + HCl$

Name & Structure

$Ph_2C=NHMe^+ \ Cl^-$

(N-methyl) diphenyl methyleneammonium chloride

m.pt.

Elemental Analysis

C	73.0	(72.6)
H	6.4	(6.1)
N	5.1	(6.0)
Sn	0.0	(0.0)
Cl	15.8	(15.3)

Empirical Formula $C_{14}H_{14}NCl$

Infra-red, ν cm⁻¹ KBr disc

3020m, 2995m, 2500m/s,b, 1650s, 1589 m/s, 1571m/s, 1490m, 1467m, 1435m/s, 1410m,shl, 1375w/m,shl, 1330m/s, 1315m/s,shl, 1305s, 1273s, 1191w/m, 1175m/s, 1167m/s, 1145m/s, 1102m, 1071m, 1028m, 1002m, 998m/s, 989m/s, 966m/s, 939m, 927m/s, 854m, 805w/m, 785s, 771s, 720m/s, 700s, 649m/s, 611m, 559s, 459m, 451m/s, 405w/m, 397w/m, 350m, 300w/m,shl.

^1H N.M.R. $CDCl_3$; Int. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.17 3.19	s s } d	-	3	Me
7.11 7.14 7.17 7.30 7.32 7.36 7.38 7.58 7.60	m	-	10	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I

Other Information ^{13}C N.M.R. (table 3.13, fig. 3.11).

Compound No.

Origin $Ph_2C=NHMe^+\ Cl^- + SnCl_4$

Name & Structure

$$Ph_2C=NHMe^+\ SnCl_5^-$$

(N-methyl) diphenyl methylammonium pentachlorostannate

m.pt.

Elemental Analysis

C	32.6	(34.2)
H	2.8	(2.9)
N	2.5	(2.9)
Sn	23.5	(24.1)
Cl	35.5	(36.0)

Empirical Formula $C_{14}H_{14}NCl_5Sn$

Infra-red, ν cm^{-1} KBr disc

3198m,b, 3060m,b, 2920w/m, 2840w, 1641 m/s, 1588m/s, 1499w, 1488w, 1457m,shl, 1435m/s, 1397w/m, 1326m,shl, 1310m,shl, 1298m/s, 1190w/m,shl, 1169m/s, 1071w/m, 1033w/m, 1001m,shl, 998m/s,sh,991m/s, shl, 936m, 911w/m, 825m/s, 775m/s, 761 s, 718m/s, 706s, 689m, 678m, 668m,shl, 641m, 555m, 460w/m, 385w/m, 310m/s, 290s.

^{1}H N.M.R. $CDCl_3$; Int. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.30	s	-	3	Me
7.57	s	-	10	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	28	269	?	8.5
103	$PhCN^+$	10	304	?	1.0
118	$PhCNMe^+$	37			
120	Sn^+	21			
155	$SnCl^+$	91			
165	$[Ph_2C - H]^+$	2.6			
180	Ph_2CN^+	2.2			
182	$Ph_2CNH_2^+$	14			
190	$SnCl_2^+$	37			
225	$SnCl_3^+$	6.9			
260	$SnCl_4^+$	10			

Other Information ^{119}Sn N.M.R. spectrum (table 3.15)

3.3.1.12 Reaction between N-methyl diphenyl methylammonium chloride and tin (II) chloride

$SnCl_2$ (0.575g, 3.0 mmoles) in THF (5 mls) was added to $(Ph_2C{=}NHMe)^+Cl^-$ (0.656g, 2.8 mmoles) in CH_2Cl_2 (15 mls) to give a clear yellow solution which upon reduction in volume in vacuo yielded a white solid (compound 3.24). This was identified as N-methyl diphenyl methleneammonium trichlorostannate $(Ph_2C{=}NHMe^+SnCl_3^-)$ (0.54g, 45%) by comparison of its spectra with those of an authentic sample.

3.3.2. Discussion of Results

3.3.2.1 As most of the spectroscopic techniques used rely on the organic parts of organometallic compounds one would not expect a significant change in the spectra upon varying the inorganic half i.e. $SnCl_3^-$ to $SnCl_5^-$ to $SnCl_6^{2-}$. The spectra of these N-methyl diphenyl methyleneammonium salts will have similar features to those discussed in the previous section, in particular N-methyl diphenyl methyleneammonium trichlorostannate, so it is not necessary to repeat the discussion except to note that the mass spectra should contain peaks attributable to $SnCl_4^+$ (260), $SnCl_5^+$ (295) and $SnCl_6^+$ (331). However, the latter two appear to be very weak or not observable at all. As a result the majority of the peaks in the mass spectrum of the hexachlorostannate are very strong in order to observe a $SnCl_5^+$ fragment peak of only 2% relative intensity, but the $SnCl_6^+$ fragment is not observed even at this magnification.

The tin (IV) chloride adduct $SnCl_4 \cdot 2Ph_2C{=}NMe$ obviously will have a different infra-red spectrum to the ionic species $(Ph_2CNHMe)_2SnCl_6$.

The imine stretching frequency is lower than that of the uncoordinated base as expected. Any changes in the ^{1}H. n.m.r spectrum are difficult to distinguish and the organic fragments of the mass spectrum will be similar to those of the salts but one unit lower. The most useful means of identification will therefore be ^{119}Sn n.m.r and Mössbauer spectroscopy, although solubility problems limit the former. ^{35}Cl n.q.r spectroscopy could be used to study whether the ligands adopt a cis or trans arrangement.

As preparation of the orthometallated compound, ortho-trichlorostannyl N-methyl diphenyl methyleneamine has been achieved it is useful to discuss here the effect of orthometallation on the spectra in comparison to those of the salts which are formed as by-products in the reaction. These observations will be useful in identifying the compounds in the following section.

There are two prominent changes upon orthometallation :-

(i) Substitution of the phenyl ring

(ii) Coordination of the tin atom.

(i) Upon orthometallation the phenyl ring becomes 1,2-disubstituted. In the infra-red spectrum this will be reflected by a new strong peak at approximately 730 cm^{-1} which may be attributed to v(C-H) for the aromatic ring taking part in orthometallation (fig. 3.14). However, this spectroscopic indication of orthometallation cannot be used for the para substituted derivatives in the next section as there is no significant change in this region (900-675 cm^{-1}) between 1,4-disubstituted and 1,2,4 trisubstituted phenyl rings [23]. The ^{1}H n.m.r. spectrum will also be affected by this change but as the aromatic proton resonance is already split into a complex multiplet any change will be difficult to distinguish.

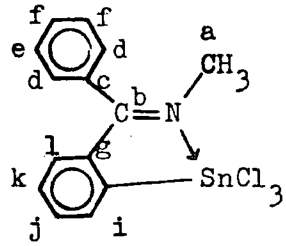
The orthometallated material lacks the N-H bond of the methyleneammonium salts so peaks attributable to it are now absent from the infra-red spectrum.

The ^{13}C n.m.r. spectrum of $2Cl_3SnC_6H_4C(Ph)C{=}NMe$, along with those of $Ph_2C{=}NHMe^+Cl^-$ and $Ph_2C{=}NHMe^+SnCl_3^-$ are given below (tables 3.11 to 3.13 and fig 3.11).

Table 3.11

^{13}C N.M.R. spectrum of

(fig. 3.11)

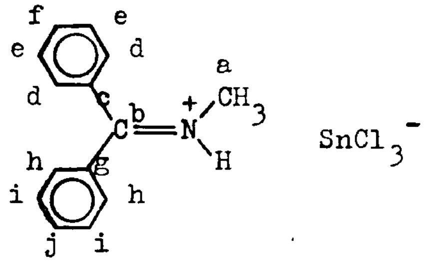


Chemical Shift, ppm*†	Assignment
37.07	a
127.18	d,e
129.42	
130.76	f,i,j,k,l
131.32	
132.33	c,g,h
132.47	f,i,j,k,l
132.61	c,g,h
133.48	
134.48	f,i,j,k,l
136.18	
170.78	b

Table 3.12

^{13}C N.M.R. Spectrum of

(fig. 3.11)



Chemical Shift, ppm*†	Assignment
37.88	a
128.29	c,g
129.00	
129.55	d,e,h,i
129.81	
129.94	
131.42	c,g,impurity
132.20	d,e,h,i
134.04	f,j
136.64	
181.48	b

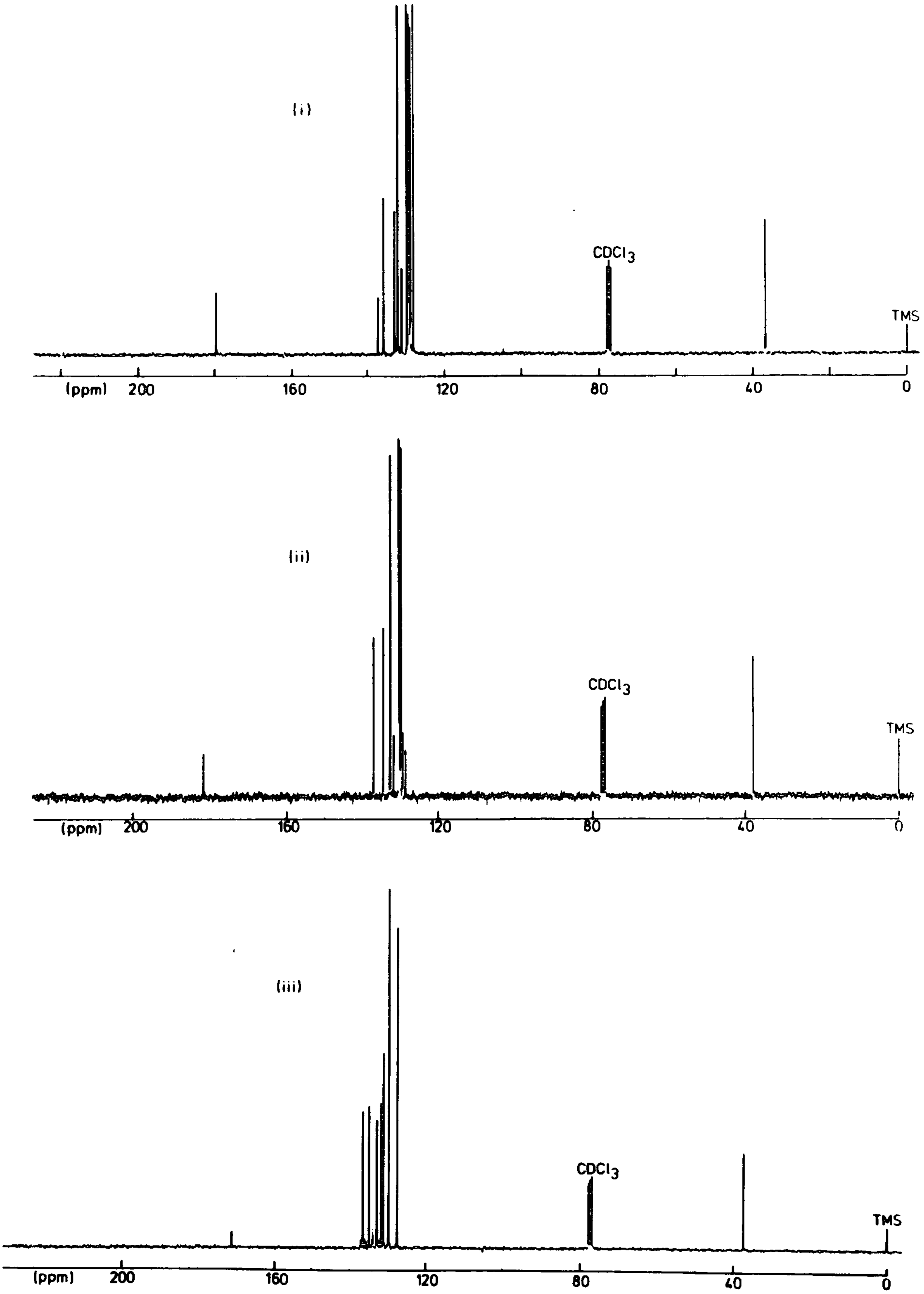
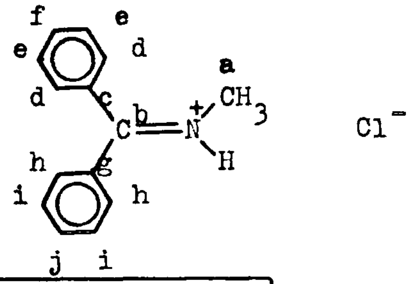


Fig. 3.11 ^{13}C N.M.R. Spectra of (i) $Ph_2C=NHMe^+Cl^-$, (ii) $Ph_2C=NHMe^+SnCl_3^-$ and (iii) $2Cl_3SnC_6H_4C(Ph)=NMe$.

Table 3.13

^{13}C N.M.R. Spectrum of

(fig. 3.11)



Chemical Shift, ppm*†	Assignment
36.33	a
127.80	d,e,h,i
128.53	
128.84	
128.99	
129.34	c,g
129.40	d,e,h,i
130.84	c,g
131.88	d,e,h,i
131.96	f,j
132.68	
135.50	
136.99	
179.32	b

* Relative to TMS, $CDCl_3$ solvent.

† All peaks are singlets and the intensities are correct for the above assignments.

In the non-orthometallated compounds the phenyl rings are equivalent whereas upon orthometallation one ring is disubstituted so different spectra are to be expected. The spectrum of the trichlorostannate has three peaks very close to one another (129.55, 129.81 and 129.94 ppm) and a separate one at 132.20 ppm assignable to carbon atoms d,e,h and i. Separation of the high frequency peak may be due to its carbon atoms being closer to the tin atom than the others.

The azomethine carbon resonance does not appear to be very dependant on the anion but is significantly higher than that of the orthometallated material.

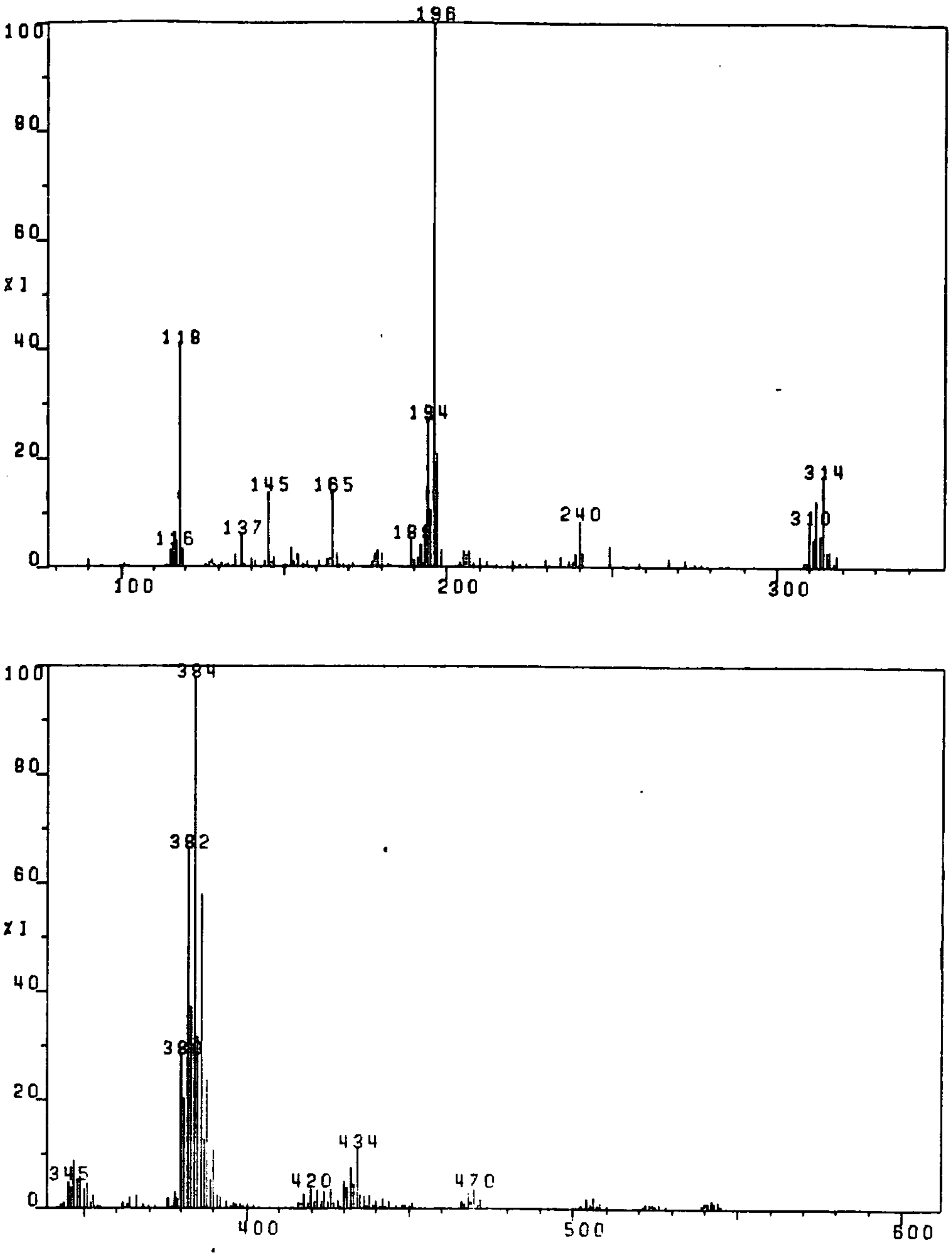


Fig. 3.12 F.A.B Mass Spectrum (positive) of $2\text{-}Cl_3\overset{\downarrow}{Sn}\text{-}C_6H_4C(Ph){=}NMe$.

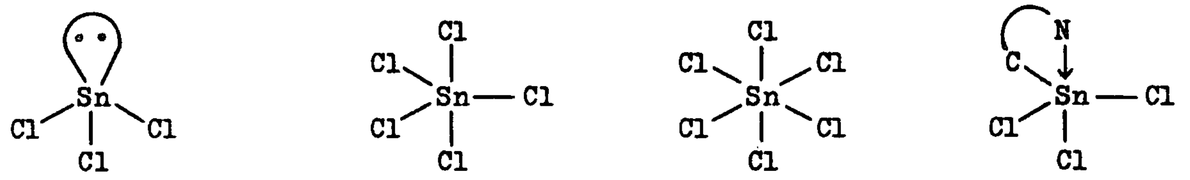
Also the mass spectra of the salts contained separate peaks for each ion and their breakdown. The mass spectrum of the orthometallated material $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NMe$ contains a parent ion peak at m/e419, although very weak. The orthometallated ring is quite stable and consequently the chlorine atoms are lost first, followed by breakdown of the ring. This is supported by the F.A.B. mass spectrum (table 3.14. fig. 3.12).

Table 3.14

F.A.B. Mass Spectrum of $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NMe$, (III.2)

m/e	Fragment Ion	I	m/e	Fragment Ion	I
118	$PhCNMe^+$	41	349	$PhC_6H_4CNMeSnCl^+$	5.8
154	$[SnCl^+ - 1]$	2.3	384	$PhC_6H_4CNMeSnCl_2^+$	97
165	$PhC_6H_4C^+$	13	420	$[PhC_6H_4CNMeSnCl_3+H]^+$ $(III.2 + H)^+$	3.6
179	$PhC_6H_4CN^+$	3.0	434	$(III.2 + Me)^+$	11
189	$[SnCl_2^+ - 1]$	4.8	470	Recombination of ions ?	3.6
196	$[Ph_2CNMe + H]^+$	100	506		2.1
240	?	8.3	526		0.7
314	$PhC_6H_4CNMeSn^+$	16	544		1.3

(ii) The change in coordination and symmetry of the tin atom upon orthometallation is illustrated in fig. 3.13.



$SnCl_3^-$ — pyramidal C_{3v}

$SnCl_5^-$ — trigonal bipyramidal D_{3h}

$SnCl_6^{2-}$ — octahedral O_h

orthometallated material — trigonal bipyramidal

Fig. 3.13

This change is observed in the infra-red spectrum fig. 3.14 in the region below 400 cm^{-1} where tin-chlorine bond vibrations occur. $2Cl_3SnC_6H_4C(Ph)=NMe$ gives two such peaks (symmetric and antisymmetric stretching) as expected for a pyramidal $SnCl_3$ group (C_{3v} symmetry). The higher energy peak, v_{as}(Sn-Cl) may be expected, although clearly this is not the case for this particular example, to be split due to distortion of the trigonal bypyramid by the chelating ligand [17].

The change in coordination at the tin atom is easily distinguished by ^{119}Sn n.m.r spectroscopy, as shown in table 3.15 where a decrease in coordination number from six (e.g.$SnCl_6^{2-}$) to five (e.g. orothometallated compound) causes a large down field shift.

Table 3.15

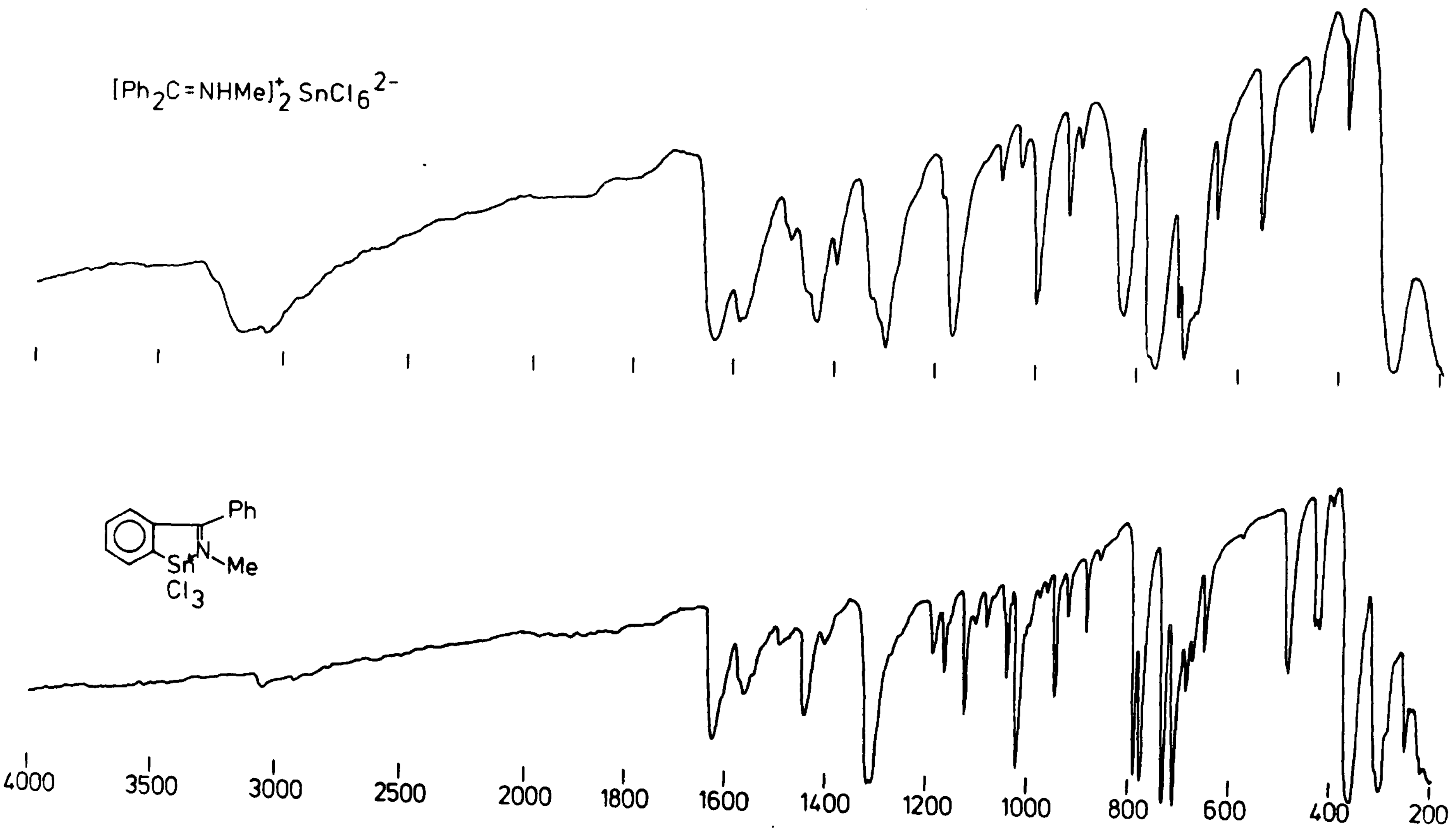
^{119}Sn N.M.R. Chemical shifts to show the effect of Orthometallation

Compound	Chemical Shift, ppm	Ref.
$2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph)=NMe^a$	-241.45	b
$2(Ph_2C=NMe).SnCl_4{}^a$	c	b
$(Ph_2C=NHMe)^+SnCl_5{}^-$ a	-516.74	b
$(Ph_2C=NHMe)^+{}_2SnCl_6{}^{2-}$ a	c	b
$Bu^t{}_2SnCH_2CH_2O$ d	-223	[24]
$Bu_3P.SnCl_4$	-573	[24]
$Bu_4N^+SnCl_5{}^-$	-479	[24]
$(Bu_4N)^+{}_2SnCl_6{}^{2-}$	-732	[24]

a = CH_2Cl_2 solvent; b = this work; c = no peak observed possibly due to low solubility; d = benzene solvent.

Further examples are given in section 3.4.

<u>Fig. 3.14</u> Infra-red Spectra of the named compounds.



^{119}Sn Mössbauer spectroscopy is also a useful tool for determining whether orthometallation has occured.

The isomer shift depends on the 's' electron density at the tin nucleus and can therefore be used to establish the oxidation state of the tin atom, the nature of the bonds to atoms or ions attached (ionic/covalent and hybridisation) and the coordination number of the tin atom. A decrease in the coordination number, for example from changing from $SnCl_6^{2-}$ (six coordinate) to the orthometallated compound (five coordinate) causes the tin atom to have a higher 's' electron density (as its use of '5d' orbitals for bonding is decreased) and consequently a higher chemical shift as illustrated below.

Table 3.16

Effect of the Coordination Number of Tin on its Mössbauer Isomer Shift

Compound	Coordination Number	Isomer Shift mm sec^{-1}	Ref.
$2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph)=NMe$	5	0.938	a
$2\text{-}Cl_3Sn,4\text{-}Me\text{-}C_6H_3C(p\text{-}tolyl)=NH$	5	1.66 b 0.874 c	[17] [17]
$2\text{-}Cl_3Sn,4\text{-}Cl\text{-}C_6H_3C(p\text{-}ClC_6H_4)=NH$	5	0.764 c	[17]
$2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph)=NH$	5	0.716 c	[17]
$Me_3SnCl.py$	5	1.53	[25]
$Bu_3SnCl.$quinoline	5	1.25	[26]
$(Ph_3C)^+\ SnCl_5^-$	5	0.63	[27]
$(Ph_2C=NHMe)_2^+\ SnCl_6^{2-}$	6	0.44	a
$(NH_4)^+_2\ SnCl_6^{2-}$	6	0.48	[28]
$(Me_4N)_2^+\ SnCl_6^{2-}$	6	0.50	[29]

a = this work; b = relative to $BaSnO_3$ ($\equiv SnO_2$ within experimental error; c = relative to $CaSnO_3$.

Table 3.16 therefore shows that the new compounds have isomer shifts within the expected regions for their respective tin atoms.

The quadrupole splitting reflects the deviation from symmetry of the '5p' valence electrons around the tin atom as a result of the spatial arrangements and electronegativities of the groups or atoms attached to it. Hexachlorostannates therefore have zero quadrupole splitting as the chlorine atoms are symmetrically placed around the tin atom. Conversely, structures with the tin atom at the centre of a trigonal bipyramid, such as the orthometallated material, should have a large quadrupole splitting. This is indeed the case for $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph)=NMe$ which has a Δ value of 1.799 $mmsec^{-1}$.

3.3.2.2 Crystallographic Studies

The X ray crystal structure of orthotrichlorostannyl (N-methyl) diphenyl methyleneamine, $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph)=NMe$, has been determined according to fig. 3.15 and table 3.17.

$C_{14}H_{12}NCl_3Sn$, M = 419.3, monoclinic, a = 11.538(2), b = 13.784(2) c = 11.442(2) Å, U = 1161.5 $Å^3$, Z = 4, D_c = 1.728g cm^{-3}, F(000) = 816, space group $P2_1/C$, Mo-K_α radiation, λ = 0.71069 Å, Stoe-Siemens AED diffractometer, graphite monochromator, Patterson synthesis.

The five coordinate tin atom forms the centre of a slightly distorted trigonal bypyramid. The metallocycle is formed with the nitrogen atom in the axial and carbon atom in the equatorial position in accordance with the rule that the less electronegative substituents (the carbon atom here) tend to occupy the equatorial sites in a trigonal bipyramidal arrangement. The chlorine atoms fill the remaining sites with the axial tin-chlorine bond longer than the

Fig. 3.15 **Crystal Structure of Orthotrichlorostannyl(N-methyl)diphenylmethyleneamine.**

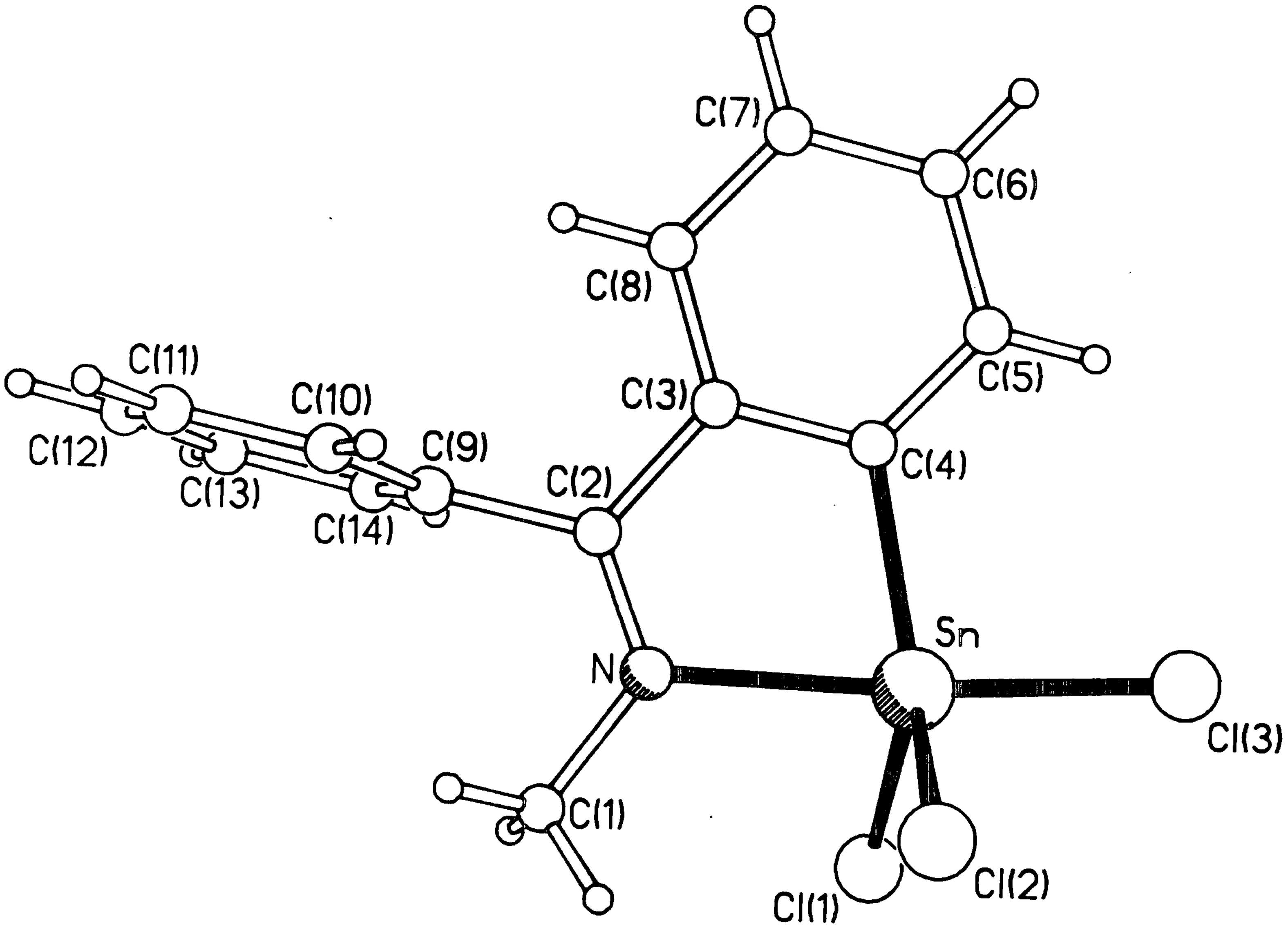


Table 3.17 Crystal Structure Data of 2Cl$_3$SnC$_6$H$_4$C(Ph)=NMe.

Bond lengths (Å)

Sn-Cl(1)	2.335(1)	Sn-Cl(2)	2.323(2)
Sn-Cl(3)	2.401(2)	Sn-N	2.284(4)
Sn-C(4)	2.115(3)	N-C(1)	1.466(7)
N-C(2)	1.273(4)	C(2)-C(3)	1.485(6)
C(2)-C(9)	1.494(6)	C(3)-C(4)	1.392(6)
C(3)-C(8)	1.385(5)	C(4)-C(5)	1.381(7)
C(5)-C(6)	1.386(6)	C(6)-C(7)	1.377(10)
C(7)-C(8)	1.398(8)	C(9)-C(10)	1.375(6)
C(9)-C(14)	1.388(8)	C(10)-C(11)	1.394(8)
C(11)-C(12)	1.368(10)	C(12)-C(13)	1.356(7)
C(13)-C(14)	1.388(8)		

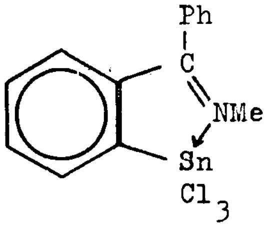
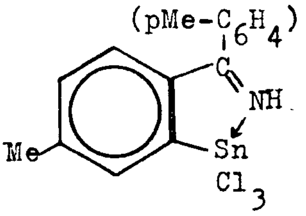
Bond angles (°)

Cl(1)-Sn-Cl(2)	105.4(1)	Cl(1)-Sn-Cl(3)	92.0(1)
Cl(2)-Sn-Cl(3)	96.7(1)	Cl(1)-Sn-N	87.0(1)
Cl(2)-Sn-N	90.0(1)	Cl(3)-Sn-N	173.2(1)
Cl(1)-Sn-C(4)	135.9(1)	Cl(2)-Sn-C(4)	115.3(1)
Cl(3)-Sn-C(4)	99.1(1)	N-Sn-C(4)	77.1(1)
Sn-N-C(1)	124.7(2)	Sn-N-C(2)	112.7(3)
C(1)-N-C(2)	122.4(4)	N-C(2)-C(3)	117.9(4)
N-C(2)-C(9)	122.8(4)	C(3)-C(2)-C(9)	119.2(3)
C(2)-C(3)-C(4)	118.3(3)	C(2)-C(3)-C(8)	121.9(4)
C(4)-C(3)-C(8)	119.8(4)	Sn-C(4)-C(3)	113.7(3)
Sn-C(4)-C(5)	125.5(3)	C(3)-C(4)-C(5)	120.8(3)
C(4)-C(5)-C(6)	119.2(5)	C(5)-C(6)-C(7)	120.6(6)
C(6)-C(7)-C(8)	120.2(4)	C(3)-C(8)-C(7)	119.3(5)
C(2)-C(9)-C(10)	122.0(5)	C(2)-C(9)-C(14)	118.4(4)
C(10)-C(9)-C(14)	119.6(5)	C(9)-C(10)-C(11)	119.7(6)
C(10)-C(11)-C(12)	120.2(5)	C(11)-C(12)-C(13)	120.1(5)
C(12)-C(13)-C(14)	120.7(6)	C(9)-C(14)-C(13)	119.5(4)

equatorial ones. Table 3.18 lists tin-chlorine bond lengths for related compounds including the four coordinate triphenyl tin chloride for comparison.

Table 3.18

Tin-Chlorine Bond lengths for some Organo Tin Compounds.

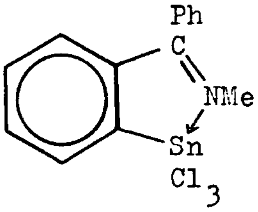
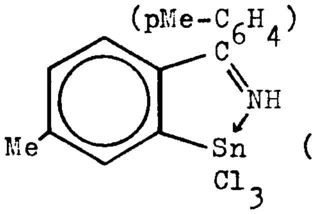
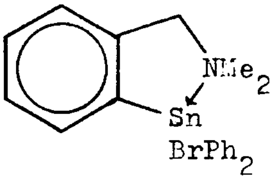
Compound	Axial Sn-Cl, Å	Equatorial Sn-Cl, Å	Ref.
	2.401(2)	2.335(1) 2.323(2)	This work
	2.416(2)	2.315(2) 2.318(2)	[16,17]
$[Me_2SnCl_3]^-$	2.540(2)	2.321(6)	[30]
Ph_3SnCl	2.318(15)	-	[31]

Angles of 77.1(1)° for N-Sn-C(4) and 99.1(1) for Cl(3)-Sn-C(4) reflect the degree of distortion from the perfect trigonal bipyramid for which these angles should each be 90°. The N-Sn-Cl(3) angle of 173.2(1), which is close to that of 180° for the ideal trigonal bipyramid, is clear evidence for intra-molecular interaction of the nitrogen atom. Conversely in its absence the tetrahedral structure adopted would require bond angles approaching 109°28'.

Evidence for the dative bond is supported by comparison of the tin-nitrogen bond length with its values for known compounds as tabulated below.

Table 3.19

Tin-Nitrogen Bond lengths for some Organo-Tin Compounds.

Compound	Sn-N Bond Length, Å	Ref.
 (III.2)	2.284(4)	This work
 (III.3)	2.260(5)	[16,17]
 (III.4)	2.511(12)	[14]
$Ph_2SnCl_2.bipy$ (III.5)	2.344(6) + 2.375(6)	[32]
cis-$(MeC{\equiv}N)_2.SnCl_4$ (III.6)	2.311(24) average	[33]
$(Ph_2C{=}N)_4Sn$ (III.7)	2.068(27)	[34,35]

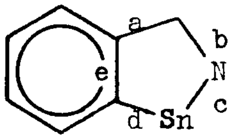
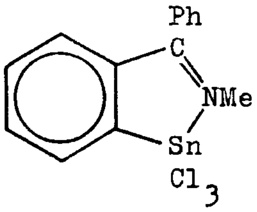
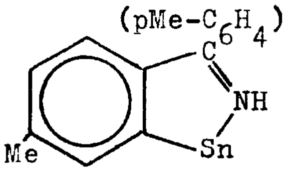
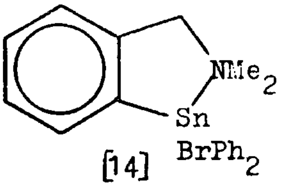
The tin-nitrogen bond length of III.2 is comparable to that of the closely related compound, III.3, and as expected is shorter than that of the third orthometallated species, III.4, due mainly to the relative C=N and C-N bond lengths. The tin-nitrogen bond lengths of compounds

III.2 and III.3 are short for tin-nitrogen dative bonds in comparison to those of the standard non-orthometallated compounds (III.5 and III.6). Also, as expected, the tin-nitrogen bond of compound III.2, being only a dative bond, is longer than that of a covalent bond, as exemplified by compound III.7. The tin-nitrogen bond length of $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NMe$ reflects the strength of the bond which depends on the Lewis basicity of the methyleneamine ligand and the strain of the five-membered ring. The ring itself is quite rigid because the two sp^2 carbon atoms restrict rotation about the C(3)-C(4) axis. Its stability is confirmed in the mass spectrum in which the tin atom loses chlorine atoms first, the metallocycle remaining intact.

The dimensions of the metallocycle are compared to those of similar orthometallated species in table 3.20.

Table 3.20

Dimensions of Orthometallated Rings*

		 [16,17]	 [14]
a	1.485(6)	1.487(8)	1.529(16)
b	1.273(4)	1.280(7)	1.477(19)
c	2.284(4)	2.260(5)	2.511(12)
d	2.115(3)	2.116(5)	2.150(12)
e	1.392(6)	1.391(7)	1.393(20)

* Å

The dimensions of the two methyleneamine metallocycles are very similar and as expected those of the amine are larger, due chiefly to its saturated carbon nitrogen bond. However, bond 'e' is identical within experimental error in each case which is not surprising. The C=N bond length is also similar to that of 1.280(7) Å for 2-$\overline{\text{Mn}(CO)_4-C_6H_4CH=N}$Ph [36]. The Sn-C(4) bond length is within the limits of 2.11-2.15 Å for $Ph_3Sn(IV)$ structures [14]. Also the distance of atom C(2) from the coordinated phenyl ring [C(2)-C(3); 1.485(6)] and from the free phenyl ring [C(2)-C(9); 1,494(6)] is identical within experimental error.

The dihedral angle between the two phenyl rings is 87.4°. The angle between the planes of the two connected rings (A and B, fig. 3.16) is 20.8°.

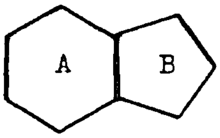


Fig. 3.16

Neither the phenyl ring nor the metallocycle is quite planar. The latter is slightly folded about the Sn-C(3) vector as illustrated in table 3.21.

Table 3.21

Deviations from Planarity of the Metallocycle

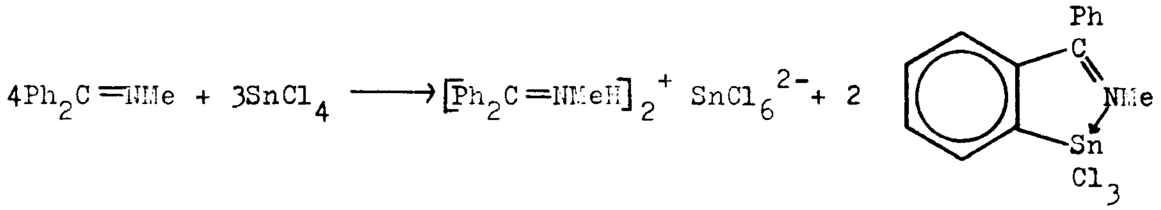
Atom	Deviation from Plane B
Sn	-0.52
N	+0.28
C(2)	+0.25
C(3)	-0.18
C(4)	+0.17

By comparison, the metallocycle of $2\text{-}Cl_3Sn,4\text{-}Me\text{-}C_6H_3C(p\text{-}tolyl){=}NH$ [16,17] is reported to be planar and coplanar with the attached phenyl ring but puckering of the metallocycle is reported for $2\text{-}(Ph_2BrSn)\text{-}C_6H_4CH_2NMe_2$ [14].

Further examples of both intra- and inter-molecular coordination trigonal bipyramidal organotin structures are given in chapter 5.

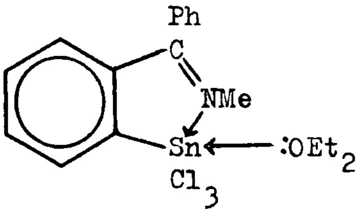
3.3.2.3. Assessment of experimental methods.

The N-methyl diphenyl methylenamine di-adduct of tin (IV) chloride has been formed in a very low yield (2%) by reaction of the two components at room temperature in toluene. However, the major product of the room temperature reactions is bis (N-methyl) diphenyl methyleneammonium hexachlorostannate of which the infra red spectra were identical to that of an authentic sample. In order to produce the hexachlorostannate, hydrogen chloride must be liberated and therefore one would expect to obtain orthometallated material also, but it was not detected. However orthotrichlorostannyl (N-methyl) diphenyl methyleneamine was obtained with thermal assistance for both the 1:1 and 2:1 ($Ph_2CNMe{:}SnCl4$) molar ratio reactions, the crystals being most easily obtained and in the best yield in the 2:1 molar ratio reaction. By changing the molar ratio to 4:3, the stoichiometric amount for the balanced equation to the orthometallated material and the hexachlorostannate (equation 3.3), the yield of the former was lower than in the 2:1 reaction so excess ligand improves the yield.



(3.3)

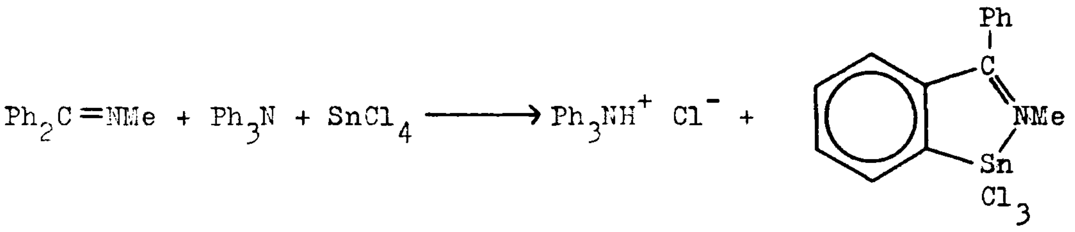
Orthometallated material was also obtained in the absence of solvent. The reaction in ether was performed to determined whether stabilisation by coordinated ether (III.8) (to give coordinatively saturated tin) would increase the ease of reaction or the yield.



III.8

Orthometallated material was obtained but with no evidence of coordinated ether in the product.

Hydrogen chloride liberation, and hence orthometallation, may be encouraged by the presence of a base and thus eliminate the need for thermal assistance.



(3.4)

However, along with orthometallated material (29%) bis (N-methyl diphenyl) hexachlorostannate, heavily contaminated with $Ph_3NH.^+ X^-$ (X = Cl, $SnCl_5$ or ½ $SnCl_6$) was obtained.

The thermally assisted 2:1 (ligand: $SnCl_4$) molar ratio reaction was chosen for investigating different ligands as it gave the best yield of orthometallated material which was easily isolated in a pure crystalline form.

The pentachlorostannate, rather than the hexachlorostannate, is formed by simple addition of tin (IV) chloride to N-methyl diphenyl methyleneamine, irrespective of the molar ratio of starting materials.

$$n\ (Ph_2C{=}NHMe)^+\ Cl^- \ +\ SnCl_4 \longrightarrow (Ph_2C{=}NHMe)^+SnCl_5^- \qquad (3.5)$$

$n = 1$ or 2.

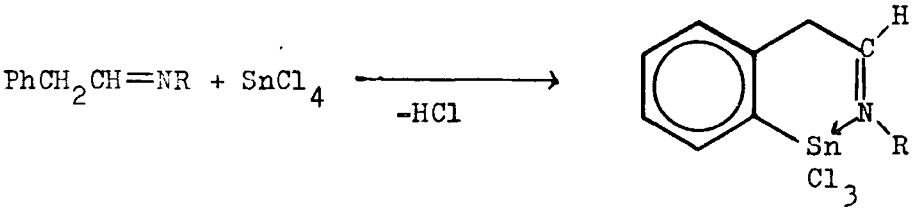
Similarily the trichlorostannate may be prepared using tin (II) chloride.

$$(Ph_2C{=}NHMe)^+Cl^- \ +\ SnCl_2 \longrightarrow (Ph_2C{=}NHMe)^+\ SnCl_3^- \qquad (3.6)$$

3.4 Preparation of Orthometallated Compounds from various Schiff's Bases

3.4.1. Introduction

Attempted orthometallation on a number of Schiff's bases was performed to show the effect of substituents in the para position of the phenyl ring (to be involved in orthometallation) and on the nitrogen atom. Also reactions aimed at forming six membered metallocycles were performed,



(3.7)

as well as attempts to achieve orthometallation via a phenyl group attached to the nitrogen atom.

3.4.2 Experimental

The Reaction between N-Phenyl 4 Methoxy phenyl methyleneamine and tin (IV) chloride.

Tin (IV) chloride (1.45 mls, 12.4 mmoles) in toluene (10 mls) was added to N-phenyl 4-methoxy phenyl methyleneamine ($MeO-C_6H_4CH{=}NPh$) (5.169g, 24.5 mmoles) in toluene (15 mls) to give an immediate precipitate. The mixture was refluxed for 8 hours and filtered hot to give both an orange solid, (compound 3.25, 5.81g) which was washed in dichloromethane, filtered and dried in vacuo and identified as bis (N-phenyl 4-methoxy phenyl methyleneamine) tin (IV) chloride, $2(MeO-C_6H_4CH{=}NPh).\ SnCl_4$, and a clear filtrate in which microcrystals were formed (compound 3.26, 0.26g) upon standing, which were identified as bis (N-phenyl 4-methoxy phenyl methyleneammonium) hexachlorostannate, $(MeO-C_6H_4CH{=}NHPh)^+_2\ SnCl_6^{2-}$ or the above tin (IV) diadduct mixed with a low yield of ortho-trichlorostannyl N-phenyl 4-methoxy phenyl methyleneamine, $2\text{-}Cl_3Sn,4\text{-}MeO-C_6H_4CH{=}NPh$.

A similar procedure was adopted for each of the bases to give the compounds listed in the following data tables where L is the base used and consequently the adducts are $2L.\ SnCl_4$, salts are $(LH)^+\ SnCl_5^-, (LH)^+_2SnCl_6^{2-}$ and the orthometallated compounds are $(L-H)SnCl_3$.

Note: from some experiments only one product has been isolated.

Compound No.	**Origin**
3.25	2 $MeOC_6H_4CH=NPh + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2[MeOC_6H_4CH=NPh].SnCl_4$

bis (N-phenyl) 4-methoxy phenyl methyleneamine tin (IV) chloride

m.pt. d158-61

Elemental Analysis

		$2L.SnCl_4$
C	49.5	49.2
H	3.8	3.8
N	4.0	4.1
Sn	17.7	17.4
Cl	22.2	20.8

Empirical Formula $C_{28}H_{26}N_2O_2Cl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3140w/m, 3060w/m, 2975vw, 2840vw, 1636 m,shl, 1580s, 1560s, 1539m/s,shl, 1532 m/s,shl, 1505m/s, 1489m/s, 1470m, 1449 m/s, 1426m,shl, 1420m, 1409m, 1369m, 1339w/m, 1314m, 1270s, 1225m, 1176s, 1125m, 1071m, 1026m,shl, 1013s, 1007s, 970m, 957w/m, 924m/s, 886m/s,830s, 813 m, 803m, 775m/s, 758m, 747m, 721w, 702 w/m, 697m/s,sh, 695m/s, 636w, 626w/m, 620w/m, 571m/s, 542m, 530s, 511m, 470 w/m, 420w, 372w, 337m, 323s, 305m, 276m.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.82	s	-	3	Me
6.92 7.08 7.13 7.23 7.27 7.77 7.90	m	-	9	Ph
8.47	s	-	1	CH

Mass Spectrum

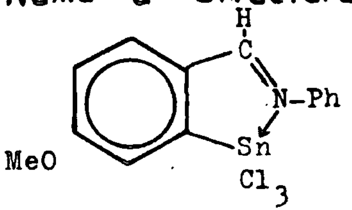
m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	40	211	$MeOC_6H_4CNPh^+$	100
77	Ph^+	99	212	$MeOC_6H_4CHNPh^+$	78
92	$PhNH^+$	8.9		or $MeOC_6H_4CNHPh^+$	
104	$PhNCH^+$	27	225	$SnCl_3^+$	50
106	$MeOC_6H_4- H^+$	1.1	260	$SnCl_4^+$	5.4
120	$MeOC_6H_4CH^+$ +/or Sn^+	17			
134	$MeOC_6H_4CHN^+$	7.8			
155	$SnCl^+$	20			
167	Ph_2CH^+	38			
179	$C_6H_4CNPh^+$	6.6			

Other Information

Compound No. 3.26

Origin 2 $MeOC_6H_4CH{=}NPh + SnCl_4 \xrightarrow{\Delta}$ microcrystals from filtrate

Name & Structure mixture of:



+ $[MeO\text{-}C_6H_4CH{=}NHPh]_2.SnCl_6$

+ $2[MeO\text{-}C_6H_4CH{=}NPh].SnCl_4$

m.pt. 217-8

Elemental Analysis

		$(L\text{-}H)SnCl_3$	L_2SnCl_6	$2L.SnCl_4$
C	45.2	38.6	44.5	49.2
H	3.4	2.8	3.7	3.8
N	3.9	3.2	3.7	4.1
Sn	20.7	27.3	15.7	17.4
Cl	23.6	24.4	28.1	20.8

Empirical Formula

Infra-red, ν cm⁻¹ KBr disc

3180w, 3055w, 1642m, 1594m/s,shl, 1577s, 1560m/s,shl, 1547m/s,shl, 1507m, 1451w/m, 1437w/m, 1407m, 1372w/m, 1312m, 1273s, 1262m,shl, 1227m, 1175s, 1076w,b, 1018s, 925m, 896w/m, 886m, 831m/s, 821m, 808m,shl, 774m, 762m, 756m, 737m, 727m, 695m, 685m, 672m, 629w,b, 566w/m, 552w, 529m/s, 464w/m, 355w/m,b, 328m,shl, 312m/s, 305m,shl, 282m,shl.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.73	s	-	3	MeO
6.87 6.97 7.10 7.33 7.70 7.83	m	-	9	Ph
8.42	s	-	1	CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	97	225	$SnCl_3^+$	31
91	PhN^+	47	245	$[210 + Cl]^+$	14
104	$CHNPh^+$	38	260	$SnCl_4^+$	1
108	$[MeOC_6H_4 + H]^+$	16	364	$[155 + 209]^+$	1.3
120	Sn^+	21	400	$[190 + 210]^+$	24
134	$MeOC_6H_4CNH^+$	13	435	$[210 + 225]^+$ i.e. $2\text{-}Cl_3Sn\text{-}4MeOC_6H_4CHNPh^+$	2.7
155	$SnCl^+$	48			
167	$C_6H_4PhCH_2^+$	93			
179	$C_6H_4PhCN^+$	9.6			
190	$SnCl_2^+$	14			
210	$MeOC_6H_4CNPh^+$	98			

Other Information ^{119}Sn N.M.R. spectrum (table 3.23)

Compound No. 3.27

Origin $2\ ClC_6H_4CH{=}NPh + SnCl_4 \xrightarrow{\Delta} \text{precipitate}$

Name & Structure

$2[ClC_6H_4CH{=}NPh].SnCl_4$

phenyl
bis 4-chloro (N-phenyl) methyleneamine tin (IV) chloride

m.pt. 160-2

Elemental Analysis

C	45.6	(45.1)
H	2.7	(2.9)
N	3.8	(4.0)
Sn	17.4	(17.2)
Cl	30.8	(30.7)

Empirical Formula $C_{26}H_{20}N_2Cl_6Sn$

Infra-red, ν cm⁻¹ KBr disc

3165w, 3060w/m, 1650m, 1605m,shl, 1581s, 1560m/s,shl, 1491m,shl, 1482m, 1451m,shl, 1425m, 1399m, 1376m, 1339vw, 1311m, 1281m, 1242m, 1210m/s, 1192m/s, 1162m, 1120w/m, 1098s,sh, 1074m, 1030m, 1014m/s, 1005m,shl, 979m, 967w/m, 949w/m 928m/s, 886m/s, 831m/s, 815s, 799m, 755m, 759m, 733s, 708m/s, 691m/s, 589w, 571m/s, 524m/s, 497m/s, 486m, 430m, 361w/m, 332s, 298m, 283m.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.24 7.33 7.40 7.53 7.78 7.93	m	-	9	Ph
8.52	s	-	1	CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	98			
91	PhN^+	15			
104	$CHNPh^+$	74			
111	$ClC_6H_4{}^+$	8.9			
124	$ClC_6H_4CH^+$	2.5			
138	$ClC_6H_4CHN^+$	3.9			
155	$SnCl^+$	15			
179	$C_6H_4CNPh^+$	10			
215	$ClC_6H_4CHNPh^+$	96			
217	$[ClC_6H_4CHNHPh + H]^+$	100			
225	$SnCl_3{}^+$	38			
260	$SnCl_4{}^+$	1			

Other Information

Compound No. 3.28

Origin $2\ Ph_2C=NPh + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$Ph_2C=NHPh^+\ SnCl_5^-$

(N-phenyl)diphenyl methyleneammonium pentachlorostannate

m.pt. 115

Elemental Analysis

		$LSnCl_5$	$(L-H)SnCl_3$
C	41.3	41.2	47.4
H	2.7	2.9	2.9
N	2.2	2.5	2.9
Sn	21.3	21.4	24.6
Cl	32.1	32.0	22.1

Empirical Formula $C_{19}H_{16}NCl_5Sn$

Infra-red, ν cm⁻¹ KBr disc

3370m,b, 1595m/s, 1560m, 1465m, 1452m, 1339m, 1302m, 1276m/s, 1207 w/m, 1185w, 1170w, 1156m,shl, 1149m, 1076w/m, 1025w/m, 997m, 961w/m, 918m, 857m/s, 828m/s, 779m/s, 764s, 726m/s, 691s, 669m,shl, 637vw, 615w, 585m/s, 547m, 498w/m, 460w/m,b, 280m/s,b.

^1H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.49 7.85	m	-	-	Ph

Mass Spectrum

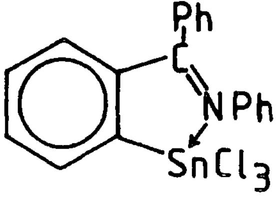
m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	97			
91	$PhCH^+$	3.5			
105	$PhCNH_2^+$	9.7			
120	Sn^+	7.2			
155	$SnCl^+$	13			
165	$[Ph_2C - H]^+$	80			
180	Ph_2CN^+	97			
190	$SnCl_2^+$	2.0			
225	$SnCl_3^+$	18			
256	$[Ph_2CNPh - H]^+$	100			

Other Information ^{119}Sn N.M.R. spectrum (table 3.23)

Compound No. 3.29

Origin $2\ Ph_2C=NPh + SnCl_4 \xrightarrow{\Delta}$ crystals from filtrate

Name & Structure



ortho-trichlorostannyl (N-phenyl) diphenyl methyleneamine

m.pt. 107

Elemental Analysis

C	47.0	(47.4)
H	3.5	(2.9)
N	2.1	(2.9)
Sn	13.9	(24.6)
Cl	23.1	(22.1)

Empirical Formula $C_{19}H_{14}NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc

3150m,b, 2920m/s, 2855m, 1920w, 1805w, 1609s, 1595s, 1578s, 1562s, 1492m/s, 1470m/s, 1455m/s, 1446m,shl, 1375w, 1332m/s, 1309m,shl, 1298m, 1275m/s, 1216m, 1184m, 1162m, 1151m, 1103w/m, 1075m, 1025m, 1000m/s, 971m,shl, 966m, 930m, 918m, 844m, 824m/s, 784s, 773m/s, 761s, 728s, 692s, 640m, 620m, 588m/s, 552s, 498m/s, 451m, 402m, 375s, 359s, 323s, 260m,

¹H N.M.R. $CDCl_3$; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
2.88	s	-	1	H_2O?
7.77 7.95 8.30 8.38 8.86	m	-	16	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	16	225	$SnCl_3^+$	6.8
51	$C_4H_3^+$	31	257	Ph_2CNPh^+	37
65	$C_5H_5^+$	11	446	$2Cl_3\overleftarrow{SnC_6H_4C(Ph)=N}Ph^+$	2.2
77	Ph^+	100			
91	PhN^+	32			
105	$PhCNH_2^+$	84			
120	Sn^+	1.9			
155	$SnCl^+$	6.3			
165	$[Ph_2C - H]^+$	16			
180	Ph_2CN^+	61			
190	$SnCl_2^+$	3.2			

Other Information ¹¹⁹Sn N.M.R. spectrum (table 3.23)

Compound No. 3.30	**Origin** $2\ PhCH{=}NPh + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2[PhCH{=}NPh] \cdot SnCl_4$

bis (N-phenyl) phenyl methyleneamine tin (IV) chloride

m.pt. 182

Elemental Analysis

C	50.2	(50.1)
H	3.8	(3.6)
N	4.1	(4.5)
Sn	19.0	(19.1)
Cl	21.8	(22.8)

Empirical Formula $C_{26}H_{22}N_2Cl_4Sn$

Infra-red, ν cm^{-1} KBr disc

3175w/m, 3050w/m,b, 1640m,shl, 1574s,b, 1482m, 1450m, 1426m, 1374m, 1330m,shl, 1318m/s, 1309m/s, 1286m, 1240m, 1207m/s 1189s, 1164m/s, 1102w/m, 1070m, 1026m, 1017m, 1000m/s, 977m, 921s, 880m/s, 838m, 829m, 786m/s, 768s, 756s, 727m, 717m/s, 707m/s, 680s, 621m, 614m, 569 m/s, 545m/s, 528m/s, 520m/s, 490w/m, 463m, 325s, 298m/s, 240m/s.

^{1}H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
7.22				
7.42	m	-	10	Ph
7.76				
8.45	s	-	1	CH

Mass Spectrum

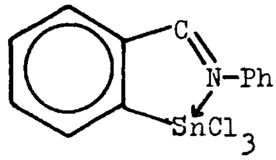
m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	100			
105	$PhCNH_2^+$	57			
120	Sn^+	3.5			
155	$SnCl^+$	19			
181	$PhCNH^+$	99			
190	$SnCl_2^+$	7.2			
225	$SnCl_3^+$	4.2			
260	$SnCl_4^+$	0.4			
269	?	1.0			

Other Information

Compound No. 3.31

Origin 2 PhCH = NPh + $SnCl_4 \xrightarrow{\Delta}$ microcrystals from filtrate

Name & Structure mixture of:



+ $(PhCH{=}NHPh)_2SnCl_6$ (heavily contaminated)

m.pt. 179

Elemental Analysis

		$(L{-}H)SnCl_3$	$(LH)_2SnCl_6$
C	49.2	38.5	44.8
H	3.1	2.5	3.5
N	3.8	3.5	4.0
Sn	21.9	29.3	17.0
Cl	21.4	26.2	30.6

Empirical Formula

Infra-red, ν cm⁻¹ KBr disc

3395w/m,b, 3190m, 3040w/m, 2920m, 2845 w/m, 2380vw,shl, 1644m/s, 1615w/m, 1596 m/s, 1586s, 1477m, 1464m,shl, 1452m, 1408m, 1374m, 1332w/m, 1310w/m,shl, 1288w, 1284w, 1245m, 1189m/s, 1166w/m, 1102w/m, 1028m, 1018m/s, 1000m, 972w, 920w/m, 868w/m, 845m, 829m, 770s, 746m, 729m, 686m/s, 535m, 520m/s, 488w, 475w, 320m/s, 295m/s, 280m,shl, 262m,shl.

^{1}H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.88	s	-	1	?
2.10	s	-	1	?
7.01 7.15 7.38 7.70	m	-	16	Ph
8.42	s	-	1	CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	98	301	$[120 + 181|^+$	1.8
105	$PhCNH_2^+$	23	309	?	8.8
120	Sn^+	8.3	335	$[155 + 180]^+$	0.5
155	$SnCl^+$	43	347	$[166 + 181]^+$	1.0
166	Ph_2C^+	4.3	371	$[181 + 190]^+$	7.4
182	$Ph_2CNH_2^+$	100	406	$[181 + 225]^+$	0.4
190	$SnCl_2^+$	19	451	$[190 + 257 + 4H's]^+$	1.3
197	$SnPh^+$	2.2			
225	$SnCl_3^+$	9.1			
257	Ph_2CNPh^+	1.3			
269	$[Cl_2SnC_6H_4{+}3H's]^+$	2.1			

Other Information

Compound No. 3.32

Origin $2\ PhCH=NBu^t + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2[PhCH=NBu^t].SnCl_4$

bis (N-butyl) phenyl methyleneamine tin (IV) chloride

m.pt. 220

Elemental Analysis

C	45.9	(45.3)
H	5.4	(5.2)
N	3.4	(4.8)
Sn	16.6	(20.4)
Cl	26.4	(24.3)

Empirical Formula $C_{22}H_{30}N_2Cl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3180m/s, 3055m, 2972m, 2918m, 1646s, 1595m/s, 1452m, 1417m, 1400w, 1385m/s, 1380m, 1342w, 1329m, 1309m, 1232m/s, 1186s, 1165m,shl, 1102w, 1030w, 1036s, 1005w, 1000w/m, 998w, 970w, 936w/m, 900m, 855m/s, 842m/s, 769m, 759s, 732s, 695m/s, 681s, 670m,shl, 609w, 503m, 475m, 465m, 426w/m, 419w/m, 337m/s, 315m,shl, 287s.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.34	s	-	1	Bu^t
7.10	s	-	1	CH
7.58	m	-		Ph
7.65				
8.30				
8.42				
8.90				

Mass Spectrum

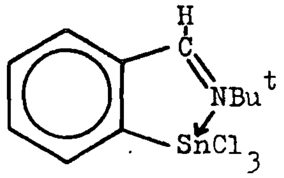
m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	24	260	$SnCl_4^+$	1.6
57	Bu^+	27			
71	NBu^+	7.1			
77	Ph^+	44			
90	$PhCH^+$	8.6			
104	$PhCHN^+$	23			
120	Sn^+	1.6			
146	$[PhCBu - H]^+$	77			
155	$SnCl^+$	3.5			
161	$PhCHNBu^+$	5.0			
225	$SnCl_3^+$	6.0			

Other Information

Compound No. 3.33

Origin $2\ PhCH=NBu^t + SnCl_4 \xrightarrow{\Delta}$ microcrystals from filtrate

Name & Structure mixture of:



$+ (PhCH{=}NBu^tH)_2SnCl_6 + 2(PhCH{=}NBu^t).SnCl_4$

m.pt. 184

Elemental Analysis

		$(L-H)SnCl_3$	$(LH)_2SnCl_6$	$2L.SnCl_4$
C	41.1	34.3	40.3	45.3
H	4.9	3.7	4.9	5.2
N	3.5	3.6	4.3	4.8
Sn	24.3	30.8	18.1	20.4
Cl	22.0	27.6	32.4	24.3

Empirical Formula

Infra-red, ν cm^{-1} KBr disc

3400w/m,b, 3160m, 3040m, 2970m, 2930m, shl, 1650m/s, 1620m/s, 1592m, 1577w/m, 1558w/m, 1452m, 1440m, 1422w/m,shl, 1395w/m, 1373m/s, 1327w/m, 1303m, 1261 m, 1224m/s, 1194s, 1117m, 1035m, 1020m, 998w/m, 980w/m, 970m,shl, 936m/s, 926 m, shl, 894w, 853m, 838m, 770s, 760s, 740s, 715m, 682m/s, 669m,shl, 654w/m, shl, 530w/m, 500m, 472m,423m, 376w, 335m/s, 288m, 274s.

^{1}H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.19	s	-		Bu^t
1.36	s	-		?
7.73	s,b	-		Ph
7.95	s,b	-		

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
57	Bu^+	100	225	$SnCl_3^+$	6.0
77	Ph^+	44	280	$[Sn + 160]^+$	3.1
104	$PhCHN^+$	23	315	$[SnCl + 160]^+$	3.0
105	$PhCHNH^+$	24	350	$[SnCl_2 + 160]^+$	1.7
106	$PhCHNH_2^+$	30			
120	Sn^+	1.6			
135	$SnNH^+$	11			
146	$PhCBu^+$	77			
155	$SnCl^+$	3.5			
161	$PhCHNBu^+$	4.9			
180	?	12			

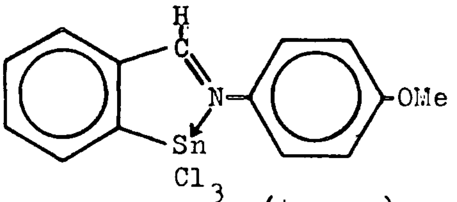
Other Information

Compound No. 3.34

Origin $2\ PhCH=NC_6H_4OMe + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2(PhCH=NC_6H_4OMe).SnCl_4$ +



(traces)

m.pt. 177-8

Elemental Analysis

		$(L-H)SnCl_3$	$2L.SnCl_4$
C	48.6	38.6	49.2
H	3.7	2.8	3.8
N	3.4	3.2	4.1
Sn	17.4	27.3	17.4
Cl	18.0	24.4	20.8

Empirical Formula

Infra-red, ν cm⁻¹ KBr disc

3180w, 3000w, 2940w,b, 2830w, 1665w/m, 1610s, 1595s, 1574m, 1560m,shl, 1540 w/m,shl, 1509m,shl, 1499m/s, 1489m,shl, 1454m, 1438m, 1415w, 1319m, 1295m, 1262 m, 1245s, 1209m, 1192m, 1174m/s, 1110m, 1030m/s, 1011m, 999m,shl, 971w/m, 943 w/m, 930w/m, 897m/s, 829m/s, 762m/s, 754m/s, 729w/m, 713m, 686m, 645m, 571m, 549m, 522m, 503w/m, 435w, 370w/m, 339 m, 322m/s.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.67	s	-	3	MeO
6.68 6.84 7.04 7.32 7.38 7.71	m	-	9	Ph
8.44	s	-	1	CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
76	$C_6H_4^+$	95	190	$SnCl_2^+$	77
77	Ph^+	96	212	$PhCHNHC_6H_4OMe^+$	93
92	$C_6H_4NH_2^+$	96	225	$SnCl_3^+$	95
104	$PhCNH^+$	61	260	$SnCl_4^+$	46
107	$C_6H_4OMe^+$	96	271	?	5.6
120	Sn^+	99	306	?	1.7
134	$CHNC_6H_4OMe^+$	98	330	$SnC_6H_4CHNC_6H_4OMe^+$ or $[SnCl_6-1]^+$	4.4
139	?	100			
155	$SnCl^+$	98	366	$[SnCl + 211]^+$	3.4
166	Ph_2C^+	98			
180	$PhCHNC_6H_4^+$	27			

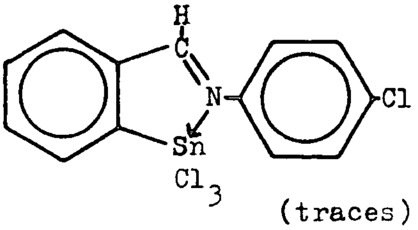
Other Information

Compound No. 3.35

Origin $2\ PhCH=NC_6H_4Cl + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2(PhCH=NC_6H_4Cl).SnCl_4$ +



(traces)

m.pt. d 165

Elemental Analysis

		2L.SnCl$_4$	(L-H)SnCl$_3$
C	44.6	45.1	35.5
H	3.0	2.9	2.1
N	3.7	4.0	3.2
Sn	17.5	17.2	27.0
Cl	30.6	30.7	32.3

Empirical Formula

Infra-red, ν cm⁻¹ KBr disc

3050vw, 1642w/m, 1601m/s, 1584s, 1571s, 1559m/s, 1539m,shl, 1480m/s, 1472m,shl, 1452m, 1429m, 1401m, 1369m, 1328w, 1320 m, 1309m, 1287m, 1270w/m, 1248w, 1207s, sh, 1190s,sh, 1174m, 1165m/s, 1109w/m, 1092s,sh, 1028w, 1017s,sh, 997m, 976m, 954w/m, 940w/m, 925w, 898s, 845w/m, 832 s, 820m/s, 781w, 765s, 746m/s, 730w/m, 682s, 639m, 630m/s, 607m, 572m/s, 544m, 520w, 432m/s, 461m, 422m, 407m,340s,320s

^{1}H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.67	s,b	-	1	H_2O ?
7.23 7.30 7.40 7.74	m	-	8	Ph
8.45	s	-	1	CH
9.85	s	-	¼	NH ?

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	15	225	$SnCl_3^+$	2.1
51	$C_4H_3^+$	15	260	$SnCl_4^+$	0.2
77	Ph^+	26	370	$[155 + 215]^+$	0.6
89	PhC^+	13	405	$[190 + 215]^+$	0.1
103	$PhCN^+$	12	439	$[225 + 214]^+$	0.4
120	Sn^+	0.5			
139	$CH_2NC_6H_4Cl^+$	2.1			
155	$SnCl^+$	0.6			
180	$PhCHNC_6H_4^+$	0.6			
190	$SnCl_2^+$	0.2			
215	$PhCHNC_6H_4Cl^+$	100			

Other Information

Compound No. 3.36	**Origin** $2\ PhCH_2CH{=}NH + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2[PhCH_2CH{=}NH].SnCl_4$

bis benzyl methyleneamine tin (IV) chloride

m.pt.

Elemental Analysis

		$2L.SnCl_4$	$(L\text{-}H)SnCl_3$	$(LH)SnCl_6$
C	43.0	38.5	28.0	33.6
H	3.5	3.6	2.4	3.5
N	4.2	5.6	4.1	4.9
Sn	23.7	23.8	34.6	20.8
Cl	22.4	28.4	31.0	37.2

Empirical Formula

Infra-red, ν cm^{-1} KBr disc

3640-3300w/b, 3180m, 3060m,b, 2905m, 2842m, 1573m, 1540m, 1473m, 1458m, 1442m, 1421m, 1400m, 1329w/m, 1300vw, 1278vw 1245m,b, 1180w, 1147m,b, 1072m, 1042w, 1025w/m, 1011w/m, 998w/m, 962w, 922w, 889w/m, 870w, 830m/s, 757s, 749s, 710m, 691s, 670m,shl, 624m, 618m, 534m, 513m, 463w/m, 446w/m, 312m/s,b, 290m,shl, 280m,shl.

^1H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
2.19	s	-		CH_2
3.70	s,b	-		H_2O?
7.43 7.47 7.51 7.77 7.82	m	-		Ph
7.75	t	36.6		NH (2)
8.87	s	-		CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
77	Ph^+	94	216	?	21
91	$PhCH_2^+$	94	225	$SnCl_3^+$	98
103	$PhCH_2C^+$	35	260	$SnCl_4^+$	7.9
120	$PhCH_2CH_2NH^+$ and Sn^+	43	269	?	7.4
127	?	48	295	$SnCl_5^+$	0.4
139	?	12	306	?	2.5
155	$SnCl^+$	92	320	?	14
165	Ph_2CH^+	20			
180	$PhCH_2CHPh^+$	19			
190	$SnCl_2^+$	51			
203	?	100			

Other Information

Compound No. 3.37

Origin 2 $PhCH_2CH=NBu^t + SnCl_4 \xrightarrow{\Delta}$ precipitate

Name & Structure

$2[PhCH_2CH=NBu^t] . SnCl_4$

bis (N-butyl) benzyl methyleneamine tin (IV) chloride

m.pt. 183

Elemental Analysis

C	50.1	(47.2)
H	5.8	(5.6)
N	4.8	(4.6)
Sn	19.0	(19.4)
Cl	23.1	(23.2)

Empirical Formula $C_{24}H_{34}N_2Cl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3438m,b, 3130m,b,shl, 3005m, 2960m, 1621s, 1603s, 1585m/s, 1479m, 1453m, 1440m, 1430m, 1400m,shl, 1391m, 1364m, 1330w, 1317vw, 1300vw, 1280w/m,shl, 1263m, 1227m, 1216m, 1178m/s, 1099m, 1015m, 980vw, 942w, 908w, 879w,750m/s, 690s, 573m, 535m, 490w/m, 440w/m, 394w, 300m,shl, 285m/s, 271m.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.12	s	-	9	Bu^t
2.63	s	-	~~3~~ 2	CH_2 ?
3.22	s	-	3	CH_2 or H_2O in DMSO
3.82	s,b	-	1	NH_2 ?
6.55 6.85 7.18 7.42	m	-	7	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	57			
51	$C_4H_3^+$	23			
58	BuH^+	91			
77	Ph^+	2.7			
118	$PhCH_2CHN^+$	27			
120	Sn^+	33			
155	$SnCl^+$	18			
175	$PhCH_2CHNBu^+$	7.4			
190	$SnCl_2^+$	67			
225	$SnCl_3^+$	96			
260	$SnCl_4^+$	8.0			

Other Information

3.4.3 Discussion of Results

The products are identified using similar reasoning to that for the previous section and the results are summarised below (table 3.22).

Table 3.22

Products from the Reaction " $2L + SnCl_4 \xrightarrow{\Delta}$" for Various Ligands, L

Ligand, (L)	Product(s)
2-MeO-$C_6H_4CH{=}NPh$	$2L.SnCl_4$ (3.25) $(L{-}H)SnCl_3 + (LH)_2^+ SnCl_6^{2-}$ or $2L.SnCl_4$ (3.26) (heavily contaminated)
2-Cl-$C_6H_4CH{=}NPh$	$2L.SnCl_4$ (3.27)
$Ph_2C{=}NPh$	$(LH)^+SnCl_5^-$ (3.28) $(L{-}H)SnCl_3$ (3.29)
$PhCH{=}NPh$	$2L.SnCl_4$ (3.30) $(L{-}H)SnCl_3 + (LH)_2^+SnCl_6^{2-}$ (3.31) (heavily contaminated)
$PhCH{=}NBu^t$	$2L.SnCl_4$ (3.32) $(L{-}H)SnCl_3 + (L{-}H)SnCl_2 + (LH)_2^+SnCl_6^{2-}$ (3.33)
$PhCH{=}NC_6H_4OMe$	$2L.SnCl_4 + (L{-}H)SnCl_3$ (traces) (3.34)
$PhCH{=}NC_6H_4Cl$	$2L.SnCl_4 + (L{-}H)SnCl_3$ (traces) (3.35)
$PhCH_2CH{=}NH$	$2L.SnCl_4$ (3.36)
$PhCH_2CH{=}NBu^t$	$2L.SnCl_4$ (3.37)

The majority of products are tin(IV) diadducts and the only pure orthometallated compound obtained was 2-trichlorostannyl diphenyl (N-phenyl) methyleneamine, 2-$Cl_3Sn{-}C_6H_4C(Ph){=}NPh$.

Infra-red peaks between 400 and 300 cm^{-1} assignable to tin-carbon stretching are easily observed for the orthometallated compounds.

Mass spectroscopy is the only method capable of revealing these compounds when only present as traces. The development of a more suitable solvent is required in order to obtain each product in a pure crystalline form.

As in the previous section, ^{119}Sn n.m.r. spectroscopy is a useful tool for identifying which of the possible products is present due to their differences in coordination and electron shielding at the tin atom as shown in table 3.23. However, the potential of this technique is seriously reduced by solubility problems. It is also possible that where there is a mixture of products only one may dissolve and the others may remain undetected.

Table 3.23.

^{119}Sn N.M.R. Studies on the products of Schiff's bases with $SnCl_4$.

Compound^{a}	Chemical Shift, ppm	Assignment
3.13	-241.45	$2\text{-}Cl_3\overset{\downarrow}{Sn}\text{-}C_6H_4C(Ph){=}NMe$
3.26	-82.14^{b} -654.63	$(LH)_2^+ \ SnCl_6^{2-}$ or $2L.SnCl_4$
3.28	-656.72	
3.29	-247.89	$2\text{-}Cl_3\overset{\downarrow}{Sn}\text{-}C_6H_4C(Ph){=}NPh$
3.36	-675.6^{c}	$2L.SnCl_4$

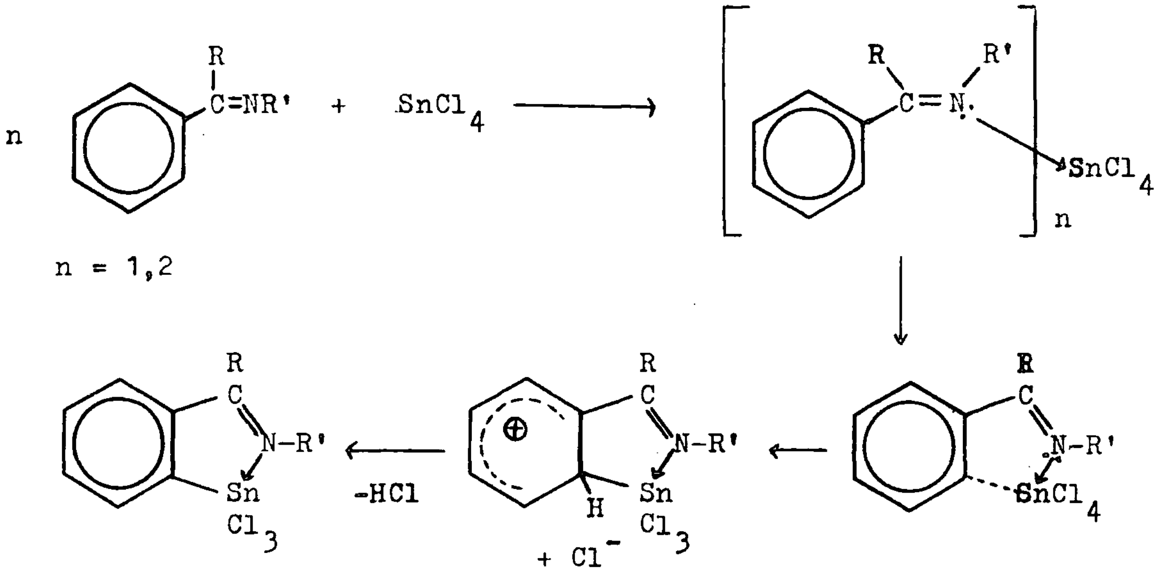
a = CH_2Cl_2 solvent; b = Approximately equal intensity; c = tentative

Note: Compounds 3.25 to 3.36 were all tested but those not listed above gave no spectra due to solubility problems in a range of solvents.

The calculated chemical shift for hexachlorostannate salts is -733.0 ppm [24,37] and deviation due to the cation should not exceed 10 ppm. Examples of related compounds are given in table 3.15 . Hence the salts and adducts have been assigned according to table 3.23.

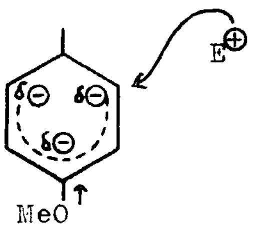
The fact that N-phenyl diphenyl methylene-amine undergoes orthometallation shows that steric hinderance of the base does not prevent the desired reaction.

A possible mechanism is one of electrophilic orthometallation which is common in transition metal chemistry. The proposed scheme is illustrated below (Scheme 3.3).

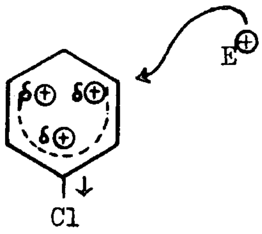


Scheme 3.3

In accordance with this mechanism both the substituents on the tin atom and on the phenyl ring undergoing orthometallation will be important. For electrophilic aromatic substitution an electron releasing substituent in the para position, such as methoxy group, will facilitate electrophilic attack in the ortho position whilst an electron-withdrawing substituent, such as chlorine, will have the opposite effect. This is illustrated by the resonance canonical forms III.9 and III.10.



III.9



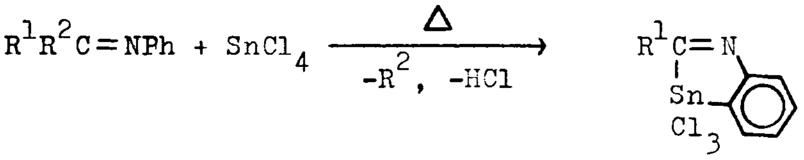
III.10

E^+ = electrophile

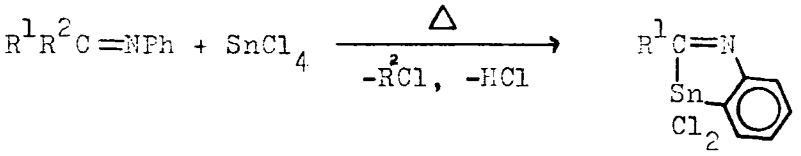
Experiments carried out to investigate these effects are inconclusive due to the impure low yields. Orthometallated material was only obtained in trace amounts for the methoxy derivative and none at all for the chloro derivative.

The substituent at the nitrogen atom is also of importance and its main effect will probably be that on the first stage of the reaction; adduct formation. An electron donating substituent, such as a methyl group, will increase the negative charge on the nitrogen atom and therefore aid the reaction and vice versa.

The phenyl group on the methylene-amine nitrogen atom does not appear to participate in orthometallation. This is hardly surprising as one of the carbon atom substituents must be expelled according to equations 3.8 and 3.9.



(3.8)



(3.9)

Attempts to form six membered metallocycles (equation 3.7) were unsuccessful. This was to be expected as they are generally less stable than their five membered counterparts. The stability of the latter lies in the fact that the bond angles and lengths cause the angle at the metal atom to be close to 90° which allows for tin in a square planar, (4 coordinate) trigonal bipyramidal (5 coordinate) or octahedral (6 coordinate) configuration.

3.5 Investigation into Alternative Routes to Orthometallated Compounds

3.5.1 Introduction

Orthometallated tin compounds may be prepared as shown in tables 3.1 & 3.3 and sections 3.3 and 3.4. A modified version of the route and preliminary investigations into alternative routes have been conducted;

(i) Orthometallation via Grignard Reagents

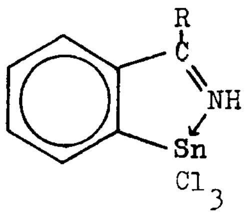
The following scheme was attempted;

$$RBr + Mg \longrightarrow RMgBr$$

$$RMgBr + R'C{\equiv}N \longrightarrow R'RC{=}NMgBr \xrightarrow{SnCl_4} R'RC{=}NSnCl_3 \qquad (III.11)$$

if R orR' is Ph;

$$RPhC{=}NSnCl_3 \longrightarrow$$



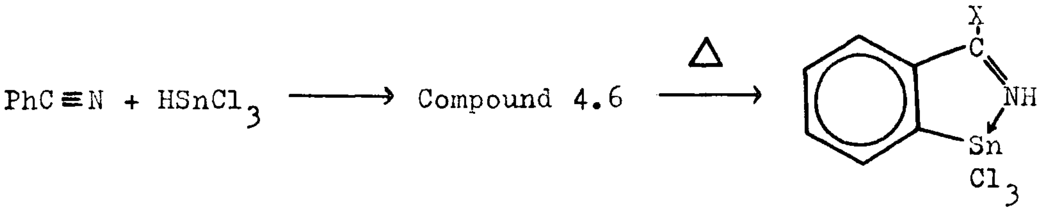
(III.12)

Scheme 3.4

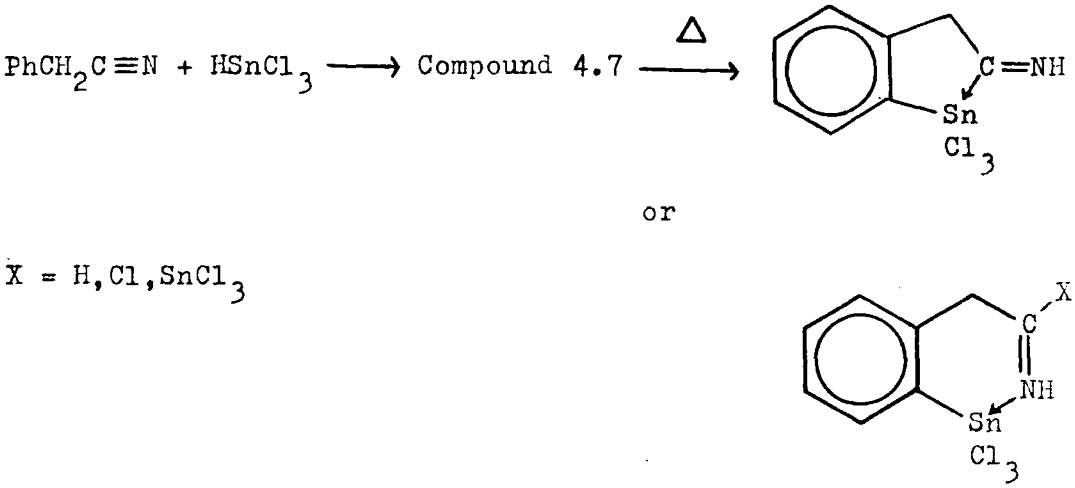
This is a compressed version of the original route avoiding isolation of the methyleneamine.

(ii) Thermal Decomposition of the Hydrostannation Products of Aryl Nitriles

Organotin products from the hydrostannation of benzo- and phenyl aceto- nitrile (chapter 4) may be thermally decomposed to give orthometallated material according to equations 3.10 and 3.11.



(3.10)



(3.11)

X = H,Cl,SnCl$_3$

(iii) Thermal Decomposition of bis(N-methyl diphenyl methyleneammonium) hexachlorostannate

If thermal decomposition of bis (N-methyl diphenyl methyleneammonium) hexachlorostannate, a side product in the orthometallation reaction between the ligand and tin (IV) chloride, yields any orthometallated material then prolonged refluxing in the original experiment may increase the yield of the required product.

3.5.2. Experimental

3.5.2.1. The Reaction between PhMgBr, benzonitrile and tin (IV) Chloride.

Phenyl bromide (3.0 mls, 25.7 mmoles) in Et_2O (15 mls) was slowly added to magnesium turnings (0.732g, 30 mmoles) in Et_2O (10 mls) and refluxed under nitrogen for 40 minutes. Benzonitrile (3.1 mls, 30 mmoles) in Et_2O (30 mls) was added slowly to the cooled mixture to give a thick white precipitate and after refluzing for 90 minutes tin (IV) chloride in toluene (30 mls) was added slowly and refluxed for 22 hours and filtered hot. After about 10 minutes crystals appeared in the filtrate and were recrystallised from Et_2O (Compound 3.38 , 0.82g.)

The residue consisted largely of magnisium halides.

The reaction was repeated but the 22 hour reflux was reduced to 2 hours upon which the yield of crystalline material was considerably lower. Preliminary investigations using para-tolylnitrile and $TiCl_4$ were conducted and gave a black intractable tar. This experiment was not taken any further.

3.5.2.2. Thermal decomposition of the hydrostannation product of benzonitrile

A small sample of the hydrostannation product of benzonitrile (compound 4.6, next chapter) (approximately 0.5g) was placed in sublimation apparatus attached to the vacuum line and a cold tap. It was heated slowly to 150°C at reduced pressure ($<$1mmHg) and a pale yellow solid (compound 3.39) sublimed onto the cold finger leaving a dark brown shiny hard solid (compound 3.40)

3.5.2.3. Thermal decomposition of the Hydrostannation product of Phenylacetonitrile

The procedure was exactly as in the previous section but gave a colourless liquid, identified as phenylacetonitrile (by comparison of its infra-red and ^1H n.m.r spectra with those of an authentic sample). The thermal decomposition product (compound 3.41) was an orange hard shiny solid.

3.5.2.4. Thermal decomposition of bis N-methyl diphenyl methyleneammonium hexachlorostannate.

The procedure was exactly as in section 3.5.2.2. and gave a white powder on the cold finger (compound 3.42) which was identified as a mixture of $2\text{-}Cl_3\overset{\downarrow}{Sn}\text{-}C_6H_4C(Ph){=}NMe$ and $Ph_2C{=}NHMe^+\ X^-$ (where X could be Cl, $SnCl_3$ or $\frac{1}{2}SnCl_6^{\ 2-}$) and a grey solid (Compound 3.43).

Compound No.	**Origin**
3.38	$PhMgBr + PhC\equiv N + SnCl_4 \xrightarrow{\Delta}$

Name & Structure

see text

m.pt.

Elemental Analysis

		$Cl_3SnC_6H_4C(Ph)NH$
C	45.0	38.5
H	3.7	2.5
N	2.8	3.5
Sn	21.0	29.3
Cl	26.2	26.2

Empirical Formula $C_{18}H_{18}NCl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3200-2800m/s,b, 1628m/s, 1591s, 1560m/s 1540m/s,shl, 1520m,shl, 1500m,shl, 1490m, 1441m, 1436m, 1404m,shl, 1367s, 1320vw, 1295w/m, 1277m, 1266m, 1187m, 1162m/s, 1138m,shl, 1117m,shl, 1089w, 1071w/m, 1026w/m, 999m, 970w,b, 930m, 916m,b, 862m,b, 845m,b, 789m/s, 765m/s, 728s, 701s, 695s, 670m,shl, 636w, 605 w/m, 558m,b, 436m, 420w/m,shl, 399w/m, 370w, 294s, 281s, 220m/s.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.38	s	-	1	H_2O ?
5.27	s	-	2	N-H ?
7.53	m	-	11	Ph
7.57				
7.60				
7.67				
7.77				
7.81				
7.83				

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	12	260	$SnCl_4^+$	3.1
77	Ph^+	99	269	?	16
90	$PhCH^+$	12	304	?	1.8
104	$PhCNH^+$	94	315	?	2.4
120	Sn^+	17	336	$[155 + 180 + H]^+$	0.3
155	$SnCl^+$	21	350	$[336 + 14]^+(N, CH_2)$	1.0
165	$C_6H_4CPh^+$	12	370	$[180 + 190]^+$	1.0
180	Ph_2CN^+ or $C_6H_4CHPhN^+$	98	406	$[180 + 225 + H]^+$	0.6
190	$SnCl_2^+$	4.0			
225	$SnCl_3^+$	67			

Other Information

Compound No. 3.39

Origin $PhC\equiv N + HSnCl_3/Et_2O \xrightarrow{\Delta}$ sublimate

Name & Structure

see text

m.pt. 120

Elemental Analysis

C	17.0
H	3.6
N	3.3
Sn	16.4
Cl	55.7

Empirical Formula $C_{10}H_{26}N_{1.7}Cl_{11}Sn$

Infra-red, ν cm⁻¹ KBr disc

3160m,b, 1680m,b, 1595w/m, 1580w/m, 1400s, 1310w/m, 1204m, 1168w/m, 828m, 780w, 747m/s, 720w, 697m, 684m, 647m, 480w,b, 450w, 330m,shl, 312s, 304s, 280m,shl.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.22	s	-	2	CH_2 ?
7.18 7.45 7.56 7.71 7.73	m	-	10	Ph
9.87	s	-	1	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	84	225	$SnCl_3^+$	20
77	Ph^+	100	260	$SnCl_4^+$	1.4
89	PhC^+	40	280	?	7.6
91	$PhCH_2^+$	13	296	$[106 + 190]^+$	34
105	$PhCH_2N^+$	79	384	$[190 + 194]^+$	24
120	Sn^+	8.4			
155	$SnCl^+$	27			
165	$[Ph_2C - H]^+$	26			
178	$[Ph_2CN - 2H's]^+$	23			
190	$SnCl_2^+$	10			
193	?	23			

Other Information

Compound No. 3.40

Origin $PhC\equiv N + HSnCl_3/Et_2O \xrightarrow{\Delta}$ residue

Name & Structure

see text

m.pt. 115

Elemental Analysis

C	46.2
H	2.8
N	4.9
Sn	
Cl	41.3

Empirical Formula $C_{11}H_8NCl_{3.5}Sn$

Infra-red, ν cm⁻¹ KBr disc

3500w/m,b, 3360w/m,b, 3200m,b, 1655w/m, b, 1590w/m,b, 1400s, 1204w, 1028w, 827w, 760m/s, 750m/s, 694s, 490w/m,b, 315s, 307m/s,shl.

¹H N.M.R. d_6DMSO; Ext. TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.24	s,b	-	1	H_2O ?
6.98	m	-	9	Ph
7.30				
7.33				
7.03	t	51.3		$NH_{(2)}$

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	72	225	$SnCl_3^+$	16
77	Ph^+	30	260	$SnCl_4^+$	1.3
91	$PhCH^+$	100	296	$[106 + 190]^+$	8.0
105	$PhCNH^+$	19	384	$[190 + 195 - H]^+$	24
106	$PhCNH_2^+$	19			
120	Sn^+	8.5			
155	$SnCl^+$	36			
165	$[Ph_2C - H]^+$	7.5			
178	$[Ph_2CN - 2H's]^+$	21			
190	$SnCl_2^+$	14			
195	$[105 + PhC]^+$?	13			

Other Information

Compound No. 3.41	**Origin** $PhCH_2C\equiv N + HSnCl_3/Et_2O \xrightarrow{\Delta}$ residue

Name & Structure

see text

m.pt. 186-8

Elemental Analysis

C	28.8
H	2.6
N	4.6
Sn	30.2
Cl	29.6

Empirical Formula $C_8H_9NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc

3200w/m,b, 3140w/m,b, 1655-1530w/m,b, 1484w/m,b, 1444w/m,shl, 1398s,b, 1072 w/m, 1025w/m, 756m/s, 696s, 515w/m,b, 455w/m,b, 314m/s, 302m,shl, 259m,shl.

¹H N.M.R d_6DMSO; Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
4.15	s,b	-	1	NH ?
7.03	t	50.7	6	$NH_{(2)}$?
7.13	m	-		Ph
7.20				
7.33				
7.37				

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	93	194	$Ph_2CH_2CN^+$	25
77	Ph^+	97	202	?	76
91	$PhCH_2^+$	95	217	?	20
105	$PhCH_2CH_2^+$	100	225	$SnCl_3^+$	1.5
116	$PhCHCN^+$	96	231	$ClSnC_6H_4^+$	94
118	$PhCH_2CNH^+$	78	258	$[231 + CNH]^+$	1.3
120	Sn^+	56	294	$[77+217]^+$ or $[104+190]^+$	3.5
135	$SnNH^+$ or $SnCH_3^+$	96	306 320	$[104+202]^+$ or $[116+190]^+$	15
149	$SnCH_2NH^+$	13	320	$[103+217]^+$ or $[165+155]^+$	72
154	$[SnCl - 1]^+$	17	336	$[258 + 77 + H]^+$	8.9
165	$[Ph_2C - H]^+$	13	422	$[232+190]^+$ or $[116+306]^+$	2.6
190	$SnCl_2^+$	8.9			

Other Information

Infra-red Spectrum of Compound 3.43, v cm^{-1}, KBr disc.

3180m, 3050m, 1645s, 1618m/s, 1590m, 1490w/m, 1460m, 1440m, 1400w/m, 1330m, 1312s, 1301s, 1167m, 1120w, 1036w, 1015w/m, 998m, 949w/m, 830m, 779m/s, 764s, 726m, 717m, 705s, 680m, 641w/m, 560m, 487w, 469w, 425w, 390w, 352m, 290m/s.

3.5.3 Discussion of Results

The possibility that the crystals from the Grignard reaction (Compound 3.38) contain orthometallated material is supported by the mass Spectrum. In the infra-red spectrum there is a peak at approximately 730 cm^{-1} for v (C-H) of the disubstituted benzene ring but there is no sharp peak for v(N-H) at approximately 3300 cm^{-1}, nor is there a strong peak between 400 and 300 cm^{-1} for v(Sn-C). The infra-red peaks do not coincide with those of an authentic sample of orthotrichlorostannyl diphenyl methyleneamine, $2\text{-}Cl_3Sn\text{-}C_6H_4C(Ph){=}NH$, [17] although the mass spectra are almost identical.

An alternative product would be that of straight forward addition; $Ph_2C{=}NSnCl_3$ (scheme 3.4). This would give a similar mass spectrum but the infra-red and ^1H n.m.r. spectra should not exhibit any peaks due to a NH_2 group. This would be feasible if the broad peak in the infra-red and that at 5.27 ppm in the ^1H n.m.r. spectrum were in fact due to the sample being wet (e.g. hydrolysed during the running of the spectrum).

Further exploratory work on this reaction is required (e.g. change of solvents and lengths of refluxing) as in theory it has good potential for orthometallation. However in the experiments performed the yield of crystalline material was low so conditions to improve it should also be sought.

Clearly, the pyrolysis experiments on the hydrostannation products of benzonitrile and phenylacetonitrile have not led to any orthometallated material as the infra-red spectra, in particular, give no supportive evidence (a sharp v(N-H) peak [6,17] or a strong peak at 730 cm^{-1}). The peak in the v(C═N) region of the infra-red spectrum of compound 3.39 is much less intense but there is a strong peak at 1400 cm^{-1} which could be due to v(C-N) indicating that the nitrile has been fully saturated. Similar trends are observed for the two residues, the peak attributable to v(C═N) having almost disappeared. Their ^1H n.m.r. spectra each contain an equal intensity triplet superimposed on the phenyl protons' multiplet. This triplet is assigned to protons attached to the nitrogen atom as in the original hydrostannation product (compound 4.6). The mass spectra suggest that complicated dimeric species may be present. Some orthometallated material was obtained upon pyrolysis of (N-methyl) diphenyl methyleneammonium hexachlorostannate but was impure, the most likely contaminant being the hydrochloride, $Ph_2C{=}NHMe^+ Cl^-$.

3.6. Conclusion

This chapter shows that the hydrostannation of methyleneamines leads to ionic species rather than addition products across the azomethine bond. Addition of tin (IV) chloride to (N-methyl) diphenyl methyleneamine leads to the diadduct and the hexachlorostannate as well as orothotrichlorostannyl (N-methyl) diphenyl methyleneamine. The tri and penta- chlorostannates have been prepared directly from the hydrochloride of the base with tin (II) and tin (IV) chloride respectively. Upon varying the bases orthometallated compounds are formed but in considerably lower yields. Alternative routes to orthometallated compounds have been sought of which the reaction involving Grignard reagents shows the greatest potential.

CHAPTER 4

THE REACTION OF SATURATED NITRILES WITH ETHEREAL TRICHLOROSTANNANE

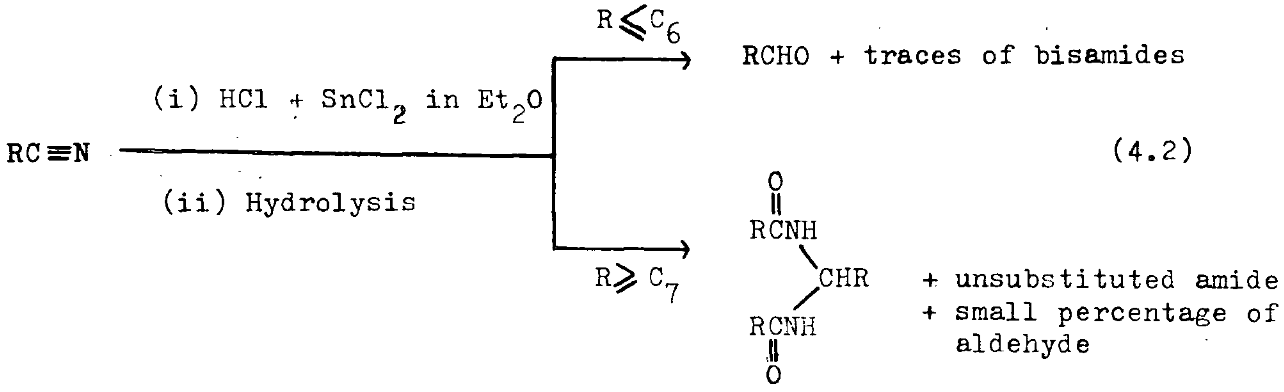
4.1 Introduction

Nitriles can be reduced to aldehydes by hydrogen chloride with tin dichloride (the Stephen reaction) [1] according to equation 4.1

$$\mathrm{RC{\equiv}N} \xrightarrow{\text{or}\left\{\begin{array}{l}\mathrm{SnCl_2/HCl/Solvent^*}\\ \mathrm{Sn}\end{array}\right.} [\mathrm{INTERMEDIATE}] \xrightarrow{\text{HYDROLYSIS}} \mathrm{RCHO}$$

* usually Et_2O (4.1)

In view of more recent research [2,3] the reaction may proceed via a trichlorostannate etherate. A number of reviews on the Stephen reaction have been published [4-6]. Although Stephen claims almost quantitative conversion to the aldehyde, alternative hydrolysis products have been isolated including primary amides, bisamides [7] and dimers and trimers of the aldehyde [8]. Consequently equation 4.2 has been suggested [9, 10].



(4.2)

The original intermediate proposed by Stephen himself [1] was $(RCH{=}NH,HCl)_2,SnCl_4$. An alternative intermediate is

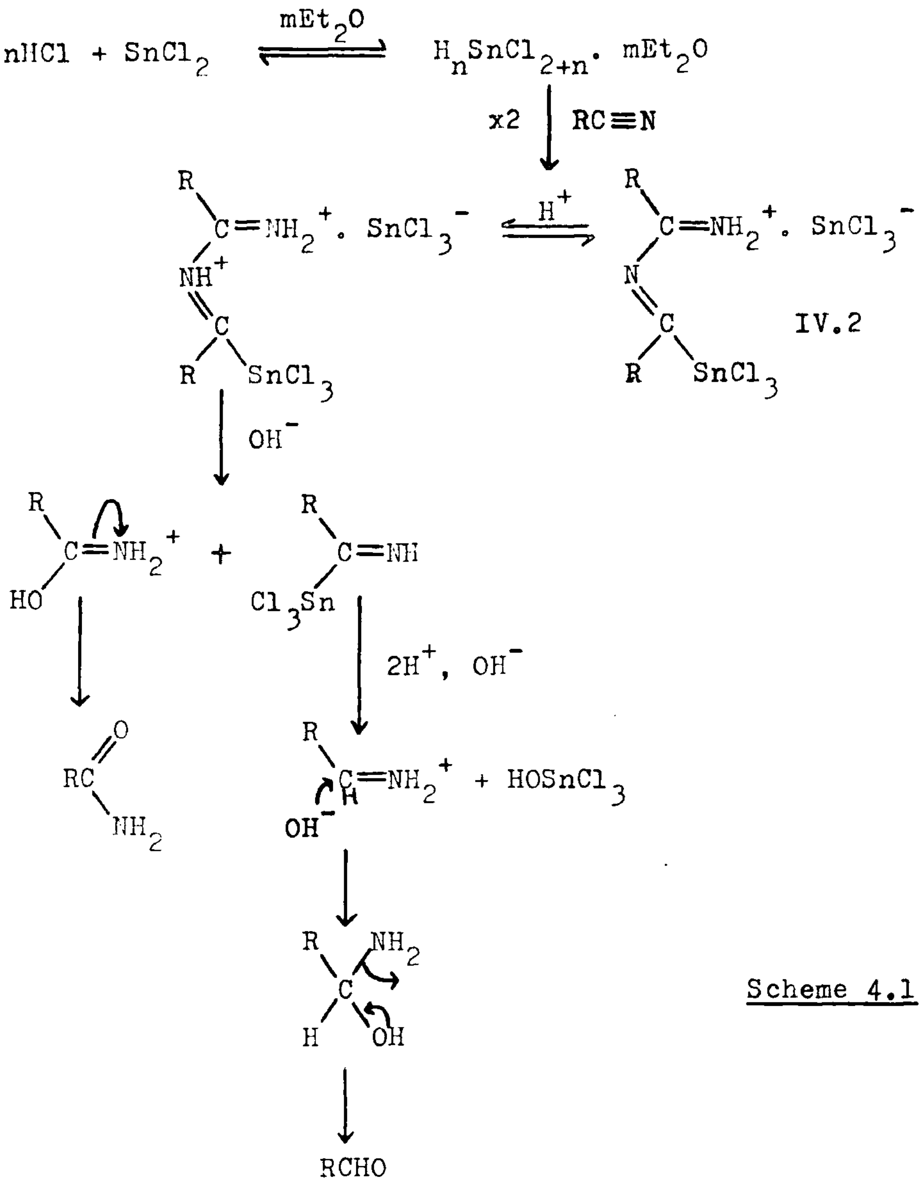
$(RCH{=}NH_2).H_2SnCl_6$ [11], presumably a misprint for $(RCH{=}NH_2)_2{}^+SnCl_6{}^{2-}$ or $(RCH{=}NH_2)^+HSnCl_6{}^-$. $(RCH{=}NH.HCl)_2SnCl_4$ may also be involved in bisamide formation [12] resulting in a condensation reaction between the imine hydrochloride and the nitrile. $[RC({=}NH)NHCHR{-}N{\equiv}CR]_2.SnCl_6{}^{2-}.2SnCl_4$ has also been proposed as an intermediate leading to the bisamide [6]. Meerwein [13] has suggested that the reaction may proceed via the nitrilium salt IV.1.

$$RC{\equiv}N + H_2SnCl_4 \longrightarrow \underset{\text{IV.1.}}{(RC{\equiv}NH)^+HSnCl_4{}^-} \qquad (4.3)$$

This is supported by kinetics studies [14].

Finally Chinese workers have prepared and determined the structure of an intermediate in the Stephen Reaction of benzonitrile and report it to be the stannic aldomonium chloride, $[PhCH{=}NH_2]^+_2\,SnCl_6{}^{2-}$. [15].

An alternative mechanism involving ethereal trichlorostannane has been postulated [3] (scheme 4.1). Indeed, Stephen reports that the ethereal suspension of tin II chloride is saturated with hydrogen chloride until the mixture separates into two layers and Pyrylova and Zil'bermann [9] declare that, for an optimum yield of aldehyde, hydrogen chloride should be passed into the ethereal solution until the solutions of nitrile and tin dichloride become homogenous. These procedures are identical to the preparation of ethereal trichlorostannane (chapter 2) but the tin containing intermediate is not isolated and characterised.


IV.2

Scheme 4.1

Compound IV.2 was isolated and characterised by comparison with the analogous products from the addition of hydrogen chloride to nitriles [16-19] . The hydrochlorination of nitriles, which has been reviewed by Schaeffer [20] may also yield an immidoyl chloride [16,17,21] , dimerisation of which may occur because of the nucleophilicity of the nitrile.

The work discussed in this chapter is a continuation of the studies of P.G.Huggett [3] by a modified method in order to obtain better quality, more stable material and possibly monomeric rather than dimeric species. Also more detailed characterisation of the products was to be undertaken, including Mössbauer studies which have not previously been performed in this area.

4.2. Experimental

The experimental procedure was as outlined below for acetonitrile to give the products listed and characterised in the data tables on pages 133 to 141 .

4.2.1. Hydrostannation of Acetonitrile

Acetonitrile (40 mls, 76.6 mmoles) was added to ethereal trichlorostannane (13.499g, 71.2 mmoles) without removal of the ethereal layer and a white precipitate began to appear within five minutes. The suspension was stirred over-night and filtered; the precipitate was washed with dichloromethane, filtered and dried in vacuo to give compound 4.1 (14.26g).

In the case of trichloroacetonitrile a yellow oil was also obtained but no pure product was isolable from this.

4.3. Discussion of Results

The complexity of ethereal trichlorostannane (chapter 2) leads to a variety of possible products from its reaction with nitriles (table 4.2) These depend largely on whether hydrogen chloride is also involved due to the equilibrium :

$$[(Et_2OH)^+]_2SnCl_4{}^{2-} \rightleftharpoons Et_2OH^+SnCl_3{}^- + HCl + Et_2O. \qquad (4.4)$$

Compound No. 4.1

Origin $MeC\equiv N + HSnCl_3$ (14.26g)

Name & Structure

see text

m.pt. 118-20

Elemental Analysis

		$RCN.HSnCl_3$
C	8.9	9.0
H	1.5	1.5
N	5.7	5.2
Sn	45.6	44.4
Cl	39.9	39.8

Empirical Formula $C_2H_4NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc.

3520m, 3470m, 3228m,b, 3100w/m,shl, 1672w/m, shl, 1635m, 1610m, 1510w, 1399m,b, 1349m, 1275m/s, 1120w, 1080w, 1030w, 958m, 880s, 740m, 535w/m, 431m/s, 318m/s

¹H N.M.R. d_6-DMSO; Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
2.02	t	16.8	4	-
2.62	s	-	2	Me
7.63	s,b	-	1	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	306	$[SnCl_4 + 44 + 2H's]^+$ or $[SnCl_3 + 82]^+$	9.3
43	$MeCNH_2^+$	100	315	$[SnCl_3+90]^+$, $[SnCl_4+55]^+$?	46
44	$C(NH_2)_2^+$, $CONH_2^+$	14	350	?	14
59	$MeC(NH_2)_2^+$	100	359	?	9.7
82	$(MeCN)_2$	31	395	?	9.0
84	$(MeCNH)_2^+$	8.1	465	?	3.0
120	Sn^+	32			
155	$SnCl^+$	69			
190	$SnCl_2$	16			
199	$[SnCl + 44]^+$	28			
225	$SnCl_3^+$	100			
234	$[SnCl_2 + 44]^+$	12			
260	$SnCl_4^+$	98			
269	$[SnCl_3 + 44]^+$	9			

Other Information ^{119}Sn Mössbauer (table 4.3, fig.4.3)

Compound No. 4.2	**Origin** EtC≡N + $HSnCl_3$	7.44g

Name & Structure

see text

m.pt. d 118-20

Elemental Analysis

		$RCN.HSnCl_3$	$RCN.2HSnCl_3$
C	7.0	12.8	7.1
H	1.0	2.2	1.4
N	2.5	5.0	2.8
Sn	51.3	42.2	46.8
Cl	37.9	37.8	41.9

Empirical Formula $C_2H_4NCl_4Sn_2$

Infra-red, ν cm⁻¹ KBr disc

3520m, 3445m, b, 3210m, b, 3120m, b, 1630m, shl, 1610m/s, 1550w, shl, 1450w, 1395m, 1368m, 1201m, 1055w, 1004w/m, 892s, 878m/s, 876m, 670m, 625w/m, 485m, b, shl, 414s, 399m, shl, 354m, 313m, 300w, shl; 280w, shl, 255m, shl

¹H N.M.R. d_6DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
0.87	t	7.0		CH_2
1.10	t	7.0		CH_2
2.97	m	4.0		
6.98	t	51.0		NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
29	$CH_3CH_2^+$	21	234	$[SnCl_2 + 44]^+$	11
36	HCl^+	91	281	$[EtCN + HSnCl_3]^+$	3.8
44	$C(NH_2)_2^+$, $CONH_2^+$	67	336	$[2EtCN + HSnCl_3]^+$	2.0
57	$EtCNH_2^+$	45			
71	$[EtC(NH_2)_2 -2H's]^+$	22			
85	$[(EtCN)_2H - CN]^+$	16			
97	$[(EtCN)_2H - N]^+$	21			
111	$(EtCN)_2H^+$	13			
120	Sn^+	91			
136	$SnNH_2^+$	14			
155	$SnCl^+$	11			
190	$SnCl_2^+$	100			
225	$SnCl_3^+$	5.5			

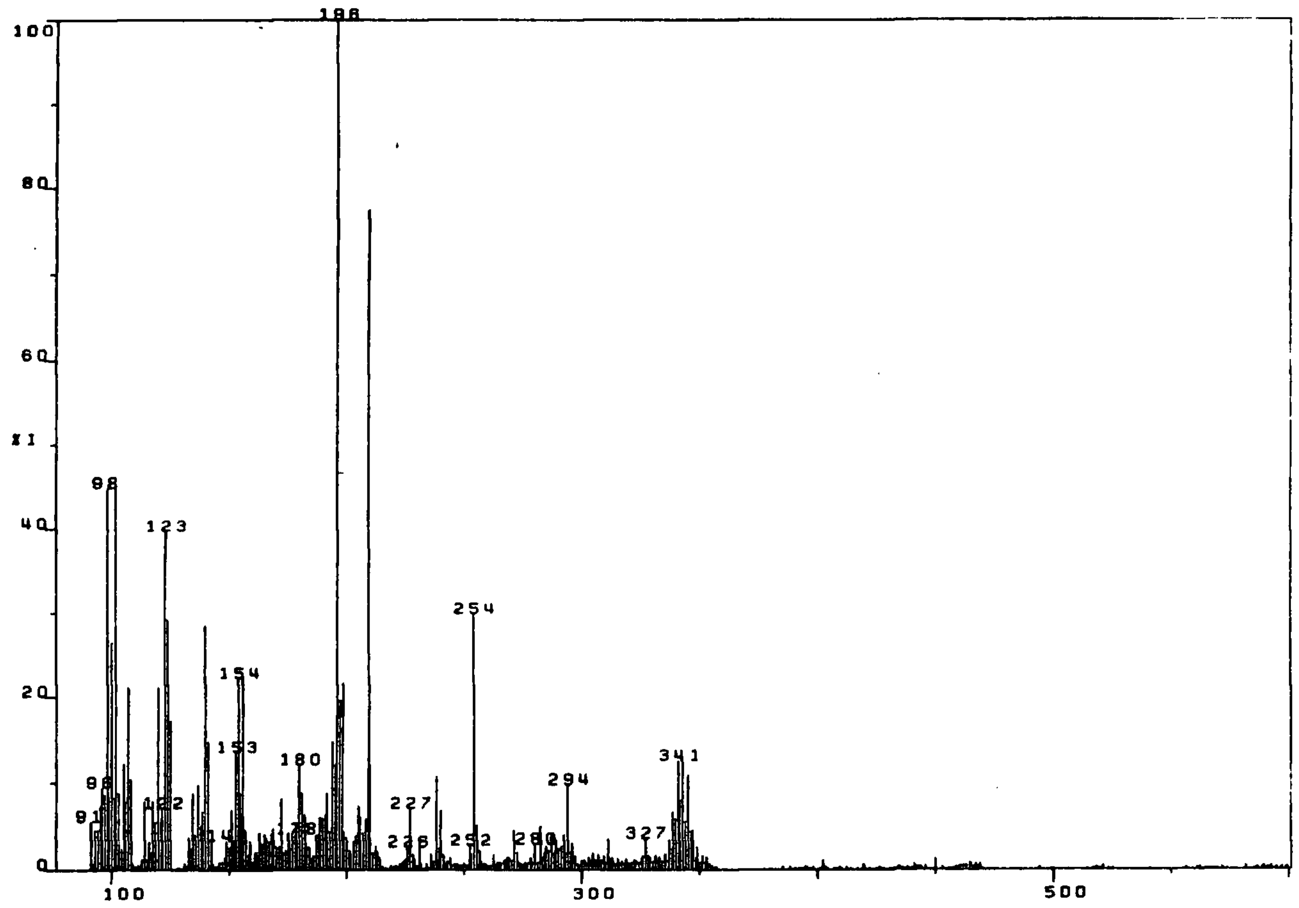
Other Information F.A.B. mass spectra (fig.4.1,table4.1) and ^{119}Sn Mössbauer (fig.4.3,table 4.3)

Table 4.1

F.A.B. Positive Mass Spectrum of Compound 4.2 (see Fig 4.1)

m/e	Fragment Ion	I	m/e	Fragment Ion	I
96	$EtC\equiv NCEt^+$	9.4	227	$[SnCl_3 + 2H]^+$	7.0
98	$[EtC=NCEt + 2H]^+$	45	238	Cl_3SnCH^+	11
108	$[(EtCN)_2 - 2H]^+$	10	254	Cl_3SnEt^+ or	30
120	Sn^+	21		$Cl_3Sn(CH)C=N^+$	
123	$[Sn + 3H]^+$	40	271	$Cl_2Sn(Et)C=NC=N^+$	4.5
140	?	29	282	$Cl_3Sn(Et)C=NH_2^+$	5.1
156	$[SnCl + H]^+$	22	294	$Cl_3Sn(Et)C\equiv NC^+$	9.6
180	?	12	311	$[Cl_3Sn(Et)C=NCNH_2 + H]^+$	3.5
190	$SnCl_2^+$	5.9	327	$[Cl_3Sn(Et)C=NCEt + 6H]^+$	3.5
196	?	100	341	$[Cl_3Sn(Et)C=NC(Et)=NH_2 + 4H]^+$	13
209	?	77			

Fig. 4.1 F.A.B. Mass Spectrum of the hydrostannation product of EtCN



Compound No.	**Origin**
4.3	$Bu^tC\equiv N$ + $HSnCl_3$ 7.74g

Name & Structure

see text

m.pt. d 190-5

Elemental Analysis		$RCN.HSnCl_3$	$RCN.HSnCl_3HCl$	$(RCH=NH_2)_2SnCl_6$
C	22.6	19.4	17.4	23.8
H	4.9	3.3	3.2	4.8
N	3.8	4.5	4.0	5.5
Sn	36.1	38.4	34.3	23.6
Cl	41.0	34.4	41.0	42.3

Empirical Formula $C_6H_{16}NCl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3305m/s, shl, 3220s, 3004w/m, 2960m, 2925w/m, shl, 2902w/m, shl, 2860w/m, shl, 2790w, shl, 1750w, shl, 1634m/s, 1544m, 1475m/s, 1455m/s, shl, 1400s, 1220w, 1179w, 1118m, 1080w/m, 1020w/m, 932w, 872s, 722w/m, 310s, 280m, 265w.

¹H N.M.R. d_6DMSO, Ext.TMS

δ ppm	**Mult.**	**J, Hz**	**Int.**	**Assign.**
0.83	s	-	18	Bu^t
0,85	t	9.0		?
7.03	t		6	NH
9.23	s	-	1	c

Mass Spectrum

m/e	**Fragment Ion**	**I**	**m/e**	**Fragment Ion**	**I**
36	HCl^+	100	260	$SnCl_4^+$	61
44	$C(NH_2)_2^+$ or $CONH_2^+$	100	269	$[SnCl_3 + 44]^+$	22
57	Bu^+	100	299	?	11
70	$BuCH^+$	100	308	$BuCNSnCl_3$	7.8
84	$BuCNH^+$	100	~349	?	3.8
98	$BuCN_2H^+$ or $BuCNHCH_2^+$	100			
120	Sn^+	79			
155	$SnCl^+$	100			
190	$SnCl_2^+$	100			
225	$SnCl_3^+$	100			

Other Information ^{119}Sn Mössbauer spectrum (table4.3,fig.4.4)

Compound No.	**Origin**
4.4	$Cl_3CC\equiv N$ + $HSnCl_3$ (0.48g)

Name & Structure

see text

m.pt. d158-60

Elemental Analysis

		$RCN.HSnCl_3$
C	8.9	6.5
H	1.8	0.3
N	5.4	3.8
Sn	28.5	32.0
Cl	51.9	57.4

Empirical Formula $C_2H_5NSnCl_4$

Infra-red, ν cm⁻¹ KBr disc fig.4.2

3500m, b, 3440m, b, 3180w/m, b,

1600m/s, 1393m/s, b, 410m/s, b, 314s

^{1}H N.M.R. d_6 DMSO, Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
7.23	t	51	1	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	225	$SnCl_3^+$	100
57	?	30	260	$SnCl_4^+$	80
66	?	88	269	$[SnCl_3 + C(NH_2)_2]^+$ or $[SnCl_3 + CONH_2]^+$	54
118	Cl_3C^+	60			
120	Sn^+	72	304	$[SnCl_4 + C(NH_2)_2]^+$ or $[SnCl_4 + CONH_2]^+$	11
136	$SnNH_2^+$ or $[Cl_3CNH_2 + 2H's]^+$	14	315	?	21
155	$SnCl^+$	100	351	?	7.5
190	$SnCl_2^+$	72			

Other Information ^{119}Sn Mössbauer (table 4.3, fig. 4.4)

Compound No.	**Origin**
4.5	$ClCH_2CH_2C\equiv N + HSnCl_3$ (3.54g)

Name & Structure

see text

m.pt.

Elemental Analysis

		$RCN.HSnCl_3$
C	12.3	11.4
H	1.1	1.6
N	2.3	4.5
Sn	47.1	37.6
Cl	39.3	44.9

Empirical Formula $C_6H_6NCl_6Sn_2$

Infra-red, ν cm⁻¹ KBr disc

3430m, b, shl, 3318m/s, b, shl, 3200s, b, 2910m, b, shl, 1684m/s, b, 1540m, b, shl, 1400s, b, 1280w/m, shl, 1260w, 1222w, 1174w, 1134w/m, 1086w, 986m, 960 w, 870m/s, 610w/m, 540w, 470w, b, 313s.

^{1}H N.M.R. d_6 DMSO, Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.15	m	-	3	
2.50	s, b	-	8	DMSO
2.93	t	3.0	6	CH_2
3.66	t	3.0	8	CH_2
6.99	t	51.5	8	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
28	$C_2H_4^+$	23	120	Sn^+	17
36	HCl^+	100	155	$SnCl^+$	70
44	$C(NH_2)_2^+, CONH_2^+$	11	190	$SnCl_2^+$	36
57	$CH_2CH_2CNH_3^+$	4.0	225	$SnCl_3^+$	100
63	$ClCH_2CH_2^+$	3.1	260	$SnCl_4^+$	27
73	?	11	317	$[ClCH_2CH_2CNHSnCl_3 + 2H's]^+$	3.0

Other Information ^{119}Sn Mössbauer (table 4.3, fig. 4.4)

Compound No. 4.6

Origin PhC≡N + HSnCl$_3$ (5.85g)

Name & Structure

see text

m.pt. 180-2

Elemental Analysis

		RCN.HSnCl$_3$	(RCH=NH$_2$)$_2$SnCl$_6$
C	26.1	25.5	30.9
H	2.5	1.8	2.9
N	4.6	4.3	5.1
Sn	35.1	36.1	21.9
Cl	38.5	32.3	39.1

Empirical Formula $C_7H_8NCl_3Sn$

Infra-red, ν cm⁻¹ KBr disc

3336m, 3240m, 3190m, 3040w/m, shl, 1692m/s, 1624m, 1593m/s, 1576m, 1531m, 1502m, shl, 1492m, shl, 1446m, 1399m, 1327m, 1310m, 1219s, 1209m, shl, 1187 m/s, 1162m/s, 1119m, 1080w/m, 1057m, 1024w, 998w, 972w, 932w, 842m, 820s, 784s, 749m, 690m/s, 660m, 650m, shl, 579w/m, 447m, 420m, 306s, 283m/s

¹H N.M.R. d$_6$DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
7.21	t	51.6	6	NH
7.57		-		
7.66	series		20	Ph
7.80	of	-		
8.17	m	-		
9.04	s	-	2	c?
10.04	s	-	3	c?

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl$^+$	100	155	SnCl$^+$	14
44	C(NH$_2$)$_2$$^+$, COHN$_2$$^+$	19	190	SnCl$_2$$^+$	7.8
51	(CN)$_2$-1$^+$ or C$_4$H$_3$$^+$	100	225	SnCl$_3$$^+$	20
77	Ph$^+$	100	260	SnCl$_4$$^+$	4.5
105	PhCNH$^+$	100	290	?	2.1
120	Sn$^+$	3.1	305	?	3.0
136	SnNH$_2$$^+$	13			

Other Information ^{119}Sn Mössbauer (table 4.3, fig. 4.4)

Compound No. 4.7	**Origin** $PhCH_2C\equiv N$ + $HSnCl_3$ (5,25g)

Name & Structure

see text

m.pt. 128 -30

Elemental Analysis

		$RCH.HSnCl_3$	$(RCH=NH_2)_2SnCl_6$
C	34.5	28.0	33.6
H	3.5	2.3	3.5
N	5.1	4.1	4.9
Sn	36.3	34,6	20.8
Cl	31.0	31.0	37.2

Empirical Formula $C_{10}H_{12}NCl_3Sn$

Infra-red, ν cm⁻¹

3520m, b, 3440m, b, 3225m, 3100m, 1630m/s, 1610m/s, 1483m, 1449w, 1400w/m shl, 1377m, 1337w/m, 1201w/m, 1189m, 1150w 1110w, 1074w, 1027w, 1000w, 930m, 920w/m shl, 909w/m, 878 s, 752m/s, 701s, 535w, 474m, 409m/s, 314m, 290m/s

¹H N.M.R. d_6DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
4.44	s	-	4	CH_2
7.67	s,b	-	3	Ph

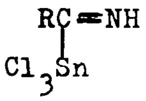
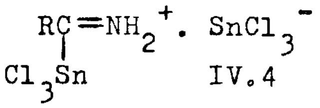
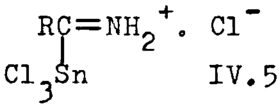
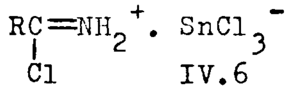
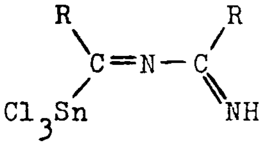
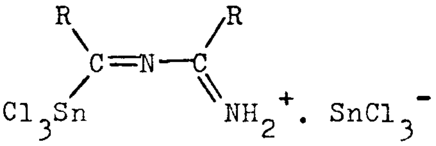
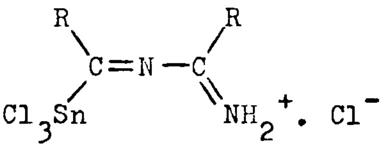
Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	32	155	$SnCl^+$	14
51	$C_4H_3^+$	81	190	$SnCl_2^+$	4.3
77	Ph^+	12	225	$SnCl_3^+$	18
91	$PhCH_2^+$	41	341	$[PhCH_2CNSnCl_3-H]^+$	13
117	$PhCH_2CN^+$	100	420	?	24
120	Sn^+	6.0	471	?	12

Other Information

Table 4.2

Possible Products of the Reaction between $RC\equiv N$ and $SnCl_2/HCl/Et_2O$

Product	Derivation
 $RC(SnCl_3)=NH$ IV.3	Hydrostannation of the nitrile bond.
 $RC(SnCl_3)=NH_2^+ . SnCl_3^-$ IV.4	Addition of $HSnCl_3$ to IV.3
 $RC(SnCl_3)=NH_2^+ . Cl^-$ IV.5	Hydrochlorination of IV.3
 $RC(Cl)=NH_2^+ . SnCl_3^-$ IV.6	Hydrochlorination followed by addition of $HSnCl_3$
 IV.7	Addition of $HSnCl_3$ to two molecules of RCN
 IV.2 	Dimerisation reactions
$(RCH=NH_2)_2^+ . SnCl_6^{2-}$ IV.8	See ref. 15

The practical results will now be discussed to differentiate which of the above possibilities are most feasible.

4.3.1. Infra-red Spectra

The solid product from trichloroacetonitrile, 4.4, is of particular interest as it has no alkyl or aryl groups to complicate its spectrum (fig. 4.2). It is therefore a useful reference for the following discussion.

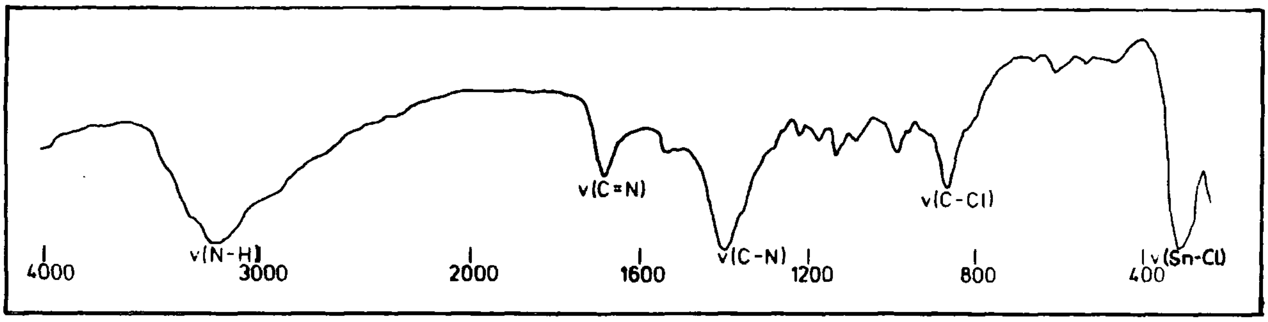


Fig. 4.2. Infra-red Spectrum of the Hydrostannation Product of $Cl_3CC\equiv N$

The most noticeable observation from the infra-red spectra is the loss of the nitrile peak $v(C\equiv N)$ (2230-2220 cm^{-1}) accompanied by the development of an azomethine absorption $v(C=N)$ (1692-1471 cm^{-1}), thus indicating that hydrostannation has occurred across the nitrile group. Compounds 4.1, 4.2, 4.6 and 4.7 each have two peaks in the azomethine region, the others have one. The latter could have a second peak hidden under the broadness of the first one. Aromatic absorptions are also present in this region to add further complications for 4.6 and 4.7 where R is Ph and $PhCH_2$. If the products are dimeric in nature, IV.2, [3] then one would indeed expect two such peaks.

However, δ(N-H) absorptions are also present in this region (1655-1515 cm^{-1}) but are characteristically weaker than $v(C=N)$ and may therefore be hidden.

The spectra all have at least two peaks in the region 3300-3100 cm^{-1} showing v(N-H) vibrations to be present, possibly from iminium salts. By comparison(N-methyl) diphenyl methylene ammonium trichlorostannate (chapter 3) has N-H stretching vibrations at 3060 and 3180 cm^{-1}. All of the compounds (except 4.3 and 4.4) have one or two additional peaks of weak to medium intensity between 3550 and 3400 cm^{-1} which may be attributed to v(N-H) of an amine or amide group.

Each spectrum also has a peak at 1400 cm^{-1} for v(C-N) as expected for the dimeric species (IV.2)

There is also a peak between 900 and 850 cm^{-1} (except for 4.6) possibly indicating a carbon-chlorine bond. It is therefore possible that hydrochlorination may have also taken place.

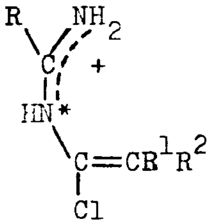
Finally a strong peak between 315 and 310 cm^{-1} appears in all of the spectra for v(Sn-Cl) [22]. Compounds 4.6 and 4.7 have an additional peak between 290 and 280 cm^{-1} representing a second tin-chlorine vibration. This second peak may be hidden in the spectra of the other compounds.

In conclusion the spectra show all the expected features for hydrostannation across the nitrile group. They give some, but not conclusive evidence for the dimeric salts.

4.3.2. ^{1}H. N.M.R. Spectra

The proton n.m.r. spectra were run in deuterated dimethyl sulphoxide due to solubility problems with all other solvents tried. There are two main observations from the spectra:

Firstly, all of the spectra exhibit a triplet of equal intensity peaks centered at approximately 7 ppm with the exception of compound 4.7, ($R = PhCH_2$) where it has spread out to a broad singlet of low intensity. The triplet is due to proton-nitrogen coupling (^{14}N has a spin of one) and only occurs if the rate of proton exchange is slower than the n.m.r. time scale. Also the nuclear quadrupole of ^{14}N increases the relaxation time which results in broadening and coalesence of the lines [23, 24] . The magnitude of the coupling constants (51-52 Hz) is comparable with values between 40 and 68 Hz for dialkylamines and tertiary alkylammonium salts [25, 26] and values of approximately 52Hz for the dimeric species IV.3 [3]. The analogous dimers from the chlorination of nitriles have three broad equal intensity signals in this region for the protons of the iminium group ($C{=}NH_2^+$) [16] In contrast the n.m.r. spectrum of (N-methyl) diphenyl methylene ammonium trichlorostannate, $Ph_2C{=}NHMe^+.SnCl_3^-$, also in d_6 DMSO, does not show proton-nitrogen coupling. Low field singlets between 9.25 and 10.25 ppm [16] in the hydro-chlorination dimers are attributed to a proton attached to the central nitrogen atom (*) of the delocalised system, IV.9.



IV.9

Singlets in the correct region are observed for some of the compounds and are denoted by a subscript (c) in the data tables still giving rise to the possibility of dimeric species.

Secondly, each n.m.r. spectrum exhibits peaks for just one type of R group (R = alkyl, aryl) which suggests that the products are monomeric rather than dimeric (where two sets of peaks would be expected for the R groups in two different environments).

4.3.3. Elemental Analysis

The elemental analyes are not particularly helpful in establishing trends of products in the series of nitriles studied but give evidence for mono and diadducts as well as products incorporating extra molecules of hydrogen chloride. Also hexachlorostannates are possible for compounds 4.3, 4.6 and 4.7. One possible reason for the poor results is that even after stringent washing and purifying methods the products are not 100% pure as indicated by the number of peaks in the Mössbauer spectra. For the interpretation of each product individually, see the data table concerned.

4.3.4. Mass Spectra

Mass spectroscopy is particularily useful in characterising chloro-tin compounds as tin has ten naturally occuring isotopes and chlorine has two. Therefore, fragments containing tin and chlorine have characteristic isotope patterns (fig. 4.3)

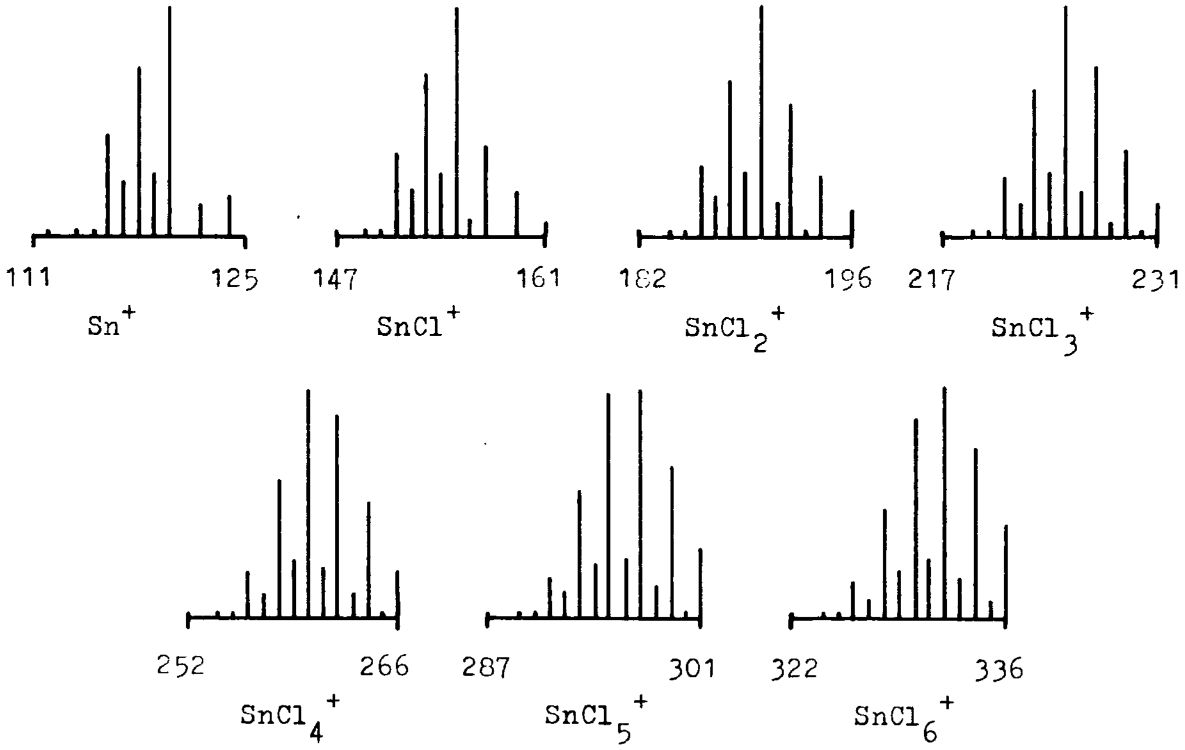


Fig. 4.3

The figures quoted in the data tables refer to the most intense peak of the group. Peaks for $SnCl_x$ (x = 1-3) show that the trichlorostannane unit is present in all compounds. In addition they all (except 4.2) exhibit a peak at m/e 260 for $SnCl_4^+$ due to recombination in the spectrometer.

$$SnCl_3^+ \xrightarrow{+Cl^-} SnCl_4 \xrightarrow{-e} SnCl_4^+ \qquad (4.5)$$

There is no evidence for $SnCl_6^+$ or $SnCl_5^+$ which would be expected if the stannic aldimonium chlorides, $(RCH{=}NH_2)_2SnCl_6$ had been formed [15]. The mass spectra strongly suggests that the compounds (from the nitrile RCN) may be dimeric due to peaks which may be assigned to $[C(NH_2)_2]^+$, $[R + C(NH_2)_2]^+$, $[SnCl_x + C(NH_2)_2]^+$, (X = 1-3), $(RCN)_2^+$ and various fragments of the dimer backbone. The spectra for the methyl and ethyl derivatives are particularily good examples. This is confirmed by the F.A.B. spectrum of compound 4.2 (fig. 4.1 and table 4.1) . The unassigned high mass peaks may be due to ion-ion or ion-molecule recombination within the mass spectrometer.

4.3.5 ^{119}Sn Mössbauer Data

The Mössbauer data are tabulated below (table 4.3) and illustrated in figure 4.4.

Table 4.3

^{119}Sn Mössbauer Data of Compounds 4.1 to 4.6

Compound	Isomer Shift, *	Tin Oxidation State	Quadrupole Splitting, *	Area %
4.1	0.527 ± 0.017	4	0.0	19.04
	0.899 ± 0.007	4	2.220 ± 0.007	41.58
	3.800 ± 0.016	2	0.0	19.17
	4.342 ± 0.017	2	0.0	20.21
4.2	0.889 ± 0.017	4	1.988 ± 0.017	30.98
	3.814 ± 0.037	2	0.0	35.15
	4.320 ± 0.032	2	0.0	33.87
4.3	0.579 ± 0.004	4	0.0	84.32
	4.133 ± 0.022	2	0.0	15.68
4.4	0.593 ± 0.002	4	0.0	100
4.5	0.286 ± 0.005	4	-	29.24
	2.399 ± 0.025	2	-	34.11
	2.831 ± 0.024	2	-	36.65
4.6	0.586 ± 0.014	4	0.0	73.77
	4.037 ± 0.045	2	0.0	26.23

* mm sec^{-1}

The expected Mössbauer features for the possible products IV.2 to IV.8 (table 4.2, page 142) are listed below (table 4.4).

Table 4.4

Expected Mössbauer Features for the Possible Hydrostannation of Saturated Nitriles

Compound(s)	Tin Oxidation State	δ, mm sec^{-1}
A IV.6	2	>2.7
B IV.3, IV.5, IV.7, IV.8	4	<2.7
C IV.2 + IV.4	2	>2.7
	+ 4	+ <2.7

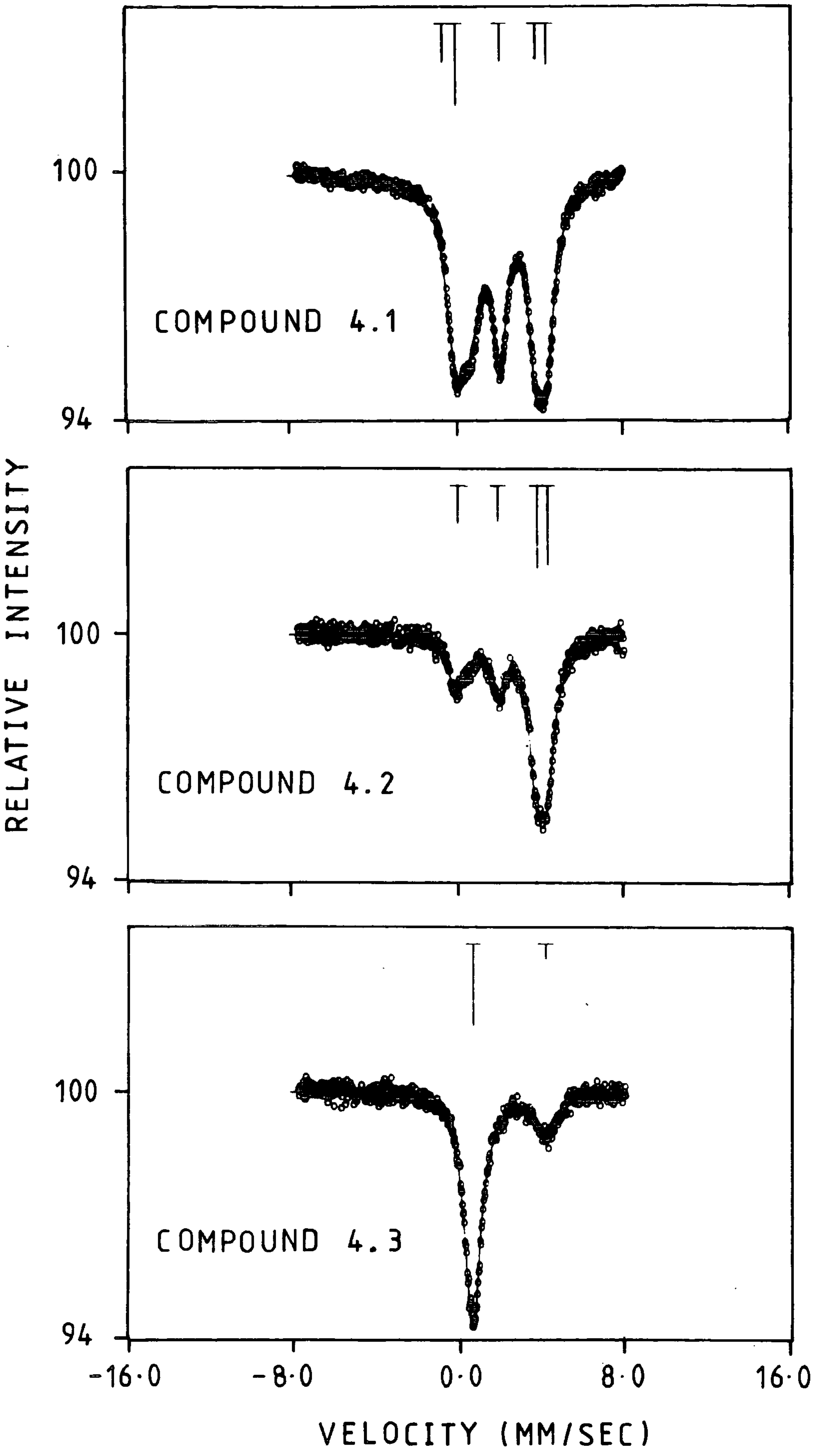


Fig. 4.4. Mössbauer Spectra of Compounds 4.1 to 4.6.

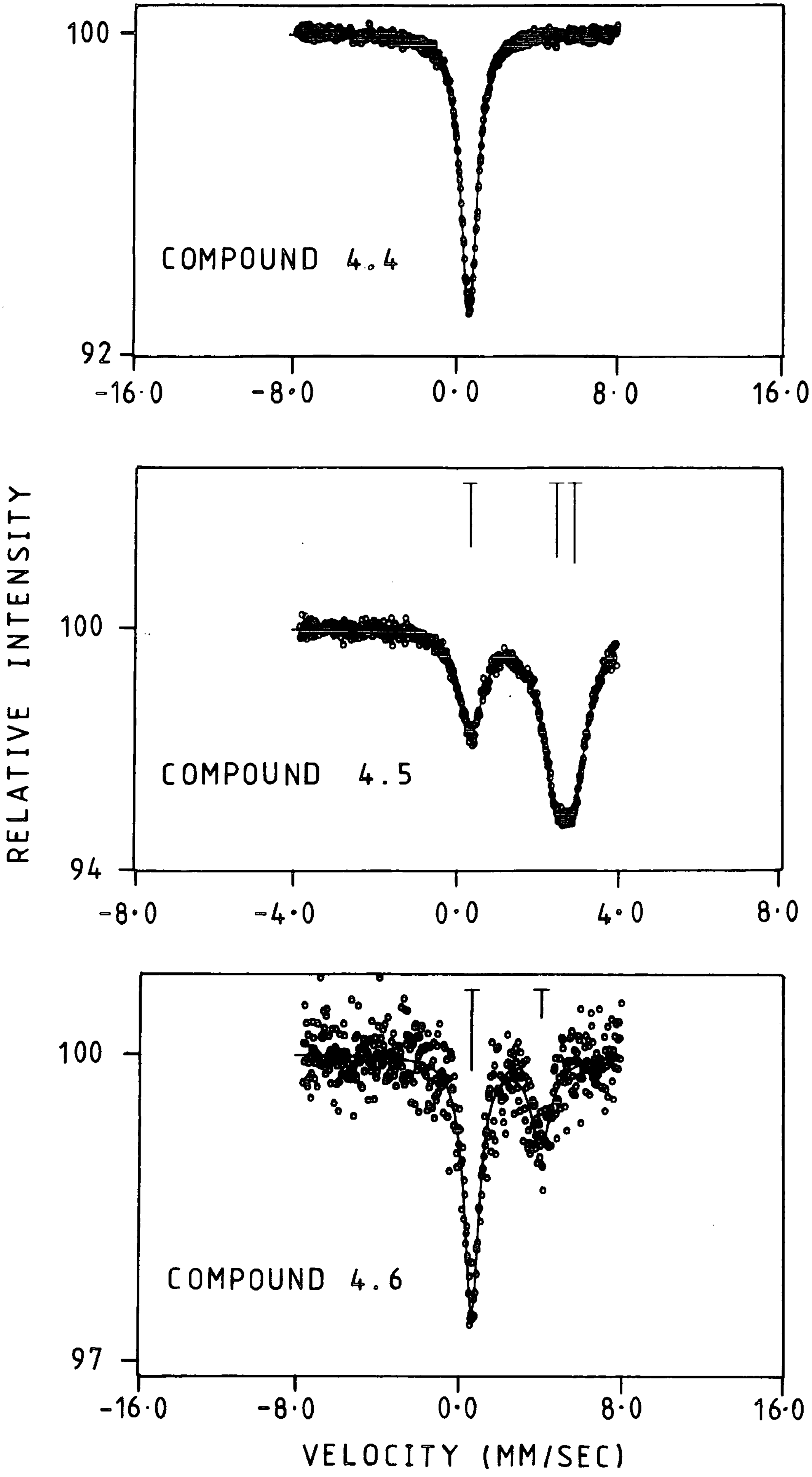


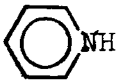
Fig. 4. 4- continued.

Compound 4.4 (from trichloroacetonitrile) gave a single peak (δ = 0.593 mm sec^{-1}) which implies that the trichlorostannane group has become covalently bonded to the nitrile (IV.3, IV.5 and IV.7) or that the hexachlorostannate (IV.8) has been formed. Likewise, the products from acetonitrile, trimethyl acetonitrile and benzonitrile gave peaks at very close shifts to that of the trichloroacetonitrile product indicating similar structural features. In addition the trimethyl acetonitrile and phenyl compounds gave a second, much weaker peak in the region for a trichlorostannate ion which implies that the samples were slightly impure or had begun to decompose. The spectrum for the methyl derivative is more complex and therefore more difficult to interpret. Both the methyl and ethyl derivatives exhibit a doublet (centered at 0.899 and 0.889 mm sec^{-1} respectively) and two singlets (at 3.800, 4.342 and 3.814, 4.320 mm sec^{-1} respectively). It is possible that the two doublets may each represent another of the alternatives in group 'B' (table 4.4) or that along with one of the high shift peaks may represent one of the possibilities of group 'C'. The other high shift peak suggests a trichlorostannate anion, most probably with an imminium cation, for example IV.6, as an impurity. The data for compound 4.5 are inconsistant with those for the rest of the compounds implying that 2-chloro-propionitrile may have reacted differently. For comparison table 4.5 shows isomer shift values of a few relevant, known compounds.

The quadrupole splitting, which depends on the spatial arrangement of the ligands on the tin atom, implies that in the majority of the compounds (4.1 to 4.6) the ligands are symetrically displaced (Δ = 0 mm sec^{-1}). Therefore the hexachlorostannate, IV.8, would be the best assignment. The elemental analyses of the trimethyl acetonitrile

Table 4.5

^{119}Sn Isomer Shifts, δ, of some Related Compounds [40]

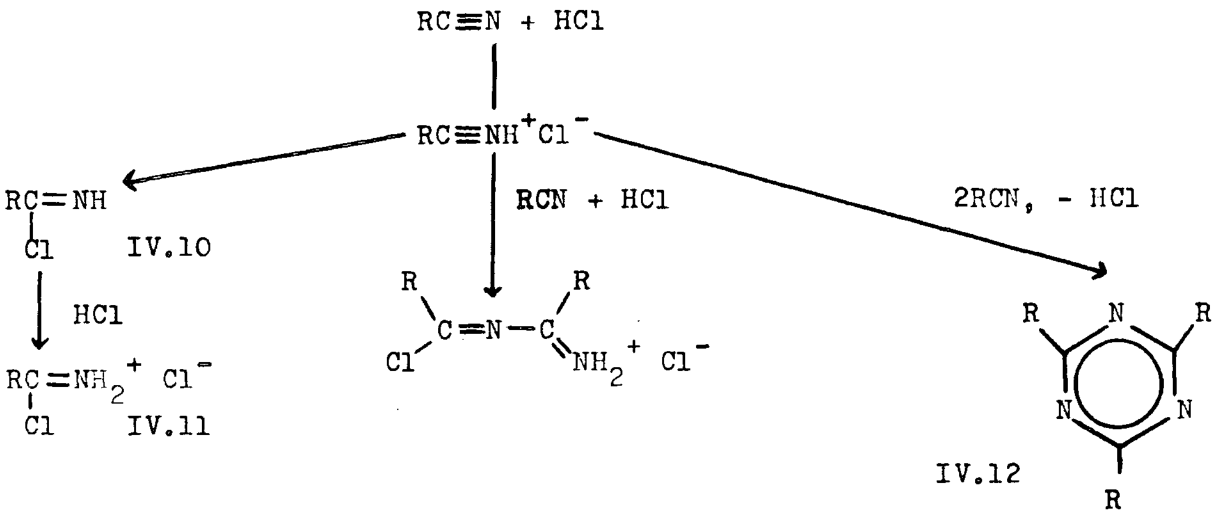
Compound	δ, mm sec^{-1}*	Ref.
$SnCl_4$	0.85	[28, 29]
$BuSnCl_3$	1.31 1.38	[30] [31]
$PhSnCl_3$	1.31 1.47 1.27 1.10	[30] [32] [33] [34]
$H^+_2\ SnCl_6^{2-}$	0.5	[35, 36]
$(Et_4N)^+_2 .\ SnCl_6^{2-}$	0.5	[36]
$Et_4N^+ .\ SnCl_3^-$	3.43 3.47	[36] [37]
 $NH^+ .\ SnCl_3^-$	3.02	[38]
$Cs^+SnCl_3^-$	3.69	[36]
$SnCl_2$	4.06 4.07	[38] [39]
$SnCl_2.2H_2O$	3.55	[29]

* Relative to SnO_2. A correcting term of +2.10 mm sec^{-1} was used where the original references used a grey (α) tin source [40].

and possibly the phenyl and benzyl derivatives do support this but there is no evidence from the mass spectra. It is also possible for a very small quadrupole splitting, or none at all, to occur when either none or all of the atoms attached to the tin atom contain a lone pair of electrons [27].

4.4 General Discussion

In general, the results for the above set of compounds imply that they are monomeric species. Products believed to be dimeric have been obtained [3] by passing hydrogen chloride gas into a suspension of tin dichloride in excess nitrile (acting as solvent as well as reactant) for six to twelve hours. The analogous chlorine dimers were formed by addition of excess hydrogen chloride to the nitrile [16]. By preparing ethereal trichlorostannane in diethyl ether and then adding the nitrile the latter is not exposed to prolonged hydrochlorination which may account for the lack of dimerisation. There may, however, be a small excess of hydrogen chloride in the ethereal trichlorostannane, for example in any ether which has not been removed from the vessel before addition of the nitrile. This could cause a low yield of the dimeric salt which may show up in the spectroscopic studies depending on their sensitivity. This explains why there is little evidence for dimerisation in the n.m.r. spectra, in which solubility difficulties were experienced, and substantial evidence in the mass spectra which would divulge the slightest impurity. Possible products are listed in table 4.2. For comparison the hydrochlorination of nitriles is summarised in scheme 4.2.



Scheme 4.2

If dimerisation is difficult then trimerisation of the nitrile IV.12 or tin containing trimers are even less likely. The imine trichlorostannane $RC(SnCl_3)=NH$ (IV.3) is unlikely for three reasons:

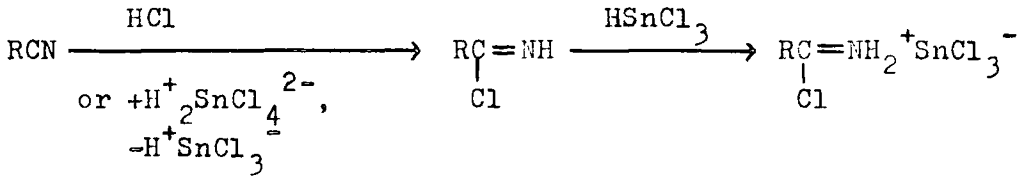
(i) In the analogous hydrochlorination reaction the imine IV.10 readily undergoes further hydrochlorination to the iminium salt, IV.11.

(ii) Integration values for the triplets representing protons attached to the nitrogen atom imply more than one proton, in the tin containing product.

(iii) The v(N-H) region in the infra-red spectra of the compounds 4.1. to 4.7 is too complex, although if a mixture of products is present then this would not be too significant.

Products involving the addition of HCl as well as $HSnCl_3$ to the nitrile are also possible IV.5 and IV.6. This is feasible if any of the hydrogen chloride is utilised in this way, rather than leading to dimerisation. Also it is possible that the intermediate species is in fact ethereal dihydrogen tetrachlorostannate, $H_2SnCl_4.2Et_2O$, (Chapter 2) which may be considered to afford addition of $HSnCl_3$ and HCl. The mass spectra all exhibit a peak for HCl^+ but there are none for $(RCN + HCl)^+$ with correct isotope patterns for chlorine.

Hydrochlorination followed by hydrostannation is therefore unlikely to occur.



$$RCN \xrightarrow[\text{or } +H^+{}_2SnCl_4{}^{2-},\ -H^+SnCl_3{}^-]{HCl} R\underset{Cl}{C}=NH \xrightarrow{HSnCl_3} R\underset{Cl}{C}=NH_2{}^+SnCl_3{}^- \qquad (4.6)$$

However the infra-red spectra do suggest the possibility of carbon-chlorine bonds.

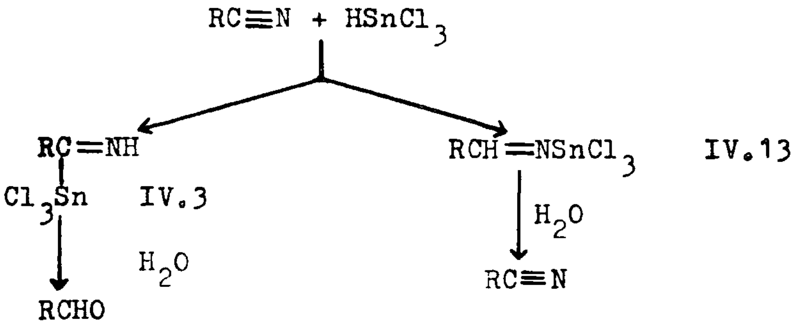
Upon hydrolysis and exposure to the air the hydrostannation product of chloroacetonitrile gave a semicrystalline product (4.8.) (after evaporation) of which the infra-red spectrum is tabulated below.

Table 4.6

Infra-red Spectrum of Compound 4.8

Frequency, cm^{-1}	Assignment
3300(shl,m)	v(N-H)
3205(s)	
1398(s)	v(C-N)
314(s)	v(Sn-Cl)

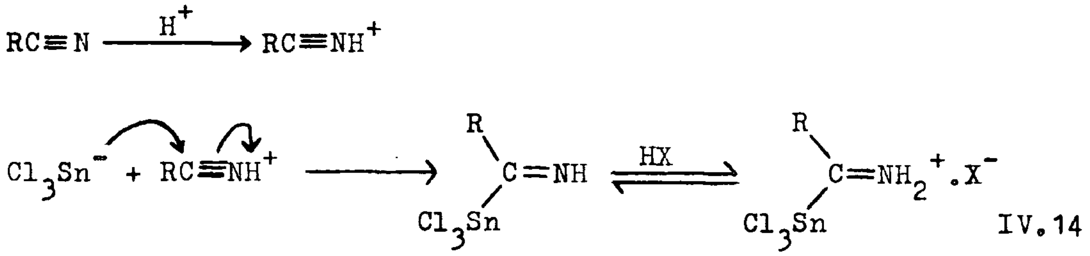
It is noticeable that peaks for v(C═N) (1689-1471cm^{-1}) and v(C-Cl) (850-550cm^{-1}) have disappeared. The liquid part gave very broad peaks in the v(O-H) regions making it difficult to obtain any conclusive results. One would expect that upon characterisation of the hydrolysis product one would be able to deduce the direction of hydrostannation of the nitrile functional group, as illustrated schematically below.



Scheme 4.3

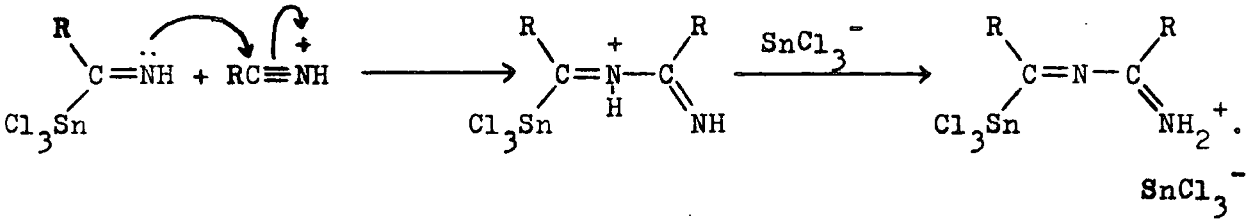
Alternatively, bromination of the hydrostannation product would cleave the carbon-tin bond (IV.3) to give a brominated alkyl derivative which could be characterised. In the case of compound IV.13 a complex organotin product would be formed which would be difficult to hydrolyse and identify.

The hydrostannation reaction is therefore very complex as there are so many possible reaction pathways involving ethereal trichlorostannane and/or hydrogen chloride. The reaction has already been discussed in terms of the possible intermediate dihydrogen tetrachlorostannate. It is highly probable that the reaction will not proceed in one direction only as indicated by the number of Mössbauer peaks for each compound and by the difficulty in fitting the elemental analysis. Formation of the imminium salt (IV.14) is represented by scheme 4.4:



Scheme 4.4

The dimerisation mechanism [3] is given in scheme 4.5:



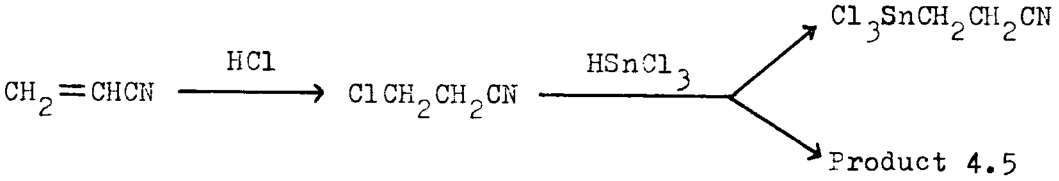
Scheme 4.5

It is apparent that the presence of excess hydrogen chloride is necessary for dimerisation to proceed. Three new nitriles have been examined, namely trichloroacetonitrile, 2-chloropropionitrile and phenylacetonitrile. Trichloroacetonitrile was used because it would be a useful reference compound having no organic substituents at the α carbon atom which would complicate the spectra. Also the effect of the electronegativily of the nitrile substituent may be observed

$Cl_3\overset{\alpha}{C}\text{-}CN$; $H_3C\text{-}CN$; $Me_3C\text{-}CN$.

The very electronegative chlorine atom should render the nitrile carbon atom more susceptible to nuclephilic attack. This may account for the yellow oil formed as well as the white powder which was isolated. Conversely, the methyl and tertiary butyl groups which are more electron donating should discourage nucleophilic attack.

The hydrostannation of 2-chloropropiontrile was performed for comparison with the acrylonitrile system (next chapter) as the presence of hydrogen chloride may affect the hydrostannation of acrylonitrile as shown below.



(4.7)

Phenylacetonitrile, along with benzonitrile, was studied to examine the potential to cause orthometallation via the products of hydrostannation, which is discussed in chapter 3.

4.5. Conclusion.

The hydrostannation of saturated nitriles results in conversion of the nitrile to an azomethine group. It is a complex reation and may lead to a range of products including iminium salts and dimeric species depending on the reaction procedure and the presence of excess hydrogen chloride. In the experimental work for this chapter a modified, much shorter, method has been developed leading to easily handled, relatively stable white powders in good yields. The range of nitriles studied has been extended by trichloroacetonitrile, 2-chloropropionitrile and phenylacetonitrile.

CHAPTER 5

2-CYANOETHYLTIN TRICHLORIDE

5.1 Introduction

Acrylonitrile has two possible sites for hydrostannation. Exploratory work has shown that addition occurs predominantly across the alkene bond, without affecting the nitrile group, to form 2-cyanoethyltin trichloride, (CETTC) [1,2] (V.1).

$$CH_2{=}CHC{\equiv}N + HSnCl_3.xEt_2O \longrightarrow \underset{\text{(V.1)}\quad\text{CETTC}}{Cl_3SnCH_2CH_2C{\equiv}N} + xEt_2O \tag{5.1}$$

The only record of CETTC in the literature is as a side product (under 3%) of the reaction between acrylonitrile, hydrogen chloride and tin in ether, the major product being the dialkyltin dichloride (V.2) [3].

$$HCl + Sn + CH_2{=}CHC{\equiv}N \xrightarrow{\text{15 hrs}} \underset{\substack{14\% \\ \text{V.2}}}{Cl_2Sn(CH_2CH_2C{\equiv}N)_2} + \underset{3\%}{Cl_3SnCH_2CH_2C{\equiv}N} \tag{5.2}$$

The analogous bromide has been prepared by brominating the triphenyl derivative [4,5] and by heating $Sn(CH_2CH_2CN)_4$ to 105°C for five hours [6,7] with $SnBr_4$.

Each molecule of CETTC contains a Lewis base nitrile unit and a Lewis acid alkyltin trichloride unit. This offers scope for some interesting coordination chemistry.

This chapter is therefore divided into four sections,

(1) Preparation and characterisation of CETTC.

(2) Coordination chemistry of CETTC.

(3) Mechanistic studies.

(4) Investigation into alternative products from the hydrostannation

of acrylonitrile including the analogous bromine system and the effect of Grignard reagents on CETTC.

5.2 THE PREPARATION AND CHARACTERISATION OF CETTC

5.2.1. Experimental

Excess acrylonitrile (22.0 mls, 334.4 mmoles) was added to ethereal trichlorostannane (14.80g, 78.3 mmoles), after removal of the ethereal layer, and stirred at room temperature for 48 hours to produce a yellow liquid. The volatile components were removed by vacuum transfer without heating, to leave crude CETTC, a pale yellow solid, which was recrystallised (10.24g, 44%) from warm toluene (60 mls). Overheating was avoided to reduce side reactions.

5.2.2. Characterisation of CETTC

Elemental Analysis

Found; C = 12.9%; H = 1.6%; N = 4.5%; Cl = 39.0%; $C_3H_4Cl_3NSn$ requires; C = 13.0%; H = 1.4%; N = 5.0%; Cl = 38.1%.

m.pt. 108-110°C
107-108°C [1].

Infra-red, v, cm^{-1}, nujol mull

3400w,b, 2950s, 2850s, 2278m, 1650w/m, 1592m, 1455m/s, 1405m, 1378m, 1310m, 1240w, 1162m, 1140m, 1010m, 910m, 888m, 720m, 690m/s, 625w/m, 530w, 470m.

Far infra-red, v, cm^{-1} [2].

387w/m, 383m, 375m, 369m/s, 365m, 350m, 338w, 320m/s, 313vs, 309vs, sh, 287w/m, 270w/m, 247vw, 233vw, 219vw, 217vw, 212vw, 203vw, 176vw, 170w, 154w, 150w, 136w, 132w, 114vw, 100vw, 84vw, 72m/s.

Raman v, cm^{-1} [2]

2279vs, 1422vw, 1165s, 1412vw, 1025w, 920vw, 633s, 616vw, 580vw, 472m, 357vs, 321m/s, 290vw, 275vw, 239w, 162w/m, 132m, 96w, 83w, 37s.

^{1}H N.M.R.

Table 5.1

^{1}H N.M.R. Spectrum of CETTC

Solvent	Chemical Shift, ppm^a Attributable to αCH_2	Coupling Hz	Chemical Shift, ppm^a Attributable to βCH_2	Coupling Hz
d_6DMSO (b)	1.54 (t)	7.0	2.67 (t)	7.0
d_6DMSO [1]	1.73 (t)	8.5	2.73 (t)	8.5
$CDCl_3$ [1]	2.51 (t)	8.0	2.00 (t)	8.0
$CDCl_3$ [2]	2.95 (t)		2.46 (t)	

(a) Relative to TMS (external). (b) Spectrum run on two samples to check authenticity with respect to that recorded by P.G.Huggett [1] and M.A.I. El Erian [2].

^{13}C N.M.R.

Table 5.2

^{13}C N.M.R. Spectrum of CETTC, d_6DMSO acting as both reference and solvent

Chemical Shift ppm	Character	Assignment
13.81	s	α CH_2
39.59	m	βCH_2 + DMSO
121.92	s	$C\equiv N$

^{119}Sn N.M.R.

Singlet at δ 462.97 ppm in DMSO (Me_4Sn reference).

Mass Spectrum

Table 5.3

Mass Spectrum of CETTC

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	40	190	$SnCl_2^+$	41
54	$CH_2CH_2CN^+$	25	225	$SnCl_3^+$	63
120	Sn^+	27	245	$Cl_2SnCH_2CH_2NH^+$	67
155	$SnCl^+$	99	280	$Cl_3SnCH_2CH_2CNH^+$	19

X Ray Crystal Structure [8] Fig. 5.1

$C_3H_4Cl_3NSn$, M = 279.12, orthorhombic, a = 10.602(4), b = 6.418(3), c = 11.738(5) Å, U = 799(1) $Å^3$, Z = 4, Dc = 2.320(3)Mg m^{-3}, F(000) = 520 space group Pna2, Mo $K\alpha$ (λ = 0.71069A).

5.2.3. Discussion of Results

CETTC has been prepared by a slightly modified method compared to previous work [1,2]. Its characterisation has been discussed extensively [1,2]. It is therefore only necessary here to consider points of relevence to the remaining sections of this chapter. The ^{13}C and ^{119}Sn n.m.r spectra and the crystal structure supply new data so are discussed in more depth.

The infra-red and ^1H n.m.r. spectra each contain peaks attributable to methylene groups and give no evidence for any remaining alkene bond. The infra-red spectrum has a single peak at 2278 cm^{-1} for v(C≡N). The mass spectrum contains a parent ion at m/e 280 for the protonated molecule in addition to peaks representing the breakdown of the trichlorostannane and cyanoethyl groups.

The ^{13}C n.m.r. spectrum has three peaks, as assigned in table 5.2. The results are comparable to the shift values tabulated below:

Table 5.4

^{13}C N.M.R. Shift values for comparison with those of $Cl_3Sn\overset{\beta}{C}H_2\overset{\alpha}{C}H_2C{\equiv}N$

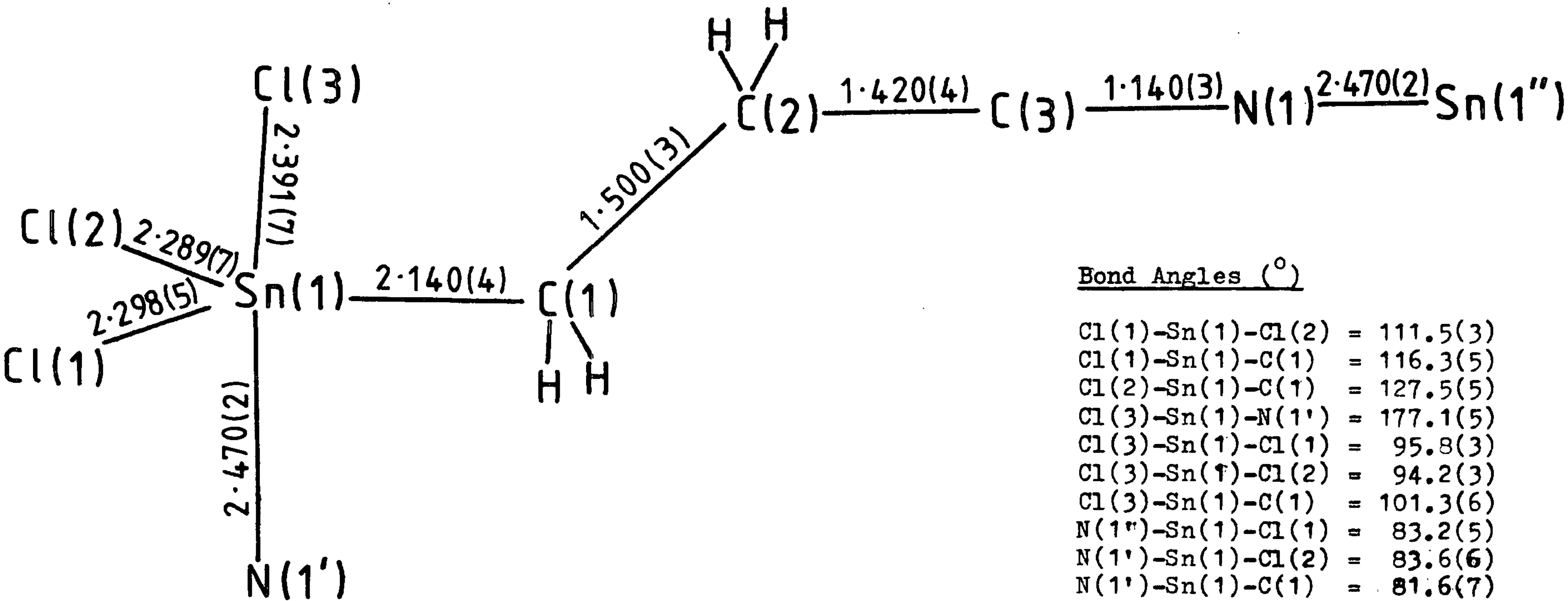
Compound	Chemical Shift	Ref.
$\overset{a}{C}H_2{=}\overset{b}{C}H\overset{c}{C}{\equiv}N$	a 137.5 b 108.1 c 117.5	[9]
$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}{\equiv}N$	a 10.6 b 10.8 c 120.8	[9]
$Cl_3Sn\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_3$	a 33.7 b 26.7 c 25.4 d 13.1	[10]

The nitrile carbon chemical shift (121.92 ppm) has only marginally increased demonstrating that the metal atom has little effect. The peak at 13.81 ppm may be assigned to the α carbon atom of CETTC by comparison with the value for the α carbon atom of ethyl cyanide. Similarily the β carbon resonance may be assigned by comparison with the resonance for the carbon atom adjacent to the trichlorostannane group of n-butyl trichlorostannane. Unfortunately the d_6DMSO resonance multiplet (centered at 39.59 ppm and ranging from 35.5 to 42.8 ppm) obscures any β carbon resonances in that region.

The ^{119}Sn n.m.r spectrum was run on a DMSO solution, the compound being hardly soluble in other solvents. CETTC is soluble in warm toluene but we were unable to do raised temperature studies. DMSO is not an ideal solvent to choose as it can easily coordinate to the tin and therefore affect the chemical shift quite drastically.

Crystallographic studies [8] (Figs. 5.1 and 5.2) show that in the crystal, CETTC is a coordination polymer; the lone pair of electrons of the nitrogen atom being coordinated, approximately

Fig. 5.1. CRYSTAL STRUCTURE OF 2-CYANOETHYLTIN TRICHLORIDE INCLUDING THE GEOMETRY OF THE COORDINATION WITH ADJACENT MOLECULES. (INDICATED BY N' AND Sn'') [8]



Bond Angles (°)

Cl(1)-Sn(1)-Cl(2) = 111.5(3)
Cl(1)-Sn(1)-C(1) = 116.3(5)
Cl(2)-Sn(1)-C(1) = 127.5(5)
Cl(3)-Sn(1)-N(1') = 177.1(5)
Cl(3)-Sn(1)-Cl(1) = 95.8(3)
Cl(3)-Sn(1)-Cl(2) = 94.2(3)
Cl(3)-Sn(1)-C(1) = 101.3(6)
N(1")-Sn(1)-Cl(1) = 83.2(5)
N(1')-Sn(1)-Cl(2) = 83.6(6)
N(1')-Sn(1)-C(1) = 81.6(7)
Sn(1)-C(1)-C(2) = 112(2)
C(1)-C(2)-C(3) = 114(2)
C(2)-C(3)-N(1) = 176(2)
C(3)-N(1)-Sn(1") = 171(2)

Bond Lengths - as shown, (Å)

Note: Details of H atom geometry are not recorded since they are placed in calculated positions.

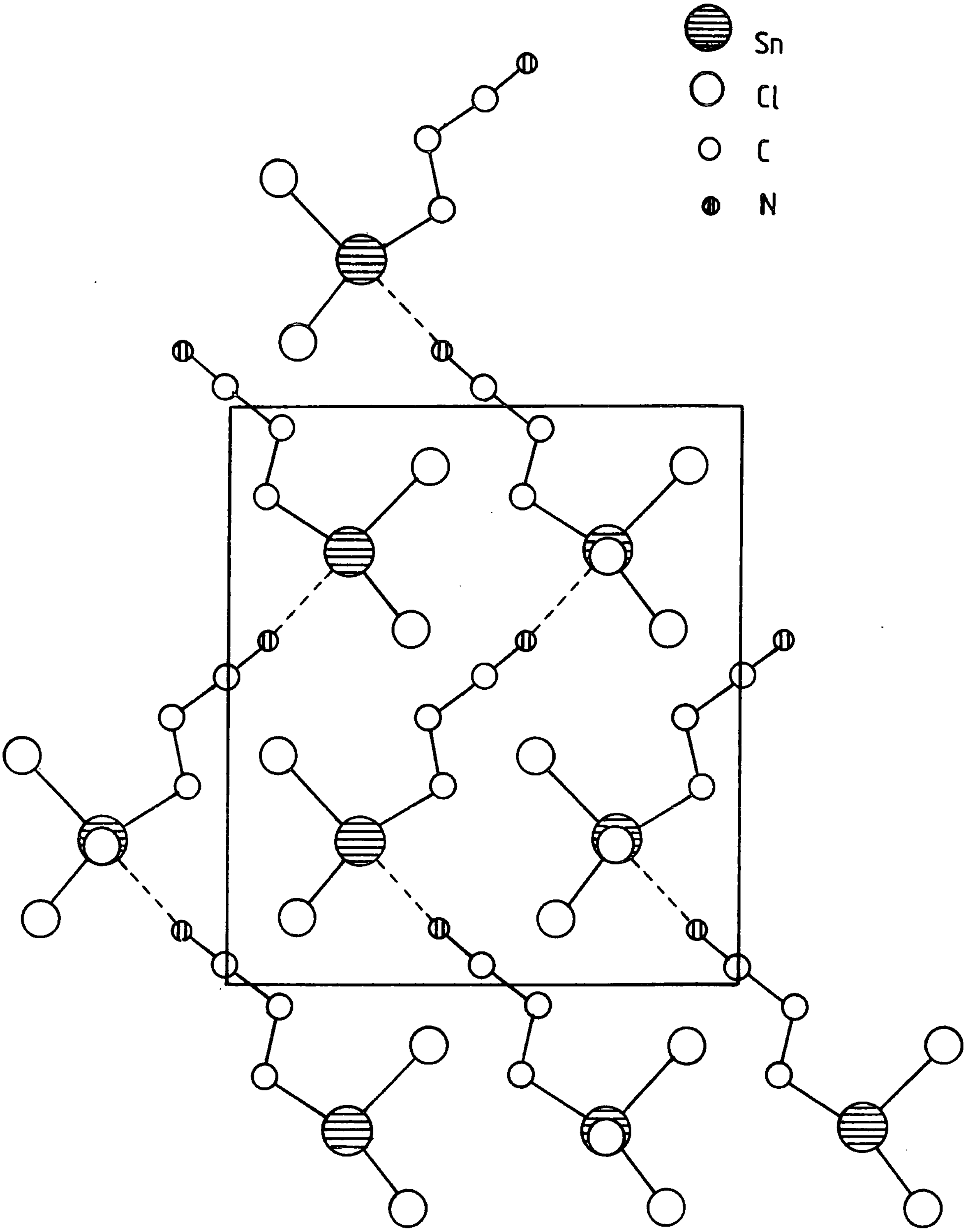


Fig. 5.2. Unit cell of $Cl_3SnCH_2CH_2C\equiv N$.

linearily (Cl(3)-Sn(1)-N(1') = 177.1(5)° and C(3)-N(1)-Sn(1'') = 171(2)°), to the tin atom of an adjacent molecule. The resultant polymer consists of a zig-zag chain along the c axis, with two such chains per unit cell (Fig. 5.2).

The arrangement around the tin atom, including the coordinate bond with the adjacent molecule, is slightly distorted trigonal bipyramidal; atoms Cl(1), Cl(2) and C(1) forming the equatorial plane with Cl(3) and N(1') in the axial positions. The two equatorial tin-chlorine bonds are of equal length, within experimental error, whilst the axial tin chlorine bond is significantly longer as expected for trigonal bipyramidal co-ordination complexes. The angle Cl(1)-Sn(1)-Cl(2) is the smallest of the equatorial angles and the angles between the equatorial and axial atoms range from 81.6 (7)°to 101.3 (6)°. As expected the angles between atom Cl(3) and the equatorial plane are larger than those between N(1') and the plane. However, unexpectedly, the bond angle Cl(3)-Sn(1)-C(1) involving the axial chlorine atom is the largest at 101.3(6)° and is approaching the tetrahedral angle.

Evidence for intermolecular co-ordination has been obtained spectroscopically. Firstly, the far infra-red spectrum of CETTC [2] exhibits peaks at 320(m/s), 313(vs) and 309(vs.sh) in the region for v(Sn-N) which suggests a form of tin-nitrogen bond. Secondly infra-red studies of 2-cyanoethyl tin tribromide [4] led Reifenberg and Considine to conclude that it comprises intermolecular complexes. The nitrile stretching frequency in nujol and in benzene appears at 2283 cm^{-1} whilst in the donor solvent THF, where intermolecular co-ordination is destroyed, the frequency is reduced by 36 cm^{-1}. Similar effects are observed for CETTC (table 5.5) and upon adduct formation (section 5.3).

Table 5.5

Effect of v(C≡N) of $Cl_3SnCH_2CH_2C{\equiv}N$ (CETTC) upon dissolving in various solvents and exposing to the atmosphere.

Condition of CETTC	V(C≡N) cm^{-1}
CETTC (Nujol mull.)	2278
CETTC in toluene	2248
CETTC in acetone	2248
CETTC exposed to moist air	2250

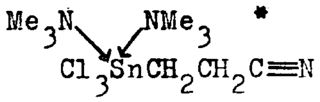
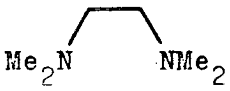
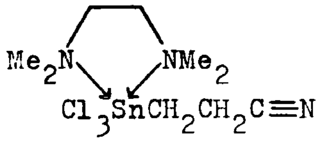
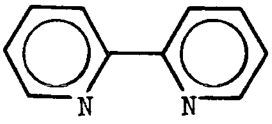
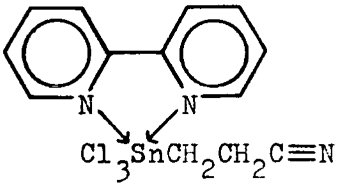
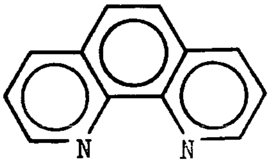
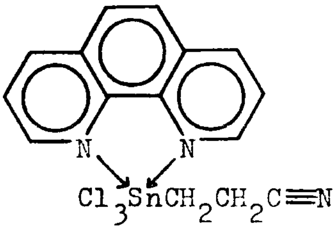
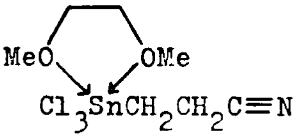
By comparison the crystal structures of $Cl_3Sn(CH_2)_2CO_2Me$ [11] and $Cl_3Sn(CH_2)_3CO_2Et$ [12] show that the tin atoms undergo intramolecular coordination to give five coordinate tin.

5.3. THE COORDINATION CHEMISTRY OF CETTC.

5.3.1. Mono-organotin compounds are generally strong Lewis acids and can be used as homogenous catalysts for esterification and transesterification reactions [13]. The Lewis acidity of organotin halides has been reviewed by Poller [14]. A quantitative measurement of the acceptor strength of organotin species may be obtained by evaluating the formation constants of complexes in solution [14-18]. For example, phenyl tin trichloride is a stronger Lewis acid than the methyl derivative which in turn is stronger than the butyl derivative towards aniline donors in diethyl ether [17]. The Lewis acidity and basicity of CETTC is studied in this section and the adducts formed are summarised in table 5.6.

Table 5.6

Adducts of CETTC

Ligand	Adduct	Yield (%)
NMe_3	 *	12
 (TMEDA)		70
 (bipy)		95
 (phen)		90
		15
$AlCl_3$	$[Cl_3SnCH_2CH_2C\equiv N]_n \longrightarrow AlCl_3$	10

* Could be cis and/or trans isomer.

The Lewis acidities of carboxyethyltin chlorides [19] and other closely related systems [12,20-22] have been reported, the results of which may be compared with those for CETTC.

5.3.2. Experimental

Either the neat ligand (if a liquid) or a solution of it in toluene (if solid) was added to CETTC, dissolved in a minimum amount of toluene, in the correct molar relationship to give the above adducts. The products from CETTC with bipy and phen precipitated out immediately whilst the TMEDA and $AlCl_3$ products took a few hours to appear. They were isolated as white powders by filtration, followed by thorough washing and drying in vacuo. In the case of aluminium trichloride, the solvent was innoculated by prior boiling with a portion of the ligand. The trimethyl amine and monoglyme products appeared as very fine precipitates and were subsequently isolated by removal of solvent. Attempts to form adducts with stannic chloride and boron trichloride yielded only the starting materials. Due to the volatility of these Lewis acids the solutions formed were reduced in volume slowly by passing a stream of dry nitrogen over the surface, but unfortunately this was of no avail.

Characterisation of the adducts formed (compounds 5.2 to 5.7) is presented in the following data tables. In addition the Mössbauer results are given in fig. 5.3.

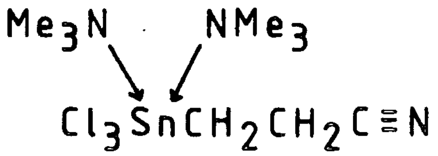
5.3.3. Discussion of Results.

The crystal structure confirmed inferences from the infrared studies that CETTC is a polymer making use of the lone pair of electrons on the nitrile moiety and the vacant orbital on the tin atom by intermolecular coordination. Addition of a Lewis acid

Compound No. 5.2

Origin $2NMe_3 + Cl_3SnCH_2CH_2C\equiv N$

Name & Structure



$(Me_3N)_2 \rightarrow Cl_3SnCH_2CH_2C\equiv N$

bis(trimethylamine) CETTC

m.pt. 118-20

Elemental Analysis

C	26.4	(26.1)
H	7.9	(5.6)
N	9.4	(10.5)
Sn	16.0	(29.9)
Cl	22.9	(26.8)

Empirical Formula $C_9H_{22}N_3Cl_3Sn$

Infra-red, ν cm^{-1} Nujol Mull

3500-3100m, b, 2900s, b, 2690w, b, 2482w, 2240m, 1650m, 1255m/s, 1150w, 1090m, b, 1015m/s, 980m, 800m.

^{1}H N.M.R. d_6DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
3.70	s	-	-	-
4.50	s, b	-	-	-

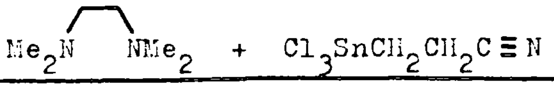
Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I

Other Information

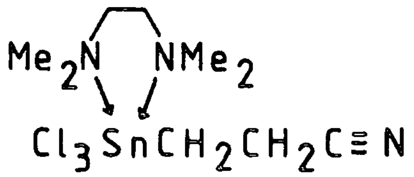
Compound No. 5.3

Origin



$Me_2N\ \ NMe_2 + Cl_3SnCH_2CH_2C\equiv N$

Name & Structure



CETTC.TMEDA

m.pt. 117-9

Elemental Analysis

C	27.3	(27.3)
H	5.1	(5.1)
N	9.1	(10.6)
Sn		(30.1)
Cl	26.5	(26.9)

Empirical Formula $C_9H_{20}N_3Cl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull

2920s, 2855s, 2565m, 2450m, 2246m, 1454s, 1375m, 1283m/s, 1235m, 1195m, 1155w, 1146w/m, 1116w/m, 1097w/m, 1060m, 1040m/s, 1004s, 980m/s, 948s, 918m, 880w/m, 794s, 760m, 720w/m, 670m, 582w/m, 511m, 481w/m, 442m.

¹H N.M.R. d_6DMSO, Int. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.57	t	8	1	CH_2^*
2.57	s	-	4	$CH_2^\ddagger$
2.73	s, b	-	1	CH_2^*
2.97	s	-	4	$CH_2^\ddagger$

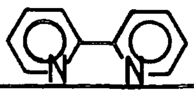
* = CETTC

‡ = TMEDA

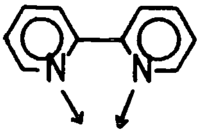
Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
28	$C_2H_4^+$	60	225	$SnCl_3^+$	48
36	HCl^+	82	245	$Cl_2SnCH_2CH_2CN^+$	31
44	NMe_2^+	15	260	$SnCl_4^+$	4.4
58	$Me_2NCH_2^+$	100	280	$Cl_3SnCH_2CH_2CN^+$	26
116	$(Me_2NCH_2)_2^+$	44	290	?	9.1
120	Sn^+	4.5	299	?	5.8
155	$SnCl^+$	32	372	?	8.2
190	$SnCl_2^+$	18			

Other Information ^{119}Sn Mössbauer, (fig. 5.3)

Compound No.	Origin
5.4	 + $Cl_3SnCH_2CH_2C\equiv N$

Name & Structure



$Cl_3SnCH_2CH_2C\equiv N$

CETTC. bipy

m.pt. 250-1

Elemental Analysis

C	34.8	(35.9)
H	3.6	(2.8)
N	8.4	(9.7)
Sn	21.0	(27.3)
Cl	22.3	(24.4)

Empirical Formula $C_{13}H_{12}N_3Cl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull

3100w, 3070w, 2248m, sh, 1160m, b, 1605m, sh, 1595m, sh, 1570m, 1490m, 1437s, sh, 1310m/s, 1260m, 1245m, 1215 1168m, 1150m, 1102m, 1065m, 1060m, 1040m, 1028s, sh, 1018m,sh, 808m,778s, sh, 724s, sh, 670m, 659m, 649m,639m, 440m.

^{1}H N.M.R. d_6DMSO Int.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.57	t	8	1	CH_2
2,70	t	8	1	CH_2
7.40 7.50 7.75 7.90 8.03 8.30 8.43 8.63	series of m	-	4	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	156	$C_{10}H_8N_2^+$ (bipy)	100
54	$CH_2CH_2CH^+$	10	190	$SnCl_2^+$	37
78	$C_5H_4N^+$	100	225	$SnCl_3^+$	49
120	Sn^+	12	245	$Cl_2SnCH_2CH_2CNH^+$	20
128	$C_{10}H_8^+$	100	280	$Cl_3SnCH_2CH_2CNH^+$	9.8
155	$SnCl^+$	100			

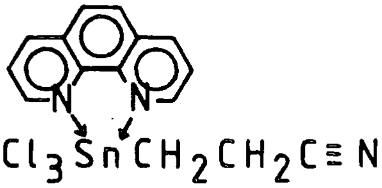
Other Information ^{119}Sn Mössbauer, (fig. 5.3)

Compound No.
5.5

Origin

+ $Cl_3SnCH_2CH_2C\equiv N$

Name & Structure



CETTC.phen.

m.pt.
255-7

Elemental Analysis

C	38.3	39.2
H	2.6	2.6
N	8.6	9.1
Sn	-	26.1
Cl	22.7	23.0

Empirical Formula $C_{15}H_{12}N_3Cl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull

3198w, 3060w, 2970s, 2930s, 2862s, 2733w, 2242m, 1640w, 1608w, 1562w/m, 1518m, 1494w, 1460s, 1442m, shl, 1427m/s 1378m/s, 1365m, shl, 1341w, 1326w, 1309w 1260w, 1225m, 1150m/s, sh, 1110m, sh, 1098w, 1070w, shl, 1019w/m, 920w, 890w 875w/m, 862s, sh, 835w, 787w, 740m/s, 725s, sh, 690w/m, 651w/m, 484w, shl, 444w

^1H N.M.R. d_6DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
2.09	s, b	-		CH_2
2.98	s, b	-		CH_2
7.21	m	-		Ph
8.05 8.41 9.18 9.94	m	-		Ph?

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	18	155	$SnCl^+$	45
54	$CH_2CH_2CN^+$	9.7	180	$C_{12}H_8N_2^+$	100
77	Ph^+	21	190	$SnCl_2^+$	6.5
90	$C_6H_4N^+$ (or $C_{12}H_8N_2^{2+}$, $phen^{2+}$)	35	225	$SnCl_3^+$	36
			245	$Cl_2SnCH_2CH_2CNH^+$	17
120	Sn^+	4.1	280	$Cl_3SnCH_2CH_2CNH^+$	9.8

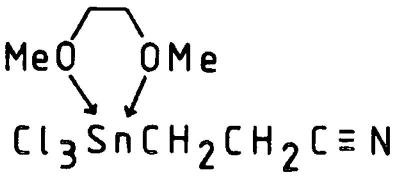
Other Information ^{119}Sn Mössbauer, (fig. 5.3)

Compound No. 5.6

Origin

+ $Cl_3SnCH_2CH_2C\equiv N$

Name & Structure



CETTC.monoglyme

m.pt. 71-3

Elemental Analysis

C	22.6	22.8
H	3.6	3.8
N	3.5	3.8
Sn		32.1
Cl	28.0	28.8

Empirical Formula $C_7H_{14}NO_2Cl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull

2964m/s, 2934m/s, 2862m/s, 2249m, 1644w/m,b,1464m/s, shl,1452m/s,1390m/s shl,1380m, 1298m, 1251m, 1210m, 1192m, 1154m, 1082m, shl,1111m, shl,1079m/s, b,1030m/s, b,1025m/s, shl,979m,900w/m, 849m/s, 804w/m, 725w/m, 690m, b, 550w/m, b,451m, b.

¹H N.M.R. d_6DMSO,Int.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.53	t	8	1	CH_2
2.63	t	8	1	CH_2
3.20	s	-	2	*Me
3.40	s	-	2	*CH_2

* Monoglyme

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	225	$SnCl_3^+$	100
44	$[MeOCH_2-H]^+$	91	245	$Cl_2SnCH_2CH_2CNH^+$	60
53	$[CH_2CH_2CN-H]^+$	100	260	$SnCl_4^+$	100
90	$(MeOCH_2)_2^+$	4.5	280	$Cl_3SnCH_2CH_2CNH^+$	35
120	Sn^+	19	290	?	2.0
155	$SnCl^+$	100	315	$Cl_3Sn(MeOCH_2)_2^+$	3.8
190	$SnCl_2^+$	45			

Other Information ^{119}Sn Mössbauer, (fig. 5.3)

Compound No. 5.7

Origin $AlCl_3$ + $Cl_3SnCH_2CH_2C\equiv N$

Name & Structure

$$(Cl_3SnCH_2CH_2C\equiv N)_n \rightarrow AlCl_3$$

CETTC.aluminium trichloride

m.pt. 112-14

Elemental Analysis

		$CETTC.AlCl_3$	$2CETTC.AlCl_3$
C	16.8	8.7	10.4
H	2.4	1.0	1.2
N	3.7	3.4	4.0
Sn			
Cl			

Empirical Formula

Infra-red, ν cm⁻¹ Nujol Mull

3350m, b,2920s, 2860s, 2304m/s,1640m/s, 1450m, b,1402m, b, 1372m, b,1242m,b, 1142m, b,1005w/m, 905m, 880w/m, 795w/m, 730m, 550w/m, b.

^1H N.M.R. d_6DMSO, Ext.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.53	s	-		
2.09	s, b	-		CH_2
2.50	s, b	-		CH_2
3.34	t	5.9		

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+				
55	$[CH_2CH_2CH\text{-}H]^+$				
120	Sn^+				
133	$AlCl_3^+$				
155	$SnCl^+$				
190	$SnCl_2^+$				
225	$SnCl_3^+$				
245	$Cl_2SnCH_2CH_2C\equiv N^+$				
260	$SnCl_4^+$				
280	$Cl_3SnCH_2CH_2C\equiv N^+$				

Other Information

or base should therefore break up the chain and form monomeric adducts, either by co-ordinatively saturating the tin atom by an electron donating ligand or by utilizing the nitrile lone pair of electrons to satisfy an independant electron acceptor ligand. This may be monitored by observing a shift in the nitrile stretching frequency in the infra-red spectrum. A coordinating ligand, by satisfying the Lewis acidity, causes v(C≡N) to decrease relative to free nitrile [23]. This is demonstrated by the CETTC adducts as tabulated below.

Table 5.7

Nitrile Infra-red stretching frequencies of free and coordinated nitriles

Compound/Adduct	v(C≡N) cm^{-1} (a)
$CH_2=CHC\equiv N$ (b)	2224 (c)
$Cl_3SnCH_2CH_2C\equiv N$ (d)	2278
$Cl_3SnCH_2CH_2C\equiv N.2NMe_3$	2240
$Cl_3SnCH_2CH_2C\equiv N$. bipy	2248
$Cl_3SnCH_2CH_2C\equiv N$. phen	2242
$Cl_3SnCH_2CH_2C\equiv N$. TMEDA	2246
$Cl_3SnCH_2CH_2C\equiv N$. Monoglyme	2249
$Cl_3SnCH_2CH_2C\equiv N$. $AlCl_3$	2304

(a) Nujol mulls, unless otherwise stated.

(b) i.e. free nitrile.

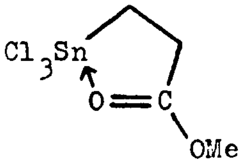
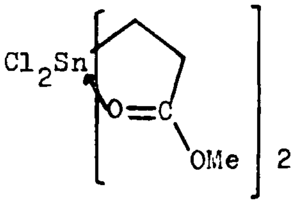
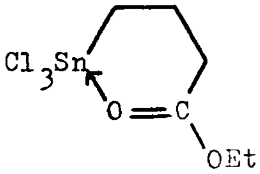
(c) liquid film.

(d) Nitrile group utilised in forming coordinating polymer.

Similarily, adduct formation from carboxyethyl and butyl tin chlorides, which themselves undergo intramolecular coordination [11,12] may be monitored by observing a change in the carbonyl stretching frequency [19] as shown in table 5.8.

Table 5.8

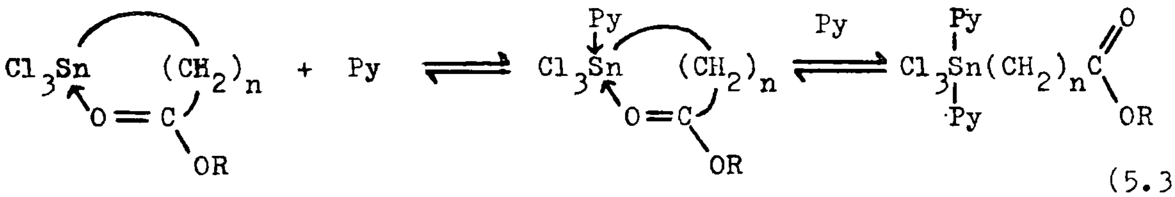
Change in carbonyl frequency upon adduct formation for certain carboxy-ethyl and butyl tin chlorides

Compound/Adduct	$v(C{=}O)Cm^{-1}$	Ref.
$CH_3CH_2CO_2Me^a$	1738^b	[24]
	1660^b 1668^c	[24]
	1677	[3]
	1663^c	[12]
$Cl_3SnCH_2CH_2CO_2Me$. bipy	1728^d	[19]
$Cl_3SnCH_2CH_2CO_2Me$. phen	$1725,\ 1735, 1745^{d,e.}$	[19]
$Cl_2Sn(CH_2CH_2CO_2Me)_2$.bipy	1728^d	[19]
$Cl_2Sn(CH_2CH_2CO_2Me)_2$.phen	$1720, 1730, 1750^{d,e}$	[19]
$Cl_3SnCH_2CH_2CH_2CO_2Me$. bipy	ca 1730^c	[12]
$Cl_3SnCH_2CH_2CH_2CO_2Me$. phen	ca 1740	[12]

(a) i.e. free carbonyl. (b) Nujol mull. (c) in CH_2Cl_2 (d) KBr disc

(e) proposed to be due to different conformations.

Similar changes in the carbonyl stretching frequency upon adduct formation between $X_2Sn\left[(CH_2)_3COOMe\right]_2$ (x = Br,Cl) and bipy have been reported [21,22]. Kuivila claimed that an equilibrium is set up between pyridine and $Me_2ClSn(CH_2)_nCOR$ (n = 2,3; R = Me,Ph) with a resultant increase in the carbonyl stretching frequency indicating adduct formation. Subsequent studies on $Cl_3Sn(CH_2)_nCOOMe$ (n = 2,3) show that one molecule of pyridine may coordinate to the tin atom without disrupting the cyclic intramolecular coordination complex. However, the ring may be broken upon addition of a second pyridine molecule (but not weaker donors) [19] as illustrated below.



(5.3)

$\nu(C{=}O)$, cm^{-1} (in CH_2Cl_2)					
n = 2,	R = Me	1668	1648	1730	[19]
n = 3,	R = Et	1663	1643	1743	[12]

The proton n.m.r. spectra of the carboxyethyl tin chlorides also support intramolecular carbonyl coordination as the peaks attributable to the methylene protons exhibit a large upfield solvent effect upon changing from chloroform to benzene [25]. Similar effects were observed for CETTC by running the proton n.m.r. spectrum in d_6DMSO and $CDCl_3$ (table 5.1). Upon adduct formation the methylene proton shifts are not affected to any great extent. Those for some of the adducts became complex multiplet structures instead of two triplets. Some peaks were hidden under those for the ligands or solvent peaks. The spectra were run in d_6DMSO due to solubility problems.

The DMSO may itself coordinate to the CETTC, consequently the methylene proton chemical shifts should not differ largely from those of CETTC itself in d_6DMSO. The remaining peaks are as assigned on the data tables, some were difficult to detect due to high background noise or low sensitivity chiefly because of the restricted solubility.

The mass spectra contain peaks representing CETTC and the ligand separately but the adducts are too weak for the parent ion to be observed.

The polymeric chain of CETTC is broken upon adduct formation because the coordinative bonds between the ligand and the tin atom are stronger than those formed by intermolecular coordination. As this causes the electronic structure around the tin atom to be altered one would expect this to be displayed in the Mössbauer spectra. Upon adduct formation the coordination number of the tin atom raises from five (coordination polymer) to six (adduct with bidentate ligand). This is reflected in the isomer shift. Changes in the quadrupole splitting are more marked as they are due to spatial arrangements and electronegativities of the groups or atoms attached.

The parameters for CETTC are comparable to those for the carboxy derivates [25] (Table 5.9).

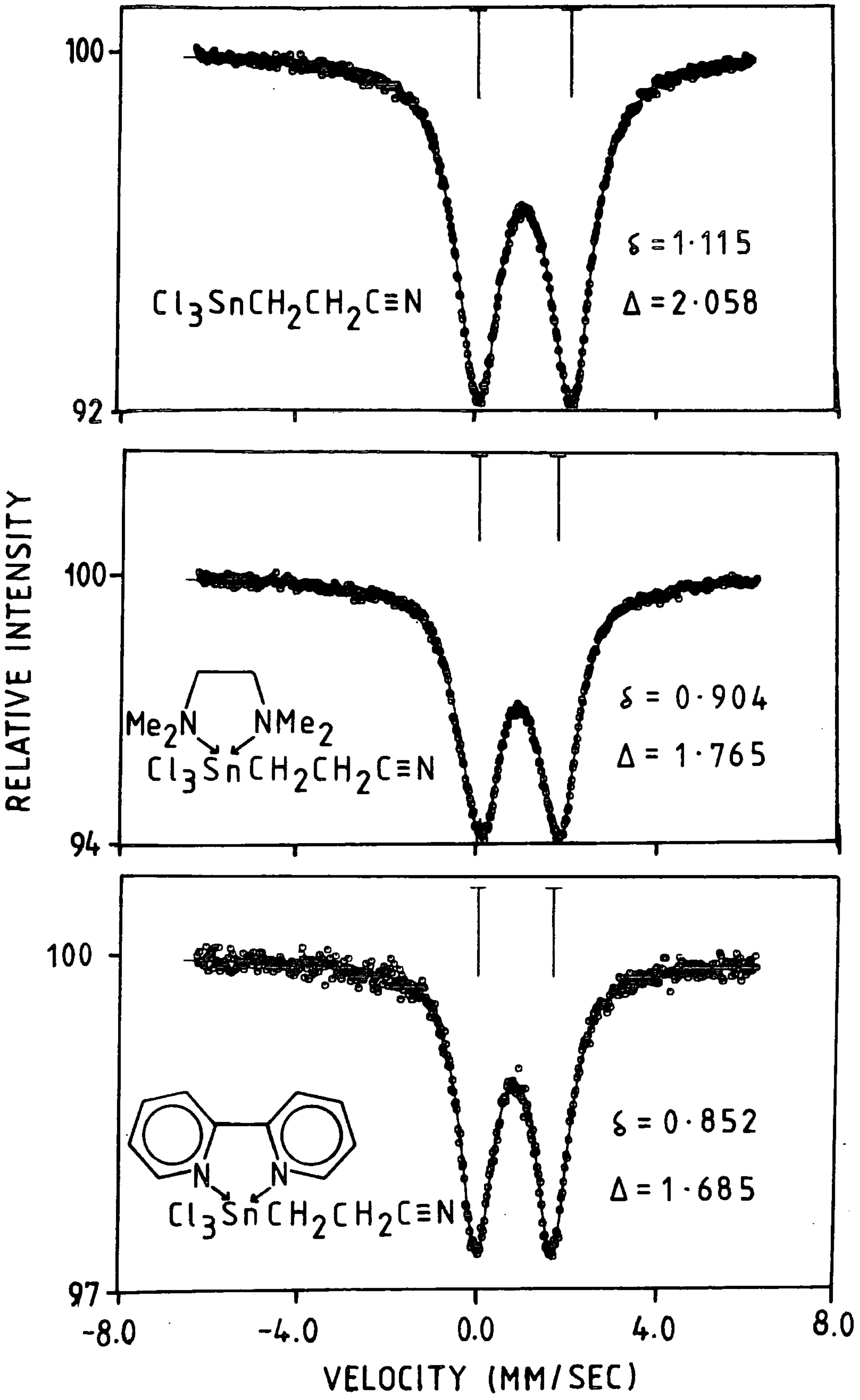


Fig. 5.3. Mössbauer Spectra of CETTC and its Adducts.

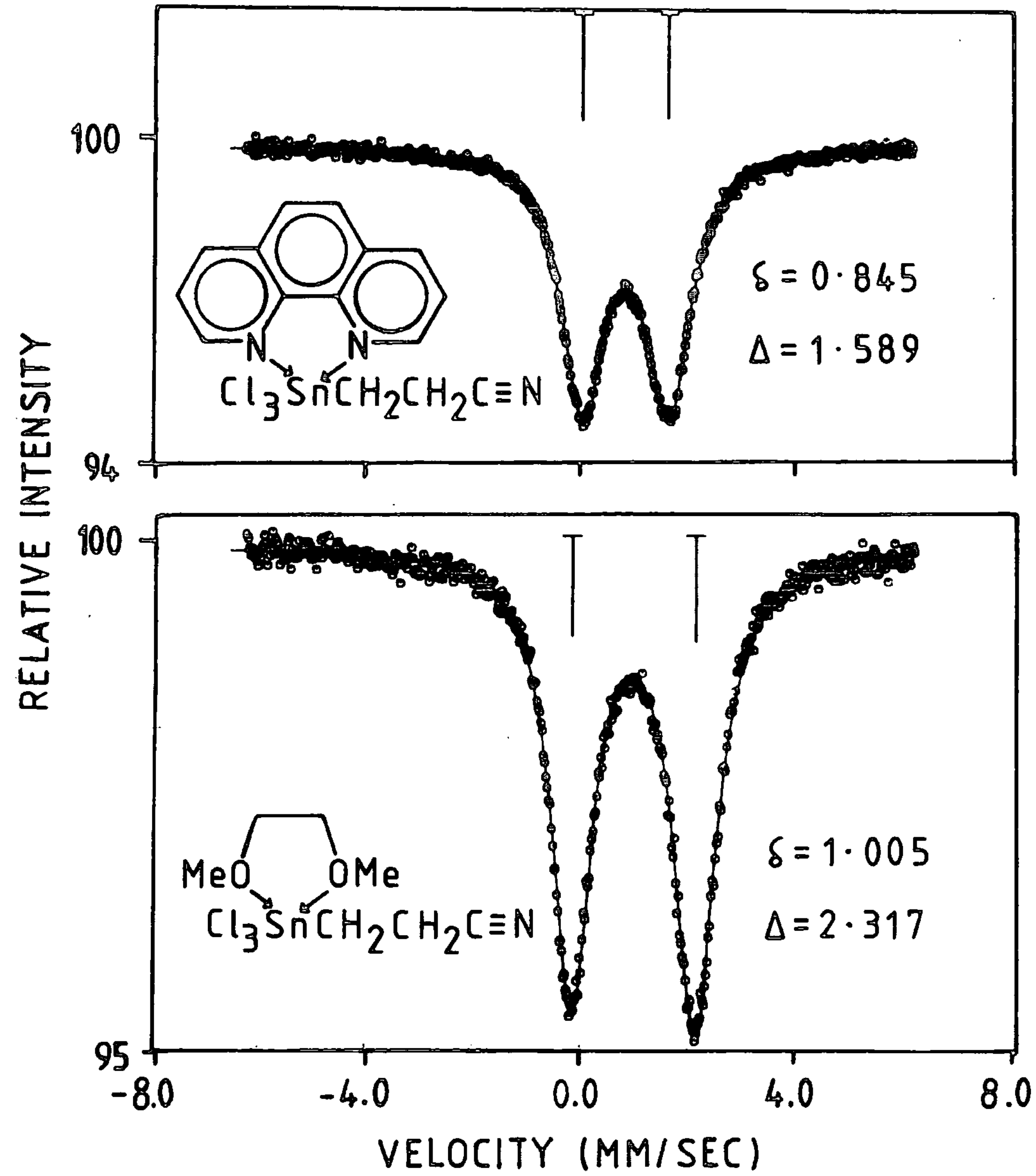


Fig. 5.3 - continued.

Table 5.9

Mössbauer Parameters for CETTC and related Carboxy Derivatives

Compound	Isomer Shift[a]	Quadrupole Splitting[a]	Ref.
$Cl_3SnCH_2CH_2C{\equiv}N$	1.115	2.058	b
$Cl_3SnCH_2CH_2CO_2R$			
R = Me	1.00	2.18	[11]
	1.08	2.04	[19]
	1.352	2.003	[25]
Et	1.164	2.040	[25]
Bu	1.105	1.947	[25]

a = mm sec^{-1} ; b = this work.

The quadrupole splitting factors suggest trigonal bipyramidal geometry [25] (as proved by crystal structure determinations [8,11]). Upon adduct formation the isomer shift is decreased and the quadrupole splitting varies from 1.589 to 2.317 mm sec^{-1}. The results are consistent with those for the carbomethoxy derivatives (table 5.10).

Table 5.10

Effect on the Isomer Shift, δ , and the Quadrupole Splitting, Δ , upon Adduct formation.

Compound/Adduct	δ*	Δ*	Compound/Adduct	δ*[19]	Δ*[19]
$Cl_3SnCH_2CH_2C{\equiv}N$	1.115	2.058	$Cl_3SnCH_2CH_2CO_2Me$	1.08	2.04
bipy adduct	0.852	1.685	bipy adduct	0.85	1.59
phen adduct	0.845	1.589	phen adduct	0.93	1.65

* mm sec^{-1}

Adduct formation with the diorganotin dichloride [19] leads to an increase in both parameters (table 5.11).

Table 5.11

Effect on the Isomer Shift, δ, and Quadrupole Splitting, Δ, of dicarbomethoxyethyltin dichloride upon adduct formation.

Compound/Adduct	δ, mm sec^{-1}	Δ, mm sec^{-1}
$Cl_2Sn(CH_2CH_2CO_2Me)_2$	1.45*	3.47*
bipy adduct	1.46	3.93
phen adduct	1.50	3.93

* δ = 1.50 ; Δ = 3.45 [11]
δ = 1.35 ; Δ = 3.45 [25]

In this case both the organotin compound and the adducts formed are all six coordinate (octahedral geometry). One would therefore expect little change in the Mössbauer parameters, δ in particular. However, for mono-organotin chlorides, adduct formation causes a change in coordination number from five to six and the geometry from trigonal bipyrimidal to octahedral. The parameters in table 5.11 correspond to octahedral complexes with trans- R_2Sn groups which agree with predictions of a quadrupole splitting value of approximately 4 mm sec^{-1} from point charge calculations [26,27] . Mössbauer spectroscopy may therefore be used to establish the stereochemistry of organotin compounds. Selected examples are given in table 5.12 and the Mössbauer spectra of the complexes of organotin halides have been listed in a review article by P.J.Smith [28] .

Table 5.12

Mössbauer Parameters for Organotin Adducts

Adduct	δ, mm sec^{-1}	Δ, mm sec^{-1}	Stereochemistry	Ref.
Me_2SnCl_2.bipy	1.35	4.02	trans	[29]
Me_2SnCl_2.phen	1.32	4.03	trans	[29]
Bu_2SnCl_2.bipy	1.56	3.83	trans	[30]
Bu_2SnCl_2.phen	1.69	4.07	trans	[30]
Ph_2SnCl_2.bipy	1.35	3.90	trans	[27]
Ph_2SnCl_2.phen	1.28	3.70	trans	[27]
Me_2Sn.oxin$_2$	0.88	1.98	cis	[31]
Ph_2Sn.oxin$_2$	0.83	1.78	cis	[27]
Ph_2Sn.oxin$_2$	0.74	2.14	cis	[27]

By comparison, therefore, the adducts of CETTC are cis octahedral isomers.

5.4 MECHANISTIC STUDIES

Several experiments were conducted in order to obtain mechanistic information on the formation of CETTC.

5.4.1 Experimental

5.4.1.1 The hydrochlorination of acrylonitrile in diethyl ether

Hydrogen chloride was bubbled into a solution of acrylonitrile (8 mls, 122 mmoles) in diethylether (25 mls) at 0°C for one hour. Removal of ether in vacuo yielded 2-chloropropionitrile (identified by comparison with the infra-red spectrum of an authentic sample)

i.e. $$HCl + CH_2{=}CHC{\equiv}N \xrightarrow{Et_2O, 0^{\circ}C,\ 1hr} ClCH_2CH_2C{\equiv}N \qquad (5.4)$$

5.4.1.2. The reaction between 2-chloropropionitrile and tin dichloride

2-chloropropionitrile (2.631g, 2.94 mmoles) was added to anhydrous tin dichloride (5.30g, 2.7 mmoles) dissolved in anhydrous acetone (100 mls). After refluxing for 72 hours the pale yellow solution was reduced in volume to give the starting materials. Similar results were obtained in the presence of ether.

i.e. $$SnCl_2 + ClCH_2CH_2CN \not\longrightarrow Cl_3SnCH_2CH_2CN. \qquad (5.5)$$

5.4.1.3. Preparation of the tin tetrachloride adduct of acrylonitrile

Tin tetrachloride (2.0 mls, 17 mmoles) was added to an excess of acrylonitrile (30 mls). The adduct (5.8) was isolated by evaporation of the solvent by drawing a stream of nitrogen over its surface.

$$2CH_2{=}CHC{\equiv}N + SnCl_4 \xrightarrow[\text{as solvent}]{CH_2=CHCN} \underset{5.8}{\begin{array}{c}(CH_2{=}CHC{\equiv}N)_2.SnCl_4 \\ (\nu(C{\equiv}N) = 2255\ cm^{-1})\end{array}} \qquad (5.6)$$

5.4.1.4 The reaction between the tin tetrachloride adduct of acrylonitrile and hydrogen chloride

The above adduct was prepared in toluene and hydrogen chloride was passed into the solution at 0°C. After 15 minutes the solution turned pale yellow and then cloudy. The solid was isolated by filtration, a small sample of which was recrystallised in toluene. (Compound 5.9)

Compound No.	**Origin**
5.9	$(CH_2=CHC\equiv N)_2SnCl_4$ + HCl

Name & Structure

see text

m.pt.

Elemental Analysis

		$L_2SnCl_4.2HCl$	$L_2SnCl_4.3HCl$
C	15.2	16.3	15.1
H	2.4	1.8	1.9
N	5.0	6.4	5.9
Sn			
Cl	41.9	48.4	55.4

Empirical Formula $C_3H_6NCl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull.

3223m,b,3102m,shl,3061m/s,2958s,2918s, 2856s,2338w,2000w,1675m,1620m/s,1602m, 1570m,1465s,1457s,1435m,shl,1415w, 1392m,1375m/s,1347w,1339w,1326m/s,shl, 1294m,sh,1259m,1151w,1122w,1069w, 1020w/m,1000s,sh,970s,sh,942m/s,shl, 936w,shl,816s,770w,shl,735w,725w,shl, 697w/m,shl,672m/s,528w,442w,shl, 435w/m,shl.

¹H N.M.R. d_6DMSO,Int.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
3.02	t	6	1	CH_2
3.82	t	6	1	CH_2
7.19	s	-	3	NH or NH_2
8.87	s	-	3	

Mass Spectrum

m/e	Fragment Ion	I
36	HCl^+	100
43	$C_2H_3NH_2^+$ or $[C(=NH_2)NH]^+$	100
44	$(CH_2)_2NH_2^+$ or $C(NH_2)_2^+$ or $CONH_2^+$	18
53	$C_2H_3CN^+$	100
57	$[(CH_2)_2CNH_2+H]^+$	74
63	$ClCH_2CH_2^+$ (relative intensity of peak at 65 incorrect for Cl)	84
67	$[107 - CH_2CN]^+$	22
83	$[107 - CN + 2H]^+$	41
97	$[Cl + 62]^+$	38
107	$C_6H_7N_2^+$ (protonated acrylonitrile dimer) or $Cl(CH_2)_2C(NH_2)_2^+$	9.1

m/e	Fragment Ion	I
111	$[(CH_2)_2CNH_2 + H]^+$	27
134	$SnCH_2^+$	16
140	?	78
155	$SnCl^+$	27
190	$SnCl_2^+$	9.2
225	$SnCl_3^+$	85
260	$SnCl_4^+$	11
269	$[SnCl_3^+ + 44]^+$	
322	$[260 + 62]^+$ $[225 + 97]^+$	47

Other Information

5.4.1.5. Hydrostannation of the tin tetrachloride adduct of acrylonitrile.

$(CH_2{=}CHCN)_2.SnCl_4$, made from acrylonitrile (5.85 mls, 88.9 mmoles) and tin tetrachloride (5.2 mls, 44.8 mmoles), was added to ethereal trichlorostannate (17.0282g, 89.6 mmoles) to yield a white solid (compound 5.10) after the removal of the volatile components by evaporation.

5.4.1.6. γ Ray initiated hydrostannation of acrylonitrile

Acrylonitrile (5.0 mls, 76.0 mmoles) was added to ethereal trichlorostannane (51.0 mmoles) in a shlenk tube and exposed to γ irradiation (^{60}Co source) for 153 hours under a blanket of dry nitrogen to produce an extremely hard white substance. The only solvent which could penetrate it was DMSO, and upon attempted removal of excess solvent yielded an intractable gelatinous gum. (5.11).

Infra-red spectrum, v, cm^{-1}, contact film.

3240m/s,shl, 2960s, 2908s, 2850s, 2700m,shl, 2950m,shl, 2440w/m, 2304w/m, 2244m/s, 1660m/s,b, 1575m/s,b, 1420s,b, 1310s,b, 1240m/s,b, 1025s,b, 935s,b, 725m/s,shl, 696m/s,b, 670m/s,b, 542w/m,shl, 450m/s,b, 384m/s,b.

5.4.2 Discussion of Results

The first two experiments (5.4.1.1. and 5.4.1.2) were conducted to determine whether CETTC could be prepared in a stepwise manner without the need for preparing the trichlorostannane intermediate.

Compound No. 5.10

Origin $(CH_2=CHC\equiv N)_2SnCl_4$ + $HSnCl_3$

Name & Structure

see text

m.pt.

Elemental Analysis

		$(Cl_3SnCH_2CH_2CH)_2SnCl_4$
C		8.4
H		0.9
N		3.3
Sn	38.5	41.7
Cl	43.1	45,7

Empirical Formula

Infra-red, ν cm⁻¹ Nujol Mull.

3418m, 3324m, 3238m, 2958s, 2920s, 2848s, 2722w, 1648m/s, 1560m, 1456s, 1404m/s, 1374m/s, 1288w, 1258w, 1240w, 1162w, 1152w, 1118w, 1080w, 1014w, 920w/m, b,842w, 720m/s, 695m, 670m.

¹H N.M.R.

δ ppm	Mult.	J,Hz	Int.	Assign.

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	120	Sn^+	47
44	$(CH_2)_2NH_2^+$, $C(NH_2)_2^+$	100	136	$SnNH_2^+$	12
	or $CONH_2^+$		155	$SnCl^+$	100
54	$CH_2CH_2CN^+$	100	190	$SnCl_2^+$	72
63	$ClCNH_2^+$	59	225	$SnCl_3^+$	100
72	$[(CH_2)_2 + 44]^+$	100	260	$SnCl_4^+$	28
83	$(CH_2)_4CNH^+$	23	270	$[SnCl_3 + 45]^+$	17
107	$C_6H_7N_2^+$	62	283	$Cl_3SnCH_2CH_2CH=NH^+$	4.2
	or $Cl(CH_2)_2C(NH_2)_2^+$		308	?	6

Other Information

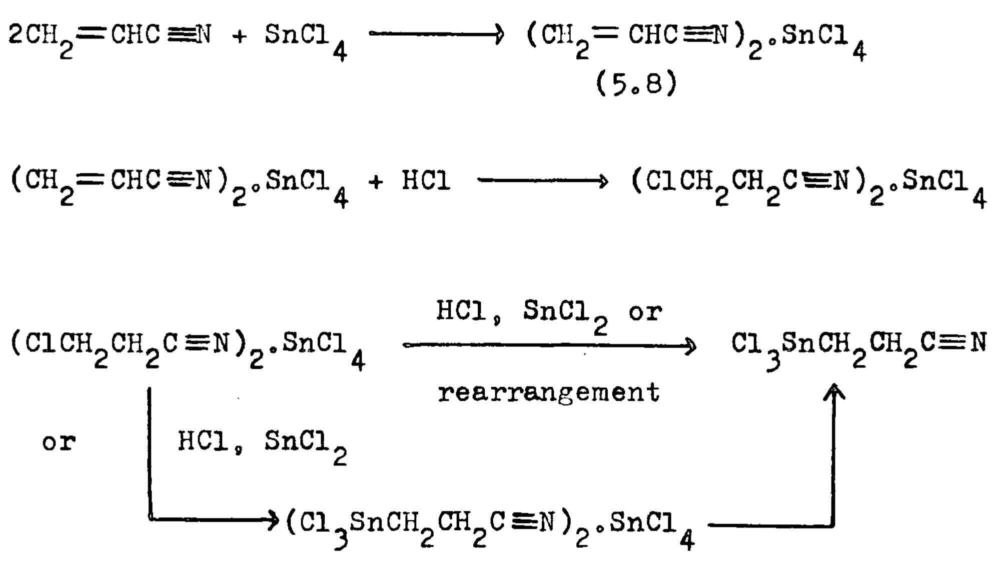
$$CH_2{=}CHCN \xrightarrow[Et_2O]{HCl} ClCH_2CH_2CN \xrightarrow[Et_2O]{SnCl_2} Cl_3SnCH_2CH_2CN \qquad (5.7)$$

Experimentally, the first stage occurs but insertion of tin chloride into the carbon chlorine bond is not possible. This is consistent with the lack of reaction between tin dichloride and 2-chloromethyl propionate [32].

$$SnCl_2 + ClCH_2CH_2CO_2Me \not\longrightarrow Cl_3SnCH_2CH_2CO_2Me \qquad (5.8)$$

The reactions involving tin (IV) chloride were performed to show that if they ultimately succeeded in producing CETTC then its preparation by the hydrostannation of acrylonitrile may involve a tin (IV) chloride adduct. This would seem feasible as on several occasions when hydrostannating acrylonitrile a precipitate was formed initially, the nature of which has not been determined. This redissolved within two hours. The amount of hydrogen chloride used during the preparation of the ethereal trichlorostannane appeared to be important. Addition of hydrogen chloride to the precipitate accelerates its rate of disappearance. If hydrogen chloride is added in excess to the ethereal trichlorostannane no precipitate forms; suggestions for possible intermediates, which could easily be involved, were discussed in connection with the Stephen reaction in the previous chapter. Failure to form such an ether insoluble precipitate was taken to indicate that the nitrile would not undergo the Stephen reaction until Lieber proved otherwise [33].

Hydrochlorination of the tin (IV) chloride adduct of acrylonitrile 5.8 was performed in an attempt to follow scheme 5.1.



$$2CH_2{=}CHC{\equiv}N + SnCl_4 \longrightarrow (CH_2{=}CHC{\equiv}N)_2.SnCl_4 \quad (5.8)$$

$$(CH_2{=}CHC{\equiv}N)_2.SnCl_4 + HCl \longrightarrow (ClCH_2CH_2C{\equiv}N)_2.SnCl_4$$

$$\begin{tikzcd}(ClCH_2CH_2C{\equiv}N)_2.SnCl_4 \arrow[rr, "{HCl,\ SnCl_2\ or}", "rearrangement"'] \arrow[d, "{or\quad HCl,\ SnCl_2}"'] & & Cl_3SnCH_2CH_2C{\equiv}N \\ (Cl_3SnCH_2CH_2C{\equiv}N)_2.SnCl_4 \arrow[urr] & & \end{tikzcd}$$

Scheme 5.1

However addition of hydrogen chloride to the acrylontrile adduct (5.8) yielded a product (5.9) which was difficult to identify. This is hardly surprising when one considers the complexity of the hydrochlorination reaction of nitriles themselves [34 - 38]. The infra-red and ^1H N.M.R. spectra give evidence for saturation of the alkene bond. The infra-red spectrum shows that the nitrile group has been converted to an azomethine group by the loss of v(C≡N) (2273-2222) and appearance of v(C=N) (1689-1471) [39]. The hydrochlorination of nitriles has been discussed in the previous chapter and similarily the nitrile group has most probably been converted into an imine or iminium chloride. The elemental analysis, which fits closest to addition of two molecules of hydrogen chloride per molecule of the adduct, suggests that, more than simple addition across the alkene bond has occured.

The mass spectrum gives evidence for possible dimerisation of acrylontrile which is consistant with the observations for the saturated nitriles (chapter 4). It also contains peaks for tin tetrachloride and its breakdown, implying that the tin tetrachloride unit has remained intact in the reaction. However, peaks at higher m/e values imply that the trichlorostannane unit may be attached to an organic group or alternatively (and less likely) recombination of ions or ions and molecules may occur within the spectrometer. These high mass peaks are at m/e values of 322, 304 and 269, the sequence of which is due to loss of fragments of m/e 18 and 35 which could represent loss of water and chlorine respectively. The mass spectrum does not give conclusive evidence for the presence of carbon-chlorine bonds although a peak is observed in the correct region of the infra-red spectrum ($850-550cm^{-1}$) [39].

Hydrostannation of the acrylonitrile adduct (5.8) was conducted to see if coordination of acrylonitrile to tin (IV) chloride (via the lone pair of electrons on the nitrile) might inactivate the nitrile functional group, and render the ligand more susceptible towards the formation of the CETTC adduct, subsequently forming CETTC, in possibly higher yield that simply from the hydrostannation of acrylonitrile.

$$\begin{tikzcd}
(CH_2{=}CHCN)_2.SnCl_4 \arrow[r, "HSnCl_3.xEt_2O"] & (Cl_3SnCH_2CH_2CN)_2.SnCl_4 \arrow[d] \\
 & Cl_3SnCH_2CH_2CN
\end{tikzcd} \qquad (5.9)$$

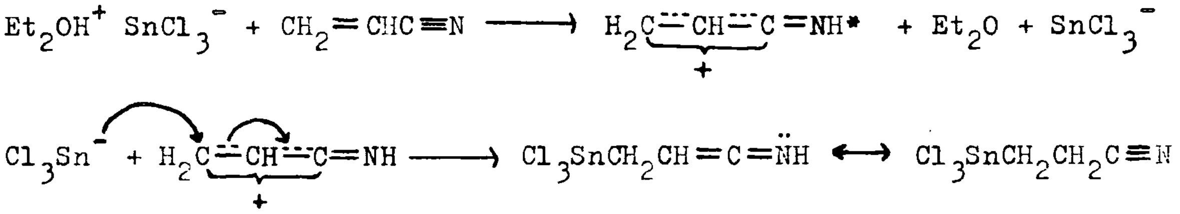
Unfortunately the reaction is complicated by the presence of excess hydrogen chloride in the ethereal trichlorostannane. Hence the nature of the final product (5.10) closely resembles that of 5.9.

Therefore equation (5.9) is not a practicable preparation of CETTC.

One may therefore conclude that it is unlikely that the hydrostannation of acrylonitrile by ethereal trichlorostannane proceeds via a tin (IV) chloride adduct.

A preliminary investigation into the attempted preparation of CETTC under the influence of γ irradiation was performed to determine whether the mechanism for the formation of CETTC is free radical in nature. As the product clearly was not CETTC then an alternative mechanism must apply. By comparison the hydrostannation of acrylonitrile by organotin hydrides (R_3SnH) under free radical conditions (u.v.light, AIBN) , leads predominantly to the β product [40] . AIBN was not used as a radical initiator for the reactions involving ethereal trichlorostannane as it would require heating and as the $CH_2{=}CHCN/HCl/SnCl_2$ system is somewhat thermally unstable this would be unadvisable. The actual reaction carried out was performed at room temperature. Care was taken to avoid excess ether and acrylonitrile which would both contribute to polymerisation under the reaction conditions. No pure products were isolated from the crude reaction mixture. The infra-red spectrum gave evidence for the presence of cyanide functional group(s) by peaks at 2304 and 2244 cm^{-1} (compared to 2224 cm^{-1} for acrylonitrile). The end product is probably a polymer of acrylonitrile with some ether and some tin- and chlorine- containing groups incorporated in the structure. Polymerisation of acrylonitrile has been studied extensively [41] and it has been reported that it will occur by a γ ray induced method in the presence of tin (II) chloride. [41a]

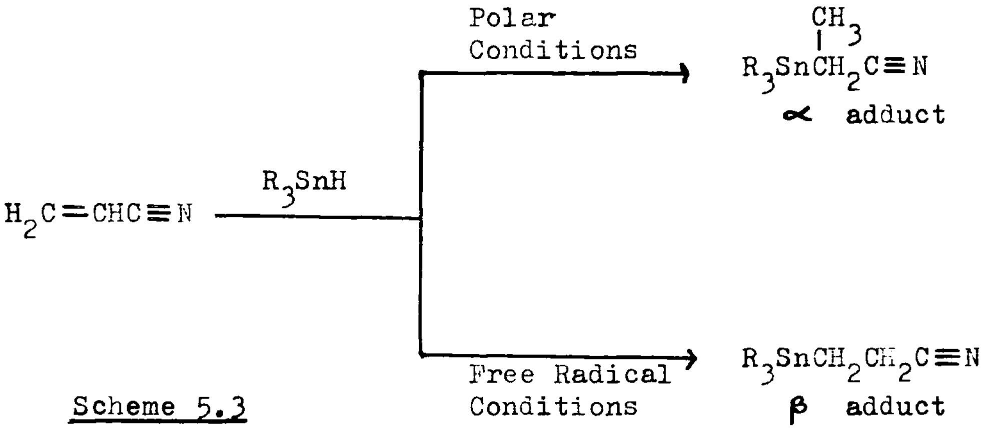
The most probable mechanism is therefore one of electrophilic attack by the proton of the ethereal trichlorostannane, proceeding via the most stable carbocation, followed by addition of the trichlorostannate anion and tautomerism to give CETTC [1] (scheme 5.2).



* Resonance stabilised
delocalised system.

Scheme 5.2

The hydrostannation of acryonitrile by organotin hydrides, R_3SnH, has been studied extensively [40, 42-49]. Polar solutions lead to the α adduct whilst the β adduct is formed under radical conditions [40] according to scheme 5.3.



Scheme 5.3

5.5 INVESTIGATIONS INTO ALTERNATIVE PRODUCTS FROM THE HYDROSTANNATION OF ACRYLONITRILE, INCLUDING THE ANALOGOUS BROMINE SYSTEM.

5.5.1 The hydrostannation of acrylonitrile appears to be very sensitive to experimental conditions. The method reported in the first section is that most conducive to formation of CETTC. An increase in temperature or the presence of moisture seriously impedes the reaction and leads to the formation of 2-chloropropionitrile and intractable polymeric gums. Hutton and Oakes, [50] in a report on the potential of hydrostannation by ethereal trichlorostannane, state that the upper temperature limit is governed by the reflux temperature of the solvent or compound undergoing hydrostannation, or by polymerisation starting to occur. In some cases the degree of polymerisation or ease of side reactions, such as hydrochlorination, is so high that the species is classed as unreactive towards ethereal trichlorostannane. The difficulties encountered with acrylonitrile may explain why its hydrostannation by ethereal trichlorostannane is absent to date from the literature.

5.5.2 Experimental

Hydrostannation of Acrylonitrile with Minor Experimental Alterations

5.5.2.1. Acrylonitrile (12.6 mls, 191.5 mmoles) was added to ethereal trichlorostannane (41.5 mmoles), without removal of the upper ethereal layer, and stirred for 48 hours at room temperature to give a pale yellow solution. Distillation at reduced pressure gave 2-chloropropionitrile (8.0 mls) leaving a yellow oil which was refluxed in toluene (40 mls) for 30 minutes, during which an orange oil was formed. The hot liquors were removed and upon cooling a few crystals (compound 5.12) appeared (0.41g). The orange oil solidified to an intractable gum.

5.5.2.2. Acrylonitrile (12.8 mls, 194.5 mmoles) was added to ethereal trichlorostannane (55.9 mmoles), without removal of the ethereal layer, to give a white precipitate (see previous section) which disappeared within 15 minutes. After 48 hours stirring at room temperature the yellow liquid was distilled gently to give hydrogen chloride, ether and 2-chloropropionitrile leaving a concentrated solution of the tin-containing species. The latter was refluxed in dry toluene for three

Compound No. 5.12	**Origin** $CH_2=CHC\equiv N$ + $HSnCl_3$

Name & Structure

see text

m.pt.

Elemental Analysis

		$Cl_3SnCH_2CH_2CONH_2$	$Cl_3SnCH_2CH_2CN$ + HCl
C	12.0	12.1	11.4
H	1.9	2.0	1.6
N	4.6	4.7	4.4
Sn			
Cl	35.2	35.7	44.9

Empirical Formula $C_3H_6NCl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull(fig.5.4)

3410m, 3330m, 3260m, 2950s, 2920s, 2850s, 2725w, 1650s, 1600w, 1562m, 1455s, 1410w, 1392w, 1375m, 1362m, 1290w/m, 1242w/m, 1120m, 1092w, 1020w, 845w, 730m, 720m, 672w/m, 612w.

¹H N.M.R. d_6DMSO, Int.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.27	t	7.6	1	CH_2
2.60	t	7.6	1	CH_2
8.80	s	-	1	NH_2

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	163	$[Sn + 43]^+$	7.6
44	$(CH_2)_2NH_2^+$; $C(NH_2)_2^+$	100	190	$SnCl_2^+$	11
	or $CONH_2^+$		225	$SnCl_3^+$	6.8
53	$C_2H_3CN^+$	100	233	$[SnCl_2 + 43]^+$	6.7
71	$(CH_2)_2CNHNH_2^+$	31	260	$SnCl_4^+$	15
83	$(CH_2)_4CNH^+$	16	272	?	3.4
97	$[83 + CH_2 \text{ or } N]^+$	15	336	$[SnCl_3 + 111]^+$	3.5
111	$[((CH_2)_2CNH)_2 + H]^+$	33.1			
120	Sn^+	12.7			
155	$SnCl^+$	25			

Other Information

hours to give crystals of CETTC (identified by comparison of its spectra with those of an authentic sample) (4.51g, 29%) from the hot liquors, along with a sticky orange solid which was pumped dry on the vacuum line and then characterised (compound 5.13).

5.5.2.3. Hydrolysis of CETTC

(i) A sample of CETTC was exposed to the atmosphere for 15 minutes and its infra-red spectrum was then recorded.

Infra-red spectrum, v cm^{-1}, KBr disc

3600-3000m,b, 2248m,b, 1610m,b, 1554m,shl 1405m, 1290m, 1239m,shl, 1160w/m, 1132m, 1004m/s, 884m, 724m, 663m/s, 618w,b, 525w/,b, 445m/s, 374w/m.

(ii) CETTC (2.47g, 88 mmoles) was dissolved in water (75 mls) and refluxed gently for 72 hours to form a white precipitate, which was filtered, washed with cold water, and dried in vacuo to give compound 5.14, the data for which are given overpage.

5.5.2.4 Bromine (2.5 mls) in toluene (20 mls) was added to compound 5.14 (0.33g) in toluene (20 mls) and stirred vigorously at room temperature for 3½ days, over which the deep red colour of the bromination mixture turned to a clear red/orange colour. This was refluxed for 2 hours and then distilled to give toluene and unreacted bromine leaving a dark coloured fuming luquid (compound 5.15).

Infra-red spectrum of compound 5.15, v cm^{-1}, contact film

3400-3100m,b, 3085m, 3055m, 3025m/s,2965m, 2915m, 1714s, 1600m, 1490m/s, 1450m/s, 1332w, 1262m/s, 1230s, 1202m, 1072m/s, 1031m, 1013w/m, 940w/m, 918m, 814m/s, 807m/s,shl, 792m, 760m/s, 748m/s, 733s, 699s, 607s, 547m, 480m, 467m,

Compound No. 5.13	**Origin** $CH_2=CHC\equiv N$ + $HSnCl_3$

Name & Structure

see text

m.pt.

Elemental Analysis

		$Cl_3SnCH_2CH_2CN$	$Cl_3SnCH_2CH_2CONH_2$
C	10.7	13.0	12.1
H	1.7	1.4	2.0
N	2.0	5.0	4.7
Sn			
Cl	24.9	38.1	35.7

Empirical Formula $C_6H_{12}NCl_5Sn$

Infra-red, ν cm⁻¹ KBr disc

3500-3000m, b, 1600s, b, 1530m, shl, 1394m, 1230m, b, 1180m, b, 1106m, 1021w/m, b, 974w, 890vw, 725m, 697m, b, 454w, 312m/s.

^{1}H N.M.R.

δ ppm	Mult.	J, Hz	Int.	Assign.
2.01 2.36 3.40 6.69 6.85 7.66 8.50	broad weak singlets			

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	225	$SnCl_3^+$	100
44	$(CH_2)_2NH_2^+$; $C(NH_2)_2^+$ or $CONH_2^+$	48	245	$Cl_2SnCH_2CH_2CNH^+$	100
			262	$[ClSn(CH_2CH_2CN)_2-H]^+$	53
54	$CH_2CH_2CN^+$	100	280	$Cl_3SnCH_2CH_2CN^+$	60
57	$[44 + CH]^+$	100	299	$Cl_2Sn(CH_2CH_2CN)_2H^+$	54
120	Sn^+	98	314	$Cl_3SnCH_2CH_2CNCl^+$	20
155	$SnCl^+$	100	333	$[Cl_3Sn(CH_2CH_2CN)_2-H]^+$	4.1
190	$SnCl_2^+$	100	394	?	8.0
208	$[ClSnCH_2CH_2CN-H]^+$	21			

Other Information

Compound No.	**Origin**
5.14	$Cl_3SnCH_2CH_2C\equiv N$ + H_2O

Name & Structure

see text

m.pt. d295

Elemental Analysis

		$ClSn(OH)_2CH_2CH_2CHO$	$ClSn(OH)_2CH_2CH_2CO_2H$
C	14.4	14.7	13.8
H	2.8	2.9	2.7
N	0.0	0.0	0.0
Sn	46.97	48.4	45.4
Cl	13.9	14.5	13.6

Empirical Formula $C_3H_6ClO_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull(fig5.5)

3620w/m, 3520w/m, b,3345m, 3144w/m,b, 2914s, 2860s, 1614m/s, 1573s, 1523s, 1458m, 1427s, 1385m/s, 1260s, 1231m, 1130m, 1058m, 1030m, 977m/s, 908m/s, 752m, 713m/s, 617m, 573m, 565w/m,540w/m 519m, 430m, 394m, shl,370m, shl.

¹H N.M.R. d_6DMSO,IntTMS(fig5.5)

δ ppm	Mult.	J,Hz	Int.	Assign.
1.41	t	8.6		CH_2
2.27	t	8.6		CH_2
1.13	s d?	12.2		OH
2.49	s			OH
3.33	s	-		OH or H_2O in DMSO

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
28	CNH_2^+, $C_2H_4^+$, CO^+	43	155	$SnCl^+$, $[Sn(OH)_2 + H]^+$	20
36	HCl^+	10	190	$SnCl_2^+$, $[Sn(OH)_2 + H]^+$ or $[SnCH_2CH_2CONH_2 - 2H]^+$	11
45	$CONH_3^+$, $\dot{C}O_2H^+$	14			
56	$(CH_2)_2CO^+$, $CH_2CH_2C=NH_2^+$	17	199	$[SnCl + 44]^+$ or $[Sn(OH)_2 + 45]^+$	4.0
73	$(CH_2)_2CO_2H^+$	12	225	$SnCl_3^+$ or $[Cl_2Sn(OH)_2 + 2H]^+$ or $[ClSnCH_2CH_2CONH_2 - 2H]^+$	4.2
120	Sn^+	7.2			
137	$SnOH^+$	2.1			

Other Information

5.5.3 Discussion of Results

For a maximum yield of CETTC care must be taken not to overheat the reaction mixture. The organotin species 5.12 is formed as a result of a thermally initiated side reaction. The elemental analysis fits most closely for the amide, $Cl_3SnCH_2CH_2CONH_2$, which could easily be formed if there were any moisture in the system. The infra-red spectrum gives no evidence for the nitrile group, but instead has peaks at 1650 and 1600 cm^{-1} which may be attributed to $v(C{=}N)$, $v(C{=}C)$ or $v(C{=}O)$. For comparison $Cl_2Sn(CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2)_2$ has a carbonyl stretching frequency of 1651 cm^{-1} [11]. The following vibrations are also evident from the spectrum; $v(N\text{-}H)$, 3410, 3330, 3260; $\delta\ NH_2$, 1410; δNH_2 and $v(C\text{-}Cl)$, 730,720,672 and $v(Sn\text{-}Cl)$ 612. The proton n.m.r. spectrum shows that the alkene bond has been saturated by the presence of peaks attributable to methylene, rather than olefinic, protons. The additional peak at 8.80 ppm is most probably due to proton(s) attached to the nitrogen atom, for example in an amide or azomethine functional group. The highest peak on the mass spectrum (m/e 336) is assignable to a species containing a trichlorostannane unit along with two acrylonitrile molecules or an acrylonitrile dimer. This opens up the possibility that the compound could involve dimerisation of the nitrile as suggested for the compounds in the previous chapter. The major peaks for $Cl_3SnCH_2CH_2CONH_2$ are not present. However, there are peaks for $SnCl_x$ (x=0-4); $SnCl_4^+$ probably being a result of recombination of ions within the spectrometer, and due to acrylonitrile and its dimer with their break down. It is also apparent that the tin atom is attached to organic groups due to peaks at m/e 163, 233 and 272 as assigned in the data table (page 195).

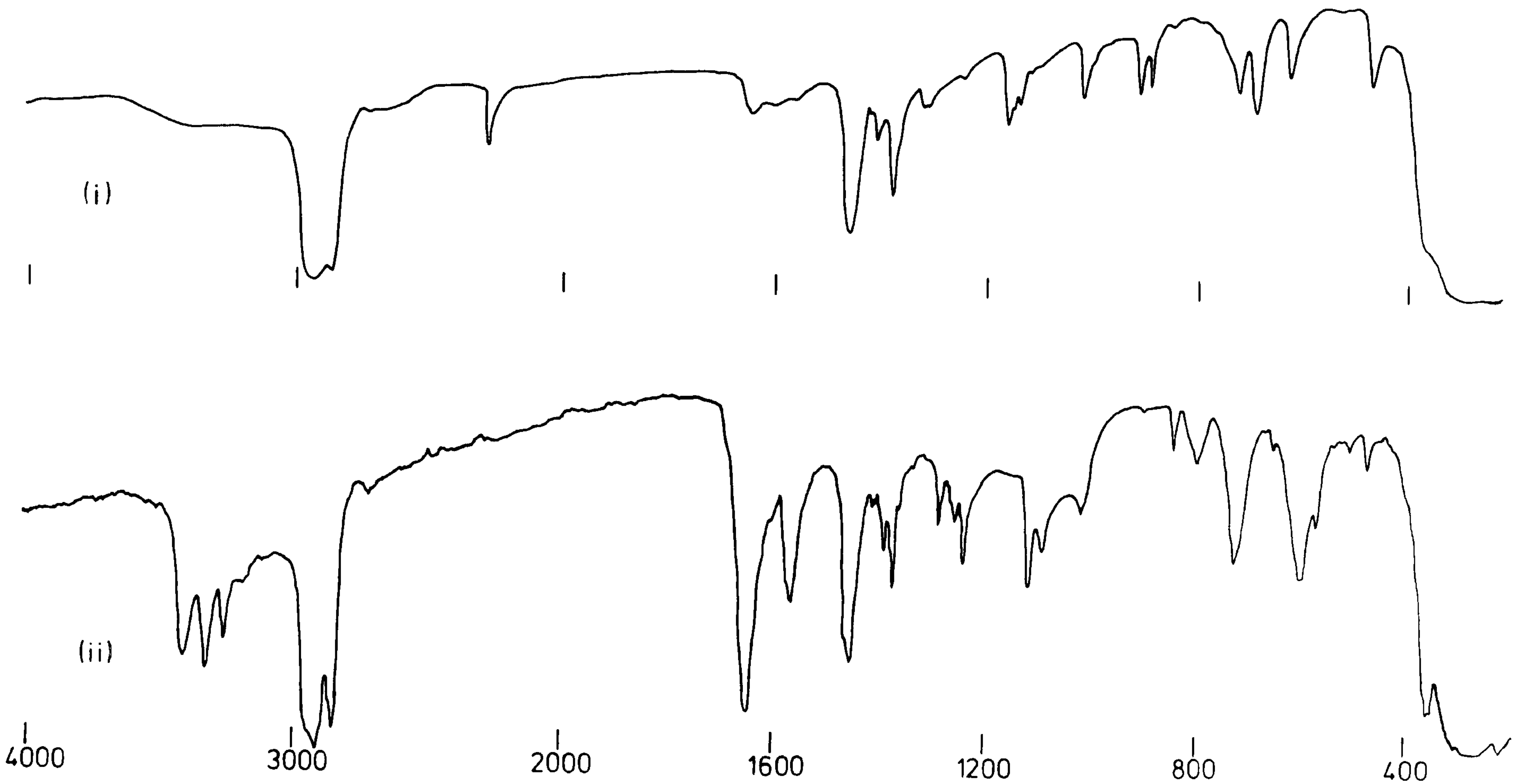
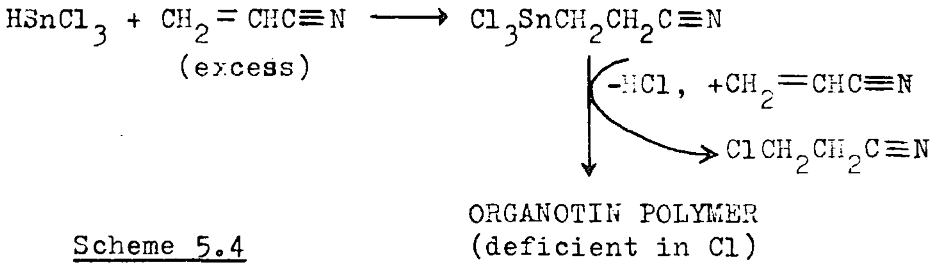


Fig. 5.4 Infra-red spectra of (i) CETTC and (ii) Compound 5.12

Compound 5.12 is therefore not simply $Cl_3SnCH_2CH_2CONH_2$, but is more likely to be a complicated species formed as a result of the complexity of ethereal trichlorostannane and the ease of loss of hydrogen chloride (thermally assisted). Unforseen moisture may also contribute to the formation of a complex species.

In each case where heat was applied to the system 2-chloropropionitrile was produced as a side product (established by comparison of the infra-red spectrum and g.l.c. trace with those of an authentic sample). The most favourable method of CETTC formation (section 5.2), in which no heating of the crude reaction mixture is involved, does not yield any 2-chloropropionitrile. On the occasions when it is formed as a side product it is accompanied by the formation of a sticky orange solid and consequently the yield of CETTC is decreased, often quite drastically. The effect of heating is probably to expel hydrogen chloride from the reaction product. The former can then react with excess acrylonitrile to form 2-chloropropionitrile as a side product. This leaves an organotin component deficient in chlorine, with a vacant coordination site on the tin atom available for bonding with another cyanoethyl group or for undergoing polymerisation (scheme 5.4).



Scheme 5.4

The elemental analyses for this compound show that the carbon to chlorine ratio is 6:5, suggesting a loss of one chlorine atom for every two CETTC molecules. Infra-red studies show that the nitrile group has disappeared but peaks at 1600 and 1560 suggest that it may have been replaced by an azomethine or carbonyl (amide) group. [39]. There is a possible (C-N) stretching frequency at 1396 cm^{-1}. The intense peaks at low frequencies (401, 310 and 290 cm^{-1}) are due to Sn-Cl stretching. The mass spectrum suggests that the $SnCl_3$ group still remains, (at least in enough molecules to be observed by the mass spectrometer), even though loss of hydrogen chloride seems to be the route to this side product. There are also peaks attributable to one or two molecules of acrylonitrile attached to the tin residue. The highest mass peak is at an m/e value of 394 and therefore shows that the product may not be polymeric when dried out.

One of the reasons for the hydrolysis experiments was to find out whether compounds 5.12 and 5.13 are formed as a result of the hydrolysis of CETTC (due to moisture in the system) which itself may actually have been prepared but subsequently reacted completely. As the data for compound 5.14 are different from those of compounds 5.12 and 5.13, unwanted hydrolytic side reactions have not led to the latter compounds, leaving the theory involving thermal assistance still viable.

Mild hydrolysis by the atmosphere was monitored by infra-red spectroscopy. Two important changes occur in the infra-red spectrum. Firstly, the cyanide stretching frequency is reduced, which is obviously due to the polymeric chain of CETTC being broken to free the nitrile group. Secondly, the region above 3000 cm^{-1} now contains a broad peak due to O-H stretching, as a result of some or all of the chlorine atoms being replaced by hydroxy groups or because of coordinated water molecules.

Slightly more forcing conditions, i.e. refluxing in water, led to a more complex product, both ends of the molecule being affected. The data imply that it is most probably $Cl(OH)_2SnCH_2CH_2R$ where R is $CONH_2$, COOH or CHO. However, even though the spectra suggest that the product could be an amide, repeated nitrogen analysis shows that compound 5.14 contains no nitrogen. Possible compounds whereby only one chlorine atom has been replaced would require a much higher chlorine content so are not feasible.

The infra-red spectrum does not contain a peak in the nitrile stretching **region** (2300-2200 cm^{-1}). The nitrile group appears to have been converted into an amide as there are peaks in the correct regions for amides (v(N-H) 3520-3400; v(C=O) 1680-1630); δ (N-H) 1655-1515; v(C-N) 1400 and N-H out of plane wagging 800-666 cm^{-1}) although the carbonyl stretching frequency is rather low. However, due to the lack of support from the elemental analysis the CETTC could have been converted into an aldehyde or a carboxylic acid, but again the carbonyl stretching frequency is too low. There is no aldehydic carbon hydrogen stretching. Carboxylic acids exhibit a broad O-H peak but the peaks above 3000 cm^{-1} for compound 5.14 are all relatively sharp (fig. 5.5). In addition there is no low field peak is the n.m.r. spectrum attributable to either an aldehyde or carboxylic acid proton. This could be overcome if the product is a carboxylate or a ketone, such as $\left[Cl_{3-x}(OH)_xSnCH_2CH_2\right]_2$ C=O. However the latter possibility is excluded on the grounds of the elemental analysis. The n.m.r. spectrum (fig. 5.5) consists of two multiplets at 1.41 and 2.27 ppm due to complex splitting interactions of the methylene protons in their new environment, possibly affected by any nearby OH group attached to the tin atom. The two highest intensity peaks in these multiplets correspond to an

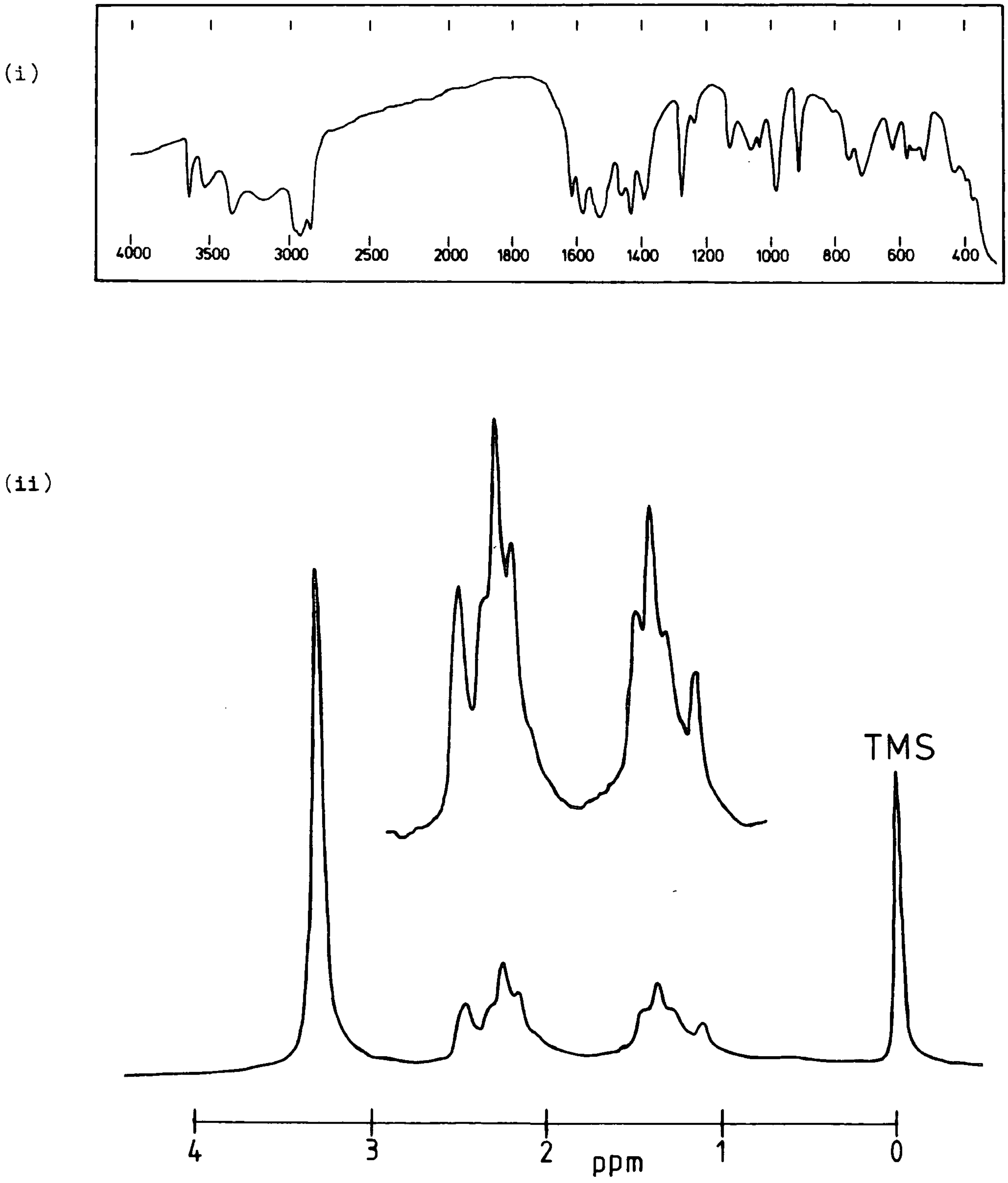


Fig. 5.5 (i) The infra-red (Nujol mull) and (ii) ^{1}H. n.m.r. spectra of the hydrolysis product of CETTC.

upfield shift compared to CETTC and the splitting value has been virtually unaffected; 8.5 to 8.6 Hz. An upfield shift implies an increase of electron density around the proton, hence the rest of the molecule must effectively be less electronegative. There is an additional singlet at 3.3 ppm which may be assigned to a hydroxy proton (or attached water molecule). Alternatively it could be due to water in the DMSO. The simplicity of the n.m.r. spectrum implies that the compound is pure.

The mass spectrum has peaks attributable to the amide functional group as illustrated on the data sheet for this compound. For the tin containing peaks it is difficult to distinguish whether a chlorine atom (mass 35) or two hydroxy groups (total mass 34) are attached. However the problem is overcome with the aid of computer simulations, due to the relative isotope intensities of tin (fig. 4.3, page 146), and chlorine, and gives evidence for both tin-chlorine and tin hydroxy groups.

Nitriles are easily hydrolysed to amides and for this particular case hydrolysis of the nitrile group may be accelerated by any hydrogen chloride being evolved from the tin end of the molecule. ^{119}Sn n.m.r. and Mössbauer studies of the hydrolysis of monoalkyltin halides [51] led to comparable results, to those discussed above, for the tin end of the molecule.

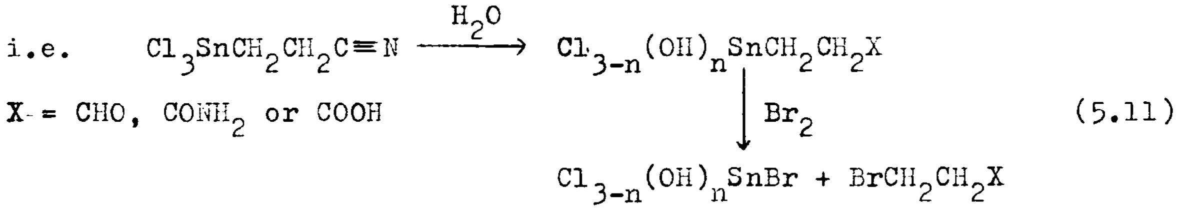
i.e. $$\mathrm{MeSnCl_3 + H_2O \longrightarrow MeSn(OH)Cl_2.2H_2O + Me(OH)_2ClSn.nH_2O + [MeSn(OH)(H_2O)_4]^{2+}.} \qquad (5.10)$$

In the Stephen reaction hydrogen chloride and tin dichloride are added to a nitrile and the subsequent mixture is hydrolysed to give an aldehyde or amide [33, 52 -55]. The hydrolysis of CETTC is effectively the last stage of the Stephen reaction on acrylonitrile.

By comparison one would expect to obtain an organotin amide or aldehyde if the compound remained intact or a separate organotin compound with the aldehyde or amide in solution. No organic products were obtained from the solution after removal of compound 5.14 by filtration.

Finally, a longer period of refluxing, or more forcing conditions, such as acid or base catalysis may remove all of the chlorine from the CETTC during its hydrolysis.

Bromination of the hydrolysis product of CETTC 5.15 was performed to separate the organic and inorganic halves of compound 5.14 which could then be characterised and identified separately.



$$\text{i.e.}\quad \begin{array}{l} Cl_3SnCH_2CH_2C{\equiv}N \xrightarrow{H_2O} Cl_{3-n}(OH)_nSnCH_2CH_2X \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow Br_2 \\ \qquad\qquad\qquad\qquad\qquad Cl_{3-n}(OH)_nSnBr + BrCH_2CH_2X \end{array} \qquad (5.11)$$

$X = CHO, CONH_2$ or $COOH$

The infra-red of the product obtained, 5.I5 strongly suggests that it, and therefore compound 5.14, is a carboxylic acid by the presence of a strong peak at 1714 cm^{-1} ($\nu(C{=}O)$) and also peaks at 1450 (δ (C-O-H) in plane), 1230 (ν(C-O)) and 918 (δ(O-H) out of plane). No further characterisation was carried out as the product needed further purification possibly via an improved isolation procedure.

In the previous chapter the hydrostannation of 2-chloropropionitrile was investigated. Comparison of its hydrostannation product with compounds 5.12 and 5.13 shows that the latter are not formed via hydrochlorination of acrylonitrile to give 2-chloropropionitrile which subsequently undergoes hydrostannation.

5.5.4 Hydrostannation of Acrylonitrile by Hydrogen Bromide and Tin (II) Bromide

5.5.4.1. Introduction

By analogy to the hydrostannation of acrylonitrile by ethereal trichlorostannane, 2-cyanoethyltin tribromide (CETTB) should be preparable from hydrogen bromide, stannous bromide and acrylonitrile in diethyl ether.

$$\mathrm{HBr} + \mathrm{SnBr_2} \xrightarrow[\mathrm{Et_2O}]{} \mathrm{HSnBr_3.nEt_2O} \xrightarrow[\mathrm{H_2C=CHC\equiv N}]{} \underset{\mathrm{(CETTB)}}{\mathrm{Br_3SnCH_2CH_2C\equiv N}} \qquad (5.12)$$

5.5.4.2. Experimental

Hydrogen bromide was bubbled into a solution of stannous bromide (4.62g, 16.6 mmoles) in diethyl ether at 0°C which immediately turned pale yellow. A dark yellow solid appeared but dissolved within ten minutes. Hydrogen bromide was added for a further 15 minutes to completely saturate the system. Excess acrylonitrile (6 mls, 90 mmoles) was added by syringe and a large amount of a crystalline product was formed over night. Attempted recrystallisation of this crude product yielded a white powder, compound 5.16, and an orange oil, compound 5.17. Small crystals were obtained from the oil, compound 5.18.

Characterisation of compound 5.16 is given on the data table over page.

Infra-red spectrum of compound 5.17, ν cm^{-1}, contact film

3300-2770s,b, 2480m,b, 1675s,b, 1575m/s,b, 1445m/s,b, 1430m/s,b, 1392m/s, 1322m, 1270s, 1230w/m, 1200w/m, 1154m/s, 1130m/s, 1087m/s, 1035w, 1005m/s, 917m, 904w/m, 822m, 788m, shl, 741s, 708m/s, 580m, 552m, shl, 472w/m.

Infra-red spectrum of compound 5.18, ν cm^{-1}, nujol mull

3150m,b, 2920s, 2850s, 1460m/s, 1392m/s, 1376m/s, 720w/m.

Compound No. 5.16	**Origin** $SnBr_2 + HBr + CH_2=CHC\equiv N \xrightarrow{Et_2O}$

Name & Structure

see text

m.pt.

Elemental Analysis		$C_3H_4NSnBr_3$	BrC_3H_4N
C	23.0	8.73	26.9
H	4.5	0.98	3.0
N	5.2	3.4	10.5
Sn			
~~**Cl**~~ Br	46.5	58.08	59.6

Empirical Formula C_3H_6NBr

Infra-red, ν cm⁻¹ Nujol Mull

3052m, b,2960s, 2922s, 2862s, 1722w/b, 1626m/s, 1562w, 1462m/s, 1449m/s,1415w, 1387m, 1370m, 1362m, 1289w, 1257m, 1197w/m, 1152m/s, 1128m, 1088m/s,1039w, 1011m, 964w, 920m, 856m, 848m, 824m, 790m, 724w/m, 572w/m, 548w/m, 486w.

¹H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.37	weak m's	-	8	CH_2
2.63				
3.58		-		
4.37		-		
7.20	t	50Hz	1	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
27	CNH^+	72	80	HBr^+	15
44	$CONH_2^+, CH_2CH_2NH_2^+,$	77	100	?	22
	COO^+		107	$CH_2CH_2Br^+$	12
54	$CH_2CH_2C\equiv N^+$	68	127	?	4
56	$CH_2CH_2C=NH_2^+$	65	134	$SnCH_2^+$, SnN^+	17
	$(CH_2)_4^+$		150	$[Br + 72]^+$	16
72	$C_3H_7CNH_2^+,$	66			
	$[C_3H_7C=O + H]^+$				

Other Information

5.5.4.3. Discussion of Results

Isolation of ethereal tribromostannane has not been reported in the literature. However, organotin bromides have been prepared by the hydrostannation of unsaturated organic species by hydrogen bromide with tin (II) bromide or tin powder using excess organic compound as solvent [50, 56] .

In this preliminary investigation into hydrostannation by hydrogen bromide and tin (II) bromide in ether to form organo tin bromides, in particular CETTB, the first observation was that tin (II) bromide is soluble in ether in contrast to tin (II) chloride which is insoluble. In the chlorine case the formation of ethereal trichlorostannane is complete when there is no undissolved tin (II) chloride left. Formation of the bromine analogue cannot be monitored in this way so hydrogen bromide was added for a longer period of time than in the chlorine case to ensure completion of the first stage.

$$HBr + SnBr_2 + Et_2O \longrightarrow HSnBr_3.nEt_2O \qquad (5.13)$$

Clearly, the desired product, CETTB, has not been prepared. Compound 5.18 is largely inorganic and therefore may be recrystallised $SnBr_2$or $SnBr_4$. Compound 5.16 is possibly a hydrobromination product. However, infra-red studies show that it is not a nitrile such as 2-bromopropionitrile, but a derivative such as ~~an~~ imine or amine. It is also feasible to form an imminium salt (bromide or tribromostannate). Any organotin bromides, such as the nitrile, imine or amide may be contained in the oily residue which was not fully characterised as further purification was necessary.

Further investigations into the handling and use of "$HSnBr_3$" are therefore required in order to establish the most conducive conditions to form CETTB and to determine other possible products.

5.5.5. Reactions to replace the chlorine atoms of $Cl_3SnCH_2CH_2C{\equiv}N$ (CETTC) by organic groups

5.5.5.1. The action of a Grignard reagent on CETTC should convert it into the corresponding organotin compound.

$$RMgBr + Cl_3SnCH_2CH_2C{\equiv}N \longrightarrow \underset{V.3}{R_3SnCH_2CH_2C{\equiv}N} \qquad (5.14)$$

If the reaction does not go to completion then additional products, $R_xCl_{3-x}SnCH_2CH_2C{\equiv}N$ (x=1,2) will be formed in the mixture. Alternatively the reaction may also involve the nitrile function, and so give ketones, $R_xCl_{3-x}SnCH_2CH_2C(=O)R$. The desired product (V.3) may be prepared by the hydrostannation of acrylonitrile by organotin hydrides, R_3SnH [40]. Keto-organostannanes have been prepared by reacting the relevant cyanoalkyl trimethylstannane with methyl and phenyl Grignard reagents or by oxidation of the corresponding alcohol [57].

5.5.5.2. Experimental

Methyl bromide (1.3g 13.7 mmoles) in diethyl ether (10 mls) was added slowly to magnesium turnings (0.35g) in diethyl ether (5 mls) and the resultant grey solution was refluxed under nitrogen for 40 minutes. Upon addition of CETTC (1.13g. 3.6 mmoles) dissolved in hot toluene (45 mls) an immediate white precipitate appeared and the mixture was refluxed for two hours. The precipitate was isolated by filtration, 5.19, and the filtrate placed in the fridge to induce crystallisation, but to no avail. A portion of compound 5.19 was suspended in ether and dioxan (6 mls) added and the amount of solid suspended increased. Removal of the solid followed by reduction of the ethereal solution yielded a yellow oil, 5.20.

Compound No. 5.19

Origin $MeMgBr + Cl_3SnCH_2CH_2C \equiv N$

Name & Structure

see text

m.pt.

Elemental Analysis

C	21.1	see table 5.13
H	4.5	
N	0.8	
Sn		
Cl	28.5	

Empirical Formula $C_9H_{22}Cl_4Sn_2$

Infra-red, ν cm^{-1} Nujol Mull

3360m/b, 2950m/s, 2918m/s, 2850m/s, 2276m, 1602s, 1448s, 1375m/s, 1283w/m, 1240w, 1182w/m, 1142m, 1117w/m, 1038m, 1032m, 994m, 884m, 827w/m, 768m.

^{1}H N.M.R. $d_6$acetone Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
1.46	s,b	-	1	
3.00	s	-	3	Me
4.88	s	-	1	

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	53	120	Sn^+	3.1
43	$C(=NH_2)NH^+, CONH^+$	34	135	$SnMe^+$	2.8
	$(CH_2)_2NH^+, CH_3CO^+$		150	$SnMe_2{}^+$	2.0
44	$C(NH_2)_2{}^+, CONH_2{}^+,$	26	155	$SnCl^+$	3.5
	$(CH_2)_2NH_2{}^+$		165	$SnMe_3{}^+$	5.8
58	$[C_2H_4C=NH_2 \quad +2H]^+$	86	176	$[Sn + 56]^+$	2.2
	$CH_2CONH_2{}^+$		185	$[Sn + 65]^+$	2.0
	$(CH_2)_3NH_2{}^+$		229	$Sn(CH_2CH_2CN)_2H^+$	2.1
65	?	8.0			
88	$C_4H_8O_2{}^+$	100			
	$(CH_2CH_2NH_2)_2{}^+$				

Other Information

Compound No. 5.20

Origin MeMgBr + $Cl_3SnCH_2CH_2C \equiv N$

Name & Structure

see text

m.pt.

Elemental Analysis

C	66.0	see table 5.13
H	12.5	
N	2.7	
Sn		
Cl	0.0	

Empirical Formula

Infra-red, ν cm⁻¹ Contact film

3445m/s, 3244w, 2930s, 2852s, 2728w, 2678w, 2282m, 2248w/m, 1725m, 1652m, 1617m, 1460s, 1374m/s, 1235m, b, 1120w/m, b, 1072w/m, 880w/m, 779m, 721m, sh, 546m, 526w/m.

¹H N.M.R. $CDCl_3$ Int.TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
0.83	m	-		CH_2
1.26	s	-		CH_3

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I

Other Information

Compound No. 5.21	**Origin** PhMgBr + $Cl_3SnCH_2CH_2C \equiv N$

Name & Structure

see text

m.pt.

Elemental Analysis

		$Ph_3Sn(CH_2)_2CN$	$Cl_2PhSn(CH_2)_2CO_2H$
C	23.9	62.4	31.8
H	2.8	4.7	3.0
N	0.6	3.5	0.0
Sn		29.4	34.9
Cl	30.5	0.0	20.9

Empirical Formula

Infra-red, ν cm⁻¹ Nujol Mull

3365m/s, b,2920s, 2858s, 2720vw, 2277w/m, 1605m/s, 1573m, 1461s, 1427m, shl,1372m/s, 1333w/m, shl,1295w/m, 1270w/m, 1185w/m, 1146m, 1118w/m,1085m 1070m, 1033m, 995m, 890w/m, 832w/m, 775m, 726m/s, 695m/s, 442m, shl.

^1H N.M.R. d_6DMSO Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
0.92	m	-	2	CH_2
2.13	s,b	-	1	CH_2
2.34	m	-		CH_2
3.16	m	-	2	CH_2
3.30		-		H_2O in solvent
7.05	m	-	5	Ph

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	15	175	$SnC_2H_3CO^+$ or	3.0
45	$CH_2CH_2OH^+, CO_2H^+$	24		$SnCH_2CH_2CNH^+$	
	or $CH_3CH_2NH_2^+$		199	$[SnPh + 2H]^+$	22
51	$C_4H_3^+$	100		or $[SnCl + 44]^+$	
77	Ph^+	100	276	$[SnPh_2 + 2H]^+$	3.0
104	$[COPh -H]^+$	23	309	Ph_2SnCl^+	2.0
120	Sn^+	8.6	348	$[Ph_3Sn -3H]^+$,	8.0
132	$C_2H_3COPh^+$	12		$[Ph_2SnCH_2CH_2COOH+H]^+$	
154	$(2xPh)^+$	75		or $[Ph_2SnCH_2CH_2CONH_2$	
				$+ 2H]^+$	

Other Information

Compound No. 5.22	**Origin** PhMgBr + $Cl_3SnCH_2CH_2C{\equiv}N$

Name & Structure

see text

m.pt.

Elemental Analysis		$Ph_3Sn(CH_2)_2CN$	$PhCl_2Sn(CH_2)_2COPh$
C	41.2	62.4	45.1
H	5.1	4.7	3.5
N	2.0	3.5	0.0
Sn		29.4	29.7
Cl	15.9	0.0	17.7

Empirical Formula

Infra-red, ν cm⁻¹ Nujol Mull

3320m, b,2960s, 2862s, 1614m, b,1600m, sh1,1590m, sh1,1460s, 1380s, 1303w/m, 1280w, 1210w, 1159w/m,1079m, 1026w/m, 1001m, sh,734m/s, 704m/s, 450w/m.

^1H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
0.95	m	-	2	CH_2's
1.98	s,b	-	1	
2.37	s,b	-	2	
3.22	s	-	4	H_2O in solvent
7.25	m	-	5	Ph

Mass Spectrum

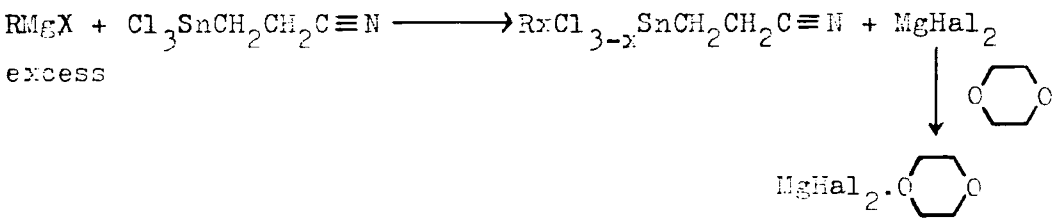
m/e	Fragment Ion	I	m/e	Fragment Ion	I

Other Information

The procedure was repeated using phenylmagnesium bromide, again producing a white solid which was removed by filtration (compound 5.21). Reduction in volume of the filtrate yielded a yellow powder (compound 5.22). Portions of this powder were used to try and establish a successful work up procedure. Neither water, hydrochloric acid (aqueous), dichloromethane, chloroform nor carbon tetrachloride would dissolve or have any effect on it, nor could it be purified by sublimation.

5.5.5.3. Results and Discussion.

The data are displayed in the tables on pages 211 to 214 . The products are likely to be moisture sensitive so careful work up procedures must be employed to isolate pure products. Consequently, the magnesium halides produced as side products were removed as dioxan adducts rather than by dissolving them in aqueous hydrochloric acid as for conventional Grignard reactions.



$$\underset{\text{excess}}{RMgX} + Cl_3SnCH_2CH_2C{\equiv}N \longrightarrow R_xCl_{3-x}SnCH_2CH_2C{\equiv}N + MgHal_2 \qquad (5.15)$$

$$MgHal_2 \xrightarrow{\text{dioxan}} MgHal_2.\text{dioxan}$$

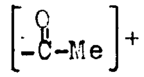
However, it is also possible that any insoluble organotin products may be lost with the dioxan precipitate due to separation difficulties. Any organotin products mixed in with the magnesium halide precipitate could conceivably be isolated by subliming them onto a cold finger, the high melting point magnesium halides ($MgCl_2$ has a melting point of 714°C and $MgBr_2$ one of 700°C) being left behind, but no organotin compounds were in fact isolated by this method. Due to the difficulties encountered it was hard to isolate pure products. Impurities present have made the spectra more complicated and therefore more difficult to interpret. Further work is necessary to develop a successful method for isolating the pure required products. Each product obtained in the experiments described above is now discussed in turn.

Compound 5.19

Infra-red studies show that the nitrile group is still present although v(C$\equiv$N) (2276 cm^{-1}) is very close to that of CETTC itself (2278 cm^{-1}). Unreacted CETTC could therefore be present as an impurity. However, the broad shoulder to the low frequency side of the peak could represent new products. Alternatively a peak at 1602 cm^{-1} implies that the nitrile has been converted to an imine group [v(C=N) = 1689-1471 [39]]. A less likely possibility for this peak would be v(C=O) for an aldehyde, ketone, carboxylic acid or amide as it is rather low. However, there is no evidence for v(C-O) between 1260 and 1000 cm^{-1} but there is a broad peak at 3360 for hydroxy stretching.

The quality of the n.m.r. spectrum was reduced by solubility problems. Subsequently, there are no triplets to represent the methylene groups of the cyanoethyl or $-CH_2CH_2R$ (R = C(=O)Me, C(=O)NH_2) groups close to the shift values of CETTC itself.

The mass spectrum shows that at least some of the CETTC must have reacted as there is evidence for $SnMe_x$ (x = 1 - 3) fragments but none for $SnCl_x$ (x = 2,3) fragments, although the latter may be present but too weak to distinguish. It also suggests the presence of amide or amine functional groups as well as some nitrile containing groups. There is also a peak at a m/e value of 43 corresponding to the


$\left[-\overset{O}{\overset{\|}{C}}-Me\right]^+$ fragment of a ketone.

Due to the purification difficulties the elemental analyses are not expected to correspond exactly to any of the suggested products. However, from table 5.13 below one is able to deduce the most probable possibilities.

Table 5.13

Elemental analysis of Compound 5.19 and some of its possible assignments.

Compound	% C	% H	% N	% Cl
Compound 5.19	21.1	4.5	0.8	28.5
$Me_3SnCH_2CH_2C{\equiv}N$	33.1	6.0	6.4	0.0
$Me_2ClSnCH_2CH_2C{\equiv}N$	25.2	4.2	5.9	14.9
$MeCl_2SnCH_2CH_2C{\equiv}N$*	18.6	2.7	5.4	27.4
$Me_3SnCH_2CH_2COMe$	35.8	6.9	0.0	0.0
$Me_2ClSnCH_2CH_2COMe$	28.2	5.1	0.0	13.9
$MeCl_2SnCH_2CH_2COMe$ *	21.2	3.7	0.0	25.7
$Me_3SnCH_2CH_2CONH_2$	30.6	6.4	5.9	0.0
$Me_2ClSnCH_2CH_2CONH_2$	23.4	4.7	5.7	13.8
$MeCl_2SnCH_2CH_2CONH_2$*	17.4	3.3	5.1	25.6
Me_3SnCl	18.1	4.6	0.0	17.8
Me_2SnCl_2	11.0	2.8	0.0	32.3
$MeSnCl_3$	5.0	1.3	0.0	44.3

* Closest fitting to compound 5.19

The data fit most closely to the calculated results for $MeCl_2SnCH_2CH_2C{\equiv}N$, $MeCl_2SnCH_2CH_2COMe$ and $MeCl_2SnCH_2CH_2CONH_2$. The product may be a mixture of compounds of the general formula $Me_xCL_{3-x}SnCH_2CH_2Y$ where Y is $C{\equiv}N$, COMe and $CONH_2$ of which the overall mixture fits the formula best for x equal to one for each value of Y. These suggestions are supported by the spectroscopic results.

Compound 5.20

The elemental analysis for the second product, obtained in the form of an oil, suggests that it is not organometallic and that it does not contain any halogens. Again due to the likelihood that it does not consist solely of one species makes the elemental analysis difficult to interpret.

There are two peaks in the nitrile stretching region of the infra-red spectrum (2282 and 2248 cm^{-1}). The higher frequency peak may represent unreacted CETTC (2278 cm^{-1}) within experimental error or alternatively the two peaks may represent two new products or one with two nitrile stretching frequencies. Amine N-H scissoring and C-N stretching occur at 1620 and 1060 cm^{-1} respectively and the wagging between 909 and 666 cm^{-1}, all of which are present in the spectrum. The peak at 3345 cm^{-1} may be v(N-H) of an amine or amide although one would expect two such peaks, one for symmetrical and one for anti-symmetrical stretching.

Alternatively this peak may be due to hydroxy stretching but there is no strong peak between 1260 and 1000 cm^{-1} for v(C-O) to accompany it.

There are three medium intensity peaks in the v(C=O) and v(C=N) region at 1725, 1652 and 1617 cm^{-1} which may be assigned as for compound 5.10.

Again the n.m.r. spectrum is of poor quality due to solubility problems and is as assigned on the data table. There is no low field peak corresponding to an aldehyde or carboxylic acid proton.

<u>Compound 5.21.</u>

Again infra-red studies indicate the presence of a nitrile group, possibly unreacted CETTC. By comparison 2-cyanoethyl triphenyl tin has a nitrile stretching frequency of 2252 cm^{-1} [58] which is not present in the spectrum of compound 5.21. Again there are features representing a carbonyl or an imine group. It is unclear whether Sn-Ph bonds are present as the region of the spectrum where such stretching occurs (280-225) is below the limitations of the KCl plates.

The ^{1}H n.m.r spectrum is as assigned in the data table and the complexity reveals its impurity. There are no low field peaks for aldehyde, carboxylic acid or amide protons.

The mass spectrum shows that some chlorine atoms of CETTC have been replaced by Ph groups as there are peaks for $SnPh_x$ (x=1,2) fragments and none for $SnCl_y$(y=2,3) fragments. There is considerable evidence for the $CH_2CH_2C(=O)Ph$ group of a ketoorganostannane.

Again the elemental analysis can only be used as a rough guide due to the probable impurity of the product. The percentage of carbon is relatively low implying that maybe replacement of only one chlorine atom has occured for the major product.

Compound 5.22.

The infra-red spectrum has similar features to those of compounds 5.19 and 5.21 with the exception that there is no peak in the nitrile stretching region. The n.m.r. spectrum is complex indicating a large proportion of impurities. The elemental analysis has a higher carbon and correspondingly lower chlorine content indicating a higher degree of chlorine replacement to compound 5.21. The mass spectrum is as assigned in the data table.

Due to the large number of possible products depending on the reaction conditions, in particular the length of time of refluxing, a number of products have therefore been obtained in an impure state. Obviously, the longer the period of refluxing means the higher degree of replacement of chlorine atoms. In addition the experiments could be repeated with a greater excess of the Grignard reagent. Difficulties in purification were experienced, however, the most probable products seem to be the ketoorganostannanes $R_xCl_{3-x}SnCH_2CH_2COR$ of which x values of one for compound 5.19 and for compound 5.21 and two for compound 5.22, fit most closely on the bases of the elemental analysis. Again an improved work up procedure is required.

5.6 Conclusion

The hydrostannation product of acrylonitrile, 2-cyanoethyltin trichloride, is an intermolecular coordination polymer due to the presence of both a Lewis acid and Lewis base site in each molecule. The polymeric chain is easily broken by Lewis bases, which coordinatively saturate the tin atom, but it is more stable towards Lewis acids.

Our investigations into the mechanism leading to CETTC from acrylonitrile show that it is necessary to prepare ethereal trichlorostannane in situ, as attempts to insert tin (II) chloride into 2-chloropropionitrile were unsuccessful. Also the reaction does not appear to proceed via a tin (IV) chloride adduct, nor via a free radical mechanism. The mechanism proposed is therefore one of electrophilic attack by the proton of ethereal trichlorostannane followed by addition of the trichlorostannane anion.

Upon hydrolysis, CETTC did not break down to propanal and an inorganic species but remained intact although both ends of the molecule were affected. Similarily, both sites were attacked by Grignard reagents, with some of the chlorine atoms being replaced by organic groups.

The hydrostannation of acrylonitrile by tribromostannate proved more difficult than by the analogous chlorine system, one of the initial problems being the different solubility of tin(II) bromide, compared to tin (II) chloride, in diethyl ether.

CHAPTER 6

HYDROSTANNATION OF UNSATURATED NITRILES

6. 1. Introduction

In the previous chapter it was shown that ethereal trichlorostannane adds predominantly across the olefinic bond of acrylonitrile but also affords products in which the nitrile group has also been affected.

In this chapter studies on substituted acrylonitrile systems $R^1CH{=}CR^2C{\equiv}N$, with both electron withdrawing and electron donating substituents on the olefinic bond, are reported. The effect of increasing the separation of the two unsaturated bonds is examined for the allyl cyanide system, $CH_2{=}CHCH_2C{\equiv}N/HSnCl_3$. The results may be compared to those for the saturated nitriles described in chapter 4. Preliminary investigations into the hydrostannation of crotonitrile, $MeCH{=}CHC{\equiv}N$, and methacrylonitrile, $CH_2{=}CMeC{\equiv}N$, were carried out by M.A.I. El Erian [1].

6. 2. Experimental

The reaction procedure adopted was similar to that most conducive to CETTC formation from acrylonitrile.

6.2.1. Hydrostannation of Crotonitrile

Crotonitrile (5.4 mls, 66 mmoles) was added to ethereal trichlorostannane (64 mmoles) without removal of the excess ether. Upon stirring for 48 hours at room temperature a white solid, pale yellow oil and upper ethereal layer were formed. The white solid was isolated by filtration, thoroughly washed in dichloromethane and dried in vacuo to give compound 6.1 (3.85g). The volatile material was removed from the filtrate by vacuum distillation and identified as hydrogen chloride and ether (g.l.c., silicone SE 30 (30%)) with no $ClMeCH{=}CH_2C{\equiv}N$. The remaining viscous yellow oil was heated gently in toluene to dissolve it, in an attempt to grow crystals, but it darkened in colour to give a brown oil, 6.2.

Data for compound 6.1 is given overpage.

Compound 6.2 infra-red spectrum, cm^{-1}, contact film

3315m/s, 3260m/s, 3205m/s, 2980m/s, 2922m/s, 1670m/s, 1645m/s, 1640m,b, 1610m, 1440m,b, 1382m, 1358m, 1270m,1221w/m, 1182w/m, 1141w/m, 1116m, 1090m, 1080m, 1070m, 1014m, 951w/m, 925w, 905w, 858w/m, 820w, 788w, 734m, 698m, 618m, 463w.

6.2.2. The experiment was repeated in an attempt to obtain crystalline material instead of the brown oil. The initial procedure was exactly as before and again a white powder (6.3, 5.89g) was obtained from crotonitrile (5.0 mls, 61.4 mmoles) and ethereal trichlorostannane (60.4 mmoles). This time the volatile components were removed by pumping until the yellow oil became a sticky paste. This was dissolved in warm toluene (100 mls) and overheating was avoided. A crystalline material (6.4, 0.15g) appeared in the solution over three weeks. Data obtained on the two products are given on the data sheets.

6.2.3. Hydrostannation of Methacrylonitrile

The reaction procedure was identical to that in section 6.2.2 using ethereal trichlorostannane (57.5 mmoles) and methacrylontrile

Compound No. 6.1

Origin $HSnCl_3/Et_2O$ + $MeCH=CHC\equiv N$

Name & Structure

see text

m.pt. d130-5

Elemental Analysis

C	13.7	
H	3.3	
N	5.4	see table 6.2
Sn		
Cl	48.5	

Empirical Formula $C_3H_8SnCl_{3.5}$

Infra-red, ν cm⁻¹ KBr disc

3320w/m, shl,3190m, b,2955vw, 2910vw, 1684m, shl,1629m/s, 1429m, shl,1403s, 1370m, shl,1320w, 1308w, 1288w, 1220s, 1180w/m, shl,1120w, b,1065m/s, 1038w/m, 962s, 921m, 840m, 824m, 776m/s, 670m, 615w/m, b,502m, 462w/m, 303s, 281m/s, shl, 250m, shl.

¹H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
2.05	d	6.5Hz	9	CH_2?
5.85	s,b	-	6	NH
7.24	t	50.5	6	NH
8.58	s,b	-	1	NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	190	$SnCl_2^+$ or $SnCH(Me)CH_2CNH_2^+$	65
44	$CH_2CH_2NH_2^+$, $C(NH_2)_2^+$ or $CONH_2^+$	76	199	$[SnCl + 44]^+$	100
56	$CH_2CH_2C=NH_2^+$		225	$SnCl_3^+$ or $ClSnCH(Me)CH_2CNH_2^+$	100
106	$[ClCH(Me)CH_2C=NH_2^+ +H]$	100	260	$SnCl_4^+$ $Cl_2SnCH(Me)CH_2CNH_2^+$ or $Sn(CH(Me)CH_2CNH_2)_2^+$	30
120	Sn^+				
132	$[Sn + 12]^+$ $[106 + CN]^+$	79	268	$[225 + 43]^+$	<1
147	$SnCNH^+$ or $SnCHCH_2^+$	65	304	$[SnCH(Me)CH_2 + 106]^+$	<1
155	$SnCl^+$	100			
175	$SnCHCH_2CNH_2^+$	46			

Other Information ^{119}Sn Mössbauer spectrum (table 6.3 and fig.6.1)

Compound No. 6.3

Origin $HSnCl_3/Et_2O$ + $MeCH=CHC\equiv N$

Name & Structure

see text

m.pt. d100-106

Elemental Analysis

C	7.9	
H	1.6	
N	2.3	see table 6.2
Sn		
Cl	42.0	

Empirical Formula $C_4H_{10}NCl_8Sn_2$

Infra-red, ν cm^{-1} KBr disc

3510m, b,3450m, b,3180m, b,1606s, 1401s, 1219m/s, 1062m, 957m, 919m, 850w/m, shl,838m, 821m, 775m, 670w, b, 495m, shl,407m/s,315s, 305m/s, shl, 260m, shl.

^1H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
2.03	d	7.5	1	CH_2
3.42	s,b	-	3	H_2O/NH_2?
7.02	t	51.5	2	NH_2

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	260	$SnCl_4^+$ $Cl_2SnCH(CH_3)CH_2C=NH_2^+$	12
56	$CH_2CH_2CNH_2^+$	100	269	$[225 + 44]^+$ (m/e44= $CONH_2^+$, $C(NH_2)_2^+$ or $CH_2CH_2NH_2^+$)	<1
70	$MeCHCH_2CNH_2^+$	100	307	?	<1
107	$[MeC(Cl)HCH_2CNH_2+2H]^+$	28	318	?	<1
120	Sn^+	18	350	?	<1
136	$SnNH_2^+$	<1			
155	$SnCl^+$	<1			
190	$SnCl_2^+$ or $[Sn +70]^+$	32			
225	$SnCl_3^+$ or $ClSnCH(Me)CH_2C=NH_2^+$	92			

Other Information ^{119}Sn Mössbauer spectrum (table6.3 & fig.6.1)

Compound No. 6.4

Origin $HSnCl_3/Et_2O$ + $MeCH=CHC\equiv N$

Name & Structure

$Cl_3SnCH(Me)CH_2C\equiv N$

1 methyl 2 cyanoethyl tin trichloride

m.pt.

Elemental Analysis

C	18.5	
H	3.1	
N	2.9	see table 6.2
Sn		
Cl	37.9	

Empirical Formula $C_4H_6NCl_3Sn$

Infra-red, ν cm^{-1} Nujol Mull

3380w/m, shl,3300w/m, b,3180m, b,2970s, 2939s, 2864s, 2280w, 1684m, 1633m/s, 1459m/s, 1378m/s, 1307w, 1293w, 1272w, shl,1231m, shl,1223m/s, 1164w/m, b, 1070m, 1043w, 967m/s, 926m, 894w, 847m, 832m, 784m, 727m, 678w/m,503w/m.

^{1}H N.M.R. d_6DMSO, Int. TMS 90MHz

δ ppm	Mult.	J, Hz	Int.	Assign.
1.33	s	-		Me
1.75	s,b	-		CH_2
5.77	s,b	-		CH
7.22	t	48.7		NH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	84			
53	$CHCH_2CH^+$	10			
69	$MeCHCH_2CNH^+$	18			
120	Sn^+	30			
155	$SnCl^+$	59			
190	$SnCl_2^+$ or $SnCH(Me)CH_2CNH_2^+$	13			
225	$SnCl_3^+$ or $ClSnCH(Me)CHCNH_2^+$	14			
279	$Cl_3SnCHCH_2C=NH^+$	1.5			

Other Information

5.0 mls, 59.7 mmoles). A white powder (6.5, 2.82 g) and semicrystalline material (6.6, 1.76 g) were obtained, the data for which are given on pages 227 and 228.

6.2.4 Hydrostannation of 2-Chloroacrylonitrile

2-Chloroacrylonitrile (5.0 mls, 63 mmoles) was slowly added to ethereal trichlorostannane (61 mmoles) without removal of the excess ether and the solution darkened in colour until, after approximately 30 minutes it was dark brown. After stirring for 48 hours it was reduced in volume and upon addition of dichloromethane a white solid (6.7, 0.39g) settled out and was isolated. No further products were obtained from the brown oil (6.8), which was involatile (possibly polymeric in nature). The data for compound 6.7 are given on page 229.

Compound 6.8; infra-red spectrum, cm^{-1}, contact film.

3240s,b, 2975m/s, 2937m/s, 2720m, 2282w,b, 1650s,b, 1545s,b, 1382s, 1367m/s, 1291m/s, 1261m/s, 1212m/s, 1182m/s, 1145m, 1121m/s, 1071m/s,b, 1006m/s, 971m/s, 924m, 893m, 843m, 805m, 762m/s, 732s,b, 671s,b, 480m, 447m.

6.2.5 Hydrostannation of Allyl Cyanide

The reaction procedure was initally identical to that in section 6.2.2 to give a white solid (6.9, 3.41g) and a yellow oil from ethereal trichlorostannane (70.0 mmoles) and allyl cyanide (5.8 mls, 72.1 mmoles). The oil was reduced in volume to give a white solid which was stirred in dichloromethane (130 mls) and subsequently isolated by filtration and further washing,

Compound No. 6.5

Origin $HSnCl_3/Et_2O$ + $CH_2=C(Me)C\equiv N$

Name & Structure

see text

m.pt. 190-1

Elemental Analysis

C	17.5	
H	4.0	
N	4.7	see table 6.2
Sn		
Cl	50.2	

Empirical Formula $C_4H_{12}NCl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3320m, shl,3150s, 2975m/s, 2930m/s, 2650w, 2560w, 2325w, 1686m, 1646m, 1575s, 1470s, 1402m/s, 1376m/s, 1328m, 1245w, 1204m, 1160m, 1131m, 1101m,1091m 1070m, shl,1060m/s, 1032w/m, 1012m, 997m/s, 928s, 875m, shl,854m/s, 798m, 762w, 705vw, 644w, 568m/s, 538m, 506m, 428w/m, 397m, 372m, 302s.

¹H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
1.70	d	6.7	3	CH_3
3.16	s,b	-	2	CH_2
5.01	s	-	1	CH
8.33	s,b	-	2	NH_2

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	225	$SnCl_3^+$ or $ClSnCH_2CH(Me)C=NH_2^+$	1
44	$CH_2CH_2NH_2^+$; $CONH_2^+$ or $C(NH_2)_2^+$	72	260	$SnCl_4^+$, $Cl_2SnCH(Me)CH_2CNH_2^+$ or $Sn(CH(Me)CH_2CNH_2)_2^+$	4.5
56	$CH(Me)CNH_2^+$	22	269	$[225 + 44]^+$	2.5
62	$ClCNH^+$ or $ClC_2H_3^+$	61	306	?	1
70	$CH_2CH(Me)CNH_2^+$	34	318	?	1
106	$[CH_2CH(Me)CNH_2+HCl]^+$	14	334	$[106 + 225]^+$	1
136	$SnNH_2^+$	2.8	354		1
155	$SnCl^+$	22			
190	$SnCl_2^+$ or $SnCH_2CH(Me)C=NH_2^+$	12			

Other Information ^{119}Sn Mössbauer spectrum(table6.3 and fig.6.1)

Compound No. 6.6

Origin $HSnCl_3/Et_2O$ + $CH_2=C(Me)C\equiv N$

Name & Structure

$Cl_3SnCH_2CH(Me)C\equiv N$

2-cyano 2-methyl ethyl tin trichloride

m.pt. 119-20

Elemental Analysis

C	18.7	
H	3.0	
N	2.6	see table 6.2
Sn		
Cl	38.4	

Empirical Formula $C_4H_6NCl_3Sn$

Infra-red, ν cm⁻¹ Nujol Mull

3250w, b,2920s, 2858s, 2260m, b,1620w/m b,1450m/s, 1407w/m, 1377m, 1310m, b, 1200w, 1155m, 1100m, b,1038m, shl, 1006m, 924w/m, 809m, 723s.

¹H N.M.R.

δ ppm	Mult.	J, Hz	Int.	Assign.
1.30	d	7	3	CH_3
1.56	d of AB's	7 and 12	2	CH_2
3.05	m	7	1	CH

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	225	$SnCl_3^+$ or $ClSnCH_2CH(Me)C=NH_2^+$	11
41	$CH_2=C=NH^+$	58			
52	$CHCHCN^+$	13	260	$SnCl_4$ $Cl_2SnCH_2CH(Me)C=NH_2^+$ or $Sn(CH_2CH(Me)C=NH_2)_2^+$	10
68	$CH_2CH(Me)CN^+$	31			
120	Sn^+	2.0			
155	$SnCl^+$	19	279	$Cl_3SnCH_2CHC=NH^+$	17
190	$SnCl_2^+$ or $SnCH_2CH(Me)C=NH_2^+$	7.2	294	$Cl_3SnCH_2CH(Me)C=NH^+$	2.0
			326	$Cl_2Sn(CH_2CH(Me)C=N)_2^+$	2.5

Other Information

Compound No.	**Origin**
6.7	$HSnCl_3/Et_2O$ + $CH_2=C(Cl)C\equiv N$

Name & Structure

see text

m.pt.

Elemental Analysis

		$RCNHSnCl_3$	$RCNH_2SnCl_3HCl$	$RCN2HSnCl_3$
C	7.8	11.5	10.3	6.7
H	3.5	1.0	1.2	1.1
N	4.3	4.5	4.0	2.6
Sn				
Cl	52.0	45.2	50.6	46.0

Empirical Formula $C_2H_{11}NCl_5Sn$

Infra-red, ν cm⁻¹ Nujol Mull

3444m, b,3180m/s, b,2952s, 2920s, 2850s, 1655m, b,1550m, b,1450m/s, 1401m, 1372m, 1288m, 1192m, 1134m, 1090w, 1068w,1001w, 950w, 880m, 720w/m, 660w/m.

^1H N.M.R. in$CDCl_3$Ext.TMSref.

δ ppm	Mult.	J,Hz	Int.	Assign.
0.90	s,b	-	2	
1.13	s,b	-	3	
1.58	s,b	-	2	
7.33	s	-	2	$CDCl_3$

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	190	$SnCl_2^+$	12
44	$CH_2CH_2NH_2^+, CONH_2^+$	35	225	$SnCl_3^+$	51
	or $C(NH_2)_2^+$		260	$SnCl_4^+$	9
55	$CH_2CHC=NH_2^+$	9	269	$[SnCl_3 + 44]^+$	2.5
	or $(CN)_2H_3^+$		274	$[Cl_3SnCH_2CHCl-3H]s^+$	1
62	$ClC=NH^+$ *	14	304	?	1
90	$CH_2CH(Cl)C=NH_2^+$ *	24	351	$[CH_2=C(Cl)CN + HSnCl_3 + HCl]^+$	1
105	?	6.0			
120	Sn^+	6.5			
136	$SnNH_2^+$	2.0			
155	$SnCl^+$	22			

*Relative intensities are incorrect for the presence of Cl

Other Information

Compound No.	**Origin**
6.9	$HSnCl_3/Et_2O$ + $CH_2=CHCH_2C\equiv N$

Name & Structure

see text

m.pt. d110-15

Elemental Analysis

C	13.7	see table 6.2
H	3.3	
N	5.0	
Sn		
Cl	45.2	

Empirical Formula $C_4H_{10}NCl_4Sn$

Infra-red, ν cm⁻¹ KBr disc

3375m/s, 3310m/s, 3245m/s, 3192s, 2725vw, 1692m/s, 1635s, 1574w/m, 1545w/m, 1522w/m, 1440m/s, 1408m, 1376m, shl, 1322vw, 1310w, 1291w/m, 1270vw, 1229s, 1221s, 1173w, b, 1065m/s, 1041w/m, 1008w, 961s, sh, 925m, 890m, b, 841m/s, 828m, 778m/s, 721w/m, 674m, 629w, b, 507m, 469m, 300m/s.

¹H N.M.R. in d_6DMSO, Ext. TMS

δ ppm	Mult.	J, Hz	Int.	Assign.
2.03	d	7.0	2	CH_2
4.25	s	-	3	H_2O, NH?
7.23	t	51.0	2	NH_2

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	147	$SnCNH^+$, $SnC_2H_3^+$	48
44	$CH_2CH_2NH_2^+$, $CONH_2^+$ or $C(NH_2)_2^+$	31	155	$SnCl^+$	100
			174	$[Sn + 54]^+$	38
56	$(CNH_2)_2^+$, $CH_2CH_2C=NH_2^+$	46	190	$SnCl_2^+$ or $Sn(CH_2)_3C=NH_2^+$	1
65	?	75	225	$SnCl_3^+$ or $ClSn(CH_3)_3C=NH_2^+$	1
70	$CH_2CH_2CH_2C=NH_2^+$	23			
106	$[CH_2CH_2CH_2C=NH_2 + HCl]^+$	66	260	$SnCl_4^+$, $Cl_2Sn(CH_2)_3C=NH_2^+$ or $Sn[(CH_2)_3C=NH_2]_2^+$	1
120	Sn^+	69			
132	SnC^+	34	293	$[SnCl_3 + 69]^+$, $Cl_3Sn(CH_2)_3C=NH^+$	1

Other Information ^{119}Sn Mössbauer (table 6.3 and fig. 6.1)

Compound No. 6.10	**Origin** $HSnCl_3/Et_2O$ + $CH_2=CHCH_2C\equiv N$

Name & Structure

see text

m.pt. d100-2

Elemental Analysis

C	7.4	
H	1.3	
N	1.9	see table 6.2
Sn		
Cl	41.9	

Empirical Formula $C_4H_8NCl_8Sn$

Infra-red, ν cm⁻¹ KBr disc

3520m, 3455m, b,3195w/m, b,3120w/m, 1655w/m, shl, 1610m, 1400m/s, 1220m, 1072w, 951m, 920w, 839w, 774w, 411m/s, 309s, 240s.

¹H N.M.R. d_6DMSO,Ext.TMS

δ ppm	Mult.	J,Hz	Int.	Assign.
2.20	d	7.0	2	CH_2?
4.01	s,b	-	6	H_2O,NH?
7.24	t	51.0	1	NH_2

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
36	HCl^+	100	155	$SnCl^+$	13
41	$CH_2C=NH^+$	41	190	$SnCl_2^+$ or $Sn(CH_2)_3C=NH_2^+$	9.5
44	$CH_2CH_2NH_2^+$, $CONH_2^+$ or $C(NH_2)_2^+$	37	225	$SnCl_3^+$ or $ClSn(CH_2)_3C=NH_2^+$	8.3
57	$[(CH_2)_2C=NH_2 + H]^+$	17	260	$SnCl_4^+$, $Cl_2Sn(CH_2)_3C=NH_2^+$ or $Sn[(CH_2)_3C=NH_2]_2^+$	2.0
70	$(CH_2)_3C=NH_2^+$	16	293	$[225 + 68]^+$, $Cl_3Sn(CH_2)_3C=NH_2^+$	3.5
86	$(CH_2)_3C(NH_2)_2^+$	20	330	$[Cl_3Sn(CH_2)_3C=NH_2 + HCl]^+$	2.0
93	?	14			
106	$Cl(CH_2)_3C=NH_2^+$	31			
111	$(CH_2)_2\text{-}\overset{\overset{NH_2}{\|}}{C}\text{-}N=C(CH_2)_2^+$	4.5			
120	Sn^+	3.8			

Other Information ^{119}Sn Mössbauer spectrum(table6.3andfig.6.1)

Compound No. 6.11

Origin $HSnCl_3/Et_2O$ + $CH_2=CHCH_2C\equiv N$

Name & Structure

$Cl_3Sn(CH_2)_3C\equiv N$ (tentative)

3 cyanopropyl tin trichloride

m.pt.

Elemental Analysis

C	17.5	
H	3.0	
N	3.5	see table 6.2
Sn		
Cl	38.1	

Empirical Formula $C_4H_6NCl_3Sn$

Infra-red, ν cm^{-1} Nujol Mull

3409m, 3349m, 3268m, 3190m, shl, 2968m/s, 2938m/s, 2860m, 2270m/s, 1640s, 1554s, 1450m/s, 1410m/s, 1387m/s, 1282m/s, 1230m, 1162m, 1118m, 1094m, shl, 1036m, 1019m, 997m/s, 932m/s, 887m, 851m, 740m, b.

^{1}H N.M.R. d_6DMSO, Int.TMS; 90MHz

δ ppm	Mult.	J, Hz	Int.	Assign.
1.28 to 1.62	Range of m			CH_2's
2.82 to 3.19	Range of m			
4.43 to 5.17	Range of m			
6.34 to 7.46	Range of m			

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I

Other Information

compound 6.10. (3.72g.)

In a second experiment the oil was dissolved in warm toluene and, after a few weeks, a semicrystalline material, (compound 6.11 approximately 0.1g) was obtained.

6. 3. Discussion of Results.

A wide range of products are possible in the reaction between unsaturated nitriles and the $SnCl_2/HCl/Et_2O$ system because of :-

(i) the complexity of $HSnCl_3$ (chapter 2) and

(ii) the availability of both an alkene and a nitrile bond for nucleophilic attack by $HSnCl_3$ and/or HCl.

Possible products are listed for the reaction involving methacrylonitrile in table 6.1.

Table 6.1. Possible products from the reaction between $CH_2{=}CMeC{\equiv}N$ and $SnCl_2/HCl/Et_2O$

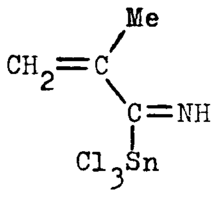
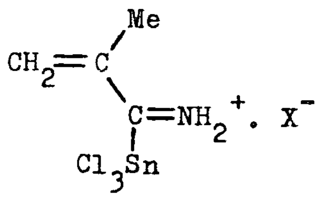
	Product	Derivation
A	$Cl_3SnCH_2CHMeC{\equiv}N$ VI.1	Hydrostannation across the alkene bond to give the CETTC analogue of methacrylonitrile.
B	 	Hydrostannation of the nitrile only.

Table 6.1 (contd.)

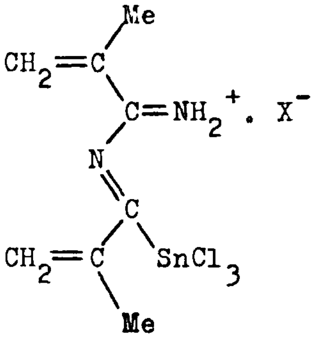
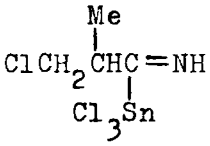
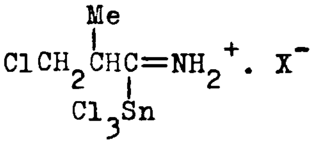
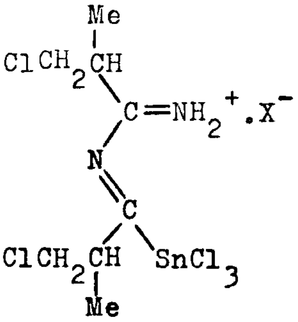
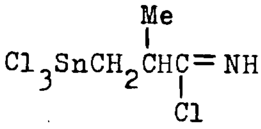
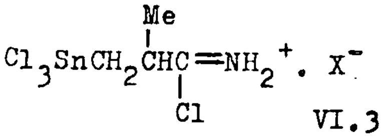
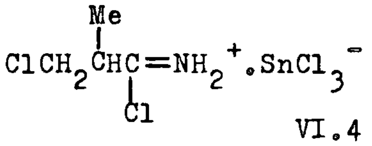
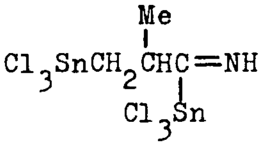
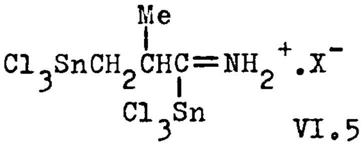
Product	Derivation
B (contd) 	
C  $\mathrm{ClCH_2\overset{Me}{C}H\underset{Cl_3Sn}{C}{=}NH}$  $\mathrm{ClCH_2\overset{Me}{C}H\underset{Cl_3Sn}{C}{=}NH_2{}^{+}.\ X^{-}}$ VI.2 	Hydrochlorination of the alkene bond with hydrostannation of the nitrile group.
D  $\mathrm{Cl_3SnCH_2\overset{Me}{C}H\underset{Cl}{C}{=}NH}$  $\mathrm{Cl_3SnCH_2\overset{Me}{C}H\underset{Cl}{C}{=}NH_2{}^{+}.\ X^{-}}$ VI.3 and dimerisation product of VI.3	Hydrostannation of the alkene bond with hydrochlorination of the nitrile bond.

Table 6.1 (contd.)

	Product	Derivation
E	 $ClCH_2\overset{Me}{C}H\underset{Cl}{C}{=}NH_2^+.SnCl_3^-$ VI.4 and dimerisation product of VI.4	Hydrochlorination of both the alkene and the nitrile bond with formation of the trichlorostannate salt.
F	 $Cl_3SnCH_2\overset{Me}{C}H\underset{Cl_3Sn}{C}{=}NH$  $Cl_3SnCH_2\overset{Me}{C}H\underset{Cl_3Sn}{C}{=}NH_2^+.X^-$ VI.5 and dimerisation product of VI.5	Hydrostannation of both the alkene and the nitrile bonds.
G	$(CH_2{=}C(Me)C{\equiv}N)_2.SnCl_4$ $(XCH_2CH(Me)C{\equiv}N)_2.SnCl_4$	Formation of $SnCl_4$ adducts from $HSnCl_3$ and HCl (possibly involving $(EtOH)_2{}^+SnCl_4{}^{2-}$ (Chapter 2)
H	$(CH_2{=}C(Me)CH{=}NH_2)_2^+.SnCl_6{}^{2-}$ VI.6 $(X\,CH_2CH(Me)CH{=}NH_2)_2^+.SnCl_6{}^{2-}$ VI.7	Formation of hexachlorostannate salts involving both $HSnCl_3$ and HCl.

X = $SnCl_3$, Cl

The experimental results show that it is possible to form the CETTC analogues (category A) and products where both unsaturated bonds have been affected (categories C-H). There is no evidence for the alkene bond remaining unaffected (category B).

By following a careful work up procedure, avoiding thermal decomposition, as in the acrylonitrile case, the analogue of CETTC has been prepared from crotonitrile (compound 6.4) methacrylonitrile (compound 6.5) and allyl cyanide (compound 6.11) but not from 2-chloroacrylonitrile.

These products are clearly identified as nitriles by a peak in the nitrile streching region of their infra-red spectra (2300-2200 cm^{-1}). The remaining infra-red frequencies may be attributed to the alkyl groups.

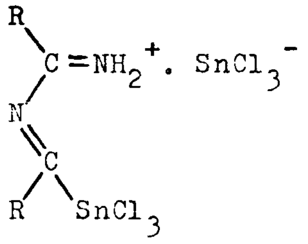
The allyl cyanide product (6.11). assigned as 3-cyanopropyl tin trichloride, has an additional peak at 1640 cm^{-1} which suggests that some of the nitrile has been reduced to an imine or iminium salt. Compound 6.11 therefore contains impurities such as compounds 6.9 and 6.10 and should therefore have been recrystallised but as the yield was already low this was not performed. (The experiment should have been repeated to obtain a pure product which would then be fully characterised).

The ^1H n.m.r. spectrum of $Cl_3SnCH(Me)CH_2C{\equiv}N$ consists of broad singlets as assigned in the data table (page 225) and a broad triplet implying the presence of N-H protons either due to impurities in the system or due to hydrolysis by the water absorbed in the DMSO. The n.m.r spectrum of 2-cyano- 2-methyl- ethyl tin trichloride, (6.6) is as tabulated on page 228 . The methyl protons resonance is split into a doublet by the tertiary protons. There is a doublet of AB's centered at 1.56 ppm which corresponds to the methylene protons which are in the same chemical, but different magnetic, environments. The multiplet at 3.05 ppm arises from the methyne proton coupled with both the methyl and methylene protons.

The n.m.r spectrum for 3-cyano propyl tin trichloride (6.11) consists of four ranges of multiplets, as shown on page 232 , which are difficult to interpret. One would indeed expect complex splitting for the three methylene groups; triplets for the α and γ methylene protons and a nonet for the β methylene group. The low field multiplets may be due to unreacted nitrile or other impurities. This is also reflected by the micro analysis results which deviate from the calculated values (table 6.2.). Again further purification by recrystallization was required.

The mass spectrum for 1-methyl 2-cyano ethyl tin trichloride, $Cl_3SnCH(Me)CH_2CN$, (compound 6.4) has peaks attributable to both the organic ($MeCHCH_2CNH^+$ at m/e 69) and inorganic ($SnCl_3^+$ at m/e 225) halves of the molecule and their break down, but no parent peak at m/e 294. Instead the highest mass peak is fifteen units lower due to loss of the methyl group. By comparison, the spectrum for $Cl_3SnCH_2CH(Me)CN$, the methacrylonitrile derivative, does have a peak at m/e 294 for the protonated parent ion. However, there is an additional peak at m/e 326 for the dichlorodiorgano tin compound, implying that bis (2-cyanoethyl 2-methyl) tin dichloride, $Cl_2Sn[CH_2CH(Me)CN]_2$, is formed as an impurity, which may account for the broad nitrile streching frequency in the infra-red spectrum and for the deviation of the elemental analysis from the calculated values for the monoorgano tin compound.

Conversely, the compounds where both alkene and nitrile groups have reacted are easily identified from their infra-red spectra by the absence of a nitrile streching frequency (2300-2200 cm^{-1} [2]), and the development of an azomethine peak (1689-1471 cm^{-1} [2]). The infra-red data for these products have many of the characteristics of those of the hydrostannation products of the saturated nitriles in Chapter 4 so a detailed discussion is unnecessary. Compounds 6.1, 6.3, and 6.10 each have a single peak in the $v(C{=}N)$ region, whilst the remaining products give more complicated spectra with additional absorbancies implying that either the product is impure or that there is more than one azomethine bond in the structure. The latter is possible if, for example, the product is a dimeric amidinium salt as suggested for the saturated nitriles [3] and illustrated below VI.8.



VI.8

Olefinic bonds also absorb in this region (1670-1640 cm^{-1} [2]) so the presence of any unreacted starting material or products whereby the nitrile group only has been affected, maintaining the olefinic bond, will complicate the spectrum. However, the n.m.r. studies show that the olefinic bonds have been completely saturated. Any nitrogen-hydrogen scissoring vibrations which naturally occur in this region will also complicate the spectra but are characteristically weaker and may therefore be hidden. The spectra all contain nitrogen - hydrogen stretching frequencies in the expected region above 3000 cm^{-1} and the implications are as discussed in Chapter 4. Aliphatic carbon - chlorine bonds have streching frequencies between 850 and 550 cm^{-1} and all of the compounds, except 6.10, have a relatively intense peak in this region. This implies that hydro-chlorination, rather than hydrostannation, may have occurred across the olefinic bond.

The starting materials crotonitrile, methacrylonitrile and allylcyanide are isomeric (C_4H_5N). Therefore with the aid of table 6.2 and separate calculations for 2-chloroacrylonitrile one can deduce that the products from the nitrile of general formula RCN may be comprised :-

(i) RCN + $HSnCl_3$ + HCl;	possibly compounds 6.1, 6.3 (from the Cl analysis), 6.5 and 6.9.
(ii) RCN + $HSnCl_3$ + 2HCl;	possibly compounds 6.1 and 6.9.
(iii) RCN + $2HSnCl_3$;	possibly compounds 6.3 (from the Cl analysis), 6.7 and 6.10.
(iv) RCN + $2HSnCl_3$ + HCl;	possibly 6.3 (from the low C analysis).
(v) RCN + H_2 + H_2SnCl_4 + 4HCl. (i.e. VI.7)	possibly 6.1 and 6.5.

These observations clearly suggest that both unsaturated bonds have been attacked as all of the possibilities listed above involve at least two molecules of HX where X is solely $SnCl_3$ or $SnCl_3$ and Cl. (See also table 6.1). Again these results imply that the compounds may not be pure and may be mixtures of products

Table 6.2

Elemental Analyses for the Possible Hydrostannation Products of the Nitriles C_4H_5N; $MeCH{=}CHC{\equiv}N$, $CH_2{=}C(Me)C{\equiv}N$ and $CH_2{=}CHCH_2C{\equiv}N$.

PRODUCT	ELEMENTAL ANALYSES (calculated)				
	% C	% H	% N	% Sn	% Cl
$C_4H_6Cl_3NSn$ $(RCN + HSnCl_3)$	16.4	2.1	4.8	40.5	36.3
$C_4H_7Cl_4NSn$ $(RCN + HSnCl_3 + HCl)$	14.6	2.1	4.2	36.0	43.0
$C_4H_7Cl_6NSn_2$ $(RCN + 2HSnCl_3)$	9.3	1.3	2.7	45.7	41.0
$C_4H_8Cl_7NSn_2$ $(RCN + 2HSnCl_3 + HCl)$	8.6	1.5	2.5	42.7	44.7
$C_4H_8Cl_5NSn$ $(RCN + HSnCl_3 + 2HCl)$	13.1	2.2	3.8	32.4	48.4
$C_8H_{11}Cl_3N_2Sn$ $(2RCN + HSnCl_3)$	26.7	3.1	7.8	32.9	29.5
$C_8H_{12}Cl_4N_2Sn$ $(2RCN + HSnCl_3 + HCl)$	24.2	3.0	7.1	29.9	35.7
$C_8H_{16}Cl_6N_2Sn$ $(RCH{=}NH_2)_2SnCl_6$ (VI.6) $(RCN + H_2 + H_2SnCl_4 + 2HCl)$	20.4	3.4	5.9	25.2	45.1
$C_8H_{17}Cl_8N_2Sn$ $(RCH{=}NH_2.HCl)_2SnCl_6$ (VI.7) $(RCN + H_2 + H_2SnCl_4 + 4HCl)$	17.7	3.3	5.1	21.8	52.2

$R = C_3H_5$

or be contaminated with tin dichloride, although the latter is not detected spectroscopically (particularily by the Mössbauer studies). Attempted recrystallization to purify these powders was unsuccessful due to solubility problems. The low solubility and consequently low signal to noise ratio, led to inconclusive n.m.r. results. The peaks obtained are assigned in the data tables for each product in turn. All of the spectra contain a low field triplet due to protons attached to the nitrogen atom. Some of the spectra contain an additional broad peak possibly due to a second type of proton attached to another N atom. If dimeric amidinium salts had been formed (VI.8) then one would expect two sets of peaks one for each R group. Clearly this is not observed in the products concerned.

The mass spectra show that the $SnCl_3$group has remained intact in the products obtained. However, the nitriles C_3H_5CN when saturated lead to the fragment $C_3H_6C{=}NH_2^+$ which has m/e 70 which is very close to the value of 71 for two chlorine atoms. Hence tin containing fragments with either one organic group or two chlorine atoms attached will be difficult to distinguish, but again with the aid of computer simulations, due to the isotope effect of the chlorine atoms, this can be overcome to a certain extent. It is possible that chlorine may be attached to the nitrile carbon as some of the spectra contain a peak at m/e 62 which may be assigned to the fragment $ClC{=}NH_2^+$, but the isotope ratio for the intensities of the peaks at 62 and 64 is incorrect for the presence of chlorine in most cases, so the evidence is by no means conclusive. Similarily a peak at m/e 106 in each spectrum, except that of the chloroacrylonitrile product, may correspond to the hydrochlorination product of the parent nitrile, but again the peak intensity ratio does not support the presence of chlorine in most cases.

Compounds 6.1 and 6.9 contain fragments at m/e 147 which may represent the $SnC{=}NH_2^+$ ion, implying that the ethereal trichlorostannane has attacked the nitrile bond in preference to the alkene bond. The possibility of dimeric species is supported by a peak at m/e 44 in each spectrum, one possible assignment of which is $C(NH_2)_2^+$, and by a peak at m/e 111 corresponding to $[(CH_2)_2C(=NH_2)-N=C(CH_2)_2]^+$ in the mass spectrum of compound 6.10.

Finally compounds 6.9 and 6.10 exhibit peaks at m/e 293 which correspond to the 1:1 ($RCN + HSnCl_3$) product and compounds 6.5 and 6.10 have peaks at approximately 330 corresponding to the ($RCN + HCl + HSnCl_3$) product. Similarily compound 6.7 from chloroacrylonitrile, has a peak at m/e 351 representing the ($RCN + HCl + HSnCl_3$) product.

Table 6.3

Mössbauer Data for the Hydrostannation Products of Unsaturated Nitriles

Compound	Isomer Shift δ (mm sec^{-1}	Quadrupole Splitting Δ (mm sec^{-1}	Intensity (%)
6.1	0.221 ± 0.001	-	94.14
	1.898 ± 0.021	-	5.86
6.3	0.217 ± 0.003	see	34.24
	1.814 ± 0.014	text	30.46
	2.095 ± 0.013		35.30
6.5	0.225 ± 0.002	-	100
6.9	0.212 ± 0.003	-	100
6.10	0.221 ± 0.003	see	34.39
	1.845 ± 0.015	text	35.24
	2.119 ± 0.014		30.37

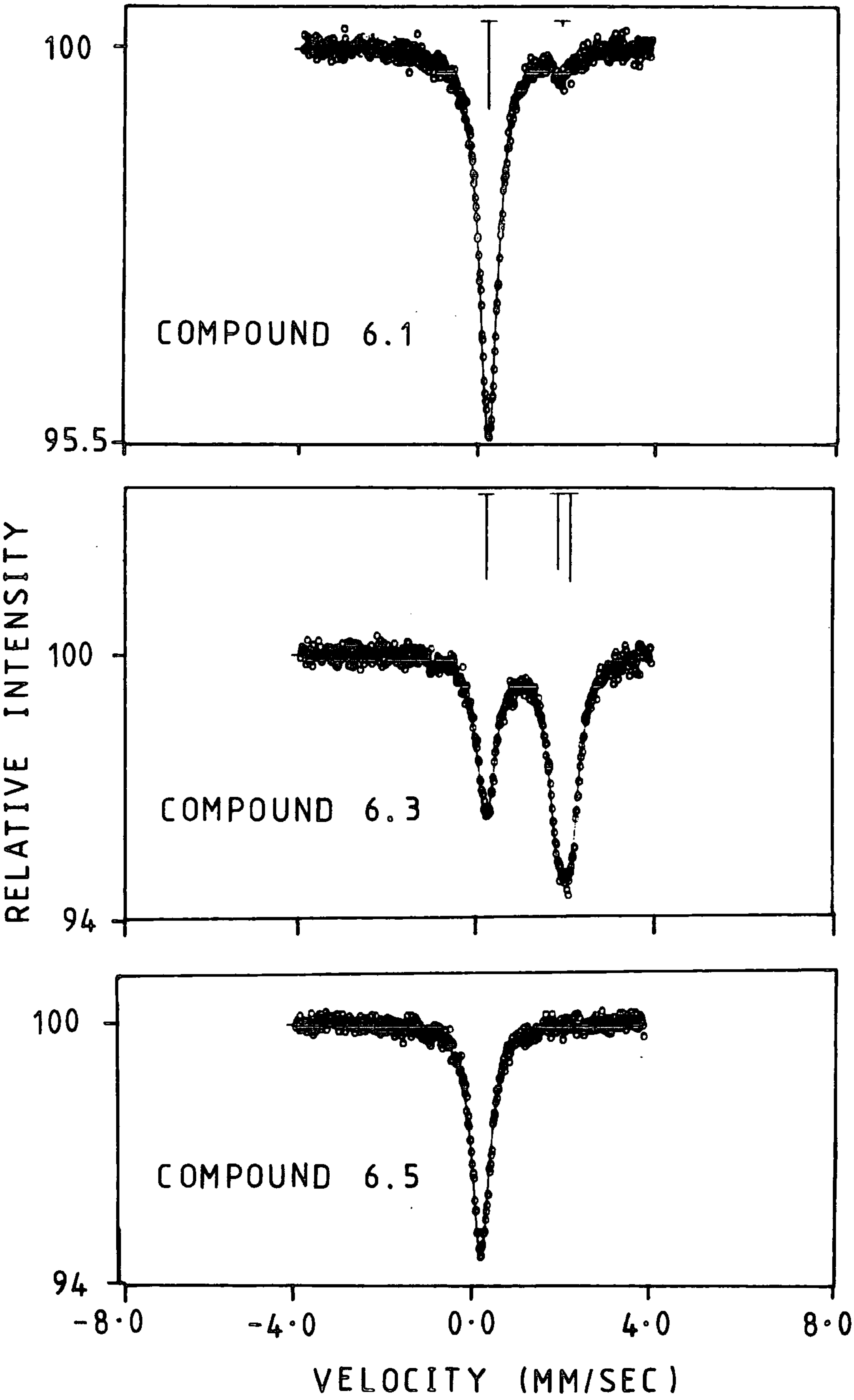


Fig. 6.1. Mössbauer Spectra of Compounds 6.1, 6.3, 6.5, 6.9 and 6.10.

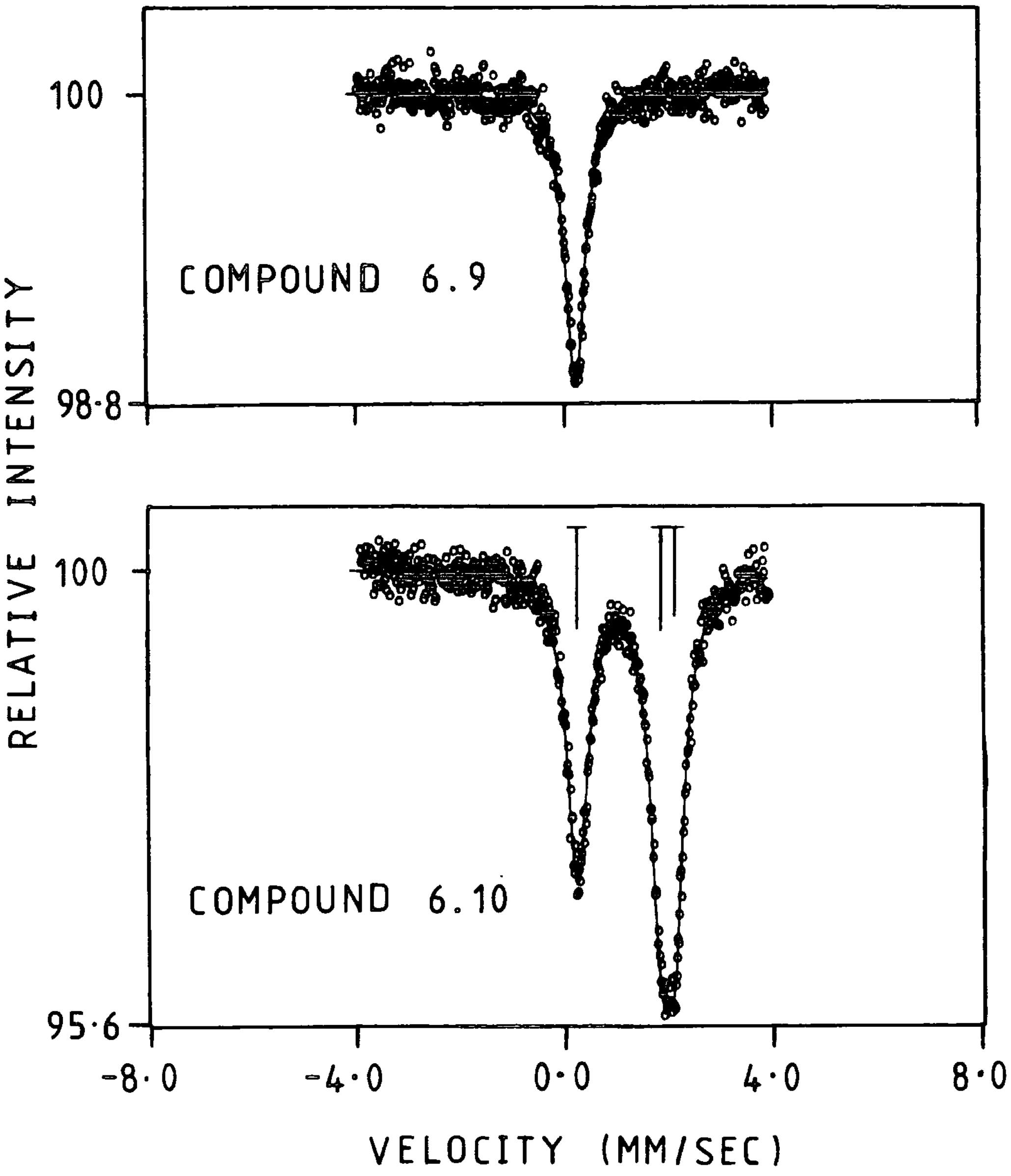
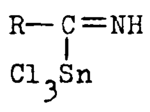


Fig. 6.1 - continued.

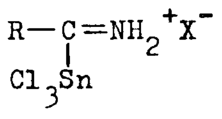
The Mössbauer data of compounds 6.1, 6.5 and 6.9 consist of singlets at approximately 0.22 mm sec^{-1} implying that the tin is in oxidation state four and that there is only one kind of tin atom. The remaining compounds 6.3 and 6.10 show a similar low velocity feature and two additional closely spaced transitions at higher energies. As the low velocity peaks are at very close isomer shifts to those of the compounds above (6.1, 6.5 and 6.9) then they most probably correspond to an analagous tin atom and it is therefore unlikely that they form part of a doublet with one of the higher energy transitions. The high energy peak is too broad (half width >0.8 mm sec^{-1}) to be considered as a singlet and therefore most probably consists of two singlets or a doublet of very low splitting constant, of which the former is the most likely. These high velocity peaks may represent a new compound which is heavily contaminated with the other product from the same nitrile which gives the low velocity singlet spectrum.

The quadrupole splitting is a measure of the electronegativity and the spatial arrangement of the groups or atoms attached to the tin atom. Surprisingly, the spectra for these compounds have no quadrupole splitting implying that the environment around the tin atom is highly symmetrical. Obviously the most likely of the possible products (table 6.1) would therefore be one of the hexachlorostannate salts (VI.6 and VI.7). However the isomer shift is low for these salts ($\simeq 0.22$ compared to $\simeq 0.5$ mm sec^{-1}) [4]. Also a tin (IV) adduct would lead to zero quadrupole splitting but this is not supported in the other spectra. Anyway, adducts of this nature would be relatively unstable whereas the compounds themselves withstood pumping under vacuum. Alternatively the zero quadrupole splitting could be as a result of the attached ligands (including chlorine atoms) having a similar electronic effect on the tin atom. It is therefore possible that the trichlorostannane group has become attached to the nitrile bond as illustrated by VI.9 and VI.10, which like the chlorine atoms is electron - withdrawing and may therefore result in a low electric field gradient at the tin atom.



$$\mathrm{R{-}\underset{\underset{Cl_3Sn}{|}}{C}{=}NH}$$

VI.9

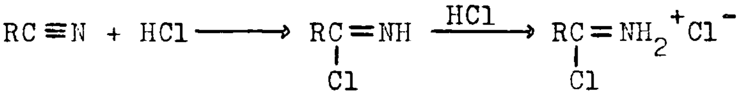


$$\mathrm{R{-}\underset{\underset{Cl_3Sn}{|}}{C}{=}NH_2{}^{+}X^{-}}$$

VI.10

Alternatively, if the alkene bond has been attacked by the $HSnCl_3$ then the organic group may not be as electron-withdrawing and would therefore be expected to give a large quadrupole splitting. It has been generalised [5,6] that for an organotin compound which contains at least one tin-carbon bond then if any of the other atoms bonded to the tin contain a lone pair of electrons, such as chlorine, then a large quadrupole splitting is to be expected. The theory has been extended [4] such that if all of the atoms attached possess a lone pair of electrons then the quadrupole splitting will be small.

We may conclude that it is possible to form the CETTC analogues with methacrylontrile, crotonitrile and allyl cyanide. Additional products where the nitrile group has also been affected are produced, often preferentially, as suggested in table (6 .1). There is some evidence, although rather slim, for dimeric amidinium salt products, but this is not supported by the n.m.r. spectra (although in some cases they do contain a broad singlet in addition to the low field equal intensity triplet implying more than one type of proton attached to a nitrogen atom). The Mössbauer spectra eliminate any species containing tin in oxidation state two so if the dimeric species do exist they would be limited to X = Cl (table 6.1). The symmetry requirements established by the zero quadrupole splitting suggest that the products could be hexachlorostannates or that the tin atom may be bonded to the nitrile carbon and this is supported by the mass spectra peak at m/e 147 for $SnC{=}NH_2^+$ in some cases. The tin IV adducts are unlikely as discussed with the Mössbauer results. Finally saturation of a nitrile group, for example by hydrogen chloride, does not usually stop after the first stage but proceeds to give the iminium salt [7].



$$RC{\equiv}N + HCl \longrightarrow R\underset{\substack{|\\ Cl}}{C}{=}NH \xrightarrow{HCl} R\underset{\substack{|\\ Cl}}{C}{=}NH_2^+Cl^- \qquad (6.1)$$

The most likely products are therefore compounds VI.2, VI.3 and VI.5 where X is Cl. Compounds VI.2 and VI.3 are effectively ($RCN + 2HCl + HSnCl_3$) whilst VI.5 is ($RCN + HCl + 2HSnCl_3$) and all of these possibilities are consistent with the elemental analysis. Species VI.5 with two trichlorostannane units may account for the more complex Mössbauer spectra for compounds 6.3 and 6.10.

6.4 Mechanistic Aspects

Difficulty was experienced in preparing CETTC from acrylonitrile as discussed in the previous chapter, and similar problems were encountered for the substituted acrylonitrile systems. Methacrylonitrile seemed to react most easily and gave 2-cyano, 2-methyl ethyl tin trichloride in moderate yield. The difficulties in obtaining the tin containing cyano derivatives may be explained by postulating possible reaction mechanisms and by studying the substituent effects of the methyl group and chlorine atom.

It is useful to consider the effects of substituents theoretically.

The Highest Occupied Molecular Orbital (HOMO), Ψ_2, and Lowest Unoccupied Molecular Orbital (LUMO), Ψ_3, for acrylonitrile [9] (fig 6.2) show that bonding at the olefinic bond is more likely as the molecular orbital coefficients are largest at these two atoms in both the HOMO and LUMO case.

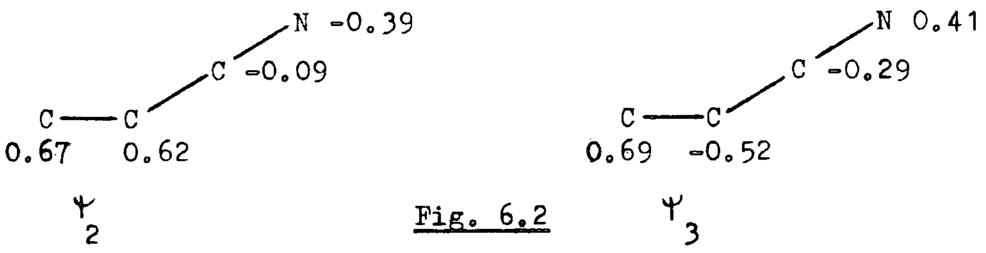


Fig. 6.2

The effect of substituents on the energy levels of substituted alkenes have been calculated [8] to give the trends below;-

$CH_2{=}CH_2$: $CH_2{=}CHMe$; $Me_2C{=}CMe_2$

π level increases $\longrightarrow$

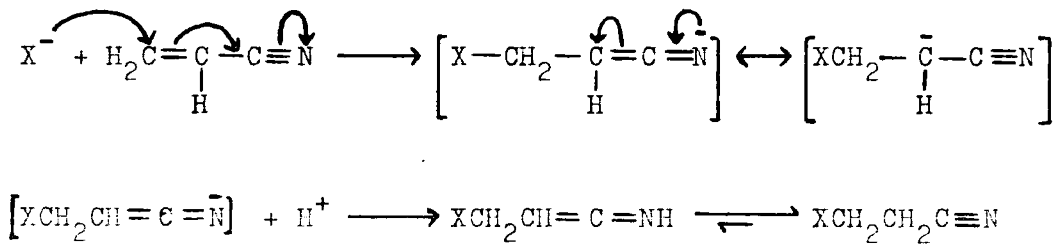
π^* level increases $\longrightarrow$

$\pi - \pi^*$ decreases $\longrightarrow$

A decrease in the difference between the HOMO and LUMO energy levels upon substitution means that the olefinic bond will be more reactive than for ethylene itself. Similarily, methyl sutstituents on acrylonitrile should facilitate reactions at its olefinic bond towards nucleophilic attack. Also, Ghio et al [10-12] have calculated the effect of substituents (both electron-withdrawing and donating) on the electron distribution of the C=C, C≡N and C-H bonds of substituted acrylonitrile systems to determine the relative importance of conjugative and inductive effects and show that the substituent effects may be fairly well represented by classical electrostatic interactions.

The mechanism proposed for the hydrostannation of acrylonitrile itself [3] is considered as protonation of the nitrile group to give a resonance stabilised carbocation, the positive charge being delocalised through the conjugated unsaturated bonds, followed by nucleophilic attack of the trichlorostannate anion, and subsequent tautomerism to the organotin nitrile (CETTC) (scheme 5.2) (page 193).

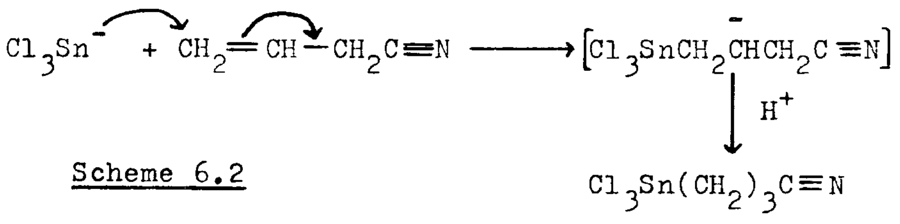
Alternatively, cyanoethylation reactions [13, 14] of HX with acrylonitrile, to give the β substituted propionitrile, proceed via nucleophilic attack of X^- on the olefin bond because of its electropositive character due to the electron withdrawing effect of the nitrile group. The second step is protonation and is followed by rearrangement according to scheme 6.1.



e.g. X = Cl

Scheme 6.1.

The above rationalisation cannot be applied to the allyl cyanide system as the two unsaturated bonds cannot achieve complete delocalisation due to the methylene group between the two unsaturated bonds.



Scheme 6.2

However, 3-cyanopropyl tin trichloride is still formed so this questions the above mechanisms.

The C=C and C≡N bonds in each of the nitriles are susceptible to attack by both Cl^- and $SnCl_3^-$ nucleophiles, the relative strengths of which must be assessed, and it is clear from the experimental results that both are involved. As CETTC was not formed from 2-chloropropionitrile (Chapter 5) then the $SnCl_3^-$ nucleophile will not be strong enough to displace a chlorine atom once hydrochlorination has taken place.

Substituent effects are obviously important to the mechanism. Steric hindrance may be significant if the substituents shield the olefinic bond from attack. Also, an electron-donating substituent, a methyl group in this case, will increase the electron density at the olefinic bond and hence make it less susceptible to nucleophilic attack, and vice versa for electron donating substituents such as chlorine. In addition back donation by the lone pair of electrons on the chlorine atom must be considered as it will reduce the overall electron withdrawing effect of that atom.

6.5 Conclusion

In this chapter the hydrostannation of unsaturated nitriles has been discussed, however the exact nature of the products is still uncertain. Further studies are therefore necessary in the following areas;

(i) to improve the work-up procedure to obtain pure products,

(ii) hydrolysis experiments which may lead to derivatives, such as aldehydes, which could be identified,

(iii) bromination experiments which could be employed to determine the site of hydrostannation. If the trichlorostannane unit was attached to the olefinic bond then cleavage by bromine would give $SnBrCl_3$ and an organobromoderivative, and

(iv) further characterisation of the products already obtained, possibly after examining their solubility in a larger range of solvents. The ultimate achievement would be to grow a crystal suitable for its structural determination.

CHAPTER 7

THE ADDITION OF ETHEREAL TRICHLOROSTANNANE TO CARBONYL COMPOUNDS

7.1 Introduction

The early work on hydrostannation by ethereal trichlorostannane involved unsaturated carbonyl compounds [1,2]. However, in these reactions the carbonyl group was only serving to activate the olefinic bond and in all cases remained unaffected.

$$CH_2{=}CHCOR + HCl + \left\{\begin{matrix} SnCl_2 \\ Sn \end{matrix}\right. \xrightarrow{Et_2O} Cl_3SnCH_2CH_2COR \text{ +/or } Cl_2Sn(CH_2CH_2COR)_2$$

$R = Me, Cl, OH, OR'(R' = \text{alkyl, aryl})$ (7.1)

In the experimental work described in this chapter hydrostannation is directed at the carbonyl bond. Organotin hydrides add across carbonyl bonds to form an alkoxide or a carbinol according to equations 7.2 and 7.3 [3-7].

$$R_3SnH + R^1R^2C{=}O \longrightarrow R_3SnOCHR^1R^2 \qquad (7.2)$$

$$R_3SnH + R_3SnOCHR^1R^2 \longrightarrow R_3SnSnR_3 + HOCHR^1R^2 \qquad (7.3)$$

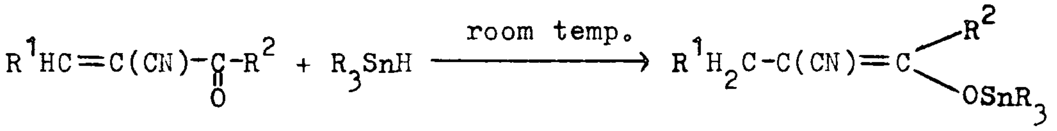
In α,β-unsaturated compounds it is usually the alkene bond which undergoes hydrostannation [8].e.g.

$$Pr^n{}_3SnH + CH_2{=}CHCO_2Me \longrightarrow Pr^n{}_3SnCH_2CH_2CO_2Me \qquad (7.4)$$

However, it is also possible to affect the carbonyl group [3]

$$Ph_2SnH_2 + CH_2{=}CHCOR \xrightarrow[\substack{\text{room temp.} \\ \text{15 hrs.}}]{\text{wet } Et_2O} CH_2{=}CH(OH)CHR + Ph_2Sn \qquad (7.5)$$

and in a limited number of cases 1,4 addition may occur, as exemplified below [9].



$$R^1HC{=}C(CN){-}\underset{\overset{\|}{O}}{C}{-}R^2 + R_3SnH \xrightarrow{\text{room temp.}} R^1H_2C{-}C(CN){=}C\left\langle\begin{matrix}R^2\\ OSnR_3\end{matrix}\right. \qquad (7.6)$$

7.2 Experimental

7.2.1 Reaction of Benzaldehyde with $HCl/SnCl_2/Et_2O$

Benzaldehyde (6.2mls, 60.8 mmoles) was added to ethereal trichlorostannane (59.2 mmoles) without removal of the excess ether, to give a yellow solution which turned deep purple within a few hours. After stirring for 72 hours the ether and a small amount of unreacted benzaldehyde were removed in vacuo to leave a dark brown/purple sticky solid which was refluxed in toluene (150mls) for one hour. Upon addition of dichloromethane a white solid separated which upon isolation was identified as tin (II) chloride. The solution was reduced in volume to give a hard purple, polymeric solid (compound 7.1, 7.23g).

7.2.2 Reaction of Benzaldehyde with Tin (II) Chloride and Hydrochloric Acid in Aqueous Conditions

Benzaldehyde (2.55mls, 25.0 mmoles), $SnCl_2.2H_2O$ (11.28g, 50.0 mmoles), hydrochloric acid (10mls) and methanol (50mls) were refluxed together for six hours to give a pale yellow solution. After addition of distilled water (100mls) and extraction with toluene (4 x 50mls) the organic solution was dried ($MgSO_4$) and reduced in volume to give a yellow oil identified as mainly benzaldehyde.

Compound No. 7.1

Origin PhCHO + $HSnCl_3/Et_2O$

Name & Structure

$-\!(\mathrm{PhCH})_n\!-$ see text

m.pt. 80-2

Elemental Analysis

		PhCHO	$(PhCH)_n$	$(PhCHO + PhCH)_n$
C	84.8	79.2	92.2	84.8
H	7.1	5.7	7.7	7.1
N	0.0			
Sn	0.0			
Cl	0.0			

Empirical Formula $C_{14}H_{14}O$

Infra-red, ν cm⁻¹ KBr disc(seefig7.1)

3380m,b,3080m,shl,3058s,3020s,2920s, 2850s,1937w/m,1875w/m,b,1795w/m,1686m, shl,1596m/s,1508m/s,shl,1486s,1448s, 1410m/s,1311w,1272w/m,1200w/m,1178m, 1153m,1105m,1072m/s,1029m/s,1000m,980w, 960w,942w,935w,910w/m,883w/m,842w/m, 751s,728s,703s,698s,596w,540w,b,479w/m, 459w/m.

¹H N.M.R. $CDCl_3$ Ext.TMS Ref.

δ ppm	Mult.	J,Hz	Int.	Assign.
1.29	s	-	2	
1.43	s	-		
2.38	s	-		
7.23	m	-	20	Ph's

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
	see text				

Other Information

7.2.3. Reaction of Ethereal Trichlorostannane with Phenyl Acetaldehyde.

The experimental procedure was exactly as in section 7.2.1. using phenyl acetaldehyde (5.0 mls, 42.7 mmoles) and gave a white solid identified as tin (II) chloride and a brown solid (compound 7.2, 3.51g.)

7.2.4. Reaction of Ethereal trichlorostannane with Benzophenone

The procedure was exactly as in section 7.2.1. using benzophenone (8.993g, 49.3 mmoles) to give a white solid identified as tin (II) chloride and a pale yellow solution from which colourless fibrous crystals were obtained (compound 7.3, 0.1 g). The experiment was repeated but only gave unreacted starting materials.

7.2.5. Reaction of Ethereal Trichlorostannane with Benzoyl Chloride

Benzoyl Chloride (6.6 mls, 72.9 mmoles) was added to ethereal trichlorostannane (72.8 mmoles), without removal of the excess ether, to give an immediate white precipitate which was stirred in dichloromethane (100 mls) filtered, dried and identified as tin (II) chloride. An IR spectrum of the filtrate showed that it was composed of a mixture of benzoyl chloride, dichloromethane and ether by comparison of its spectrumwith those of authentic samples. It was reduced in volume to give fibrous crystals (0.12g) identified as a tin (II) chloride with a trace of Benzoic acid (from the infra red spectrum).

7.2.6. Reaction of Ethereal Trichlorostanne with Phenylisocyanate

The procedure was exactly as in section 7.2.4. using phenyl isocyanate (3.5 mls, 32.2 mmoles) to give a white solid precipitate (compound 7.4, 4.82g).

Compound No.	Origin
7.2	$PhCH_2CHO + HSnCl_3/Et_2O$

Name & Structure

see text

m.pt. 78-9

Elemental Analysis

		$PhCH_2CH_2$	$PhCH_2CHO$	$PhCH_2CH_2$ + PhCHO
C	78.1	91.4	80.0	85.0
H	7.0	8.6	6.7	7.6
N	0.0			
Sn	0.0			
Cl	0.0			

Empirical Formula C_8H_9O

Infra-red, ν cm⁻¹ KBr disc

3440w/b,3050m,3009m/s,2906m/s,2848m, shl,1935w/m,1865w/m,1798w/m,1675m,shl, b,1590m/s,1534m,b,1480m/s,1442s,1365m, b,shl,1178w/m,1151m,1074m/s,1028m/s, 906w/m,752s,698s,520m,b,324m/s,b.

¹H N.M.R. $CDCl_3$ Ext.TMS Ref.

δ ppm	Mult.	J,Hz	Int.	Assign.
1.20	s,b	-	1	CH_2's
1.67	s,b	-	1	
7.17	m	-	14	Ph's

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
45	$COOH^+$	18	131	?	8.1
77	Ph^+	12	149	?	4.6
91	$PhCH_2^+$	100	167	Ph_2CH^+	6.9
105	$PhCH_2CH_2^+$	20	181	$[(2\times91) - H]^+$	15
115	?	8.5	193	$[115 + PhH]^+$	2.8
118	$[PhCH_2CHO-2H]^+$	4.0	214	$[91 + 122 + H]^+$?	32
120	$PhCH_2CHO^+$	1.9	222	$[105 + 118 - H]^+$?	2.0
122	$[PhCH_2CHO + 2H]^+$ $PhCH_2CH_2OH^+$?	3.8			

Other Information

Compound No. 7.3	**Origin** Ph_2CO + $HSnCl_3/Et_2O$

Name & Structure

see text

m.pt. 320

Elemental Analysis

C	1.3
H	5.4
N	
Sn	
Cl	47.7

Empirical Formula

Infra-red, ν cm^{-1} KBr disc

3500m, b,1735m, 1640w/m, 1600s,1430w/m, 1302w/m, 1230m/s, 1160w, 1141w, 1080w, 930w/m, 780w/m, 690m/s, 620w, 420m/s, 300m/s.

^{1}H N.M.R.

δ ppm	Mult.	J,Hz	Int.	Assign.
No distinguishable peaks, solubility problems.				

Mass Spectrum

m/e	Fragment Ion	I	m/e	Fragment Ion	I
28	CO^+	68	165	$[Ph_2C\ \ - H]^+$	1.0
36	HCl^+	67	182	Ph_2CO^+	100
77	Ph^+	97	190	$SnCl_2{}^+$	18
91	$PhCH_2{}^+$	1.0	225	$SnCl_3{}^+$	3.6
105	$PhCO^+$	93	261	$[SnCl_4 + H]^+$? $[182 + 77 + 2]^+$? or $[106 + 155]^+$ ie.$PhHCOSnCl_2$	0.4
120	Sn^+	13			
139	?	0.6			
155	$SnCl^+$	52			

Other Information

Compound No. 7.4	**Origin** PhN = C = O + $HSnCl_3/Et_2O$

Name & Structure

see text

m.pt. 217-18

Elemental Analysis		$C_7H_6Cl_3NOSn$
C	13.9	24.4
H	1.4	1.8
N	2.5	4.1
Sn	40.9	34.4
Cl	43.9	30.8

Empirical Formula

Infra-red, ν cm^{-1} KBr disc

3590w/m,shl,3520m,3140m,shl,3080m,b, 2550w,b,1606m/s,1594m/s,shl,1562m,b, 1539m,shl,1475m/s,1337w,1321w/m,1283w, 1221w/m,1181w/m,1102vw,1079m/s,1062m, shl,1027m,739s,681m/s,615w,519m,464m/s 410m,b,371m/s,304s,293m,shl,279m/shl.

^1H N.M.R. d_6 DMSO,Ext.TMS Ref.

δ ppm	Mult.	J,Hz	Int.	Assign.
7.27 7.30	m	-	-	Ph's

Mass Spectrum

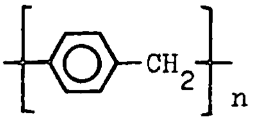
m/e	Fragment Ion	I	m/e	Fragment Ion	I
43	$NCOH^+$	25	137	$[120 + OH]^+$ or $[120 + NH_2 + H]^+$	3.2
77	Ph^+	23			
93	$PhNH_2^+$	95	155	$SnCl_2^+$	41
106	$PhNH_2CH^+$	29	165	$[120 + 45(NCOH_3)]^+$	31
119	$PhNCO^+$	6.6	190	$SnCl_2^+$	15
120	$PhNCOH^+$ and/or Sn^+	13	225	$SnCl_3^+$	16

Other Information

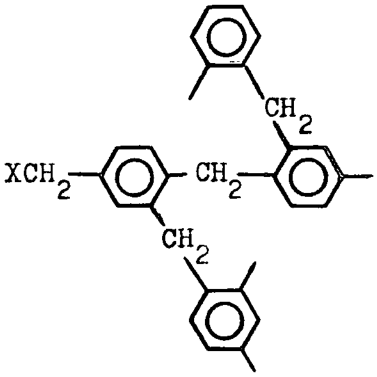
7.3 Discussion of Results

7.3.1. The Aldehyde Reactions

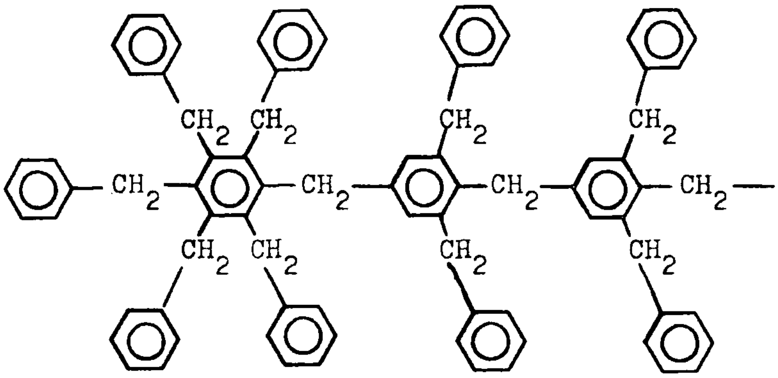
The mass spectrum of the product from ethereal trichlorostannane and benzaldehyde (7.1.) clearly shows that it is polymeric in nature. In general, aromatic aldehydes, such as benzaldehyde, do not undergo polymerisation or condensation reactions as readily as aldehydes, such as formaldehyde, which have an α hydrogen atom [10]. However, it has been reported that the reaction between benzaldehyde and antimony pentachloride [11], ferric chloride [11] or aluminium chloride [12, 13,] results in the formation of a dark polymeric solid. This is accompanied by the evolution of hydrogen chloride [11] and for the latter two cases the evolution of carbon monoxide is reported. Raff et al [10] claim that attempts to homopolymerise benzaldehyde by γ irradiation or by stirring between 0° and 25° C for 90 minutes with a series of ionic and co-ordination catalysts, including $AlCl_3$, $TiCl_4$, $SnCl_4$, $VOCl_3$, silica gel, $Bu^n Li$, tetra butyl titanate, diisobutyl aluminium hydride (DIBAH), DIBAH-$TiCl_4$ and DIBAH- $VOCl_3$, failed to give any polymeric material. However they were successful upon heating benzaldehyde with $BF_3.Et_2O$ and obtained a brown powder which was identified as polybenzyl by comparison of its infra-red spectrum with that of an authentic sample [14-16]. They also remark on its similarity to toluene. The spectrum for this polymer [10] is identical to that of the polymer obtained in the hydrostannation reaction so we may conclude that it too is polybenzyl (Fig. 7.1). The exact structure of polybenzyl is still to be elucidated. It has been proposed [17] that it is a linear methylene-p-phenylene structure (VII.1) or more probably a branched variation as illustrated by VII.2 [18] and VII.3. [10,14].



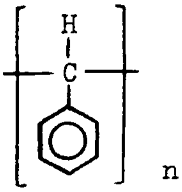
VII.1



VII.2



VII.3

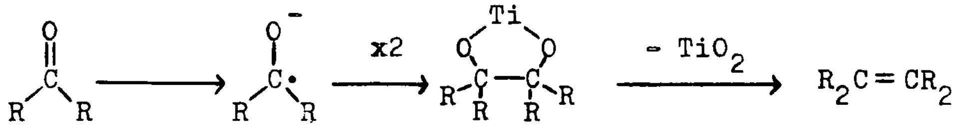


VII.4

Conversely,[14] the pendant type structure, VII.4 for polymers is formed from compounds such as benzyl fluoride due to the instability of a single fluorine atom on an aliphatic side chain by a Friedel Crafts type mechanism [10].

One may compare the above reactions with the reductive coupling of carbonyl compounds by reduced forms of titanium [19] such as Zn-$TiCl_4$ [20], Mg(Hg)-$TiCl_4$ [21], Zn-Cu-$TiCl_3$ [22], Mg-$TiCl_3$ [23] and $LiAlH_4$-$TiCl_3$ [24] to give diols and alkenes as shown, for example, for benzophenone in scheme 7.1.

$$Ph_2C{=}O \xrightarrow[\text{THF Reflux overnight}]{LiAlH_4\ (1\ eq)\ -\ TiCl_3\ (2.5\ eq)} \underset{95\%}{Ph_2C{=}CPh_2}$$



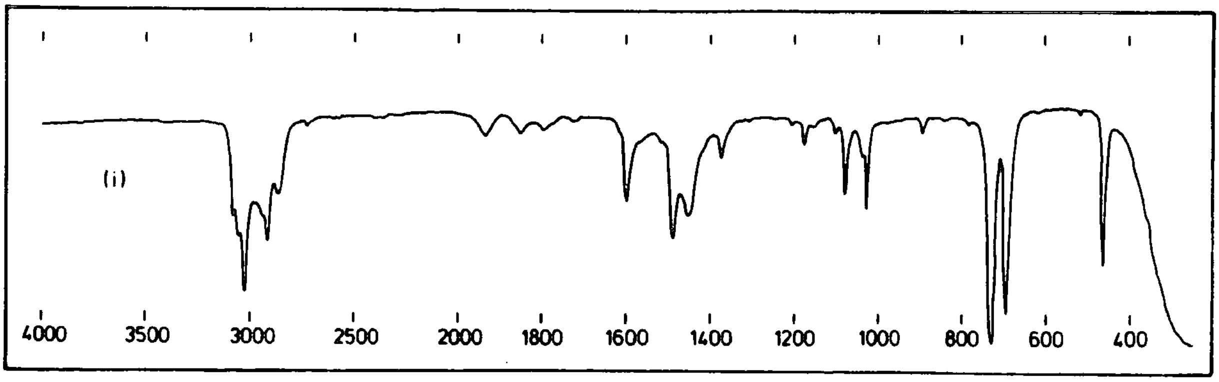
Scheme 7.1

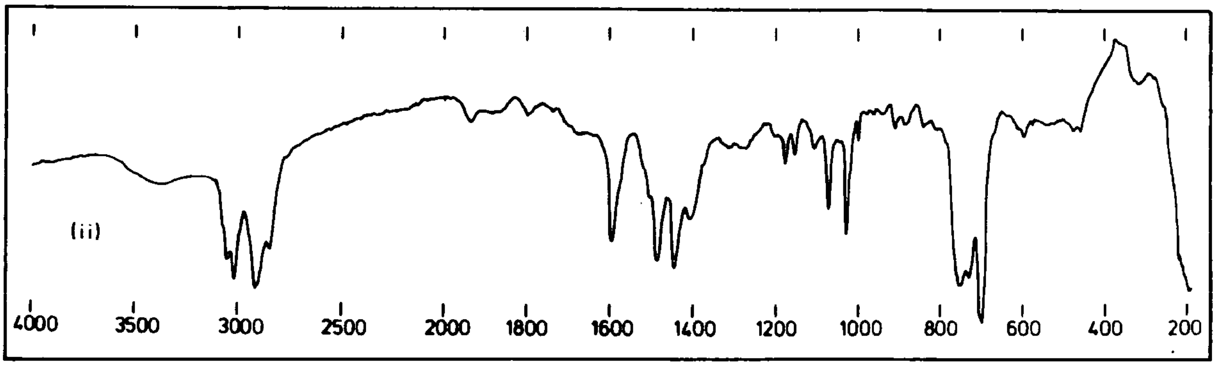
eq = equivalent

The hydrostannation product of benzaldehyde is characterised on page 254 . As mentioned above and illustrated in Fig. 7.2 the infra red spectrum of compound 7.1 is identical to that of polybenzyl [10] and very similar to that of toluene. There is evidence in the infra red spectrum for alkyl and **aryl** groups but none for ether linkages. A medium intensity peak at $3380cm^{-1}$ is possibly due to hydrolysis of the product and there is very little other support for the presence of any alchol groups.

The ^1H n.m.r. spectrum shows that there are predominantly aromatic protons in the structure as assigned in the data table. There is a broad peak at 3.95ppm which may be assignable to an alcohol proton. For comparison the ^1H N.M.R. spectrum of toluene has resonances at 2.32 and 7.17 whilst there are peaks at 2.38 and 7.23 in the spectrum of this compound implying a similar basic structure. The peaks at 1.29 and 1.43ppm imply slight complications such as branching or possible impurities.

The simplicity of this and the infra red spectrum imply that the structure is not very complex and should be relatively easy to solve.





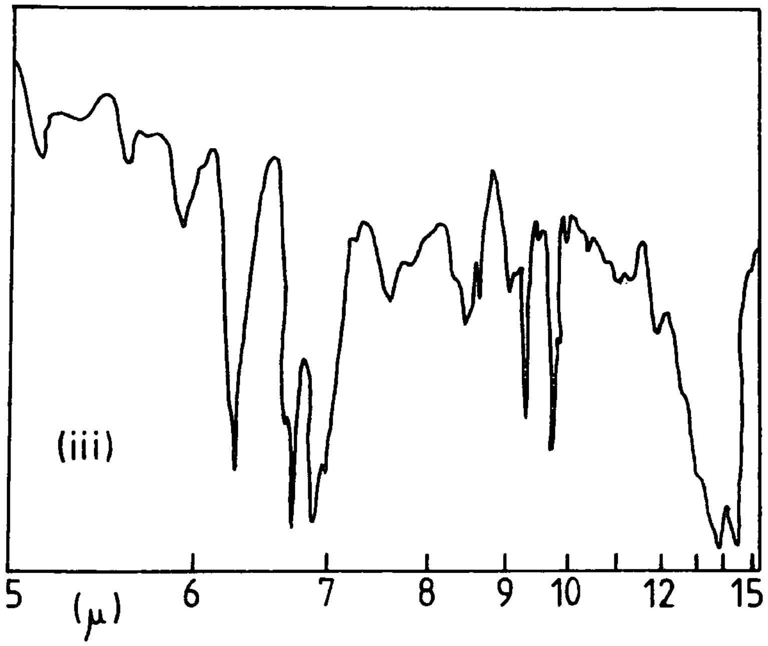


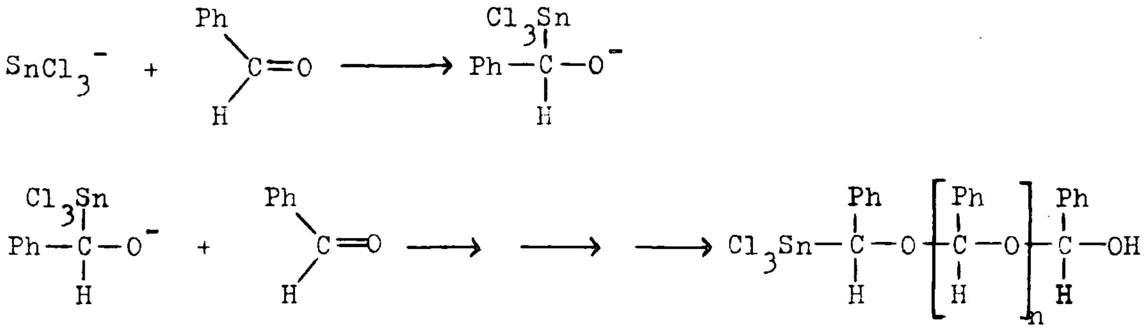
Fig. 7.2 Infra-red Spectra of (i) Toluene (ii) Compound 7.1 and Polybenzyl [10].

The mass spectrum, which is tabulated below (table 7.1) suggests that it is a polymer of relatively low molecular weight.

Table 7.1 Mass Spectrum of Compound 7.1

m/e	Fragment Lost *	Fragment Ion	I
77		Ph^+	38
91		$PhCH_2^+$	100
105		$PhCO^+$ or $PhC_2H_4^+$	100
115		$PhC_3H_2^+$	40
129		$PhC_4H_3^+$	31
141	90	$PhC_5H_3^+$	20
152		$PhC_6H_3^+$ or $2(C_6H_4)^+$	22
167		Ph_2CH^+	100
181		$Ph_2C_2H_3^+$	100
191		$Ph_2C_3H^+$	66
205		$Ph_2C_4H_3^+$	100
215		$[2(PhCHOH) + H]^+$	87
291	76		75
383	92		57
473	90		41
562	89		41
588	26 90	* 26 = $C_2H_2^+$	22
652	90	76 = $C_6H_4^+$	61
678	90	89 = PhC^+	33
742	90	90 = $PhCH^+$	36
768	90	92 = $[PhCH + 2H]^+$	21
832	90		11
858	90		7.2
922	90		2.5
948	90		2.2
1012	90		0.2
1038			0.3

If the polymer was simply built up from benzaldehyde units, as a result of catalysis by ethereal trichlorostannane according to scheme 7.2, then peaks at a distance m/e 106 apart in the mass spectrum would be expected.



Scheme 7.2

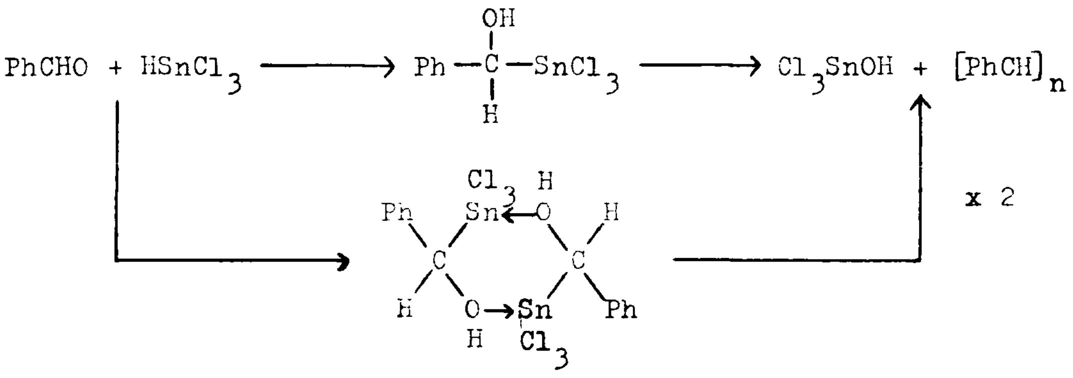
VII.5

However table 7.1. shows that clearly this is not the case. Instead the polymer is built up from units of m/e 90 which represent the cationic benzylidene fragment $[PhCH]^+$. There are two such sets of peaks in phase, separated by a m/e value of 26 which corresponds to $[C_2H_2]^+$. By comparison if the structure was as suggested by VII.5 then the loss of (C-O) and (O-C-O) units of masses of 28 and 44 would be expected instead.

Assuming that the polymer is composed chiefly of PhCH units then there are two possible ways in which they could be linked according to VII.1 and VII.4. The former suggestion may account for its colour. The pendant type polymer, VII.4 could easily give rise to peaks in the mass spectrum for a m/e value of 26 such would be less feasible from the alternative structure. Also VII.4 should readily lose Ph units; VII.1 should not.

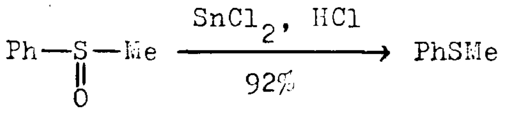
The elemental analysis reveals an absence of both tin and chlorine and fits more closely for the loss of one oxygen atom per pair of benzaldehyde molecules. This does not support the sole presence of -PhCH- chains but may be accounted for by oxidation during analysis.

The overall reaction therefore seems to be one of reductive polymerisation as the oxygen content has been drastically reduced, if not eliminated altogether, compared to that of benzaldehyde itself. It is not clear whether the polymer is comprised of para linkages (VII.1) (which could be joined in a head to tail or head to head manner), a pendant type structure (VII.4) or a mixture of both. It is quite possible that it is a branched structure similar to VII.2 or VII.3. The ethereal trichlorostannane may simply have catalysed the reaction and then decomposed to its starting materials. Alternatively a tin hydroxy species may have been formed according to scheme 7.3.



Scheme 7.3

Also in aqueous conditions tin (II) chloride and hydrochloric acid will reduce sulphoxides to their sulphides [25] .



$$\mathrm{Ph{-}S({=}O){-}Me} \xrightarrow[92\%]{\mathrm{SnCl_2,\ HCl}} \mathrm{PhSMe} \qquad (7.7)$$

$$\mathrm{Ph_2S{=}O} \xrightarrow[93\%]{} \mathrm{Ph_2S} \qquad (7.8)$$

$$\mathrm{(^nBu)_2S{=}O} \xrightarrow[62\%]{} \mathrm{(^nBu)_2S} \qquad (7.9)$$

The aqueous reaction between tin (II) chloride, hydrochloric acid and benzaldehyde was carried out using exactly the same experimental procedure to that for the sulphoxides [25] but gave only the unreacted starting materials rather than following the analagous reaction according to equation 7.10.

$$\mathrm{PhCHO} \xrightarrow[\times]{\mathrm{SnCl_2,HCl(aq)}} \mathrm{PhCH{=}CHPh}. \qquad (7.10)$$

The hydrostannation reation was extended to phenyl acetaldehyde to determine whether its homopolymer with an additional methylene group in the polymer unit could be prepared. The product obtained was very similar in appearance to that from benzaldehyde but successive mass spectral studies revealed that it was not polymeric. However the infra-red spectrum is almost identical to that of compound 7.1 from benzaldehyde. The ^{1}H n.m.r. and mass spectra are as assigned in the data tables on page 256. Again the elemental analysis fits partial loss of oxygen from the aldehyde and there is no evidence for any tin or chlorine in the product.

7.3.2. The other Carbonyl Compounds

The scope of the reaction has also been extended to benzophenone for two reasons. Firstly to determine whether the aldehyde proton is vital for the reaction to occur, which may lead to some speculation on the reaction mechanism. Secondly, the reaction may be affected by steric hindrance. It was immediately obvious that the reaction had not followed the same course as there was no colouration of the reaction mixture. The main products are the unreacted starting materials along with a very small amount of fibrous crystals of which the infra-red spectrum implies that the product is heavily contaminated with tin (II) chloride. The medium intensity peaks assignable to organic bond vibrations exhibit a peak due to v(C=O) at 1735 cm^{-1} compared to 1640 cm^{-1} for benzophenone and 1675 cm^{-1} for benzoic acid. The peak at 1230 cm^{-1} may be assigned to the asymmetric (C-O-C) streching of an ether. The mass spectrum of compound 7.3 implies that a new organometallic compound has been formed as the highest peak may be assigned to the fragment ion $[Cl_2SnPhCHO]^+$. There are also peaks due to both Ph_2CO (m/e182) and $SnCl_3$ (m/e 225) and their break down. However, the elemental analysis does not support the 1:1 product but the high tin and chlorine content could be accounted for if the product is heavily contaminated with tin (II) chloride.

Finally, the research was extended to the carbonyl compounds benzoyl chloride and phenyl isocyanate. The former gave only unreacted starting materials with only a trace of benzoic acid which may be an actual product or may have been formed as a result of hydrolysis of the benzoyl chloride during the course of the reaction.

The phenyl isocyanate reaction did yield a new organometallic product the characterisation of which appears on page 258. The most noticeable change in the infra-red spectrum compared to that of phenyl isocyanate itself in the loss of the peak at 2280 due to v(N=C=O) which proves that this group has reacted and this is supported by minor changes in the region between 1650 and 1400 cm^{-1} where C=N and C=O stretching frequencies are observed. The ^1H n.m.r spectrum has peaks in the phenyl region but none assignable to protons attached to the nitrogen atom, nor to an alcohol proton, nor any high field peaks due to aliphatic protons, all of which would imply saturation of the isocyanate group. The mass spectrum is as assigned in the data table and has fragments associated with both isocyanate and trichlorostannane units. The elemental analysis does not fit for the 1:1 product, and again this may be due to heavy contamination with tin (II) chloride.

7.4. Conclusion

The hydrostannation of carbonyl compounds by ethereal trichlorostannane does not occur readily to give organotin products, instead, in each case, (with the possible exception of phenyl isocyanate) unreacted tin (II) chloride was recovered. Benzaldehyde, but not phenyl acetaldehyde, yielded a hydrocarbon polymer in a reaction comparable to that between benzaldehyde and $BF_3 . Et_2O$. Of the remaining carbonyl compounds, benzophenone, benzoyl chloride and phenyl isocyanate only the last gave a significant amount of organometallic product, which has been characterised but not identified completely.

CHAPTER 8

NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPIC STUDIES

8.1 Introduction

Nuclear quadrupole resonance (n.q.r.) spectroscopy reflects the electric field gradient (e.f.g.) in a solid sample using the quadrupolar nucleus as the probe. The resonant frequency therefore corresponds to the energy of coupling between the nuclear quadrupole moment and the molecular e.f.g.. As a result a variable frequency detector is required, the nuclear quadrupole interactions ranging from 100kHz to 1000 MHz.

The nucleus must be in an unsymmetrical environment, have a nuclear spin quantum number, I, greater than 1/2 and have a reasonably high natural abundance. For example, the nuclei involved in this chapter namely ^{35}Cl and ^{79}Br, each with $I = 3/2$, have natural abundances of 75.40% and 50.57% respectively. However, the isotopes ^{37}Cl and ^{81}Br of natural abundances 24.60% and 49.43% respectively, again with $I = 3/2$, may also be studied. The sample must be a solid, preferably crystalline, as molecular motions in liquids and gases cause the e.f.g. to be reduced to zero.

N.Q.R spectroscopy is a particularily valuable tool for studying inorganic compounds and some of its chief applications are listed below. It gives information on :-

(i) Chemical bonding in the solid state. This is because the e.f.g. arises mainly from 'p' and 'd' orbital electron contributions to the symmetry of the nucleus, the 's' orbital electrons being spherically symmetrical in the absence of hybridisation.

(ii) Molecular structures. For example, cis and trans isomers in organometallic complexes may be distinguished due to their differing symmetries.

(iii) Crystallographic structures. If there is more than one quadrupolar nucleus of the same atom within the molecular formula then any crystallographic inequivalencies will be divulged by line splitting, i.e. more than one resonance per spectrum. Among the factors affecting the n.q.r. frequency will be the bond lengths and the overall size of the anions and cations in ionic compounds.

(iv) Phase transitions within the crystal structure.

The latter two will be discussed in further detail. The detection of phase transitions is illustrated in a temperature dependence study on caesium tribromostannate in the experimental work for this chapter. The research has been extended to other trihalostannates and to some of the compounds prepared in the previous chapters, including (N-methyl) diphenyl methylene ammonium trichlorostannate, ($[Ph_2C{=}NHMe]^+ SnCl_3^-$), for which the results are compared with the crystal structure.

8.2 Temperature Dependence N.Q.R. Sppectroscopy Studies on Caesium Tribromostannate, $Cs^+SnBr_3^-$

8.2.1 Phase transitions in the solid state can be studied due to the ability of n.q.r. spectroscopy to detect crystallographic inequivalence, including both inter- and intra- molecular forces. The transition is recognised either by a change in the number of resonance lines or by an abrupt change in the temperature coefficient, (for frequency against temperature). Phase transitions have been studied for a number of hexachlorostannates [1 - 7] and some investigations have already been carried out for $CsSnBr_3$ [8].

8.2.2 Experimental

All operations were carried out under an atmosphere of dry nitrogen and all solvents were deoxygenated, due to the high sensitivity of the desired product to oxidation to the hexabromostannate. Any oxidation of $CsSnBr_3$ which is black is easily monitored as Cs_2SnBr_6 is yellow.

8.2.2.1 Preparation of $CsSnBr_3$

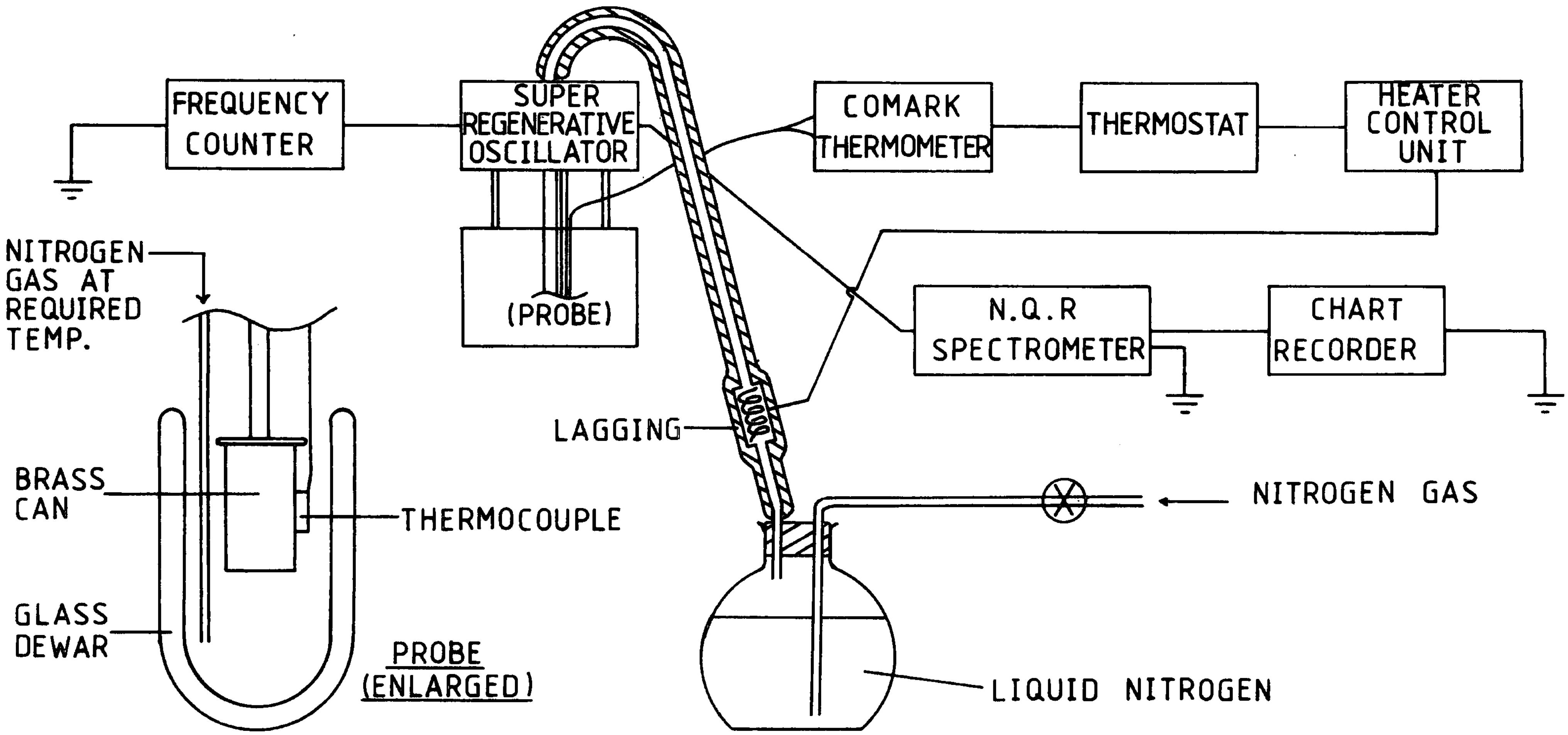
Caesium Bromide (6.952g, 32.7 mmoles) in concentrated hydrobromic acid (50 mls) was added by syringe to tin (II) bromide (9.216g, 33.1 mmoles) in concentrated hydrobromic acid (50 mls) to give an immediate black precipitate of caesium tribromostannate which was filtered, washed and dried in vacuo (8.54g, 54%).
Elemental analysis; Cs = 26.7% ; Br = 48.3% ; $CsSnBr_3$ requires; Cs = 27.1% ; Br = 48.8% .

8.2.2.2 Temperature Dependence N.Q.R. Spectroscopy Studies

Approximately 2g of $CsSnBr_3$ was packed in a small sample bottle and placed in the coil. The apparatus used for the range -110 to 25°C, a variable temperature cryostat, is ilustrated in fig 8.1.

The sample was cooled down by a flow of cold nitrogen gas which had been passed through liquid nitrogen and maintained at the required temperature using a thermostatically controlled heating unit. The thermostat was set at the desired temperature and by adjusting the flow of nitrogen gas the required temperature was achieved. After approximately twenty minutes when thermal equilibrium had been reached, with the aid of careful lagging with cotton wool, an accuracy of ± 0.1°C was attained. A Comark copper-constantan thermometer was attached to the outside of the brass can which contained the coil and in turn the sample. Due to the thermal conductivity of brass the temperature recorded is close

Fig. 8.1. APPARATUS FOR TEMPERATURE DEPENDENCE N.Q.R. STUDIES.



to that of the sample. Temperatures below - 110°C were achieved by adding dropwise just enough liquid nitrogen into the dewar around the can, for which an accuracy of only ± 1 °C was possible.

The frequency region was scanned at least twice for each temperature, and for the temperature range over which the phase transition occured readings were taken for both cooling (20 - 12°C) and heating (12 - 20°C) of the sample. The results are given in tables 8.1 to 8.3 and illustrated graphically in figures 8.2 and 8.3.

Table 8.1

N.Q.R. Frequencies for $CsSnBr_3$ for cooling from 25 to -5°C * uncertain

Temperature, °C	Frequency, MHz	Temperature, °C	Frequency, MHz
25	62.960	11	62.810 63.325*
24	62.940	10	62.810
23	62.935	9	62.790
22	62.950	8	62.775 63.330*
21	62.955	7	62.800
20	62.950	6	62.775 63.375*
19	62.975	5	62.775
18	62.975	4	62.775 63.420*
17	62.885	3	62.775 63.410
16	62.980	2	62.775 63.435
15	62.975	1	62.780
14	62.955 63.380*	0	62.775 63.450*
13	62.825 63.255*	-5	62.770 63.470
12	62.810 63.300*		

Table 8.2.

N.Q.R. Frequencies for $CsSnBr_3$ for Heating from 12 to 20° C.

Temperature, °C	Frequency, MHz	Temperature, °C	Frequency, MHz
12	62.820	17	62.985
13	62.820	18	62.970
14	62.820	19	62.980
15	62.840	20	62.980
16	62.840		

Table 8.3

N.Q.R. Frequencies for $CsSnBr_3$ over the Range - 10 to - 196 °C.

Temp. °C	Frequencies, MHz[a]	Temp. °C	Frequencies, MHz[a]
-10	62.775, 63.515	-110	62.810, 64.160
-20	62.750, 63.540	-120	62.820, 64.285
-30	62.745, 63.550	-130	62.840, 64.400
-40	62.750, 63.645	-135	62.850, 64.640
-50	62.770, 63.700	-145	62.875, 64.775
-60	62.760, 63.760	-155	62.910, 64.865
-70	62.765, 63.805	-165	62.960, 64.970
-80	62.760, 63.890	-175	62.980, 65.100
-90	62.795, 63.995	-185	62.950, 65.180
-100	62.790, 64.090	-196	62.950[b], 64.820[b]

a = Relative intensities 2 : 1

b = Uncertain

Fig. 8.2 Temperature Dependence of the ^{81}Br N.Q.R. Frequencies of $CsSnBr_3$ over the Range -5 to +25 ^{o}C.

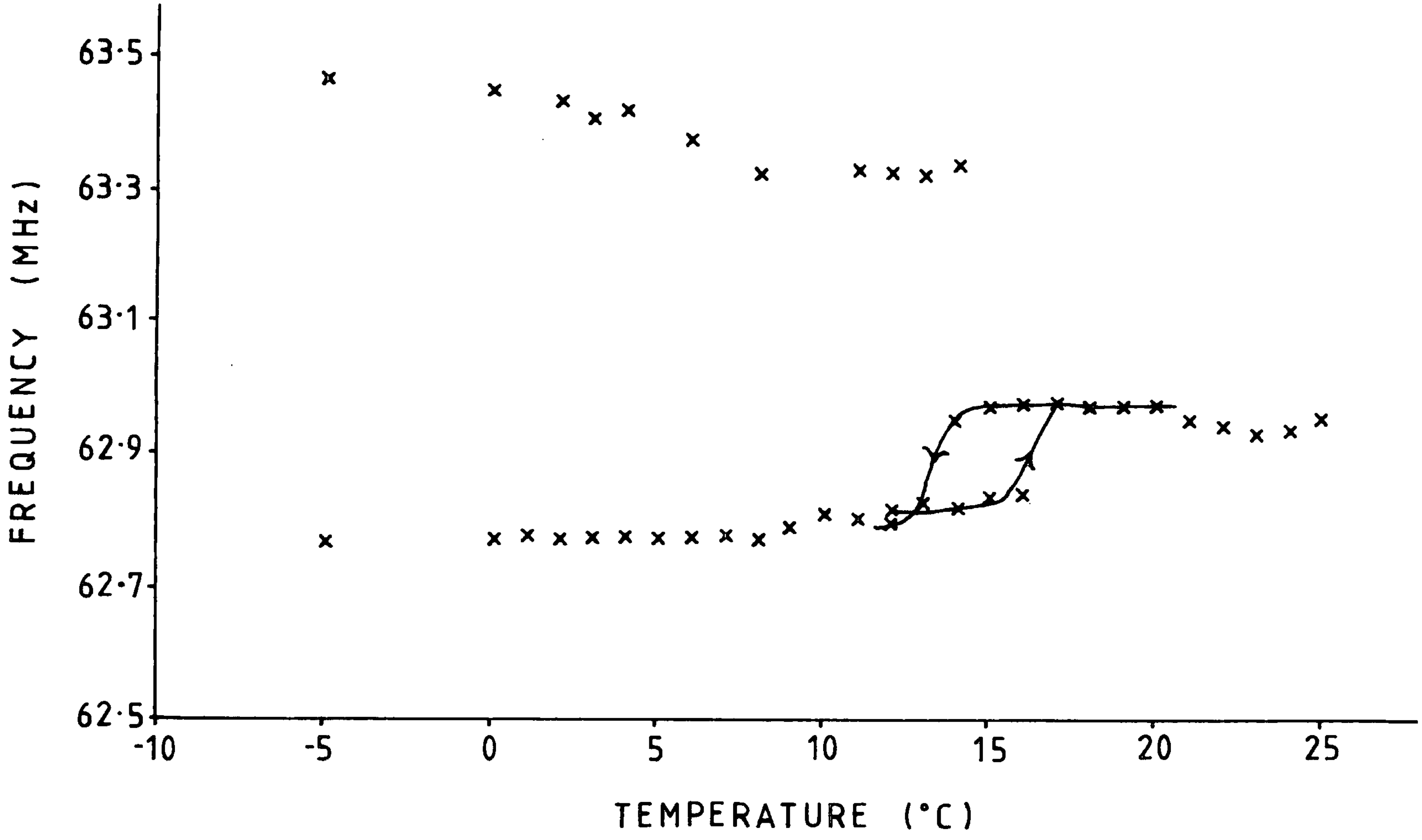
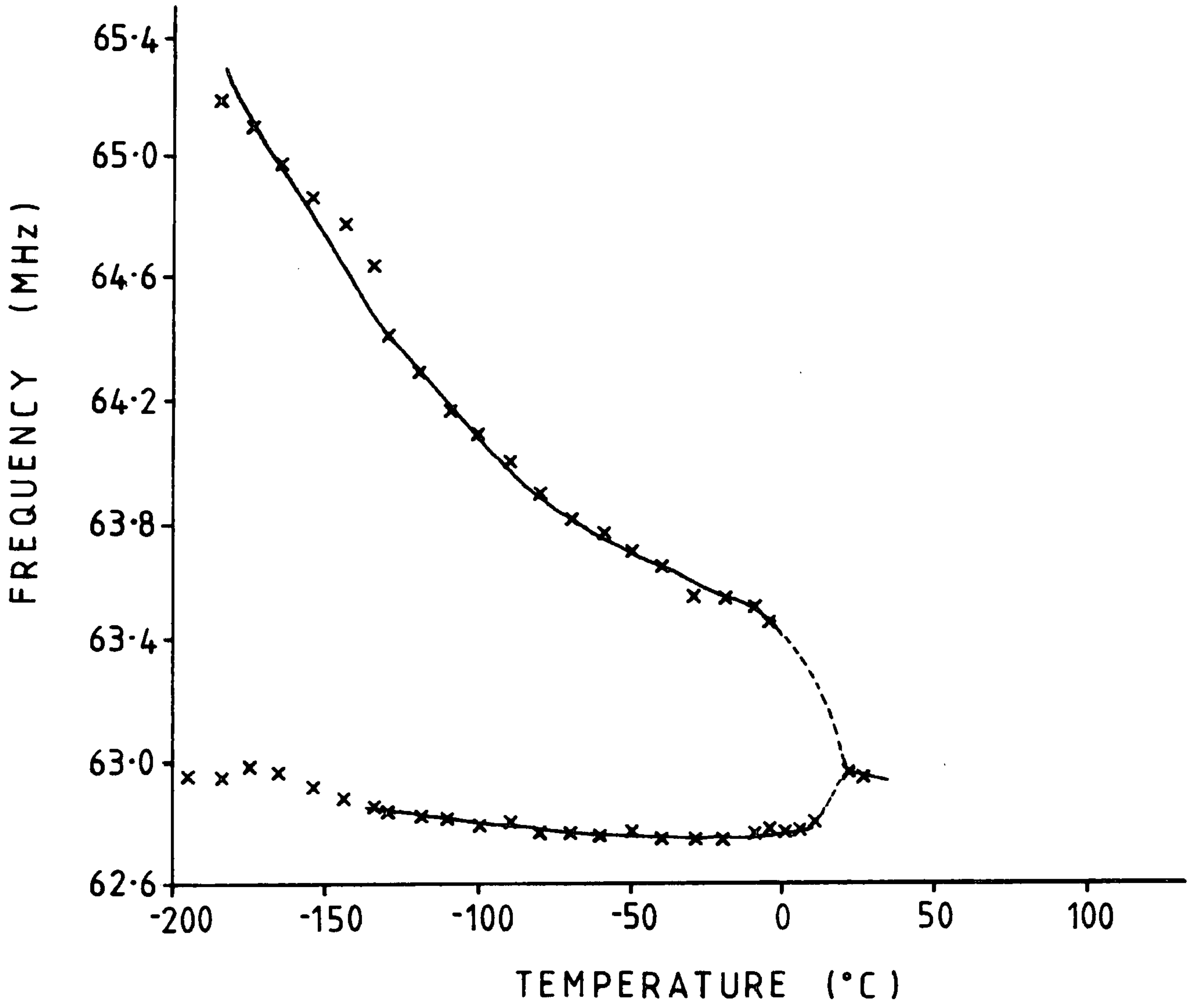


Fig. 8.3 Temperature Dependence of the ^{81}Br N.Q.R. Frequencies of $CsSnBr_3$ over the Range -196 to +25 °C.



8.2.3. Discussion of Results

Some n.q.r. temperature dependence studies of $CsSnBr_3$ have already been performed [8]. However, the experiment was repeated for two reasons; firstly, to deduce whether the phase transition is first or second order. The former would give rise to complete disappearance of the two lines at the transition with replacement by a single line at approximately the intensity weighted mean frequency, whilst a second order transition is recognised by the two lines progressively merging into one. Scaife et al [8] were uncertain on the transition order but favour a first order transition by comparison of their results with those of $CsPbCl_3$ [9, 10] which itself undergoes a first order transition. Secondly Scaife et al [8] only looked at the region between - 100 and + 100 °C. We have extended this study to the liquid nitrogen temperature (-196°C).

Scaife et al [8] assigned the peaks observed to the ^{81}Br isotope, rather than the ^{79}Br isotope which also has a nuclear quadrupolar moment, although they do not give any reasoning for this assignment. However, following this assumption and using the formula:

$$\frac{^{79}Br}{^{81}Br} \text{ frequency} = 1.19707$$

from their results the predicted resonance for the ^{79}Br isotope is 75.502 MHz (Temp $\geqslant$ 20° C). Unfortunately this was not detected on our particular spectrometer which does not scan this region.

The crystal structure of caesium tribromostannate has been determined [11] and is cubic pervoskite at room temperature with all three tin - bromine bond lengths of 2.94Å. This is reflected by the single n.q.r. line at this temperature. Upon cooling below the phase transition temperature a second peak appears. By comparison with the $CsPbCl_3$ system the higher frequency peak has been assigned to bromine atoms in sites of four fold symmetry and the lower frequency peak to bromine atoms in two fold sites [8].

Detailed studies were made in the phase transition region (tables 8.1 and 8.2 and fig. 8.2). Above 19°C there is a single peak at 62.95 MHz which is close to that at 63.073 MHz quoted by Scaife et al [8]. By decreasing the temperature the frequency remains constant until, at 14°C, it starts to drop and this coincides with the appearance of a possible second peak at a higher frequency which implies a first order phase transition. For the low temperature results the low frequency peak is twice as intense as that at a higher frequency and consequently, any high frequency peaks at these higher temperatures will be difficult to distinguish. However, by doing each run in duplicate their authenticity can be confirmed to a certain extent. A decrease in temperature by one degree to 13°C results in a reduction in the frequency by 0.13 MHz. The frequency value then levels off, any further reduction in temperature having very little effect. The results for the opposite direction i.e. heating are given in table 8.2 and Fig. 8.2. There is evidence for hysteresis as the low frequency peak does not increase in value until the temperature reached 17°C. Thus the phase transition temperature lies between 13 and 17°C. By comparison Scaife et al [8] give a phase transition temperature of approximately 10°C and report that it occurs relatively rapidly upon increasing the temperature but much slower upon cooling.

Upon cooling further (table 8.3 and fig. 8.3) the lower frequency peak initially remains in approximately the same position, but the frequency gradually increases as the temperature is reduced below - 120°C. The high frequency peak steadily increases in frequency until at the liquid nitrogen temperature it is difficult to discern. A tentative peak is reported at 64.32 MHz but it is possible that the actual frequency is beyond the scope of the spectrometer (see next section) and the scale of the graph.

The region above 25°C has not been investigated further as extensive studies have already been carried out [8], and show that the single resonance decreases in frequency at a rate of -3.21 KHz /°C.

8. 3. N.q.r. spectroscopic studies on related trihalostannates

The n.q.r. study has been extended to tetra ethyl- and tetra n-propyl ammonium tribromostannate and to tetraphenyl phosphonium trichloro- and tribromostannate

8.3.1. Experimental

A similar procedure to that for caesium tribromostannate was adopted, care being taken to avoid oxidation.

8.3.1.1. Preparation of tetra ethyl ammonium tribromostannate.

Tetra ethyl ammonium bromide (5.199g, 24.7 mmoles) in concentrated hydrobromic acid (50 mls) was added to tin (II) bromide (6.865g, 24.7 mmoles) in concentrated hydrobromic acid (50 mls) to give a pale yellow solution. This was reduced in volume in vacuo and left to stand overnight during which the required crystals were formed and subsequently isolated. The elemental analysis is presented in table 8.4.

The n-propyl analogue was prepared in an identical manner. The phosphonium salts were similarly prepared but due to severe solubility problems the bromide was dissolved in deoxygenated dichloromethane. For the trichlorostannate both the tin (II) chloride and the tetraphenyl phosphonium chloride were dissolved in deoxygenated water with a trace of hydrogen bromide. The two phosphonium trihalostannates came out of solution immediately . Attempted recrystallizations from dichloromethane were unsuccessful.

Table 8.4

Elemental Analyses for the Trihalostannates Prepared for N.Q.R. Studies. (calculated values in parenthesis)

Compound	% C	% H	% N or P	% Halogen
$[(CH_3CH_2)_4N]^+ SnBr_3^-$	19.8 (19.7)	4.4 (4.1)	2.5 (2.9)	45.3 (49.1)
$[(CH_3CH_2CH_2)_4N]^+ SnBr_3^-$	26.3 (26.5)	5.3 (5.2)	2.6 (2.6)	41.0 (44.0)
$[(C_6H_5)_4P]^+ SnBr_3^-$	37.3 (41.3)	3.0 (2.9)	- (4.4)	39.1 (34.4)
$[(C_6H_5)_4P]^+ SnCl_3^-$	47.6 (51.1)	2.2 (3.6)	5.9 (5.5)	20.8 (18.9)

8.3.1.2. N.q.r. spectra were recorded for each sample at 25°C (room temperature), -77°C (CO_2(s)) and -196°C (N_2(l)). The frequency range swept for ^{79}Br was between 42 and 236 MHz with the exception of the regions between 65 and 93 MHz and between 132 and 160 MHz over which the departmental spectrometer does not operate, but concentrating on frequencies between 40 and 65 MHz by comparison with $CsSnBr_3$. The range swept for ^{35}Cl was between 8 and 20 MHz. The results are as tabulated (table 8.5).

Table 8.5

The Br[a] and ^{35}Cl N.Q.R. frequencies of some Trihalostannates.

Compound	N.Q.R. Frequency b,c at		
	-196°C	-77°C	25°C
$Et_4N^+ SnBr_3^-$	57.75 61.05[d]	45.95 62.22[e]	-
$Pr_4N^+ SnBr_3^-$	57.92[d] 60.05[d]	-	54.65
$Ph_4P^+ SnBr_3^-$	-	-	-
$Ph_4P^+ SnCl_3^-$	13.43 } (2)[f] 13.47 } 13.765 (1)	-	-

(a) The bromine resonances cannot be assigned unequivocally to ^{79}Br or ^{81}Br isotopes although the lower frequency signal from Et_4NSnBr_3 at -77°C is more likely to arise from ^{81}Br nuclei,
(b) MHz, (c) ± 0.10 MHz, (d) Tentative but reproducible
(e) Tentative but not reproducible, (f) Relative intensities.

8.3.2. Discussion of Results

The only tribromostannate for which n.q.r. studies are reported is caesium tribromostannate [8]. A preliminary investigation into ammonium tribromostannates, for the cations Me_3NH^+, Me_4N^+ and NH^+ [7] has given no N.Q.R. peaks. However the trichlorostannates have proven more rewarding and peaks in the region of 10 to 12 MHz have been reported for the cations $Me_2NH_2^+$ and Me_4N^+ [7] and between 5 and 12 MHz for $CsSnCl_3$ [8] and $[SnCl(H_2O)_2]^+ SnCl_3^-. H_2O$ [12].

The results for the tribromostannates in table 8.6 are only tentative, as indicated. The 'peaks' are very weak, often with a signal : noise ratio as low as 2:1 or 3:1. They are recognised by a broadening and 'rounding off' of the lines compared to the background noise. Each spectrum was run at least three times as reproducibility of the peaks, however weak, would support their authenticity. Also by examining the spectra at different temperatures the presence of peaks at approximately the same frequencies, allowing for the fact that the frequency decreases with an increase in temperature, confirms their authenticity.

There are a number of explanations for the poor quality of these spectra. Firstly the quality of the sample is important. Crystalline material is preferable as, in the absence of possible lattice defects, it will have a well ordered and regular structure.

Therefore any quadrupolar nucleus will have identical surroundings to all the other similar nuclei and consequently the quadrupole moments will all lie in approximately the same direction. The two ammonium salts are crystalline whilst the phosphonium salts are powders so this may account for the dearth of signals for tetraphenyl phosphonium tribromostannate.

The percentage of bromine should also be considered. The cations here are quite large compared to Cs^+ for which the tribromostannate gives definite peaks. The small ammonium ions studied previously [7] gave no spectra, so it is not surprising that these compounds, with larger cations and therefore a lower percentage of bromine for the same amount of material, give poor spectra. This explanation is supported by the fact that studies on the hexabromostannates [7] which have a higher bromine content are more successful. Also good spectra will be difficult to obtain as the natural abundance of ^{79}Br is only approximately two thirds of that of ^{35}Cl for which adequate spectra have been obtained for a limited number of samples [7]. Finally the low sensitivity of the spectrometer may contribute to the poor results.

Inspite of tetra phenyl phosphonium trichlorostannate being a powder a satisfactory spectrum was recorded at -196°C.

The spectrum may be interpreted by comparison with the crystal structure which has been determined [13]. The tin-chlorine bond lengths are 248.8 (2), 245.6 (2) and 246.7 (2) Å (Figures in parenthesis are the standard deviation). Lower frequencies usually correspond to longer bond lengths [10, 13], because with increasing bond length (where there is little π bonding) the ionic character of the halogen increases. Hence its e.f.g. and consequently the n.q.r. frequency becomes lower. The peak at 13.765 Hz could represent the shortest Sn-Cl bond, with the two lower frequency peaks representing the longer bonds even though one of them is closer in length to the shortest. The assumption above is confirmed graphically by a linear plot of the n.q.r. frequency against the relevant bond lengths. Such a graph for certain trichlorostannates [7] predicts frequencies at 25°C between 12.5 and 13.5 MHz for tin-chlorine bonds as short as those concerned, and the observed result is indeed very close. However, it is also possible for a partial reverse to occur [7], as could be the case for this compound.

8.4. Other systems

^{35}Cl n.q.r. spectra have been run for some of the compounds prepared in previous chapters. Of these, only (N-methyl) diphenyl methylene ammonium trichlorostannate gave a result. Also tested were ethereal trichlorostannane and its products with proton sponge and tertiary butyl cyanide. The former two are discussed in chapter 2. The tertiary butyl cyanide product was examined in an attempt to identify the hydrostannation products in chapter 4. The results for $Ph_2C{=}NHMe^+SnCl_3^-$ are tabulated below.

Table 8.6 N.Q.R. Spectra for $Ph_2C{=}NHMe^+SnCl_3^-$

Temperature /°C	Frequency of Peak /MHz
- 196	No distinguishable peaks
- 77	10.175 (1), 11.070 (1), 13.125
25	11.800

Figures in parenthesis represent the relative intensities.
The higher resonance was recorded separately and is reproducible.

The results may be interpreted in terms of the crystal structure which is discussed in Chapter 3. There are three different cations and anions in the structure giving nine different tin-chlorine bond lengths which may be grouped according to table 8.7.

Table 8.7

Sn-Cl bond lengths for $Ph_2C{=}NHMe^+ \ SnCl_3^-$

Group / Sn-Cl Bond length, Å	A	B	C	D	E
	2.455(2)	2.472(2)	2.502(2)	2.511(1)	2.533(1)
		2.473(1)		2.513(1)	
		2.479(2)		2.514(1)	

The correlation between bond length and n.q.r. frequency at 20°C [7] predicts frequencies ranging from 10.4 MHz (2.533 Å) to 12.3 MHz (2.455 Å) . The only resonance observed at this temperature, 11.8 MHz is within the expected region. At -77°C the results are more interesting. The peaks at 10.175 and 11.070 MHz possibly represent the chlorine atoms in groups "E" and "D" respectively whereby their relative intensities should be 1:3. In practice as the peaks are so weak part of the intensity may have been spread out into the background noise and is therefore not observed. The third resonance, 13.125 MHz, may be assigned to chlorine atoms in either group "A" or "B", the latter being most likely as its chlorines are more abundant.

One normally expects the n.q.r. frequency to be inversly dependent on the temperature. Whilst it is still possible for the room temperature signal at 11.800 MHz to arise from a movement of the

11.070 MHz signal at -77°C it is more likely to come from movement of the 13.125 MHz signal to a lower frequency. It would therefore represent the chlorine atoms in group "B" As the temperature dependence is much bigger than normal the resonances for the other chlorine atoms will be correspondingly affected. Therefore the other main group, "D" may result in a considerably lower resonance, and may have been undetected for this reason.

8.5 Conclusion

N.q.r. studies on a series of trihalostannates have been performed. A temperature dependance study on caesium tribromostannate reveals a first order phase transition between 13 and 17 °C with evidence for hysteresis. Difficulties were encountered in obtaining satisfactory spectra for tetra ethyl- and tetra n-propyl ammonium tribromostannate, one of the main reasons being the larger cation sizes and hence dilution of bromine atoms. The results for tetra phenyl phosphonium- and (N-methyl) diphenyl methylene ammonium- trichlorostannate have been discussed in terms of their crystal structures.

APPENDIX 1

EXPERIMENTAL DETAILS

1. General

Many of the compounds described in this thesis were sensitive to the atmosphere, either through hydrolysis or oxidation. All operations were carried out under vacuum or an atmosphere of pure dry nitrogen. Liquids and solutions were transferred by syringe against a counter current of nitrogen and with the aid of suba seals. Air sensitive solids were handled in a nitrogen filled glove box.

2. Nitrogen Gas

Nitrogen gas was supplied as the boil/off from a tank containing liquid nitrogen. Traces of oxygen were removed in a heated copper tower at 300°C and water was removed by a liquid nitrogen trap followed by a tower packed with phosphorous pentoxide. The purified gas was then delivered to the glove box and to a multiple outlet system.

3. Glove Box

The dry nitrogen atmosphere was maintained by continuous purge and by recycling through a phosphorous pentoxide tower to remove residual water. All external tubing was of nylon or glass and all joints were sealed with silicone rubber.

4. Vacuum System

Evacuation was effected using a rotary oil pump and all volatile compounds were collected in two connected traps maintained at 77 K. This vaccum system was used for separation and purification of volatile materials by distillation, for filtration, reduction in solvent volume and for the drying of involatile materials.

5. Solvents

Diethyl ether and other hydrocarbon solvents were dried with sodium wire. Toluene and the chlorinated solvents were dried over activated molecular seive (3A and 4A). THF was dried over potassium hydroxide followed by potassium metal and was freshly distilled before use. Deuterised solvents used for n.m.r. studies were commercial samples stored under dry nitrogen.

6. Starting Materials

Anhydrous tin (II) chloride was used as purchased. Anhydrous tin (II) bromide was prepared from tin (II) powder and hydrobromic acid. Tin (IV) chloride was purified by vacuum distillation and stored under dry nitrogen.

The Schiff's bases were prepared by condensation of the relevant aldehyde or ketone with an amine using a Dean-Stark apparatus.

$$R^1R^2C{=}O + R^3NH_2 \xrightarrow{\text{toluene}} R^1R^2C{=}NR^3 + H_2O$$

The mixture was refluxed until no more water separated and then distilled to remove excess amine and toluene. Finally, the methyleneamine itself was distilled and collected.

Acrylonitrile was stirred for 6 hours with calcium hydride (10g/l) and then distilled onto fresh calcium hydride to remove the water and stabilizer (hydroquinone). After refluxing for 6 hours and fractionally distilling onto activated 3A molecular sieve it was stored in the dark to prevent u.v. initiated polymerisation in the absence of the stabilizer. The other nitriles used were distilled over phosphorus pentoxide and stored over molecular sieve.

The carbonyl compounds used in chapter 7 were distilled onto molecular sieve and stored under dry nitrogen.

The purchased ammonium and phosphonium bromides and chlorides were recrystallised before use. The aqueous hydrobromic acid used was as purchased.

7. Instrumentation

(i) Infra-red Spectra

Infra-red spectra in the range 4000-200 cm^{-1} were recorded on a Perkin Elmer 457 or 577 grating spectrometer. KBr discs were prepared in the glove box and used immediately. Nujol mulls, also prepared in the glove box, and neat liquids were sandwiched between KBr plates.

(ii) N.M.R. Spectra

^{1}H n.m.r. spectra were recorded on a Varian A56/60D spectrometer operating at 60MHz. The samples were either neat liquids or concentrated solutions in an appropriate solvent. TMS was used as an external or internal reference.

The ^{13}C n.m.r. spectra were recorded at Newcastle University on a Brüker spectrometer operating at 66MHz, except that of CETTC which was recorded at the University of Edinburgh.

The ^{119}Sn n.m.r. spectra were recorded on a home built Fourier Transform multinuclear spectrometer driven by a PDP11/34 computer constructed at the university by Dr. A. Royston. A 1.4T magnet from a Perkin Elmer R10 instrument with a special tin probe was used. The temperature of the probe was maintained at 307.2K by a thermostat. Concentrated solutions were placed in tubes of external diameter 8.4mm and tetramethylstannane was used as an external reference with the downfield direction taken as positive. Due to the low natural abundance (8.9%) * and low magnetic moment (-1.046 nuclear magnetons) * of ^{119}Sn

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* CRC Handbook of Chemistry and Physics, 60th Edition.

several thousand scans had to be accumulated for a satisfactory spectrum to be obtained. The spectra were displayed on an oscilloscope and printed on a plotter.

(iii) N.Q.R. Spectra

Cl n.q.r. spectra were obtained using a commercial mid range Decca spectrometer operating between 5 and 55 MHz and for the Br n.q.r spectra a Decca spectrometer with a high frequency head was used. The frequency ranges scanned were determined by selection of an appropiate radiofrequency coil. The spectrometers were of a super regenerative oscillator type operating with a 1MHz crystal for Cl and one of 5MHz for Br. They were used in the Zeeman modulation mode with quench frequencies of 25kHz and 50kHz respectively. The frequencies were measured at the start and finish of each run using an Advanced Instruments TC16 frequency counter and intermediately by the frequency marks of the instrument. The resonance frequencies were measured manually from the marker scales.

(iv) Mass Spectra

Mass spectra were recorded on an AEI MS9 instrument. The samples were introduced by direct insertion into the ion source. The F.A.B. spectra were recorded in thioglycerol at U.K.A.E.A. Harwell.

(v) Mössbauer Spectra

These were run at Birkbeck College, University of London. All data reported were recorded at 77K with a SnO_2 reference, unless otherwise stated.

(vi) Elemental Analyses

Carbon, hydrogen and nitrogen were determined using a Perkin Elmer 240 Elemental Analyser. The samples were sealed in a preweighed aluminium capsule in the glove box. Chlorine was determined by oxygen flask combustion followed by potentiometric titration of the chloride ions. Tin was determined using a Perkin Elmer 5000 elemental analyser with an electric filament lamp. Alternatively, tin was determined gravimetrically as SnO_2 . Unfortunately the presence of halogens often caused the loss of tin and therefore gave rise to low results.

APPENDIX 2

COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing :

(a) details of the first-year postgraduate induction course.

(b) all research colloquia, research seminars and lectures arranged by the Department of Chemistry and the Durham University Chemical Society during the period of the writer's residence as a postgraduate student.

(c) all research conferences attended and papers read out by the writer of the thesis during the period when the research for the thesis was carried out.

A. POSTGRADUATE INDUCTION COURSE

A series of lectures was given to explain the services available in the department.

Departmental organisation	- Dr. E.J.F.Ross
Safety matters	- Dr. M.R. Crampton
Electrical appliances and infra red Spectroscopy	- Mr. R.N. Brown
Chromatography and microanalysis	- Mr. T.F. Holmes
Atomic absorption spectrometry and inorganic analysis	- Mr. R.Coult
Mass spectrometry	- Dr. M. Jones
N.M.R. spectrometry	- Dr. R.S. Matthews
Glassblowing techniques	- Mr. W.H. Fettis and Mr. R. Hart.

B. DEPARTMENTAL COLLOQUIA AND DURHAM UNIVERSITY CHEMICAL SOCIETY (D.U.C.S.) LECTURES

14-10-81. Prof. E. Klúk (University of Katowice). "Chemoluminescence and photo-oxidation".

22-10-81. Dr. P.J. Corish (Dunlop Ltd.) "What would life be like without rubber ?". (D.U.C.S.)

28-10-81. Dr. R.J.H.Clark (University College, London). "Resonance Raman spectroscopy".

29-10-81. Miss J.M. Cronyn (University of Durham). "Chemistry in archaeology". (D.U.C.S.)

6-11-81. Dr. W. Hoddeman (Monsanto Research Labs., St. Louis, Missouri), "High energy materials".

12-11-81. Prof. A. I. Scott (University of Edinburgh), "An organic chemist's view of life in the N.M.R. tube". (D.U.C.S.)

18-11-81. Prof. M.J. Perkins (Chelsea College, London). "Spin trapping and nitroxide radicals".

19-11-81. Prof. B.L. Shaw (University of Leeds), Big rings and metal-carbon bond formation". (D.U.C.S.)

25-11-81. Dr. M. Baird (University of Newcastle), "Intramolecular reactions of carbenes and carbinoids".

26-11-81. Dr. W.O. Ord (Northumbrian Water Authority), "The role of the Scientist in a regional water Authority". (D.U.C.S.)

30-11-81. Dr. B.T.Heaton (University of Kent), "N.M.R. studies of carbonyl clusters".

2-12-81. Dr. G. Beamson (University of Durham), "Photoelectron spectroscopy in a strong magnetic field.

3-12-81. Dr. R.E.Hester (University of York), "Spectroscopy with lasers". (D.U.C.S.)

20-1-82.	Dr. M.R. BRYCE (University of Durham). "Organic metals".
27-1-82.	Dr. D.L.H. Williams (University of Durham), "Nitrosation and nitrosoamines".
28-1-82.	Prof. I. Fells (University of Newcastle), "Balancing the energy equation". (D.U.C.S.)
3-2-82.	Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".
10-2-82.	Dr. D. Pethrick (University of Strathclyde), "Conformation of small and large molecules".
11-2-82.	Dr. D.W. Turner (University of Oxford), "Photoelectrons in a strong magnetic field". (D.U.C.S.)
17-2-82.	Prof. R. D. Chambers (University of Durham), "Recent reactions of fluorinated internal olefins".
18-2-82.	Prof. R.K.Harris (University of East Anglia), N.M.R. in the 1980's". (D.U.C.S.)
24-2-82.	Dr. L. Field (University of Oxford), "Applications of N.M.R. to biosynthetic studies on penicillin".
25-2-82.	Prof. R.O.C. Norman (University of York), "Turning points and challenges for the organic chemist". (D.U.C.S.)
3-3-82.	Dr. P. Bamfield (I.C.I. Organics Division). "Computer aided design in synthetic organic Chemistry".
4-3-82.	Dr. R. Whyman (I.C.I. Runcorn), "Making metal clusters work". (D.U.C.S.)
17-3-82.	Prof. R. J. Haines (University of Natal), "Clustering around Ruthenium, Iron and Rhodium".
7-4-82.	Dr. A. Pensak (DuPont, U.S.A.), "Computer aided synthesis".

5-5-82. Dr. G. Tennant (University of Edinburgh), "Exploitation of the aromatic nitro-group in the design of new heterocyclisation reactions".

7-5-82. Dr. C.E. Garner (Iniversity of Manchester), "The structure and function of Molybdenum centres in enzymes".

26-5-82. Dr. A. Welch (University of Edinburgh), "Conformation patterns and distortion in carbometalloboranes".

14-6-82. Prof. C.M.J. Stirling (University College of Wales, Bangor). "How much does strain affect reactivity ?".

28-6-82. Prof. D.J. Burton (University of Iowa), "Some aspects of the chemistry of fluorinated phosphoniun salts and their phosphonates".

2-7-82. Prof. H.F. Koch (Ithaca College, U.S.A.), "Proton transfer to and elimination reactions from localized and delocalized carbanions".

13-10-82 Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".

14-10-82 Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".

14-10-82 Mr. F. Shenton (County Analyst, Durham), "There is death in the pot". (D.U.C.S.)

27-10-82 Dr. C.E. Housecroft (Oxford High School/Notre Dame University, USA), "Bonding capabilities of butterfly-shaped Fe_4 units; implications for C-H bond activation in hydrocarbon complexes".

28-10-82 Prof. M.F. Lappert, F.R.S.,(University of Sussex), "Approaches to asymmetric synthesis and catalyses using electron-rich olefins and some of their metal complexes".

"The Chemistry of some Unusual Subvalent Compounds of the Main Group IV and V Elements". (D.U.C.S.)

4-11-82	Dr. D.H. Williams(University of Cambridge), "Studies on the Structures and Modes of action of antibiotics". (D.U.C.S.)
11-11-82	Dr. J. Cramp (I.C.I. Ltd.), "Lasers in Industry". (D.U.C.S.)
15-11-82	Dr. G. Bertrand (University of Toulouse, France), "Curtius rearrangement in organometallic series. A route for hybridised species".
24-11-82	Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmuir-Blodgett films: solid state polymerisation of diacetylenes".
25-11-82	Dr. D.H. Richards (P.E.R.M.E., Ministry of Defence), "Terminally functional polymers; their synthesis and uses". (D.U.C.S.)
2-12-82	Dr. G.M. Brook (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".
8-12-82	Dr. G. Wooley (Trent Polytechnic), "Bonds in transition metal cluster compounds".
12-1-83	Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".
27-1-83	Prof. D.W.A. Sharp (University of Glasgow), "Some redox reactions in fluorine chemistry". (D.U.C.S.)
3-2-83	Dr. R. Manning (Department of Zoology, University of Durham), "Molecular mechanisms of hormone action". (D.U.C.S.)
9-2-83	Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.- N.M.R. and high pressure N.M.R. line broadening".
10-2-83	Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "U.K. Research Ltd.". (D.U.C.S.)

17-2-83	Prof. A.G. MacDiarmid (University of Pennsylvania, USA), "Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their derivatives". (D.U.C.S., R.S.C. Centenary Lecture).
21-2-83	Dr. R. Lynder-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN".
2-3-83	Dr. D. Bloor (Queen Mary College, University of London), "The solid state chemistry of diacetylene monomers and polymers".
3-3-83	Prof. A.C.T. North (University of Leeds), "The use of a computer display system in studying molecular structures and interactions". (D.U.C.S.)
8-3-83	Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".
9-3-83	Dr. D.M.J. Lilley (University of Dundee), "DNA, sequence, symmetry, structure and supercooling".
11-3-83	Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on sulphur" , "Fluorine substitutions in radicals". (Musgrave lecture).
16-3-83	Dr. I Gosney (University of Edinburgh), "New extrusion reactions: organic synthesis in a hot tube".
25-3-83	Prof. F.G. Baglin (University of Nevada, USA), "Interaction induced Raman spectroscopy in supra-critical ethane".
21-4-83	Prof. J. Passmore (University of New Brunswick, Canada), "Novel selenium-iodine cations".
4-5-83	Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of".
10-5-83	Prof. K. Burger (Technical University of Munich, FRG), "New reaction pathways from trifluoromethyl substituted heterodienes to partially fluorinated heterocyclic compounds".

11-5-83	Dr. N. Isaacs (University of Reading), "The application of high pressures to the theory and practice of organic chemistry".
13-5-83	Dr. R. de Koch (Caloin College, Michigan, USA / Free University, Amsterdam, Netherlands), "Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces".
16-5-83	Prof. R.J. Lagow (University of Texas, USA), "The chemistry of polylithium organic compounds. An unusual class of matter".
18-5-83	Dr. D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".
25-5-83	Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".
15-6-83	Dr. A. Pietrzykowski (Technical University of Warsaw, Poland / University of Strathclyde), "Synthesis, structure and properties of aluminoxanes".
22-6-83	Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase on structure".
5-7-83	Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".
5-10-83	Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterisation of cations".
12-10-83	Dr. C.W. McLeland (University of Port Elizabeth, Australia), "Cyclisation of aryl alcohols through the intermediacy of alkoxy and aryl radical cations".
19-10-83	Dr. N.W. Alcock (University of Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".
20-10-83	Prof. R.B. Cundall (University of Salford), "Explosives", (D.U.C.S.)

26-10-83	Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymers".
3-11-83	Dr. G. Richards (University of Oxford), "Quantum pharmacology". (D.U.C.S.)
10-11-83	Dr. J. Harrison (Stirling Organic Ltd.), "Applied chemistry and the pharmaceutical industry". (D.U.C.S.)
24-11-83	Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions". (D.U.C.S.)
30-11-83	Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".
1-12-83	Dr. J.D. Coyle (The Open University), "The problem with sunshine". (D.U.C.S.)
14-12-83	Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".
10-1-84	Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".
18-1-84	Prof. R.K. Harris (University of East Anglia), "Multi-nuclear solid state magnetic resonance".
26-1-84	Prof. T.L. Blundell (Birkbeck College, University of London), "Biological recognition: Interactions of macromolecular surfaces". (D.U.C.S.)
2-2-84	Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy- a radical approach". (D.U.C.S.)
8-2-84	Dr. B.T. Heaton (University of Kent), "Multi-nuclear n.m.r. studies".
15-2-84	Dr. R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".

16-2-84 Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry- a light entertainment". (D.U.C.S.)

23-2-84 Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesise metal clusters" (D.U.C.S. The Waddington Memorial Lecture)

1-3-84 Prof. A.J. Leadbetter (Rutherford Appleton Laboratory), "Liquid crystals". (D.U.C.S.)

7-3-84 Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemotherapy".

8-3-84 Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques". (D.U.C.S.)

21-3-84 Dr. P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".

23-3-84 Dr. A. Ceulemans (Catholic University of Leuven, Belgium), "The development of field-type models of the bonding in molecular clusters".

28-3-84 Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects". (D.U.C.S. R.S.C. Centenary Lecture)

2-4-84 Prof. K. O'Driscoll (University of Waterloo, Canada), "Chain ending reactions in free radical polymerisation",

3-4-84 Prof. C.H. Rochester (University of Dundee), "Infrared studies of adsorption at the solid-liquid interface".

25-4-84 Dr. R.M. Acheson (Department of Biochemistry, University of Oxford), "Some heterocyclic detective stories".

27-4-84 Dr. T. Albright (University of Houston, USA), "Sigmatropic rearrangements in organometallic chemistry".

14-5-84	Prof. W.R. Dolbier, Jr. (University of Florida, USA), "Cycloaddition reactions of fluorinated allenes".
16-5-84	Dr. P.J. Garratt (University College, London), "Syntheses with dilithiated vicinal diesters and carboximides".
22-5-84	Prof. F.C. De Schryver (Catholic University of Leuven, Netherlands), "Configurational and conformational control in excited state complex formation". "The use of luminescence in the study of micellar aggregates".
23-5-84	Prof. M. Tada (Waseda University, Japan), "Photochemistry of dicyanopyrazine derivatives".
29-5-84	Dr. A. Haaland (University of Oslo, Norway), "Electron diffraction studies of some organometallic compounds".
11-6-84	Dr. G.B. Street (I.B.M. San Jose, USA), "Conducting polymers derived from pyrroles".

C. CONFERENCES ATTENDED

1st Graduate Symposium, University of Durham, April 1982.

2nd Graduate Symposium, University of Durham, April 1983.

Annual Chemical Congress, Royal Society of Chemistry, University of Lancaster, April 1983.

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