

SOME REACTIONS OF STANNIC CHLORIDE
WITH SILICON HYDRIDES AND SOME NOVEL
GROUP IV DERIVATIVES OF MERCURY

BY

NARAYAN S. HOSMANE

THESIS PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
UNIVERSITY OF EDINBURGH

1974



CONTENTS

Preface	i
Acknowledgements	ii
Summary	iii
<u>PART ONE: Some Reactions of Stannic Chloride with Silicon Hydrides.</u>	
<u>Chapter 1. Introduction.</u>	1.
<u>Chapter 2. Experimental Techniques and Preparation of Starting Materials.</u>	6.
<u>Chapter 3. Reaction of Silane, Disilane, Alkyl substituted Monosilanes and Monohalo-substituted Monosilanes with Stannic Chloride.</u>	
3.1 Introduction	14.
3.2 Me_3SiH	14.
3.3 Me_2SiH_2	15.
3.4:1 MeSiH_3	16.
3.4:2 MeSiH_2Cl	17.
3.5:1 SiH_4	18.
3.5:2 SiH_3Cl	19.
3.6 Si_2H_6	20.
3.7 SiH_3F	21.
3.8 SiH_3Br	24.
3.9 Discussion	24.
<u>Chapter 4. Reaction of Stannic Chloride with SiH_3-Derivatives of Different Types of Carbon Compounds.</u>	
4.1 Introduction	29.
4.2 $\text{SiH}_3\text{.C}\equiv\text{CH}$	30.
4.3 $\text{SiH}_3\text{.C}\equiv\text{C-CF}_3$	32.
4.4 $\text{SiH}_3\text{.CH=CH}_2$	34.
4.5 $\text{SiH}_3\text{.CH}_2\text{-CH=CH}_2$	38.

4.6	$\text{SiH}_3 \cdot \text{C}_5\text{H}_5$	40.
4.7	$\text{SiH}_2(\text{C}_4\text{H}_6)$	42.
4.8	$\text{SiH}_3 \cdot \text{C}_6\text{H}_5$	43.
4.9	Discussion	45.

Chapter 5. Reaction of Stannic Chloride with SiH_3 -Derivatives of

Elements of Groups V and VI.

5.1	Introduction	54.
5.2	$(\text{Me}_2\text{SiH})_2\text{O}$	54.
5.3	$(\text{SiH}_3)_2\text{O}$	56.
5.4	$(\text{SiH}_3)_2\text{S}$	58.
5.5	$(\text{SiH}_3)_3\text{P}$	60.
5.6	$(\text{SiH}_3)_3\text{N}$	61.
5.7	Discussion	65.

Chapter 6. Reaction of Silyl-transitionmetal-carbonyl Compounds with
Stannic Chloride.

6.1	Introduction	75.
6.2	$\text{SiH}_3 \cdot \text{Mn}(\text{CO})_5$	75.
6.3	$\text{SiH}_3 \cdot \text{Co}(\text{CO})_4$	77.
6.4	Discussion	78.

Chapter 7. Preparation and Chlorination of Trimethylsilylsilane.

7.1	Introduction	81.
7.2	The preparation of $\text{Me}_3\text{Si} \cdot \text{SiH}_3$	81.
7.3	The chlorination of $\text{Me}_3\text{Si} \cdot \text{SiH}_3$	83.
7.4	The chlorination of $\text{Me}_3\text{Si} \cdot \text{SiH}_2\text{Cl}$	85.
7.5	Discussion.	87.

References.	93.
-------------	-----

PART TWO: Some Novel Group IV Derivatives of Mercury.

<u>Chapter 8.</u>	Introduction	97.
<u>Chapter 9.</u>	<u>Preparation and Identification of Some Novel Group IV Derivatives of Mercury.</u>	
9.1	Introduction	100.
9.2:1	$\text{Me}_3\text{SiHgSiH}_3$	100.
9.2:2	$\text{SiH}_3\text{HgSiH}_3$	101.
9.2:3	$\text{Me}_3\text{SiHgGeH}_3$	102.
9.2:4	$\text{GeH}_3\text{HgGeH}_3$	103.
9.2:5	$\text{Me}_3\text{SiHgCH}_3$	104.
9.3	Nuclear Magnetic Resonance Spectra	105.
9.4	Infrared and Raman Spectra	108.
9.5	Discussion	108.
References:		121.
<u>Appendix 1.</u>	<u>Determination of Chemical Shifts and Correction of Observed Frequencies.</u>	122.

PREFACE

The work described in this thesis is the original work of the author except where specific reference is made to other sources. It has not been submitted, in whole or in part, for any degree at any other University.

Narayan S. Hosmane.

ACKNOWLEDGEMENTS

I am extremely grateful to my supervisors, Professor E.A.V. Ebsworth and Dr S. Cradock, for the help, encouragement and advice which they have continually given me. My thanks are also due to all the members of the Department of Inorganic Chemistry who have helped me either by passing on their practical skills or by taking part in many helpful discussions; especially to Dr R.A. Whiteford, who helped me in preparing some of the starting materials, and to Dr K.M. Mackay, for his helpful discussions. My thanks are also due to all the members of the technical staff who have helped me; especially to Mr. John Miller for his help during the INDOR spectral recordings, to Mr S.D. Henderson for his practical assistance, and to Miss Diana Wilson for typing my thesis so patiently.

I would like to thank all of my friends; especially Dr David Mellor, Dr Gourie Nag, and Dr Bernard Ransom for reading the manuscript.

I am grateful to the University of Edinburgh for a maintenance grant without which this work could not have been carried out.

SUMMARY

The first part of the thesis describes a study of reactions of silane, disilane, alkyl substituted monosilanes, monohalo-substituted monosilanes, SiH_3 -derivatives of different types of unsaturated carbon compounds, SiH_3 -derivatives of elements of groups V and VI, SiH_3 -transitionmetal-carbonyl compounds, and trimethylsilylsilane with stannic chloride. The new compounds, (SiH_2ClF) , $\text{ClSiH}_2\cdot\text{C}\equiv\text{CH}$, $\text{ClSiH}_2\cdot\text{C}\equiv\text{C}-\text{CF}_3$, $\text{ClSiH}_2\cdot\text{CH}=\text{CH}_2$, $\text{Cl}_2\text{HSiCH}=\text{CH}_2$, $\text{ClSiH}_2\cdot\text{CH}_2-\text{CH}=\text{CH}_2$, $\text{ClSiH}(\text{C}_4\text{H}_6)$, $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$, $(\text{ClSiH}_2)_3\text{N}$, $\text{Me}_3\text{Si}\cdot\text{SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si}\cdot\text{SiHCl}_2$ obtained during this study were partially characterised by n.m.r., mass, infrared and Raman spectroscopy. In addition to the chlorination reactions, a new method of preparing $\text{Me}_3\text{Si}\cdot\text{SiH}_3$ is also described.

The preparation and identification of some novel group IV derivatives of mercury ($\text{Me}_3\text{SiHgSiH}_3$, $(\text{SiH}_3)_2\text{Hg}$, $\text{Me}_3\text{SiHgGeH}_3$, $(\text{GeH}_3)_2\text{Hg}$ and $\text{Me}_3\text{SiHgCH}_3$) have been studied in the second part of the thesis. Although ^{199}Hg and ^{29}Si INDOR spectroscopy was the major tool for the identification of these compounds, vibrational spectroscopy was used to confirm this identification.

PART ONE

SOME REACTIONS OF
STANNIC CHLORIDE WITH
SILICON HYDRIDES

CHAPTER ONE

INTRODUCTION

CHAPTER ONEINTRODUCTION

Silanes and germanes may be halogenated by a variety of reagents, including free halogens^{1,2}; hydrogen halides³, boron halides⁴ and heated silver halides⁵. Each of these reagents has its own advantages and disadvantages; the most general and serious disadvantages are the apparently inevitable formation of a mixture of mono-, di- and tri- halogenated products, and formation of a polymer in some cases. Boron trichloride has been claimed to chlorinate selectively⁶. Even if there is a selective halogenation, the conversion is often very low. Although side reactions, resulting in the formation of unnecessary products are less common, it is rather a waste of time to purify the required products. Part of the work described in this thesis is concerned with the use of stannic chloride as a halogenating agent for silanes. An attempt will be made in this chapter to describe the main differences between stannic chloride and other halogenating agents. The differences are not many, but may be traced to some that are fundamental.

For the first time in 1971, stannic chloride⁷ was used for the monochlorination of monosilane and monogermane; with disilane, digermane or trisilane, a mixture of mono- and di- chlorinated compounds is formed, but no products resulting from disubstitution at a single silicon or germanium atom have been detected among the initial reaction products, and the Si-Si or Ge-Ge bonds are not broken.

Now a question arises, why stannic chloride is a selective chlorinating agent for silanes and germanes.

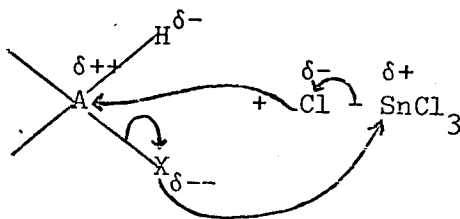
It is assumed in most of the halogenation reactions^{1,2,3,4,5}

behave in a similar way but stannic chloride differs from other chlorinating agents mainly in the initial formation of monochloro derivatives of silanes and germanes.

It may be believed that the tin atom of a stannic chloride molecule is ready to exchange with the silicon or germanium atom of the silanes or germanes by donating a chloride ion to the silicon or germanium and accepting a hydride ion. This results in the formation of an unstable intermediate compound, HSnCl_3 , which will yield stannous chloride, a white solid, and hydrogen chloride, a gas. It is found that the stannous chloride produced in this reaction is inert in this system, and does not influence further reaction⁸. However, we have not detected the presence of HSnCl_3 directly. Is there any possibility of the dichlorination, when the stannic chloride is reacted with the silanes or germanes?

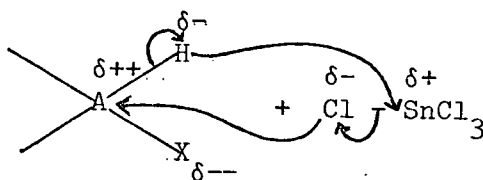
The dichlorination is less probable than the monochlorination. This may be explained by the following considerations.

In the case of chlorination of the monochloro derivative of silanes or germanes, the stannic chloride has a choice between hydrogens and the chlorine on the silicon or germanium atom. In this case, the exchange between chlorine atoms of each of these molecules is more probable than the exchange of a hydrogen atom of the monochloro derivative of silicon or germanium hydrides and a chlorine atom of stannic chloride. This may be mainly due to the bond polarity of the monochlorosilyl or germyl molecule, caused by its chlorine atom which removes an electron from silicon or germanium as in the following.



In other words, the chlorine which is more negative than hydrogen, makes the silicon or germanium more positive and hence the donation of chlorine is more probable than the donation of hydrogen from a monochloro- derivative of silanes or germanes to stannic chloride. Therefore, more examples of an exchange of halogen atoms between monochlorosilyl and stannic chloride are noticed than the exchange between hydrogen and chlorine.

Although, there are a few examples of dichlorination in this system, the yield is often very low due to the following mechanism.



There are some advantages of stannic chloride over other halogenating reagents. Out of those, the most important, are higher conversion of silanes or germanes to their corresponding monochloro derivatives; the possibility of watching the formation of white thin film on the inner walls of the reaction ampoule, the involatility of stannous chloride, and the separation of the main reaction product from the other reaction products more efficiently.

But, there are some disadvantages of stannic chloride. Firstly it dissolves and then reacts with the grease in the vacuum line joints, which frequently causes a leak in the high vacuum system. It also may react with starting materials before their estimation. Therefore it is necessary to clean the detachable sections of the

vacuum line whenever a new reaction is started. A greaseless vacuum line section is also essential. The second disadvantage of stannic chloride relates to its low vapour pressure at room temperature. It is very difficult to measure the pressure on the scale and/or on mercury. Therefore, the stannic chloride for the reaction should be weighed every time if an accurate estimation is required.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES AND
PREPARATION OF STARTING MATERIALS.

CHAPTER TWO2.1 Experimental Techniques2.1:1 Apparatus for preparations

All manipulations of volatile compounds were carried out in a pyrex vacuum system of conventional design. A high vacuum, necessary for the exclusion of air and moisture from the materials being handled, was maintained by a mercury diffusion pump backed by a rotary oil pump. The pressures of the materials inside the apparatus were measured using a spiral gauge with a mirror, employed as a null point instrument with a lamp and scale and the pressure in the system was monitored by a pirani gauge.

The vacuum line was made of detachable sections, which aided cleaning. This was frequently necessary to remove nonvolatile solids (stannous chloride and mercury silyl species) and volatile species (stannic chloride and cyclopenta-3-ene derivatives) which themselves either dissolve or reacted in the grease of the vacuum line joints. Apiezon L and N greases were used on the stop-cocks and ground glass joints. Most of the detachable reaction ampoules were fitted with 'Rotaflo' or 'Sovirel' teflon greaseless taps, care being taken to keep them away from liquid nitrogen which rapidly causes leaks. Using a molecular weight bulb the line was calibrated for volume which, combined with pressure readings, allowed rapid quantitative estimations of the amount of volatile materials present.

2.1:2 Criteria of purity

A number of methods were used to establish the purity of the samples.

Samples and impurities were identified by infrared spectroscopy, the impurities being removed by trap-to-trap distillation in one of the two trap sections through traps surrounded by slush-baths of known temperature. For less well characterised samples, vapour-phase molecular weight determinations and vapour pressure determinations at various temperatures were made together with proton n.m.r. spectra to determine any impurities. The constancy of vapour pressure was taken as a criterion of purity.

2.1:3 Infrared spectroscopy

Infrared spectra were recorded using a Perkin-Elmer 457 grating spectrophotometer. The vapour cell (10 cm) was fitted with CsI or KBr. plates using Apiezon W cement. Less volatile samples were frozen in using cotton wool soaked in liquid nitrogen. Mull spectra were recorded using CsI plates; nujol, dried by molten potassium and hexachlorobutadiene were used as mulling agents.

Where particularly high resolution spectra were required or where it was necessary to run the low frequency region down to 200 cm^{-1} , a Perkin-Elmer 225 grating infrared spectrophotometer was used.

2.1:4 Raman spectroscopy

Raman spectra of samples sealed in pyrex glass tubes (2x0.5 cm) were run on a Cary 83 spectrometer excited with a blue laser line great care being taken to ensure that sample tubes were mounted at the correct angle.

2.1:5 Nuclear magnetic resonance spectroscopy

Proton nuclear magnetic resonance and inter nuclear double

resonance (INDOR) spectra were recorded on a Varian Associates HA 100 spectrometer at approximately 100 MHz. An external Schlumberger frequency supply unit was fitted to generate radiation for heteronuclear double resonance; an accurate frequency of the spectrometer was measured during decoupling experiments. This spectrometer was also used for INDOR spectral recordings fitted with a variable temperature probe and an external recorder similar to that used in chromatography. Fluorine, ^{29}Si , ^{13}C and some INDOR spectra were recorded on an XL 100 instrument operating at 100 MHz for protons. This XL 100 instrument was used in the FT mode for ^{13}C , ^{29}Si and in the CW mode for ^{19}F and ^1H . Samples were sealed with ground glass bottoms in conventional pyrex tubes of 5mm diameter for reading in the HA 100 spectrometer and in tubes of 10mm diameter for the XL 100 spectrometer.

2.1:6 Mass spectrometry.

Mass spectra were recorded on an A.E.I. MS9 mass spectrometer normally operated with an ionising potential of 70 eV. Most compounds examined contained chlorine which has a characteristic isotope distribution.

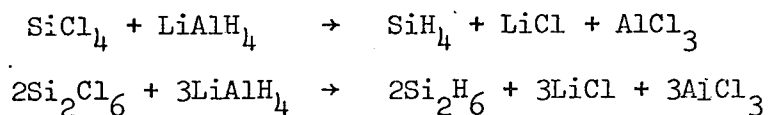
$$^{35}\text{Cl} = 75.53\% \quad ^{37}\text{Cl} = 24.47\%$$

Moisture in the mass spectrometer hydrolysed most of the halogenated silicon compounds and some organic impurities were also noted. Since the observed fragments were not derived mainly from pure parent ions, it was necessary to determine the accurate mass of the parent ions after a mass spectrum had been run. Exact mass measurements were also used to help to characterise new compounds.

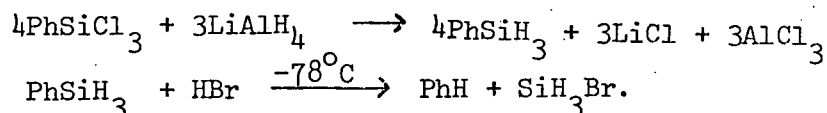
2.2 Preparation of starting materials

Procedures for preparation and/or purification of the many compounds used during this work are listed below. The silyl starting materials were generally prepared by well documented techniques. The appropriate references and any modifications attempted are given. Most of the halides used were commercially available, and for these the purity checks applied are recorded.

2.2:1 Monosilane and disilane were prepared by the standard method⁹ on a 20m. mole scale. The reduction was carefully carried out in di-n-amyl ether under 60 cms nitrogen pressure kept constant as the reaction progressed.

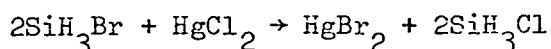


2.2:2 Phenylsilane and silyl bromide were prepared by the method of Kummer and Fritz on a 200m mole scale¹⁰.

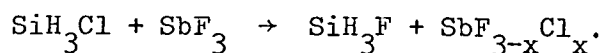


Purification and separation was achieved by distillation from -96°C into -120°C . The reduction was carefully carried out under nitrogen in di-n-amyl ether.

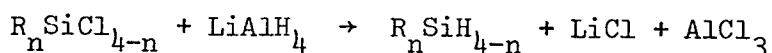
2.2:3 Silyl chloride was prepared by streaming silyl bromide through an excess of dried mercuric chloride¹¹, giving a conversion of about 95%. Separation was achieved by passage through -120°C and into -130°C .



2.2:4 Silyl fluoride was prepared by streaming silyl chloride through an excess of antimony trifluoride¹².



2.2:5 Monomethyl-, dimethyl- and trimethylsilanes were prepared by the standard method as for silane and disilane in di-n-butyl ether under nitrogen.

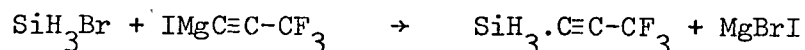


where R - methyl group

n - number of methyl groups

2.2:6 Silylacetylene - a small amount of pure compound prepared by the standard method¹³ was kindly provided by Dr D.W.W Anderson.

2.2:7 Silylperfluoromethylacetylene was prepared for the first time by addition of silyl bromide to perfluoromethylacetylene magnesium iodide in diglyme¹⁴.



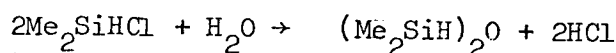
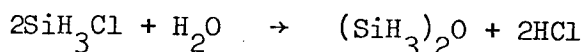
The purity of silylperfluoromethylacetylene was checked by its molecular weight determination, infrared and n.m.r. spectra.

2.2:8 Vinylsilane and allylsilane were prepared by reducing their corresponding trichloro species with lithium aluminium hydride in di-n-amyl ether under 60 cm nitrogen pressure kept constant as the reaction proceeded. The products were pumped through -96°C into -120°C . The infrared spectrum of each showed that a very small quantity of silane passed through. No trichloro species of the starting materials were trapped at -96°C . The purity of each compound was checked by comparison of observed and published¹⁵ i.r. spectrum.

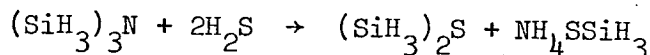
2.2:9 Sila-cyclopenta-3-ene was prepared by reduction of commercial dichloro-sila-cyclopenta-3-ene with lithium aluminium hydride in di-n-amyl ether, under a reduced pressure of dry nitrogen.

2.2:10 Silylcyclopentadiene - a small amount of pure compound prepared by the standard method¹⁶ was kindly provided by Dr Hans Moretto.

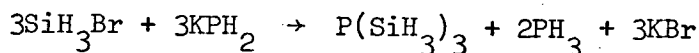
2.2:11 Disiloxane and tetramethyldisiloxane were prepared by reacting their corresponding monochloro derivative of monosilane with water vapour¹⁷.



2.2:12 Disilylsulfide was prepared by the reaction between H_2S and trisilylamine¹⁸.

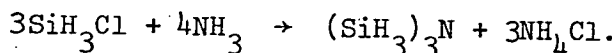


2.2:13 Trisilylphosphine was prepared by reaction of silyl bromide on KPH_2 at -64°C in dimethyl ether¹⁹.



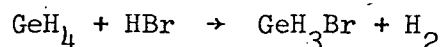
The purity was checked with an i.r. spectrum²⁰.

2.2:14 Trisilylamine was prepared by the gas phase reaction of ammonia with excess silyl chloride to avoid base-catalysed decomposition²¹.



2.2:15 Silylmangenesepentacarbonyl and silylcobalt-tetracarbonyl - the pure compounds prepared by the standard method²² were kindly provided by Mr Alastair Robertson.

2.2:16 Germyl bromide was prepared by the standard method²³ of bromination of germane with HBr using an aluminium bromide catalyst and excess germane.



2.2:17 Ammonia obtained from a commercial cylinder was fractionated to remove water (-78°C bath) and stored over sodium in a bulb on the vacuum line.

2.2:18 Hydrogen sulfide and phosphine were kindly provided by Mr W. John Savage.

2.2:19 Bis(trimethylsilyl)mercury was prepared by a modification of the method used before²⁴.

To the Na/Hg in a greaseless ampoule, excess trimethylchlorosilane was added and was degassed. The ampoule was then shaken for about 14 days. No other solvent was used since the $(\text{Me}_3\text{Si})_2\text{Hg}$ is highly soluble in Me_3SiCl . After 14 days, the ampoule was placed in a dry bag, containing N_2 gas; where the mercury was removed by inverting the ampoule and opening the tap. (Since Hg is dense, it stays at the bottom). The excess Me_3SiCl was removed from the yellow solution by vacuum distillation, leaving yellow crystalline solid. This yellow crystalline solid is bis(trimethylsilyl)mercury.

Hydrogen bromide, ¹⁵N ammonia, mercury, trimethylsilyl chloride, dimethyldichlorosilane, monomethyltrichlorosilane, silicon tetrachloride, hexachlorodisilane, vinyltrichlorosilane, allyltrichlorosilane, phenyltrichlorosilane, dichloro-sila-cyclopenta-3-ene and stannic chloride were all obtained commercially, dried on the vacuum line

and fractionated to remove any impurities as appropriate. Various solvents used were purified or available purified as follows:-

- | | | |
|-------------------------------|---|---|
| Benzene | - | Analar grade, dried over sodium wire. |
| Toluene | - | Analar grade, dried over sodium wire. |
| Monoglyme | - | Shaken with K/anthracene and distilled. |
| Diglyme | - | Shaken with K/anthracene and distilled. |
| Tetramethylsilane | - | Spectroscopic grade, dried over molecular sieve. |
| n-Pentane | - | Spectroscopic grade, dried over molecular sieve. |
| n-Hexane | - | Spectroscopic grade, dried over molecular sieve. |
| Arcton CCl_3F | - | Commercial grade, distilled. |
| Carbon tetrachloride | - | Spectroscopic grade, dried over molecular sieve. |
| Dimethyl ether | - | Commercial grade, distilled. |
| Di-n-amyl ether | - | Commercial grade, dried over lithium aluminium hydride. |
| C_6D_6 | - | Spectroscopic grade, dried over molecular sieve. |

CHAPTER THREE

REACTION OF SILANE, DISILANE, ALKYL
SUBSTITUTED MONO-SILANES, AND MONOHALO-
SUBSTITUTED MONO-SILANES WITH
STANNIC CHLORIDE.

CHAPTER THREEReaction of silane, disilane, alkyl substituted mono-silanes,
and mono-halo-substituted mono-silanes with stannic chloride.3.1 INTRODUCTION

This chapter describes a study of reactions of stannic chloride with trimethylsilane, dimethylsilane, monomethylsilane, monosilane, disilane, silyl fluoride, silyl chloride and silyl bromide. Although the reactions of stannic chloride with monosilane and disilane have been studied,⁷ they have been repeated for comparison with reactions between stannic chloride and alkyl substituted monosilanes. This work was done largely to study the effects on the chlorination reaction of changing the number of methyl groups on the silicon atom of silane and of changing the nature of the electronegative group on silicon. All of the following characteristics of chlorination have been examined in detail; the possibility of dichlorination, the stability of silicon-carbon bonds, the time required to complete reaction, the percentage conversion of the starting compound, the effect of the quantity of stannic chloride, and the influence of produced stannous chloride and hydrogen chloride during the reaction.

From the reaction of stannic chloride with silyl fluoride, a new compound, monochloro-monofluorosilane SiH_2ClF was obtained. The partial characterisation of this compound is reported in this chapter.

3.2 The reaction of trimethylsilane with stannic chloride

Pure trimethylsilane (1m mole) and stannic chloride (1.4m moles, 0.366 gm) were condensed into a 35ml reaction ampoule on a

conventional vacuum line and allowed to warm to room temperature. A white thin film on the inner walls of the reaction ampoule began to form almost immediately and the reaction appeared complete in 3 hours at this temperature. The stannic chloride was quantitatively reduced to stannous chloride (1m mole or 0.193 gm), an involatile white solid which remained in the reaction ampoule.

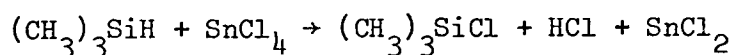
Trap-to-trap distillation of the remainder gave hydrogen chloride (1m mole) passing through the -120° trap, the trimethylchlorosilane (1m mole; ca. a 100% yield) passing through the -78° trap, and stannic chloride (0.31m mole or 0.081 gm) was left. The remaining stannic chloride was dissolved in the grease of the vacuum line joints. No products formed by breaking the Si-C bonds were detected.

HCl was identified by the rotational fine structure in its infrared spectrum between 2700 and 3000 cm^{-1} , stannous chloride by comparison of the observed and published powder photograph²⁵, and trimethylchlorosilane by comparison of the observed and published infrared spectrum²⁶.

An increase in stannic chloride to a 1:3 ratio of reactants has no influence on the reaction products.

Trimethylchloro silane (0.5m mole) was condensed in an ampoule containing stannous chloride (2m moles or 0.379 gm) allowed to warm to room temperature and then held at that temperature for 4 days. After 4 days, all trimethylchlorosilane (0.5m mole) was recovered.

The reaction:



3.3 The reaction of dimethylsilane with stannic chloride.

Dimethylsilane (1m mole) and stannic chloride (1.16m moles, 0.304 gm)

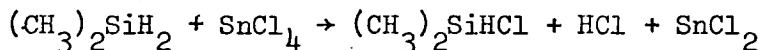
were condensed into a 35ml reaction ampoule and allowed to warm to room temperature. A white solid formed immediately and the reaction appeared complete in 20 minutes at this temperature. The stannic chloride was quantitatively reduced to stannous chloride (1m mole, 0.190 gm). The remaining stannic chloride (0.16m mole) was dissolved in the grease of the vacuum line joints.

Trap-to-trap distillation of the remainder gave hydrogen chloride (1m mole) passing through the -120° trap and dimethylchlorosilane (1m mole; $\sim 100\%$) was left. No other products by breaking the Si-C bonds were detected. Dimethylchlorosilane was identified by comparison of the observed and published infrared spectrum²⁷.

An increase in proportion of stannic chloride to a 1:3 ratio of reactants has no influence on the reaction, since neither Me_2SiCl_2 nor any other products of decomposition were detected among the products.

Dimethylchlorosilane (0.6m mole) was condensed into an ampoule containing stannous chloride (2m mole or 0.380 gm), a white crystalline solid, allowed to warm to room temperature and then held at that temperature for 4 days. After this period, all dimethylchlorosilane (0.6m mole) was recovered unchanged.

The reaction could be expressed by the equation:



3.4:1 The reaction of methylsilane with stannic chloride

Pure methylsilane (1.02m moles) and stannic chloride (1.43m moles, 0.294 gm) were condensed into a 35ml reaction ampoule and allowed to warm to room temperature. A white, thin film on the inner walls of the reaction ampoule began to form almost immediately and the reaction appeared complete after 4 hours. The stannous chloride produced (1.05m moles, 0.2 gm) remained in the reaction ampoule

and since no stannic chloride was recovered any remaining may have been dissolved in grease of the vacuum line joints.

Trap-to-trap distillation of the remainder gave hydrogen chloride (1.03m moles) passing through the -120° trap, methylchlorosilane (0.87m mole) passing through -96° , and methyldichlorosilane (0.15m mole) which still contains a very small quantity of the monochloro species was left. No other products that might have been formed by breaking the Si-C bonds were detected. The mono-chloro and dichloro derivatives of methylsilane were identified by measuring the exact mass of their parent ions and by comparison of the observed and published infrared spectra^{28,27}.

3.4:2 The reaction of methylchlorosilane with stannic chloride.

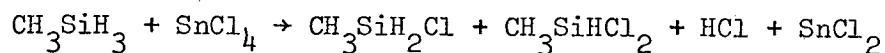
When pure methylchlorosilane (0.37m mole) and stannic chloride (0.39m mole or 0.101 gm) were condensed into a 35ml reaction ampoule and allowed to warm to room temperature, a white solid began to form very slowly. The reaction was not complete even after 3 days at room temperature, but it was stopped after this period and products were fractionated. The stannic chloride was quantitatively reduced to involatile, white stannous chloride (0.22m mole or 0.04 gm) which remained in the reaction ampoule.

Trap-to-trap distillation of the remainder gave hydrogen chloride (0.21m mole) passing through -120° , ca. 39% of the methylchlorosilane (0.14m mole) passing through -96° , methyldichlorosilane which still contained a small quantity of the monochloro species (0.23m mole) passing through the -78° trap and unreacted stannic chloride (0.15m mole or 0.04 gm) was left. The remaining unreacted stannic chloride was dissolved in grease of the vacuum line joints; no MeSiCl_3 was detected among the products.

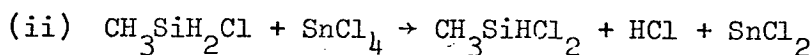
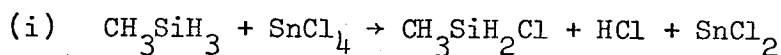
MeSiH₂Cl (0.8m mole) was condensed in an ampoule containing SnCl₂ (2m moles or 0.38 gm) and allowed to react at room temperature for 4 days. After this period all of the MeSiH₂Cl (0.8m mole) was recovered, demonstrating that MeSiH₂Cl was not affected by stannous chloride.

After a small quantity of pure MeSiH₂Cl was kept in a clean glass ampoule at room temperature for 4 days, no decomposition products were found, so that there was no detectable influence of glass, light or room temperature on the compound.

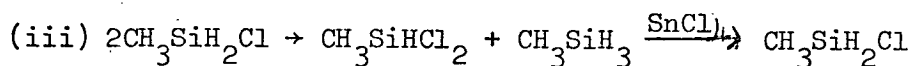
The reaction between methylsilane and stannic chloride may be expressed by the equation:



In steps:



or



3.5:1 The reaction of silane with stannic chloride

Pure silane (0.47m mole) and stannic chloride (0.56m mole, 0.147 gm) were condensed into a 35ml reaction ampoule and allowed to warm to room temperature. A white, thin film on the inner walls of the reaction ampoule began to form very slowly. The reaction was not complete even after 18 hours at room temperature, but it was stopped then and the products were fractionated. The stannic chloride was quantitatively reduced to involatile, white stannous chloride (0.15m mole, 0.029 gm), which remained in the reaction ampoule.

Trap-to-trap distillation of the remainder gave a mixture of hydrogen chloride and silane (0.47m mole) passing through -130° , monochlorosilane (0.11m mole) passing through -120° , dichlorosilane (0.04m mole) passing through -78° , and unreacted stannic chloride (0.35m mole, 0.091 gm) was left. The remaining unreacted stannic chloride must have been dissolved in the grease of the vacuum line joints. No hydrogen, SiHCl_3 or SiCl_4 were detected among the products.

The above mixture of hydrogen chloride and silane (0.47m mole) was allowed to react with pure ammonia (0.6m mole) in a reaction ampoule at room temperature. Ammonium chloride, a white solid, was formed immediately and remained in the reaction ampoule.

Trap-to-trap distillation of the volatile products gave SiH_4 (0.32m mole) passing through -130° , and unreacted NH_3 (0.13m mole) was recovered. The quantity of HCl produced during the reaction (0.15m mole) was estimated from the weight of NH_4Cl (0.0081 gm).

The monochloro- and dichloro derivatives of silane were identified by comparing their observed and published infrared spectra^{29a,b}.

When silane (3m moles) reacted with stannic chloride (0.5m mole) at room temperature over night, all stannic chloride was consumed and SiH_3Cl (0.5m mole), HCl (0.5m mole), SnCl_2 (0.5m mole) and unreacted SiH_4 (2.5m moles) were obtained.

3.5:2 The reaction of monochlorosilane with stannic chloride

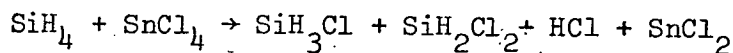
Pure monochlorosilane (0.47m mole) and stannic chloride (1.03m moles, 0.268 gm) were condensed into a 35ml reaction ampoule, allowed to warm to room temperature and then held there for 24 hours. A white, thin film on the inner walls of the reaction ampoule began

to form very slowly. Although the reaction was not complete after 24 hours it was stopped at this stage and the products were fractionated.

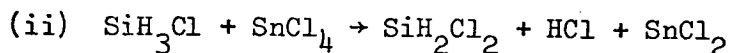
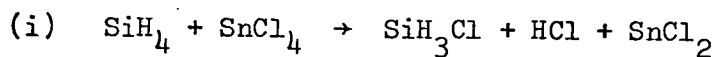
The stannic chloride was quantitatively reduced to stannous chloride (0.13m mole, 0.024 gm) which remained in the reaction ampoule.

Trap-to-trap distillation of the remainder gave hydrogen chloride (0.13m mole) passing through -130° , ca. 72% of the monochlorosilane (0.34m mole) passing through -120° , dichlorosilane (0.13m mole) passing through -78° and unreacted stannic chloride (0.88m mole, 0.230 gm) was left. SiHCl_3 and SiCl_4 were not detected among the products.

As in the previous reactions, a small quantity of SiH_3Cl was allowed to stand with a large excess of stannous chloride, SnCl_2 , for several days at room temperature. No reaction took place and all the SiH_3Cl was recovered. The overall reaction between silane and stannic chloride may be expressed by the equation:



In steps:



3.6 The reaction of disilane with stannic chloride

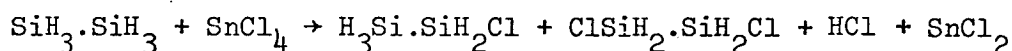
Pure disilane (1m mole) and stannic chloride (1.01m moles, 0.265 gm) were condensed into a 35ml reaction ampoule, allowed to warm to room temperature and held there for 18 hours. A white solid began to form almost immediately; the reaction was complete after 18 hours. The stannic chloride was quantitatively reduced to

stannous chloride (1.01m mole or 0.192 gm) which remained in the reaction ampoule.

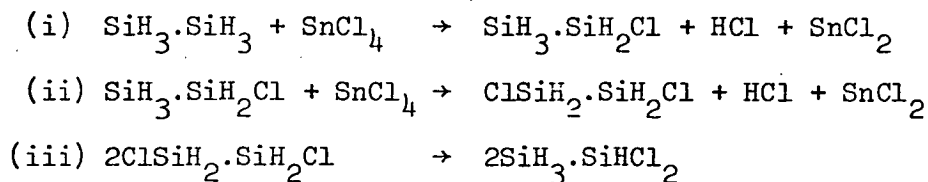
Trap-to-trap distillation of the remainder gave hydrogen chloride (1m mole) passing through the -130° trap, unreacted disilane (0.52m mole) passing through the -120° trap, monochloro-disilane (0.25m mole) passing through the -78° trap and 1,2-dichlorodisilane ($\text{ClSiH}_2\text{.SiH}_2\text{Cl}$; 0.23m mole) was left. A negligible quantity of 1,1-dichlorodisilane ($\text{H}_3\text{Si.SiHCl}_2$) was detected when pure $\text{ClSiH}_2\text{.SiH}_2\text{Cl}$ was kept in an ampoule for at least a day at room temperature.

Monochloro- and dichlorodisilanes were identified by comparing their observed and published infrared⁴ and n.m.r. spectra³⁰.

When disilane (3m moles) react with stannic chloride (0.5m mole) at room temperature over night the consumption of all stannic chloride occurred and $\text{ClSiH}_2\text{.SiH}_3$ (0.5m mole), HCl (0.5m mole), SnCl_2 (0.5m mole) and unreacted disilane (2.5m moles) were obtained. Neither $\text{ClSiH}_2\text{.SiH}_2\text{Cl}$ nor $\text{SiH}_3\text{.SiHCl}_2$ was detected among the products. The overall reaction between disilane and stannic chloride may be expressed by the equation:



In steps:



3.7:1 The reaction of silyl fluoride with stannic chloride

Pure silyl fluoride (1m mole) and stannic chloride (1.17m moles, 0.305 gm) were condensed into a 35ml reaction ampoule on a conventional vacuum line and allowed to warm to room temperature

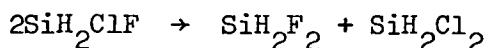
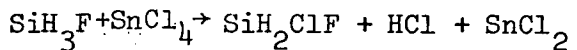
A white, thin film on the inner walls of the reaction ampoule began to form very slowly; the reaction was complete after 18 hours. The stannic chloride was quantitatively reduced to stannous chloride (1m mole, 0.191 gm) which remained in the reaction ampoule.

Trap-to-trap distillation of the remainder gave hydrogen chloride (1m mole) passing through the -160° trap, a mixture (I) of SiH_2F_2 and SiH_2ClF passing through a trap at -130° and another mixture (II) of SiH_2ClF and SiH_2Cl_2 was held at -130° but volatile at -78° ; unreacted stannic chloride (0.11m mole) was left.

Trap-to-trap repeated distillation of mixture (I) gave SiH_2F_2 (0.3m mole), volatile at -130° , and SiH_2ClF (0.3m mole) was left. Similarly, repeated trap-to-trap distillation of mixture (II) gave SiH_2ClF (0.1m mole) volatile at -120° and dichlorosilane (0.3m mole) was left.

No SiH_3F was recovered among the products. SiH_2Cl_2 and SiH_2F_2 were identified by comparison of the observed and published infrared spectra 29b, 31

The reaction of silyl fluoride with stannic chloride precedes by chlorination and then disproportionation, may be represented by the equations:-



Since monochloro-monofluorosilane (SiH_2ClF) is a new compound, an attempt will be made in this chapter to characterise the molecule in detail.

3.7:2 Nuclear magnetic resonance spectraProton n.m.r. of SiH_2ClF

TMS was used as solvent and reference standard.

doublet at 4.52T, 5.07T

∴ chemical shift $\tau = 4.79$ ppm.

$${}^2J(\text{HSiF}) = 56 \text{ Hz.}$$

 ${}^{19}\text{F}$ n.m.r. of SiH_2ClF

CCl_3F was used as solvent and reference standard.

The spectrum showed a triplet.

Chemical shift " δ " related to $\text{CCl}_3\text{F} = 146.4$ ppm

$${}^2J(\text{HSiF}) = 56 \text{ Hz.}$$

3.7:3 Mass spectrum

Since SiH_2ClF was very sensitive to moisture, most of it was hydrolysed with the moisture present in the mass spectrometer.

Therefore, it was necessary to obtain the exact mass of the parent ions.

Chlorine has two isotopes of ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$ with natural abundance of 75.53% and 24.47%, respectively.

Exact mass of parent ions:

	Calculated	Measured	Error
${}^{28}\text{Si}_1\text{H}_2{}^{35}\text{Cl}_1\text{F}_1$	83.959833	83.959229	less than 8 p.p.m.
${}^{28}\text{Si}_1\text{H}_2{}^{37}\text{Cl}_1\text{F}_1$	85.956884	85.956166	less than 9 p.p.m.

3.7:4 Infrared spectrum

The observed infrared spectrum for SiH_2ClF may be found in tables 1 and 2. The assignments of this spectrum have been justified in the discussion (3.9)

3.8 The reaction of silyl bromide with stannic chloride

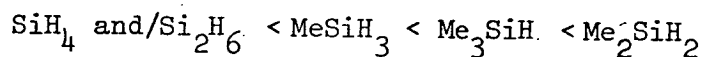
Pure silyl bromide (1m mole) and stannic chloride (1m mole, 0.260 gm) were condensed into a 35ml reaction ampoule, allowed to warm to room temperature and held there for one hour. A white, thin film on the inner walls of the reaction ampoule with some colourless crystals began to form very slowly; the reaction was complete after one hour.

Trap-to-trap distillation of these products gave only pure silyl chloride (1m mole) passing through the -78° trap and other liquid-solid products were left at -78° trap. This was identified as a mixture of SnBr_4 and SnCl_4 by their infrared spectra, showing strong Sn-Br stretching and very strong Sn-Cl stretching vibrations.

No traces of SiH_2ClBr , SiH_2Cl_2 , SiH_2Br_2 and SiH_3Br were detected among the products.

3.9 DISCUSSION

In this chlorination study the reaction rates increased in the following order:

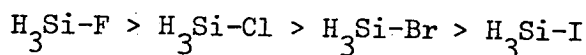


with reaction times of approximately 18-20 hours for monosilane and disilane, 4 hours for monomethylsilane, 3 hours for trimethylsilane and 20 minutes for dimethylsilane. Since an inductive effect increases

or the steric effect decreases as the number of methyl groups increases on silicon; the time required to complete the chlorination reaction would be expected to decrease as the number of methyl groups on silicon increases. The observed reaction times agree with this prediction, except for Me_3SiH . This discrepancy may have been due to the steric hindrance caused by the three bulky methyl groups on silicon in the Me_3SiH molecule.

In all the above reactions the initial products were only monochloro- derivatives. A very low yield of dichloro- derivatives was obtained only when stannic chloride reacted again with the monochloro- derivative. A direct dichlorination on a single silicon atom was never observed.

The reaction of stannic chloride with SiH_3Br , SiH_3Cl and SiH_3F gave SiH_3Cl , a considerable quantity of SiH_2Cl_2 and SiH_2ClF respectively. The bond strengths to silicon increases in the following order³².



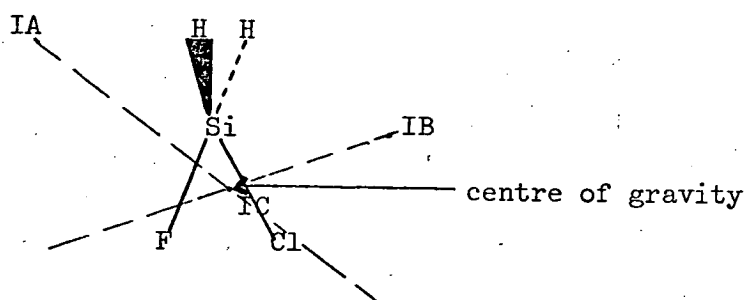
An exchange of halogen atoms between the above halo-substituted silane and stannic chloride may be expected. In fact, SiH_3Br was converted to SiH_3Cl and SiH_3Cl showed some change or produced a considerable yield of SiH_2Cl_2 , whereas SiH_3F was completely converted into a new compound SiH_2ClF . Although the first two reactions support the halogen exchange prediction, the last contradicts it. This may be explained by the following consideration. Since the Si-F bond is stronger than the bonds between Si and Cl, Br or I, the exchange of halogen atoms between SiH_3F and SnCl_4 molecules is less probable than the exchange of hydrogen on Si in SiH_3F and chlorine on Sn in SnCl_4 molecule.

The disproportionation of SiH_2ClF may be due to the instability of the molecule either towards glass, light and/or temperature.

The new compound SiH_2ClF was characterised by proton n.m.r. ^{19}F n.m.r., mass and infrared spectroscopy. The mass spectrum showed exact mass of the parent ions of SiH_2ClF which is consistent with the calculated mass, with an error of less than 9 p.p.m.

The proton n.m.r. demonstrates the presence of one fluorine atom and ^{19}F n.m.r. proves the presence of two protons. As the observed doublet in the p.m.r. spectrum by coupling with one fluorine is within the range of the $-\text{SiH}_2\text{Cl}$ region published for other $-\text{SiH}_2\text{Cl}$ compounds³³, this is consistent with the compound being SiH_2ClF . The formulation of the compound as SiH_2ClF may be further proved by comparison of its observed infrared spectrum with the published infrared spectra of SiH_3F ³⁴, SiH_2Cl_2 ^{29b}, and SiH_2F_2 ³¹. A correlation diagram of infrared spectra for SiH_3F , SiH_2Cl_2 , SiH_2F_2 and SiH_2ClF is shown in fig. 1.

Assuming a mirror plane symmetry element SiH_2ClF would have Cs symmetry. The centre of gravity of this molecule is believed to be between Cl and F as these two atoms are heavier than hydrogen.



I_c is perpendicular to the plane of symmetry and I_A , I_B are perpendicular to each other.

Where I = moment of inertia and A,B,C are the direction of the principal axis.

The nine normal modes, numbered according to Herzberg's convention³⁵, are described in table 1. The assignment of the normal modes is facilitated by the use of band contours³⁶; A' modes should give rise to bands with contours of type A, B or AB hybrids, with a PQR structure or a doublet structure, and A'' modes to type C bands with a prominent Q branch. The observed frequencies are listed in table 2, with the proposed assignments.

The Si-H stretchings and Si-Cl stretching modes appear in the expected regions; ν_7 gives rise to a type C band at 2242 cm^{-1} , ν_1 to a type A band at 2200 cm^{-1} and ν_5 to a type A band at 570 cm^{-1} . ν_6 may also be readily assigned as the type A band at 235 cm^{-1} .

The remaining five normal modes are between 1000 and 600 cm^{-1} . Of these, ν_4 is assigned as the type A band at 922 cm^{-1} , by comparing with ν_4 for SiH_3F and SiH_2F_2 and the remaining four normal modes are assigned as $-\text{SiH}_2$ deformations (ν_2, ν_3, ν_8 and ν_9).

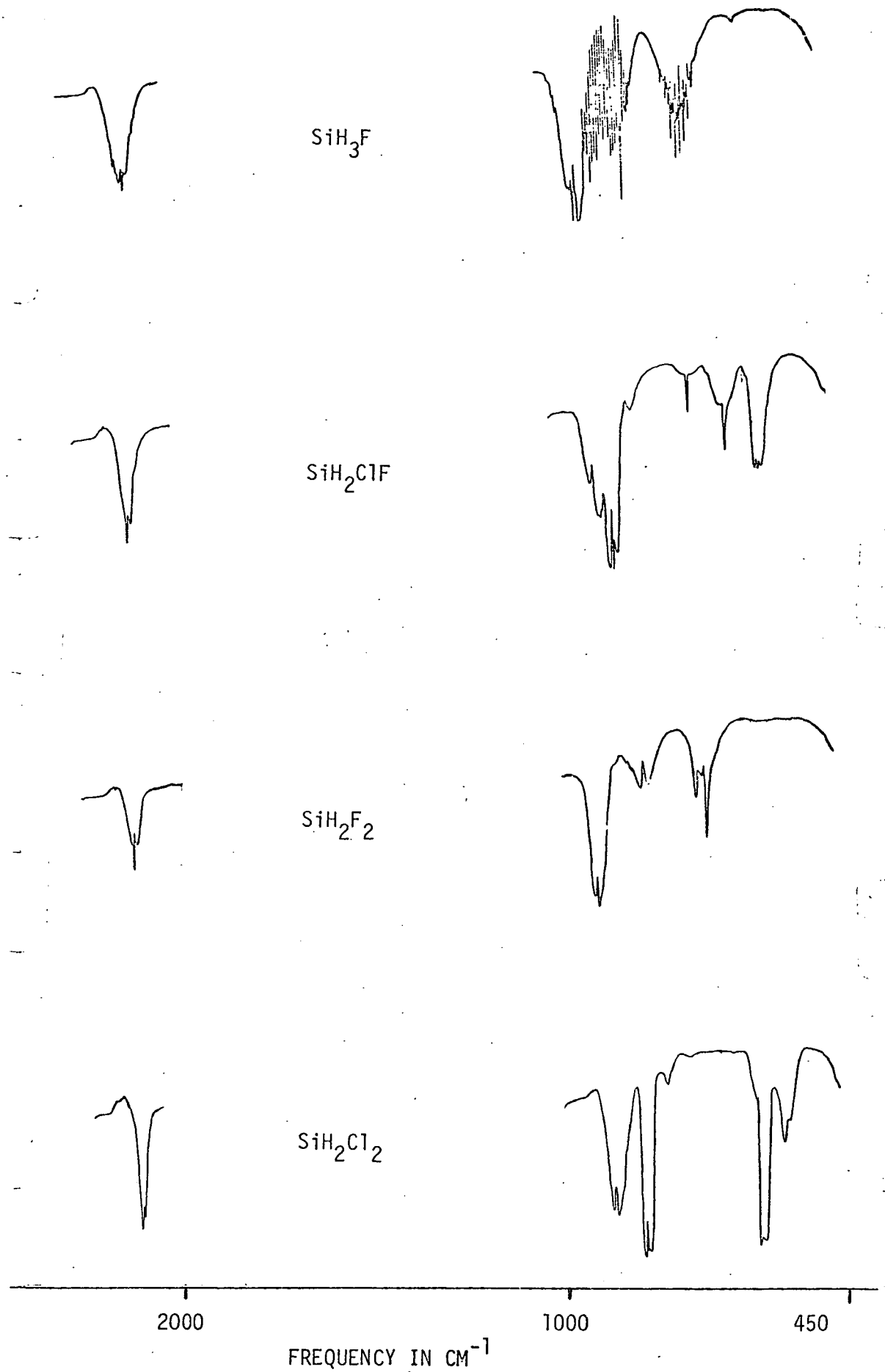


FIGURE 1: CORRELATION DIAGRAM OF THE INFRARED SPECTRA OF HALOGENATED MONOSILANES

Table 1. NOTATION OF NORMAL MODES FOR SiH₂ClF

approximate description of mode	symmetry class	
	A'	A''
SiH stretching	ν_1	ν_7
SiH ₂ deformations	ν_2, ν_3	ν_8, ν_9
SiF stretching	ν_4	
SiCl stretching	ν_5	
SiF deformation	ν_6	
band contour	A or B or mixture of these two	C

Table 2. BANDS OBSERVED FOR SiH₂ClF

frequency, cm ⁻¹	intensity, contour	assignment
2242	vs C	ν_7 (A'')
2200	s A	ν_1 (A')
978	m mixture of A,B	ν_2 (A')
952	s mixture of A,B	ν_3 (A')
922	vs A	ν_4 (A')
735	w C	ν_8 (A'')
649	m C	ν_9 (A'')
570	vs A	ν_5 (A')
235	w A	ν_6 (A')

CHAPTER FOUR

REACTION OF STANNIC CHLORIDE WITH
SiH₃ - DERIVATIVES OF DIFFERENT TYPES
OF CARBON COMPOUNDS.

CHAPTER FOUR

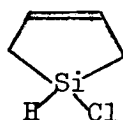
Reaction of stannic chloride with SiH_3 -derivatives of different types of carbon compounds.

4.1 INTRODUCTION

A study of reactions of stannic chloride with silylacetylene, silylperfluoromethylacetylene, vinylsilane, allylsilane, silylcyclopentadiene, sila-cyclopenta-3-ene and phenylsilane is described in this chapter. This work was done largely to study the effects on the chlorination reaction of changing the number of carbon atoms and of changing the nature of the carbon-carbon bonds in the organosilyl compounds. All of these following characteristics of chlorination have been examined in detail; the possibility of chlorination, the stability of silicon-carbon bonds, the percentage conversion of the starting materials, and the effect of the quantity of stannic chloride during the reaction.

A study of reactions of BCl_3 with allylsilane and silylcyclopentadiene is also described in this chapter. This work was done largely for comparison with the reactions of stannic chloride with allylsilane and silylcyclopentadiene.

From the reactions of SnCl_4 with the organosilyl compounds, the new compounds, $\text{ClSiH}_2.\text{C}\equiv\text{CH}$, $\text{ClSiH}_2.\text{C}\equiv\text{C}-\text{CF}_3$, $\text{ClSiH}_2.\text{CH}=\text{CH}_2$, $\text{Cl}_2\text{SiH}.\text{CH}=\text{CH}_2$, ; and from the reaction of



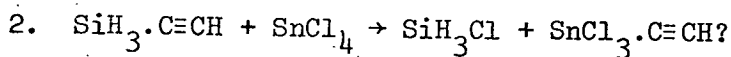
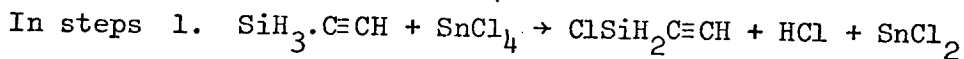
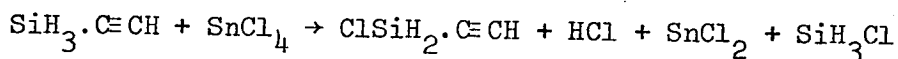
BCl_3 with allylsilane, a new compound $\text{ClSiH}_2.\text{CH}_2-\text{CH}=\text{CH}_2$ were obtained. The partial characterisation of these molecules are reported in this chapter.

4.2:1 The reaction of silylacetylene with stannic chloride

Silylacetylene (1m mole) and stannic chloride (1.5m moles, 0.4 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form almost immediately and the reaction appeared complete in 18 hours.

Trap-to-trap distillation of the volatile products gave HCl (0.5m mole) volatile at -130° , SiH_3Cl (0.07m mole) volatile at -126° , unreacted SiH_3CCH (0.43m mole) volatile at -120° , ClSiH_2CCH (0.5m mole) volatile at -78° , and unreacted SnCl_4 (~ 0.8 m mole, 0.2 gm) was left at -78° . The stannous chloride produced during the reaction remained in the ampoule. No trace of Cl_2SiHCCH was detected among the products.

The reaction between silylacetylene and stannic chloride may be expressed by the equation:



The step 2. can be regarded as side reaction.

Since monochlorosilylacetylene ($\text{ClSiH}_2.\text{C}\equiv\text{CH}$) is a new compound, an attempt will be made in this chapter to describe the characterisation of the compound.

4.2:2 The molecular weight determination of $\text{ClSiH}_2.\text{C}\equiv\text{CH}$

The molecular weight was measured by the Dumas method.

Molecular weight:

Calculated = 90.5

Measured = 91.3

4.2:3 Proton magnetic resonance spectrum

TMS was used as solvent and reference standard.

Chemical Shifts in ppm

T (CH)

T (SiH)

7.52 (triplet) 5.21 (doublet)

 $^4J(\text{HSiCCH}) = 1.0 \text{ Hz}$ 4.2:4 Mass spectrum

Exact mass of parent ions:

	Calculated	Measured	Error
$^{35}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_2 \text{H}_1$	89.969256	89.968993	less than 3 ppm
$^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_2 \text{H}_1$	91.966306	91.966740	less than 5 ppm

4.2:5 Infrared and Raman spectra

The observed infrared and Raman spectra for ClSiH_2CCH may be found in table 3. The assignments of these spectra have been justified in the discussion (4.9).

4.2:6 Boiling point by the vapour pressure curve method

VAPOUR PRESSURE (cm.Hg)

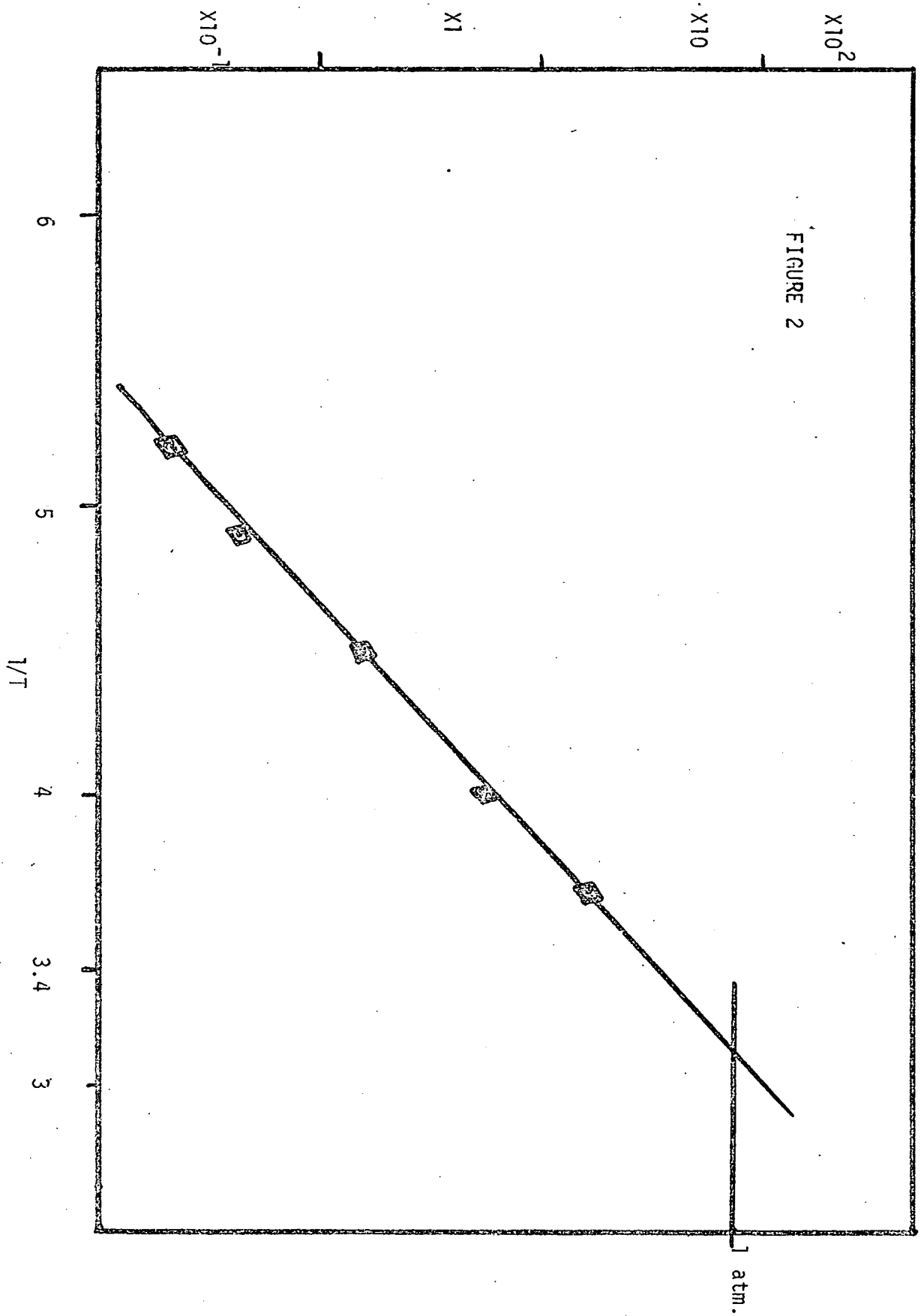


FIGURE 2

atm.

TABLE 4

Observed Temperature in °C	Absolute Corrected Temperature in °K	1/T	Vapour Pressure (cm Hg)
+ 0.05	273.05	0.00366	16.20
- 23.0	249.7	0.00400	5.10
- 51.0	222.0	0.00450	1.61
- 69.0	204.0	0.00490	0.40
- 81.0	192.0	0.00521	0.20

All the temperatures of different slush baths were measured by the calibrated n-pentane thermometer. The boiling point of ClSiH_2CCH at one atmosphere pressure was calculated from the log. graph (Fig.2).

$$3.12 = 0.00312$$

$$= 320.5 \text{ } ^\circ\text{K}$$

$$\therefore \text{Boiling Point} = 47.5^\circ\text{C} \pm 2^\circ$$

4.3:1 The reaction of silylperfluoromethylacetylene with stannic chloride

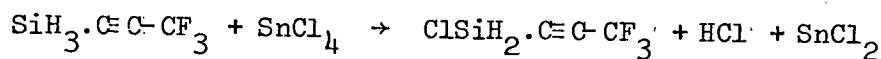
Silylperfluoromethylacetylene (1m mole) and stannic chloride (0.95m mole, 0.248 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form immediately and the reaction was complete in 18 hours.

Trap-to-trap distillation of the volatile products gave HCl

(0.95m mole) volatile at -120° , unreacted $\text{SiH}_3.\text{C}\equiv\text{C}-\text{CF}_3$ (0.05m mole) volatile at -96° , and $\text{ClSiH}_2.\text{C}\equiv\text{C}-\text{CF}_3$ (0.95m mole) was obtained at -96° .

The stannous chloride (0.95m mole, 0.18 gm) produced during the reaction remained in the ampoule. Neither $\text{Cl}_2\text{SiHCCCF}_3$ nor any other products that might have been formed by breaking the Si-C bond were detected among the products.

The reaction between silylperfluoromethylacetylene and stannic chloride may be expressed by the equation:



Since chlorosilylperfluoromethyl acetylene ($\text{ClSiH}_2.\text{C}\equiv\text{C}-\text{CF}_3$) is a new compound, an attempt will be made in this chapter to describe the characterisation of the compound.

4.3:2 The molecular weight determination of $\text{ClSiH}_2.\text{C}\equiv\text{C}-\text{CF}_3$

The molecular weight was measured by the Dumas method.

Molecular weight

Calculated = 158.5

Measured = 158

4.3:3 Nuclear magnetic resonance spectra

Proton n.m.r. of $\text{ClSiH}_2\text{CCCF}_3$

TMS was used as solvent and reference standard.

quartet at 5.12 T

$${}^1J (\text{H}^{29}\text{Si}) = 265 \pm 2 \text{ Hz}$$

$${}^5J (\text{HSiCCCF}) = 1.3 \text{ Hz}$$

${}^{19}\text{F}$ n.m.r. spectrum

1:2:1 triplet at 5026.95 Hz up field from

CCl_3F at 94, 190, 472 Hz.

Therefore, ^{19}F Chemical Shift " δ " of $\text{ClSiH}_2\text{CCCF}_3$ related to CCl_3F
 $= + 53.42 \text{ ppm}$

$$^5\text{J} (\text{FCCCSiH}) = 1.3 \text{ Hz}$$

4.3:4 Mass spectrum

	Calculated	Measured	Error
$^{35}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_3 \text{F}_3$	157.956638	157.956151	less than 4 ppm
$^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_3 \text{F}_3$	159.953688	159.953273	less than 3 ppm

4.3:5 Infrared and Raman spectra

The observed infrared and Raman spectra for $\text{ClSiH}_2\text{CCCF}_3$ may be found in table 5. The assignments of these spectra have been justified in the discussion (4.9)

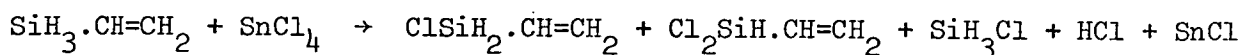
4.4:1 The reaction of vinylsilane with stannic chloride

Vinylsilane (1m mole) and stannic chloride (1.5m moles, 0.4 gm) were condensed in a 35 ml reaction ampoule and allowed to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form almost immediately and the reaction was complete in 18 hours.

Trap-to-trap distillation of the volatile products gave HCl (1.11m moles) volatile at -130° , SiH_3Cl (0.108m mole) volatile at -120° , $\text{ClSiH}_2\text{CH=CH}_2$ (0.672m moles) volatile at -78° , $\text{Cl}_2\text{SiH.CH=CH}_2$ (0.212m mole) volatile at -64° , and unreacted SnCl_4 (0.25m mole, 0.07 gm) was recovered at -64° . The stannous chloride produced during the reaction remained in the ampoule.

When vinylsilane (2m moles) reacted with stannic chloride (1.5m moles, 0.397 gm) at room temperature for 4 hours all stannic chloride was consumed and $\text{ClSiH}_2\text{.CH=CH}_2$ (1.5m moles), HCl (1.5m moles), SnCl_2 (1.5m moles, 0.289 gm) and unreacted $\text{SiH}_3\text{.CH=CH}_2$ (0.5m moles) were obtained. No traces of $\text{Cl}_2\text{SiH.CH=CH}_2$ and SiH_3Cl were detected among the products.

The reaction between vinylsilane and stannic chloride may be expressed by the equation:



In steps:

1. $\text{SiH}_3\text{.CH=CH}_2 + \text{SnCl}_4 \rightarrow \text{ClSiH}_2\text{.CH=CH}_2 + \text{HCl} + \text{SnCl}_2$
2. $\text{ClSiH}_2\text{.CH=CH}_2 + \text{SnCl}_4 \rightarrow \text{Cl}_2\text{SiH.CH=CH}_2 + \text{HCl} + \text{SnCl}_2$
3. $\text{SiH}_3\text{.CH=CH}_2 + \text{SnCl}_4 \rightarrow \text{SiH}_3\text{Cl} + \text{SnCl}_3\text{.CH=CH}_2?$

The step (3) can be regarded as a side reaction.

Since monochloro- and dichloro-derivatives of vinylsilane ($\text{ClSiH}_2\text{.CH=CH}_2$ and $\text{Cl}_2\text{SiH.CH=CH}_2$) are new compounds, an attempt will be made in this chapter to characterise these molecules in detail.

4.4:2 The molecular weight determination of chlorinated vinylsilanes

The molecular weights were measured by the Dumas method.

Molecular weight:

	Calculated	Measured
$\text{ClSiH}_2\text{.CH=CH}_2$	92.5	93.6
$\text{Cl}_2\text{SiH.CH=CH}_2$	127	127.8

4.4:3 Proton magnetic resonance spectra

Chemical shifts in ppm

<u>Compound</u>	$^3J(\text{HSiCH})$	$T(\text{SiH})$	$T(\text{CH} = \text{CH}_2)$
$\text{ClSiH}_2 \cdot \text{CH} = \text{CH}_2$	1.5 Hz	5.14 (doublet)	~ 3.85 (multiplets)
$\text{Cl}_2\text{SiH} \cdot \text{CH} = \text{CH}_2$	1.0 Hz	4.42 (doublet)	~ 3.85 (multiplets)

4.4:4 Mass spectraExact mass of parent ions:

	Calculated	Measured	Error
$^{35}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_2 \text{H}_3$	91.983915	91.984073	less than 2 ppm
$^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{C}_2 \text{H}_3$	93.981955	93.980767	12 ppm.
$^{35}\text{Cl}_2 \text{ } ^{28}\text{Si}_1 \text{H}_1 \text{C}_2 \text{H}_3$	125.945934	125.945308	less than 5 ppm
$^{35}\text{Cl}_1 \text{ } ^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_1 \text{C}_2 \text{H}_3$	127.942985	127.943422	less than 4 ppm
$^{37}\text{Cl}_2 \text{ } ^{28}\text{Si}_1 \text{H}_1 \text{C}_2 \text{H}_3$	129.940035	129.940345	less than 3 ppm

4.4:5 Infrared and Raman spectra

The observed infrared and Raman spectra for $\text{ClSiH}_2 \cdot \text{CH} = \text{CH}_2$ and $\text{Cl}_2\text{SiH} \cdot \text{CH} = \text{CH}_2$ may be found in tables 6 and 7. The assignments of these spectra have been justified in the discussion (4.9).

4.4:6 Boiling point by vapour pressure curve method

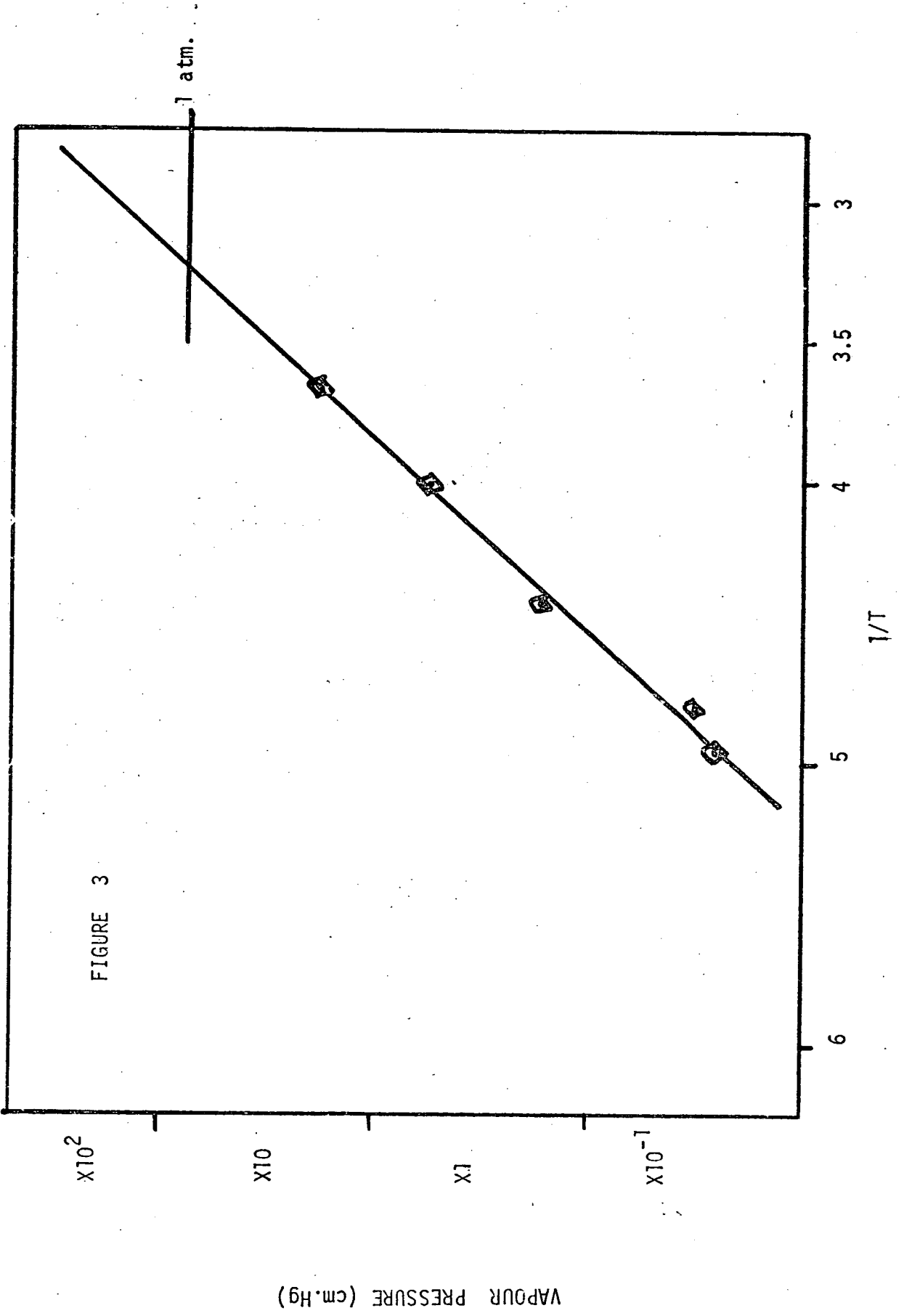


FIGURE 3

TABLE 8

Observed Temperature in °C	Absolute Corrected Temperature in °K	1/T	Vapour Pressure (cm Hg)
+ 0.05	273.05	0.00366	18.0
- 24.0	249.0	0.00402	5.4
- 47.5	225.5	0.00443	1.65
- 64.5	208.5	0.00480	0.30
- 71.25	201.8	0.00496	0.25

The boiling point of $\text{ClSiH}_2\text{CH}=\text{CH}_2$ at one atmosphere pressure was calculated from the log. graph (Fig.3).

$$3.22 = 0.00322$$

$$= 311.0^\circ\text{K}$$

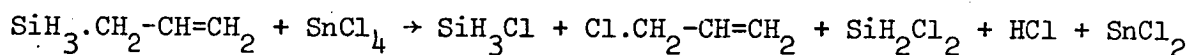
$$\therefore \text{Boiling Point} = 38^\circ\text{C} \pm 2$$

4.5:1 The reaction of allylsilane with stannic chloride

Allylsilane (1m mole) and stannic chloride (1.2m moles, 0.312 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A white, solid was formed almost immediately and the reaction was complete in two hours.

Trap-to-trap distillation of the volatile products gave HCl (0.12m mole) volatile at -130° , SiH_3Cl (0.6m mole) volatile at -126° , $\text{Cl}\cdot\text{CH}_2\text{-CH}=\text{CH}_2$ (0.8m mole) volatile at -120° and SiH_2Cl_2 (0.4m mole) involatile at -120° . The stannous chloride produced during the reaction was remained in the ampoule. No trace of chlorinated allylsilane ($\text{ClSiH}_2\cdot\text{CH}_2\text{-CH}=\text{CH}_2$) was detected among the products. HCl, SiH_3Cl and SiH_2Cl_2 were identified by their i.r. spectra as in the previous reactions (chapter 3). $\text{Cl}\cdot\text{CH}_2\text{-CH}=\text{CH}_2$ was identified by comparison of the observed and published infrared spectrum.³⁷

The reaction between allylsilane and stannic chloride may be expressed by the equation.



In steps:

1. $\text{SiH}_3\cdot\text{CH}_2\text{-CH}=\text{CH}_2 + \text{SnCl}_4 \rightarrow \text{SiH}_3\text{Cl} + \text{Cl}\cdot\text{CH}_2\text{-CH}=\text{CH}_2 + \text{SnCl}_2$
2. $\text{SiH}_3\text{Cl} + \text{SnCl}_4 \rightarrow \text{SiH}_2\text{Cl}_2 + \text{HCl} + \text{SnCl}_2$

The step (2) can be regarded as side reaction.

4.5:2 The reaction of allylsilane with boron trichloride

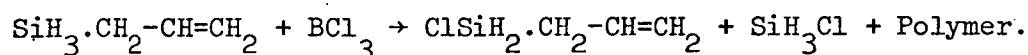
Allylsilane (1m mole) and boron trichloride (0.34m mole) were condensed in a 35ml reaction ampoule and allowed to warm to room

temperature. The reaction was complete after 3 days at room temperature with the formation of a solid probably a polymer at the bottom of the reaction ampoule.

Trap-to-trap distillation of the volatile products gave SiH_3Cl (0.2m mole) volatile at -120° , unreacted $\text{SiH}_3\text{CH}_2\text{-CH=CH}_2$ (0.22m mole) volatile at -96° and $\text{ClSiH}_2\text{-CH}_2\text{-CH=CH}_2$ (0.25m mole) involatile at -96° . The transparent polymer produced during the reaction was remained in the ampoule. No traces of HCl , B_2H_6 and $\text{Cl}_2\text{SiHCH}_2\text{-CH=CH}_2$ were detected among the products.

When the above reaction was carried out for $5\frac{1}{2}$ hours at -78° by reacting allylsilane (1m mole) with boron trichloride (0.34m mole); $\text{ClSiH}_2\text{CH}_2\text{-CH=CH}_2$ (0.45m mole), SiH_3Cl (0.15m mole) and unreacted $\text{SiH}_3\text{CH}_2\text{-CH=CH}_2$ (0.21m mole) were obtained with the formation of a polymer as in the above reaction. No traces of diborane, hydrogen chloride and dichloro-derivative allylsilane were detected among the products.

The reaction between allylsilane and boron trichloride may be expressed by the equation:



Since allylchlorosilane ($\text{ClSiH}_2\text{CH}_2\text{-CH=CH}_2$) is a new compound, an attempt will be made in this chapter to characterise the molecule.

4.5:3 The molecular weight determination of $\text{ClSiH}_2\text{CH}_2\text{-CH=CH}_2$

The molecular weight was measured by the Dumas method.

Molecular Weight:

Calculated = 106.5

Measured = 105.0

4.5:4 Proton magnetic resonance spectrum

TMS was used as solvent and reference standard.

	<u>Chemical Shifts in ppm</u>	
T (-CH=CH ₂)*	T(-SiH ₂)	T(-CH ₂)
between 4 and 5.2	5.39(triplet)	8.1(heptet)
two triplets (J=7.5Hz)	¹ J(H ²⁹ Si)=212.0Hz	-
with the separation of		
26Hz,		
One quartet (J=7.5 Hz)	³ J(HSiCH)=3.2Hz	³ J(HSiCH)=3.2Hz
and multiplets		

* Since the n.m.r. analysis of the vinyl region of allylsilane has already been done³⁸, the detailed n.m.r. analysis of the vinyl region for ClSiH₂.CH₂-CH=CH₂ was not attempted.

4.5:5 Mass spectrum

Exact mass of parent ions:

	Calculated	Measured	Error
³⁵ Cl ₁ ²⁸ Si ₁ H ₂ C ₃ H ₅	106.000555	106.00026	less than 5 ppm
³⁷ Cl ₁ ²⁸ Si ₁ H ₂ C ₃ H ₅	107.997605	107.996998	less than 6 ppm

4.5:6 Infrared and Raman spectra

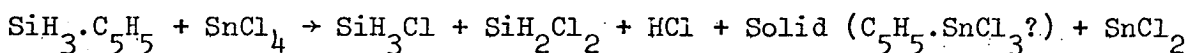
The observed infrared and Raman spectra for ClSiH₂.CH₂-CH=CH₂ may be found in table 10. The assignments of these spectra have been justified in the discussion (4.9).

4.6:1 The reaction of silylcyclopentadiene with stannic chloride

Silylcyclopentadiene (0.5m mole) and stannic chloride (0.7m mole,

0.18 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A grey-white solid was formed immediately and the reaction was complete in 3 minutes.

Trap-to-trap distillation of the volatile products gave HCl (0.07m mole) volatile at -130° , SiH_3Cl (0.43m mole) volatile at -120° and SiH_2Cl_2 (0.07m mole) involatile at -120° . The grey-white, solid produced during the reaction was remained in the ampoule and the remaining unreacted SnCl_4 might have been dissolved in the grease of the vacuum line joints as there was no recovery of SnCl_4 . No trace of $\text{ClSiH}_2\text{C}_5\text{H}_5$ or $\text{Cl.C}_5\text{H}_5$ was detected among the products. The reaction between silylcyclopentadiene and stannic chloride may be expressed by the equation:



In steps:

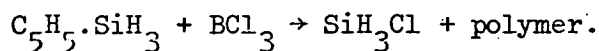
1. $\text{SiH}_3\text{C}_5\text{H}_5 + \text{SnCl}_4 \rightarrow \text{SiH}_3\text{Cl} + \text{C}_5\text{H}_5\text{.SnCl}_3\text{?}$
2. $\text{SiH}_3\text{Cl} + \text{SnCl}_4 \rightarrow \text{SiH}_2\text{Cl}_2 + \text{HCl} + \text{SnCl}_2$.

The step (2) can be regarded as side reaction.

4.6:2 The reaction of silylcyclopentadiene with boron trichloride

When silylcyclopentadiene (1m mole) was reacted with boron trichloride (0.4m mole) at room temperature for 4 hours, SiH_3Cl (0.6m mole) was obtained with the formation of a polymer which remained at the bottom of the reaction ampoule. No traces of chlorinated silylcyclopentadiene and HCl were detected among the products.

The reaction between silylcyclopentadiene and boron trichloride may be expressed by the equation:

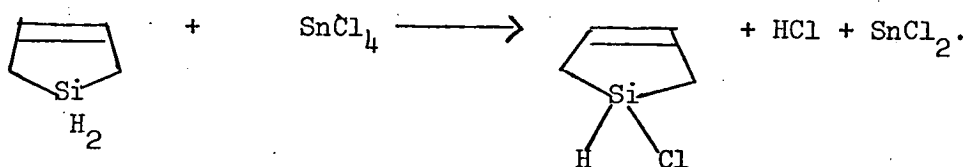


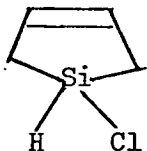
4.7:1 The reaction of sila-cyclopenta-3-ene with stannic chloride.

Sila-cyclopenta-3-ene (1m mole) and stannic chloride (1.03m moles, 0.27 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A white, thin film on the inner walls of the reaction ampoule began to form almost immediately and the reaction was complete in 30 minutes.

Trap-to-trap distillation of the volatile products gave HCl (1m mole) volatile at -78° and monochlorosila-cyclopenta-3-ene (1m mole) involatile at -78° . The stannous chloride (1m mole, 0.19gm) produced during the reaction remained in the ampoule and remaining unreacted SnCl_4 might have been dissolved in the grease of the vacuum line joints. No trace of dichlorosila-cyclopenta-3-ene was detected among the products.

The reaction between sila-cyclopenta-3-ene and stannic chloride may be expressed by the equation:



Since monochlorosila-cyclopenta-3-ene, , is a new

compound, an attempt will be made in this chapter to characterize the molecule.

4.7:2 Proton magnetic resonance spectrum

TMS was used as solvent and reference standard.

	<u>Chemical Shifts in ppm</u>	
T(-SiH)	T(-CH ₂)*	T(-CH=CH-CH ₂)*
5.33 (triplet)	~8.1 (multiplets) between 4 and	5.2 (multiplets)
³ J(HSiCH)=2.8Hz	-	-

* Since the n.m.r. analysis of the regions -CH₂ and -CH=CH-CH₂ of sila-cyclopenta-3-ene has already been done,³⁹ the detailed n.m.r. analysis of above regions for chlorosila-cyclopenta-3-ene was not attempted.

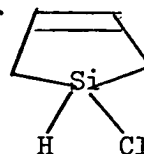
4.7:3 Mass spectrum

Exact mass of parent ions:

	Calculated	Measured	Error
³⁵ Cl ₁ ²⁸ Si ₁ C ₄ H ₇	118.000555	118.000813	less than 3ppm
³⁷ Cl ₁ ²⁸ Si ₁ C ₄ H ₇	119.997605	119.997921	less than 3ppm

4.7:4 Infrared and Raman spectra

The observed infrared and Raman spectra for



may be found in table 11. The assignments of these spectra have been justified in the discussion (4.9).

4.8 The reaction of phenylsilane with stannic chloride

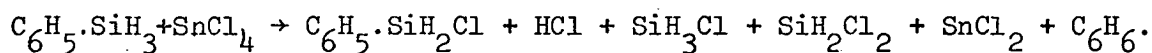
Phenylsilane (1m mole) and stannic chloride (1.5m moles, 0.4 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature. A white, thin film on the inner walls of the reaction

ampoule began to form almost immediately and the reaction was complete in 15 minutes.

Trap-to-trap distillation of the volatile products gave HCl (0.92m mole) volatile at -130° , SiH_3Cl (0.04m mole) volatile at -120° , SiH_2Cl_2 (0.02m mole) volatile at -78° unreacted SnCl_4 and benzene (0.5m mole) volatile at -22° , and phenylchlorosilane (0.912m mole) involatile at -22° . The stannous chloride produced during the reaction was remained in the ampoule.

No trace of phenyldichlorosilane was detected among the products. The benzene⁴⁰ and phenylchlorosilane⁴¹ were identified by comparison of the observed and published infrared spectra.

The reaction between phenylsilane and stannic chloride may be expressed by the equation:



In steps:

1. $\text{C}_6\text{H}_5\cdot\text{SiH}_3 + \text{SnCl}_4 \rightarrow \text{C}_6\text{H}_5\cdot\text{SiH}_2\text{Cl} + \text{HCl} + \text{SnCl}_2$
2. $\text{C}_6\text{H}_5\cdot\text{SiH}_3 + \text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{C}_6\text{H}_6$
3. $\text{C}_6\text{H}_5\cdot\text{SiH}_2\text{Cl} + \text{HCl} \rightarrow \text{SiH}_2\text{Cl}_2 + \text{C}_6\text{H}_6$
4. $\text{SiH}_3\text{Cl} + \text{SnCl}_4 \rightarrow \text{SiH}_2\text{Cl}_2 + \text{HCl} + \text{SnCl}_2$

The steps (2), (3) and (4) can be regarded as side reactions.

4.9 DISCUSSION

From the reactions of SnCl_4 with some organosilyl compounds ($\text{SiH}_3\text{C}\equiv\text{CH}$, $\text{SiH}_3\text{CH}=\text{CH}_2$ and $\text{C}_6\text{H}_5\text{SiH}_3$) a small quantity of SiH_3Cl , and with $\text{SiH}_3\text{CH}_2\text{-CH}=\text{CH}_2$ and $\text{C}_5\text{H}_5\text{SiH}_3$ a large quantity of SiH_3Cl was obtained. This may be explained by the following considerations. The statement often is made that "substitution at carbon makes the Si-C bond more easily broken,"^{42a} by which is meant that the substitution of common functional groups of organic chemistry within an alkyl or aryl group attached to silicon weakens the Si-C bond toward attacking reagents. This indeed is so, and the reason for it lies in the fact that the common functional groups ($-\text{OH}$, $-\text{COOH}$, $-\text{CO}-$, $-\text{O}-$, $-\text{NH}_2$, $-\text{NH}-$, $-\text{N}=\text{N}-$, $-\text{C}=\text{N}$, $-\text{X}$, $-\text{OR}$ etc.) contain highly electronegative elements and so serve to accentuate the already -too-high polarity of the Si-C bond. Negative substituents on a β -carbon atom pose a special threat, for a β -elimination reaction takes place in the presence of a good acceptor in the shape of the silicon atom; β -chloroalkylsilanes, for example, readily cleave at the Si-C bond when heated to give the energetically favored Si-Cl bond and an alkene. The enhanced reactivity of fluorocarbonsilanes and siloxanes (especially if there be fluorine on the α - or β -carbon atom) also is readily understood in terms of this principle. The rapid increase in ease of basic cleavage of the Si-C bond in the series Si-CH_3 , $\text{Si-CH}_2\text{Cl}$, Si-CHCl_2 , and Si-CCl_3 ^{42b} offers a further example. In the same way, the domination of methyl silicones in the field of silicon polymers (rather than ethyl, propyl, butyl, or organofunctional ones) is readily understood. The Si-C bonds of $\text{Si-C}=\text{C}$ and $\text{Si-C}\equiv\text{C}$ systems are much more reactive than those of

the corresponding methyl compounds, and act like those of Si-CHCl₂ and Si-CCl₃ groups. The ethynyl group is split from silicon even by cold water. Therefore the formation of SiH₃Cl in the reactions of SnCl₄ with most of the above unsaturated organosilyl compounds is not surprising.

The formation of a very small quantity of SiH₂Cl₂ in most of the above reactions may be due to the chlorination of SiH₃Cl with the excess SnCl₄ present in the systems.

The new chlorinated organosilyl compounds produced in this study were all characterised partially by n.m.r., mass, and vibrational spectroscopy. The measured molecular weight of each of these compounds are in close agreement with the calculated ones.

The mass spectrum of each of these new compounds showed exact mass of the parent ions which are consistent with the calculated mass, within the allowed error.

The proton n.m.r. spectra demonstrate the presence of two sets of protons in ClSiH₂.C≡CH, three fluorine atoms (coupled to -SiH₂ protons) in ClSiH₂CCCF₃, three sets of protons in ClSiH₂.CH=CH₂ and Cl₂SiH.CH=CH₂, three sets of protons in ClSiH₂.CH₂-CH=CH₂ and three sets of protons in C₄H₆SiHCl which themselves are coupled to each other. ¹⁹F n.m.r. spectrum of ClSiH₂CCCF₃ proves the presence of two protons. The observed proton chemical shifts due to -SiH₂Cl or -SiHCl₂ and the ²⁹Si coupling constants (¹J(H²⁹Si)) in these molecules are within the range published for other -SiH₂Cl and -SiHCl₂ compounds.³³ Since the n.m.r. analyses of the -CH=CH₂ regions of vinyl and allyl-silanes³⁸ and -CH=CH-CH₂ regions of sila-cyclopent-3-ene³⁹ had already been done, the detailed analyses

of these regions in the n.m.r. spectra of chlorinated vinyl, allyl-silanes, and chlorosilacyclopent-3-ene were not attempted.

The formulations of the compounds as ClSiH_2CCH , $\text{ClSiH}_2\text{CCCF}_3$, $\text{ClSiH}_2\cdot\text{CH}=\text{CH}_2$, $\text{Cl}_2\text{SiH}\cdot\text{CH}=\text{CH}_2$, $\text{ClSiH}_2\cdot\text{CH}_2-\text{CH}=\text{CH}_2$ and $\text{C}_4\text{H}_6\text{SiHCl}$ may be further proved by comparison of their observed and published vibrational spectra for $\text{SiH}_3\cdot\text{C}\equiv\text{CH}$ ⁴³, $\text{SiH}_3\cdot\text{C}\equiv\text{C}-\text{CF}_3$ ⁴⁴, $\text{SiH}_3\cdot\text{CH}=\text{CH}_2$ ⁴⁵, $\text{SiH}_3\cdot\text{CH}_2-\text{CH}=\text{CH}_2$ ⁴⁶, and silacyclopent-3-ene.⁴⁷

The C-H, Si-H, $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, Si-C, C-F and Si-Cl stretching modes appear in the expected regions and most of these bands in the Raman spectra are strongly polarised (tables 3,5,6,7,10 and 11). The bands in the region $960-710\text{ cm}^{-1}$ (most of these are depolarised in the Raman spectra) may readily be assigned as SiH_2 and/or SiH deformations for most of the chlorinated organosilyl compounds. In some cases CH_2 rocks appear in the same region. The bands in the region $480-130\text{ cm}^{-1}$ may be due to CF_3 , CCC, SiCC, and ClSiC bending modes. The one of the CF_3 deformations for $\text{ClSiH}_2\cdot\text{CCCF}_3$ molecule appears at 620 cm^{-1} which is depolarised in the Raman spectrum.

All these assignments for chlorinated organosilyl compounds are in close agreement with the assignments for the corresponding SiH_3 -analogues.

TABLE 3

Raman and Infrared Spectra of $\text{ClSiH}_2\text{C}\equiv\text{CH}$

Liquid		Vapour		
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignments	
3310	vvw	p?	3313.8 s	v CH
			2247.3 w	?
2220	vvs	p	2219.1 vs	v SiH(asym)
			2215 s	v SiH(sym)
			2204.4 s	?
2060	vs	p	2061.8 s	v $\text{C}\equiv\text{C}$
			1362 m	2x692 (overtone)
950±1	s,broad	dp?	955 s	δ SiH_2
			934±1 m	?
870	w,broad	dp?	874.6 vs	δ SiH_2
			815 w	δ SiH_2
810	vvw,broad	dp?		
735	m,broad	dp?	729.8 w	C_2H_2 impurity?
710	w,broad	dp?	692 s	ρ SiH_2
670±2	w	p??	663 w	v SiC
620±5	w,broad	dp?	628? m	δ CCH(asym)
			615 m	δ CCH(sym)
535	vvs	p	548 m	v SiCl
325	w,broad	p?	322 w	SiCC bend(sym)
222	s	dp?	- -	SiCC bend(asym)
132	vs	dp?	- -	ClSiC bend

Where s = strong, m = medium, w = weak, v = very, p = polarised and dp = depolarised.

TABLE 5

Raman and Infrared Spectra of $\text{ClSiH}_2\text{CCCF}_3$

LIQUID		VAPOUR	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignment
2238 vs	p	2226 s	v SiH(asym)
		2221.5 s	v SiH(sym)+v $\text{C}\equiv\text{C}$
1265 vvw, br	dp	1252.6 vs	} v C-F
1225 vvw	dp	1223 s	
1172 vw, br	dp	1180 vvs	
948 s	dp	947 s	δ SiH_2
880 s	p	-	?
865 m	dp	868 vs	δ SiH_2
742 m	p	760 vvw	δ SiH_2
731 m	dp	726 vvw	ρ SiH_2
702 w	p	698 vvw	v SiC
620 m	dp	610 m	δ CF_3
558 vs	p	564 s	v SiCl
462 m	dp	467 vvw	δ CF_3
378 m	dp?	372 m	δ CF_3
305 vs	p	302 vvw	CCC bend?
243 \pm 1 vvs	dp	-	SiCC bend?
151 vvs	dp?	-	ClSiC bend?

Where s = strong, m = medium, w = weak, br = broad, v = very,
p = polarised and dp = depolarised.

TABLE 6

Raman and Infrared Spectra of $\text{ClSiH}_2\text{.CH=CH}_2$

LIQUID		VAPOUR	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignment
3080 vw	dp?	3071.4 m	} v CH
3005 s	p	2988.6 w	
2975 vw	p?	2964.2 w	
2195 vvs	p	2194.0 vs	v SiH(asym)
		2188.0 s	v SiH(sym)
1600 vs	p	1600.0 w	v C=C
1410 s	p	1410.0 m	δ CH ₂
1270 vs	p	1271.2 vvw	δ CH
1015 vvw, br	dp?	1007.0 \pm 0.5 s	δ CH ₂
		1001.8 \pm 0.1 m	δ CH ₂
		961.0 s	δ SiH ₂
955 \pm 2 s, br	dp?	955.0 \pm 1 s	ρ CH ₂
865 m, br	dp?	869.0 vs	δ SiH ₂
810 vvw, br	dp?	808.8 vw	δ SiH ₂
745 vs, br	p	731.4 w	(555+180)
708 \pm 2 s, br	p?	703.0 m	v SiCl
675 vw, br	dp	634.2m	ρ CH?
618 vvw	dp	609.8 m	ρ SiH ₂ ?
535 vvs	p	555.0 s	v SiCl
468 vvs	p	471.0 vw	?
380 w, br	dp?	375.0 vw	?
295 s, br	p?	-	SiCC bend
180 s, br	dp?	-	ClSiC bend

Where s = strong, m = medium, w = weak, br = broad, v = very,

p = polarised, dp = depolarised

TABLE 7

Raman and Infrared Spectra of $\text{Cl}_2\text{SiH.CH=CH}_2$

LIQUID		VAPOUR	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignment
3079 \pm 1 w	dp?	3073.4 vw 3029.6 vvw	v CH (1605+1412)
3000 \pm 1 vs	p	2998.0 vvw	} v CH
2968 \pm 1 w	p?	2965.0 \pm 1 vw	
2222 vvs	p	2218.0 \pm 1s 1942.0 vvw	v SiH (971.2x2)
1598 vs	p	1605 vw	v C=C
1405 vs	p	1412 m	δ CH_2
1268 vs	p	1275 \pm 1 vvw	δ CH
1010 vw	dp?	1010 \pm 1 m	δ CH_2
-	-	996.8 s	δ CH_2
975 \pm 2 vvw	dp?	977.0 s	δ SiH
810 \pm 0.5 vvs	dp	971.2 m 810.2 vvs 768.0 \pm 1 vvw	ρ CH_2 δ SiH (375x2)?
730 vw	dp?	729.0 m	v SiC
698 \pm 1 w	p?	694.6 w 667.4 vvw	ρ CH impurity?
579 s	dp	590.6 \pm 1 vs	v SiCl(asym)
525 vvs	p	535.4 s	v SiCl(sym)
479 vvs	p	480.0 \pm 2 w	SiCC bend(asym)
371 m	dp?	375.0 \pm 1 vw	SiCC bend(sym)
325 s	p	325.0 \pm 2 vvw	?
229 m	dp?	-	Cl_2SiC bend?
179 vvs	dp?	-	ClSiCl bend?

Where s = strong, m = medium, w = weak, br = broad, v = very, p = polarised and dp = depolarised.

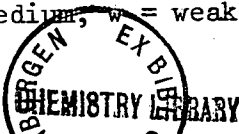


TABLE 10

Raman and Infrared Spectra of $\text{ClSiH}_2\text{CH}=\text{CH}_2$

LIQUID		VAPOUR	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignments
3108 \pm 2 vvw	dp	3095 w	} ν CH
3025 \pm 2 w	p?	3000 sh	
2995 sh	dp?	2980 w	
2950 sh	dp	2920 w	
2915 w	p?	2910 sh	
2195 vvs	} p	2191 vs	ν SiH(asym)
2178 vs		2186 vs	ν SiH(sym)
1640 vs	p	1637.5 m	ν C=C
1425 w	dp?	1440 sh	} δ CH ₂
1405 w	p?	1410 w	
1308 s	p	1305 m	δ CH
1170 m,br	p	1165 \pm 1 w	δ CH ₂
		1037.5 w	δ CH ₂
950 m,br	dp	953.0 vvs	δ SiH ₂
860 vvw	dp?	881.0 vvs	δ SiH ₂
768 sh	dp?	761.0 w	δ SiH ₂
745 s	p	748.0 w	ρ CH?
708 \pm 1 vs,br	p	694.0 vw	ν SiC
608 s	p	598.0 s	ρ SiH ₂ ?
528 vs,br	p	532.0 vs	ν SiCl
416 m	p?	-	CCC bend?
355 m	p	-	SiCC bend?

Where s = strong, m = medium, w = weak, sh = shoulder, br = broad,
 ν = very, p = polarised and dp = depolarised

TABLE 11

Raman and Infrared Spectra of $\text{ClSiH}(\text{C}_4\text{H}_6)$

LIQUID		VAPOUR	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignment
3101 \pm 1 vvw	dp	3085 \pm 2 vvw	} v CH
3054 m	p?	3039 w	
3020 vw	dp		
3005 vvw	dp?	2960 sh	
2918 s	p	2920 w,br	
2870 \pm 5 sh	dp?	2850 sh	
2195 vs	p	2175 s	v SiH
1612 m	p	1610 \pm 2 vw	v C=C
1420 sh	dp	1410 vw,br	δ CH_2
1405 m	dp	-	δ CH_2 (in plane)
1305 w	p	-	δ CH (out of plane)
1285 sh	p?	1270 vvw	δ CH_2
1211 m	p	1212 vvw	δ CH_2 (in plane)
1109 w	dp?	1108 m	δ CH (in plane)
1010 vvw	dp	999 vvw	ring deform
954 \pm 1 w	dp	955 w	δ SiH
918 s	p	920 vw	ring deform
865 vw	dp	857 \pm 2 s	δ SiH
763 m	dp?	755.0 m	ρ CH_2 (in plane)
718 vs	p	-	ring deform
678 vw	dp?	-	ring deform
640 s	dp	643 m,br	ring deform
520 vvs, br	p	528 \pm 1 m,br	v SiCl
440 w,br	p?	-	ring deform
380 vw	dp	-	C=C twist
362 sh	p?	-	?
235 m	p?	-	?
197 s	dp	-	ClSiC ₂ bend?

Where s = strong, m = medium, w = weak, sh. = shoulder, br = broad, v = very
 p = polarised and dp = depolarised

CHAPTER FIVE

REACTION OF STANNIC CHLORIDE WITH
SiH₃-DERIVATIVES OF ELEMENTS OF
GROUP V AND VI.

CHAPTER FIVEReaction of stannic chloride with SiH_3 - derivatives of elements of groups V and VI.5.1 INTRODUCTION

This chapter describes a study of reactions of stannic chloride with tetramethyldisiloxane, disiloxane, disilyl sulphide, trisilylphosphine, and trisilylamine. This work was done largely to examine whether there is a possibility of chlorination of the above silyl-compounds, something not previously achieved by many research workers using other halogenating agents. The effects of stannic chloride towards Si-X bonds (X = O, S, P or N) in silyl-derivatives of elements of groups V and VI have also been examined in detail.

From the reaction of stannic chloride with trisilylamine, new compounds, $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$ and $(\text{ClSiH}_2)_3\text{N}$ were obtained. The partial characterisation of these compounds is reported in this chapter.

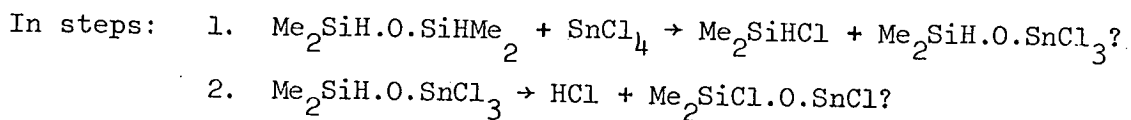
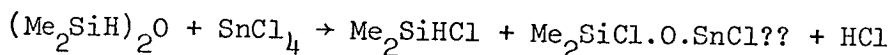
5.2:- The reaction of tetramethyldisiloxane with stannic chloride

Pure tetramethyldisiloxane (0.5m mole) and stannic chloride (0.56m mole, 0.147 gm) were condensed in a 35ml reaction ampoule and allowed to warm to room temperature for 3 minutes. A bluish-white, thin film on the inner walls of the reaction ampoule formed immediately with a vigorous bubbling. All the products which were volatile at room temperature were removed at this stage and the infrared spectrum of these products showed the presence

of only Me_2SiHCl (0.5m mole) which was consistent with the infrared spectrum published for Me_2SiHCl ²⁷. When the reaction was allowed to continue for 10 minutes, only HCl (0.5m mole) was produced and the involatile bluish white solid remained in the ampoule. The infrared spectrum of this solid was obtained using nujol as a mulling agent and this spectrum indicated the possible presence of $\text{Me}_2\text{SiCl.O.SnCl}$.

When the above reaction was carried out for one hour at -22° by reacting $(\text{Me}_2\text{SiH})_2\text{O}$ (1m mole) with SnCl_4 (1m mole, 0.265 gm), only Me_2SiHCl (1m mole) was obtained as a volatile product, and no trace of HCl or $(\text{Me}_2\text{SiH})_2\text{O}$ was detected among the volatile products. HCl (1m mole) was produced when the reaction ampoule was warmed to room temperature for 20 minutes after the removal of all the volatile products produced during the first stage of reaction.

The reaction between tetramethyldisiloxane and stannic chloride may be expressed by the equation:



5.2:2 Proton magnetic resonance study of the reaction

Tetramethyldisiloxane (0.25m mole) and stannic chloride (0.25m mole) were taken in an n.m.r. tube with cyclopentane and sealed. (Cyclopentane was used as solvent and reference standard).

at -50°

Chemical Shifts in p.p.m.

	T(CH)	T(SiH)
$(\text{Me}_2\text{SiH})_2\text{O}$	9.85	5.27
	(doublet)	(heptet)

at -22°

for one hour

Me_2SiHCl	9.55	5.11
	(doublet)	(heptet)
$\text{Me}_2\text{SiH.O.SnCl}_3?$	9.31	5.29
	(doublet)	(heptet)

at $+28^{\circ}$

for 30 minutes

Me_2SiHCl	9.55	5.11
	(doublet)	(heptet)
$\text{Me}_2\text{SiCl.O.SnCl?}$	9.91	-
	(singlet)	

5.2:3 Infrared spectrum

The observed infrared spectrum for the unknown bluish white solid, produced during the reaction (5.2:1) may be found in Table 12. The tentative assignments of this spectrum have been described in the discussion (5.7)

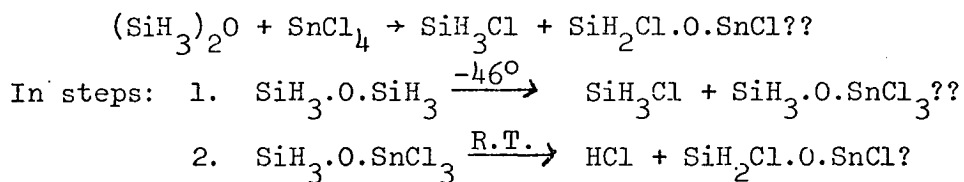
5.3:1 The reaction of disiloxane with stannic chloride

Pure disiloxane (0.5m mole) and stannic chloride (0.5m mole, 0.132 gm) were condensed in a 35 ml reaction ampoule and allowed to warm to room temperature for 5 minutes. A bluish white, thin film on the inner walls of the reaction ampoule formed immediately with a vigorous bubbling. All the products which were volatile at room temperature were removed at this stage and the infrared spectra

of these products showed the presence of SiH_3Cl (0.5m mole) and HCl (0.5m mole) which are consistent with the i.r. spectra published for SiH_3Cl and HCl . When this reaction was allowed to proceed further for 15 minutes, no more volatile products were obtained and the involatile bluish white solid remained in the ampoule. The infrared spectrum of this solid was obtained using nujol as a mulling agent, and this spectrum indicated the possible presence of $\text{ClSiH}_2\cdot\text{O}\cdot\text{SnCl}$.

When the above reaction was carried out for two hours at -46° by reacting $(\text{SiH}_3)_2\text{O}$ (0.5m mole) with SnCl_4 (0.5m mole, 0.131 gm), only SiH_3Cl (0.5m mole) was obtained as a volatile product, and no trace of HCl or $(\text{SiH}_3)_2\text{O}$ was detected among the volatile products. HCl (0.5m mole) was produced when the reaction ampoule was warmed to room temperature for 30 minutes after the removal of all the volatile products produced during the first stage of reaction.

The reaction between disiloxane and stannic chloride may be expressed by the equation:



5.3:2 Proton magnetic resonance study of the reaction

Disiloxane (0.25m mole) and stannic chloride (0.25m mole) were taken in an n.m.r. tube with cyclopentane and sealed. (Cyclopentane was used as solvent and reference standard)

		<u>Chemical Shifts in p.p.m.</u>
at -50°		$\tau(\text{SiH})$
	$\text{SiH}_3 \cdot \text{O} \cdot \text{SiH}_3$	5.37
		(singlet)
at -46°		
for 2 hours	SiH_3Cl	5.41
		(singlet)
	$\text{SiH}_3 \cdot \text{O} \cdot \text{SnCl}_3?$	
	or	5.29
	$\text{ClSiH}_2 \cdot \text{O} \cdot \text{SnCl}_3?$	(singlet)
at $+28^{\circ}$		
for 45 minutes	SiH_3Cl	5.41
		(singlet)
	$\text{ClSiH}_2 \cdot \text{O} \cdot \text{SnCl}_3?$	5.29
		(singlet)

5.3:3 Infrared spectrum

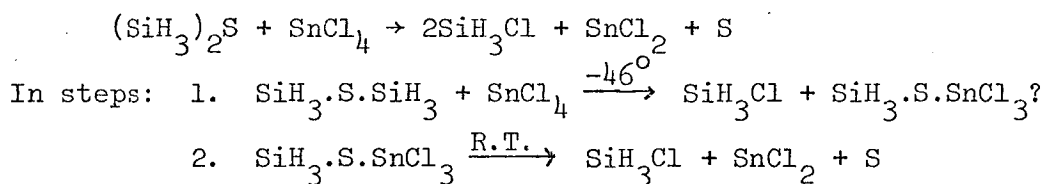
The observed infrared spectrum for the unknown bluish white solid produced during the reaction (5.3:1) may be found in Table 13. The tentative assignments of this spectrum have been described in the discussion (5.7)

5.4:1 The reaction of disilyl sulphide with stannic chloride

Pure disilyl sulphide (1m mole) and stannic chloride (1m mole, 0.265 gm) were condensed in a 35 ml reaction ampoule and allowed

to warm to -46° for two hours. No white, thin film formed on the inner walls of the reaction ampoule. All the products which were volatile at -46° were removed at this stage and then infrared spectrum of these products showed the presence of only SiH_3Cl (1m mole). When this reaction was allowed further for 30 minutes at room temperature, SiH_3Cl (1m mole) was obtained with the formation of a white, thin film and a yellow solid, on the inner walls of the reaction ampoule and at the bottom of the reaction ampoule respectively. No trace of HCl was detected among the products. The attempt to obtain the infrared spectra of white and yellow solids was unsuccessful. Therefore, the white solid may be considered as SnCl_2 and the yellow solid may be free sulphur.

The reaction between disilyl sulphide and stannic chloride may be expressed by the equation:



5.4:2 Proton magnetic resonance study of the reaction

Disilyl sulphide (0.25m mole) and stannic chloride (0.25m mole) were taken in an n.m.r. tube with cyclopentane and sealed. (Cyclopentane was used as solvent and reference standard)

Chemical Shifts in p.p.m.

at -50°		T (SiH)
	$\text{SiH}_3\cdot\text{S}\cdot\text{SiH}_3$	5.65
		(singlet)
at -46°		5.65
for 30 minutes	$\text{SiH}_3\cdot\text{S}\cdot\text{SiH}_3$	(singlet)

SiH_3Cl		5.41
		(singlet)

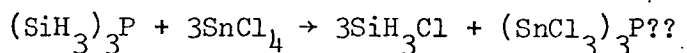
at $+28^\circ$

for 2 minutes	only SiH_3Cl	5.41
		(singlet)

5.5:1 The reaction of trisilylphosphine with stannic chloride

Pure trisilylphosphine (0.2m mole) and stannic chloride (0.6m mole, 0.156 gm) were condensed in a 20 ml reaction ampoule and allowed to warm to room temperature for 3 minutes. A yellowish brown solid formed immediately. All the products which were volatile at room temperature were removed and the infrared spectrum of these products showed the presence only of SiH_3Cl (0.6m mole). No traces of HCl and PCl_3 were detected among the products. The involatile yellowish brown solid remained in the reaction ampoule and the attempt to obtain the infrared spectrum of this solid was unsuccessful.

The reaction between trisilylphosphine and stannic chloride may be expressed by the equation:



5.5:2 Proton magnetic resonance study of the reaction

Trisilylphosphine (0.2m mole) and stannic chloride (0.6m mole) were taken in an n.m.r. tube with TMS and sealed. (TMS was used as solvent and reference standard).

Chemical Shift in p.p.m.

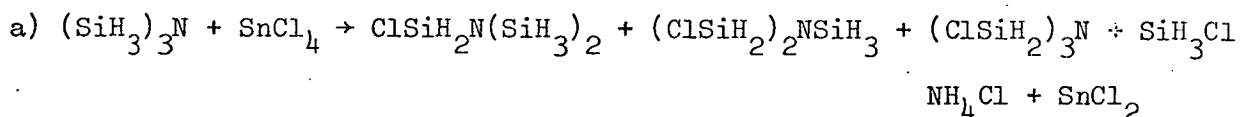
at $+28^\circ$		T(SiH)
for 3 minutes		5.41
	only SiH_3Cl	(singlet)

5.6:1 The reaction of trisilylamine with stannic chloride

Pure trisilylamine (1m mole) and stannic chloride (1m mole, 0.265 gm) were condensed in a 35 ml reaction ampoule and allowed to warm to room temperature for 15 minutes. A white solid formed immediately. Trap-to-trap distillation of the volatile products gave SiH_3Cl (0.82m mole) volatile at -120° , unreacted $(\text{SiH}_3)_3\text{N}$ (0.27m mole) volatile at -78° , and a mixture of new compounds $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$ and $(\text{ClSiH}_2)_3\text{N}$ (0.45m mole) involatile at -78° . Trap-to-trap distillation of this mixture gave $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$ (0.2m mole) volatile at -64° , $(\text{ClSiH}_2)_2\text{NSiH}_3$ (0.15m mole) volatile at -46° , and $(\text{ClSiH}_2)_3\text{N}$ (0.1m mole) involatile at -46° . No trace of HCl was detected among the products. The white solid was identified as the mixture of SnCl_2 and NH_4Cl by qualitative analysis for Sn^{2+} and for NH_4^+ ions.

When pure $(\text{SiH}_3)_3^{15}\text{N}$ (0.38m mole) was reacted with SnCl_4 (0.34m mole, 0.09 gm), a mixture of chlorinated trisilylamines, $\text{ClSiH}_2^{15}\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2^{15}\text{NSiH}_3$ and $(\text{ClSiH}_2)_3^{15}\text{N}$ (0.091m mole), SiH_3Cl (0.35m mole) and unreacted $(\text{SiH}_3)_3^{15}\text{N}$ (0.11m mole) was obtained. The monochloroderivative of trisilylamine was prepared by another method,^{48a} reacting dichlorosilane with $(\text{SiH}_3)_3\text{N}$ at room temperature for a few hours. SiH_3Cl was produced as a by-product.

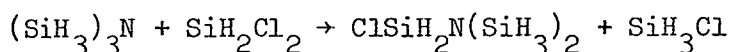
The reaction of trisilylamine with stannic chloride may be represented by the equation:



In steps:

1. $(\text{SiH}_3)_3\text{N} + \text{SnCl}_4 \rightarrow (\text{ClSiH}_2)_x\text{N}(\text{SiH}_3)_{3-x} + \text{HCl} + \text{SnCl}_2$
2. $(\text{SiH}_3)_3\text{N} + 4\text{HCl} \rightarrow 3\text{SiH}_3\text{Cl} + \text{NH}_4\text{Cl}$

b) The reaction between trisilylamine and dichlorosilane may be represented by the equation:



Since the chlorinated trisilylamines are new compounds, an attempt will be made in this chapter to characterise these molecules in detail.

5.6:2 Nuclear magnetic resonance spectra

TABLE 14

Proton n.m.r. of chlorinated trisilylamines

TMS was used as solvent and reference standard.

	$\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$	$(\text{ClSiH}_2)_2\text{NSiH}_3$	$(\text{ClSiH}_2)_3\text{N}$
SiH_2 T(ppm)	4.90	4.85	4.80
$^1\text{J}({}^{29}\text{SiH})$, Hz	258.0	260.0	264.0
SiH_3 T(ppm)	5.56	5.54	-
$^1\text{J}({}^{29}\text{SiH})$, Hz	212.0	224.0	-
The ratio of integration	1:3	4:3	-

TABLE 15

^{29}Si Chemical Shifts " δ " in ppm relative to Me_4Si (-ve to low frequency)

a) (i)	$\text{Cl}^{29}\text{SiH}_2\text{N}(\text{}^{28}\text{SiH}_3)_2$	=	-17.7
	corrected ^{29}Si frequency	=	19.866832 MHz
	(ii) $\text{Cl}^{28}\text{SiH}_2\text{N}(\text{}^{29}\text{SiH}_3)_2$	=	-39.8
	corrected ^{29}Si frequency	=	19.866392 MHz
b) (i)	$(\text{Cl}^{29}\text{SiH}_2)_2\text{N}^{28}\text{SiH}_3$	=	-17.16
	corrected ^{29}Si frequency	=	19.866842 MHz
	(ii) $(\text{Cl}^{28}\text{SiH}_2)_2\text{N}^{29}\text{SiH}_3$	=	-47.31
	corrected ^{29}Si frequency	=	19.866243 MHz
c)	$(\text{Cl}^{29}\text{SiH}_2)_3\text{N}$	=	-20.23
	corrected ^{29}Si frequency	=	19.866781 MHz.

TABLE 16

^{15}N n.m.r. of chlorinated trisilylamines

TMS was used as solvent and reference standard.

	$\text{ClSiH}_2^{15}\text{N}(\text{SiH}_3)_2$	$(\text{ClSiH}_2)_2^{15}\text{NSiH}_3$	$(\text{ClSiH}_2)_3^{15}\text{N}$
SiH_2 T(ppm)	4.92 (doublet)	4.84 (doublet)	4.79 (doublet)
$^2\text{J}(\text{HSi}^{15}\text{N})$, Hz	6.2	6.1	6.0
$^1\text{J}(\text{}^{29}\text{SiH})$, Hz	258.0	260.0	264.0
SiH_3 T(ppm)	5.57 (doublet)	5.54 (doublet)	-
$^2\text{J}(\text{HSi}^{15}\text{N})$, Hz	4.0	4.0	-
$^1\text{J}(\text{}^{29}\text{SiH})$, Hz	212.0	224.0	-

TABLE 17

^{15}N Chemical Shifts " δ " in ppm relative to $(\text{CH}_3)_4^{15}\text{N}^+\text{I}^-$ (+ve to high frequency)

a) $\text{ClSiH}_2^{15}\text{N}(\text{SiH}_3)_2 = -51.32$
 corrected ^{15}N frequency = 10.132832 MHz

b) $(\text{ClSiH}_2)_2^{15}\text{NSiH}_3 = -22.11$
 corrected ^{15}N frequency = 10.133128 MHz

c) $(\text{ClSiH}_2)_3^{15}\text{N} = +1.18$
 corrected ^{15}N frequency = 10.133364 MHz

5.6:3 Mass spectra

Since the chlorinated trisilylamines were very sensitive to moisture, most of these were hydrolysed with the moisture present in the mass spectrometer. It was also found that these compounds were more stable losing a proton in mass spectra when the ionising voltage was 70 eV. Therefore, it was necessary to obtain the exact mass of the parent ions.

Exact mass of parent ions

	Calculated	Measured	Error
$^{35}\text{Cl}_1^{28}\text{Si}_1\text{H}_2^{14}\text{N}_1(^{28}\text{Si}_1\text{H}_3)_2$	140.965311	140.965004	less than 3 ppm
$^{37}\text{Cl}_1^{28}\text{Si}_1\text{H}_2^{14}\text{N}_1(^{28}\text{Si}_1\text{H}_3)_2$	142.962361	142.962144	less than 2 ppm

$(^{35}\text{Cl}_1\ ^{28}\text{Si}_1\text{H}_2)_2\ ^{14}\text{N}_1\ ^{28}\text{Si}_1\text{H}_3$	174.926339	174.926011	less than 2 ppm
$^{35}\text{Cl}_1\ ^{37}\text{Cl}_1\ (^{28}\text{Si}_1\text{H}_2)_2\ ^{14}\text{N}_1\ ^{28}\text{Si}_1\text{H}_3$	176.923389	176.923120	less than 2 ppm
$(^{37}\text{Cl}_1\ ^{28}\text{Si}_1\text{H}_2)_2\ ^{14}\text{N}_1\ ^{28}\text{Si}_1\text{H}_3$	178.920439	178.920312	less than 1 ppm
$(^{35}\text{Cl}_1\ ^{28}\text{Si}_1\text{H}_2)_3\ ^{14}\text{N}_1$	208.887368	208.886433	less than 5 ppm
$^{35}\text{Cl}_2\ ^{37}\text{Cl}_1\ (^{28}\text{Si}_1\text{H}_2)_3\ ^{14}\text{N}_1$	210.884418	210.883342	5 ppm
$^{35}\text{Cl}_1\ ^{37}\text{Cl}_2\ (^{28}\text{Si}_1\text{H}_2)_3\ ^{14}\text{N}_1$	212.881468	212.879540	9 ppm
$(^{37}\text{Cl}_1\ ^{28}\text{Si}_1\text{H}_2)_3\ ^{14}\text{N}_1$	214.878518	214.877434	less than 6 ppm

5.6:4 Infrared and Raman spectra

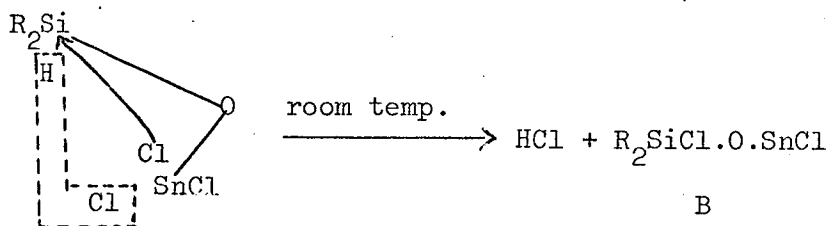
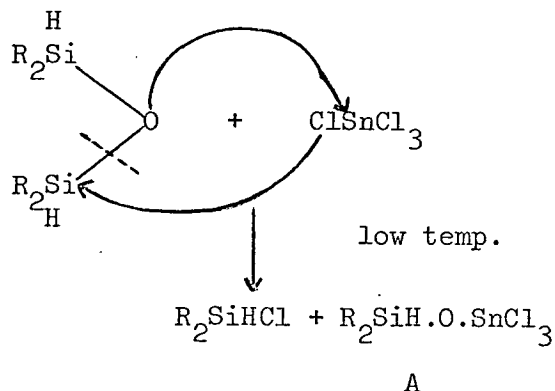
The observed infrared and Raman spectra for the chlorinated trisilylamines and corresponding ^{15}N labelled derivatives may be found in Tables 18 and 19. The assignments of these spectra have been justified in the discussion (5.7). A correlation diagram of infrared spectra for $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$ and $(\text{ClSiH}_2)_3\text{N}$ is shown in figure 5.

5.7 DISCUSSION

One m.mole of each of $(\text{Me}_2\text{SiH})_2\text{O}$, $(\text{SiH}_3)_2\text{O}$ and $(\text{SiH}_3)_2\text{S}$ was reacted with a m.mole of stannic chloride at low temperature and gave a m.mole of Me_2SiHCl , SiH_3Cl and SiH_3Cl respectively. No formation of HCl at this stage suggests that a solid, $\text{R}_2\text{SiH.Y.SnCl}_3$ (where $\text{R}=\text{Me}$ or H , $\text{Y}=\text{O}$ or S) might have been formed as an intermediate compound. Later this solid was warmed to room temperature for 20 minutes. The oxygen compound gave only a m.mole of pure HCl; in the disilyl sulphide reaction with SnCl_4 , another m.mole of

SiH_3Cl was obtained together with free sulphur and stannous chloride.

The above reactions may proceed as follows:



(where R = H or Me)

Although the n.m.r. study of the reaction of stannic chloride with tetramethyldisiloxane at different temperatures is consistent with the presence of A and B (5.2:2), the same reaction with disiloxane showed just a singlet at 5.29 T in the n.m.r. spectrum at -46° , and at room temperature the chemical shift of that singlet was not altered. This may be due to insolubility of the white solid, produced during the reaction, in cyclopentane. The attempt to trace the ^1H n.m.r. chemical shift due to HCl was not successful possibly due to its insolubility in cyclopentane or because of its exchange. The n.m.r. study of the reaction of stannic chloride with disilyl sulphide at -46° showed the presence of

$(\text{SiH}_3)_2\text{S}$ at 5.65 T (singlet) and SiH_3Cl at 5.41 T (singlet). No trace of the possible intermediate compound $\text{SiH}_3\cdot\text{S}\cdot\text{SnCl}_3$ was detected in the n.m.r. spectrum even after 30 minutes and at room temperature, only a singlet due to SiH_3Cl was observed. Similarly the reaction of stannic chloride with $(\text{SiH}_3)_3\text{P}$ showed a singlet due to SiH_3Cl when the reaction was allowed to warm to room temperature for 3 minutes.

The infrared spectra of the white solids, produced during the reaction of SnCl_4 with $(\text{Me}_2\text{SiH})_2\text{O}$ and $(\text{SiH}_3)_2\text{O}$ were obtained using nujol as a mulling agent. The significant Si-Cl (560 cm^{-1} in $\text{Me}_2\text{SiCl}\cdot\text{O}\cdot\text{SnCl}$ and 520 cm^{-1} in $\text{SiH}_2\text{Cl}\cdot\text{O}\cdot\text{SnCl}$), Sn-Cl (390 cm^{-1} in $\text{Me}_2\text{SiCl}\cdot\text{O}\cdot\text{SnCl}$ and 410 cm^{-1} in $\text{SiH}_2\text{Cl}\cdot\text{O}\cdot\text{SnCl}$), and Si-H ($2180 - 2140\text{ cm}^{-1}$ in $\text{SiH}_2\text{Cl}\cdot\text{O}\cdot\text{SnCl}$) stretching modes appear in the expected regions. The bands in the region $1170-1025\text{ cm}^{-1}$ may be due to Sn-O-Si stretching modes in both the molecules. The bands at 975, 940 and 920 cm^{-1} in $\text{SiH}_2\text{Cl}\cdot\text{O}\cdot\text{SnCl}$ molecule are in the expected regions of SiH_2 -deformations and the strong band at 1260 cm^{-1} in $\text{Me}_2\text{SiCl}\cdot\text{O}\cdot\text{SnCl}$ may readily be assigned as CH_3 -deformation. The remaining bands in the infrared spectra for the molecules $\text{Me}_2\text{SiCl}\cdot\text{O}\cdot\text{SnCl}$ and $\text{SiH}_2\text{Cl}\cdot\text{O}\cdot\text{SnCl}$ are not significant. Although some of these infrared vibrations support the presence of above mentioned new compounds, it is rather difficult to justify their existence.

The attempt to obtain infrared spectrum of the yellowish brown solid, formed during the reaction of SnCl_4 with $(\text{SiH}_3)_3\text{P}$ was unsuccessful, and this solid may be considered as $(\text{SnCl}_3)_3\text{P}$ as there were no other products in addition to SiH_3Cl .

The reaction of stannic chloride with trisilylamine gave a mixture of mono-, di- and trichlorinated trisilylamines

$\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$, and $(\text{ClSiH}_2)_3\text{N}$. Each of these new compounds was characterised by proton n.m.r., ^{15}N n.m.r., mass, infrared and Raman spectroscopy.

The mass spectra showed exact masses of the parent ions of the chlorinated trisilylamines, which are consistent with the calculated masses, within the allowed error (5.6:3).

The proton m.m.r. demonstrates the presence of two sets of protons in the cases of $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$ and $(\text{ClSiH}_2)_2\text{NSiH}_3$ which themselves are not coupled to each other. The ratio of integration proves the number of protons in each set. The proton chemical shifts and the ^{29}Si coupling constants $^1\text{J}(\text{H}^{29}\text{Si})$ of chlorinated trisilylamines are within the range of the $-\text{SiH}_2\text{Cl}$ and $-\text{SiH}_3$ regions published for other $-\text{SiH}_2\text{Cl}$ and $-\text{SiH}_3$ compounds³³; these results are consistent with the compounds being $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$ and $(\text{ClSiH}_2)_3\text{N}$. The ^{29}Si chemical shifts are obtained by the heteronuclear double resonance method, which will be discussed in the second part of this thesis in detail.

The proton n.m.r. of $(\text{ClSiH}_2)_3^{15}\text{N}$ showed a doublet by coupling to ^{15}N which has a spin of $\frac{1}{2}$. When one of these two lines was irradiated by the ^{15}N frequency using a secondary frequency supply unit (Schlumberger frequency) the other one also collapsed and a new peak appeared exactly in the middle of these two lines. The position of this line is the proton chemical shift of $(\text{ClSiH}_2)_3^{15}\text{N}$ molecule. The difference between these two lines in Hz is the coupling constant $^2\text{J}(\text{HSi}^{15}\text{N})$ and the ^{15}N chemical shift of $(\text{ClSiH}_2)_3^{15}\text{N}$ at exactly 100 MHz was calculated in p.p.m. relative to $(\text{CH}_3)_4^{15}\text{N}^+\text{I}^-$. Similarly the ^{15}N n.m.r. parameters for $\text{ClSiH}_2^{15}\text{N}(\text{SiH}_3)_2$ and $(\text{ClSiH}_2)_2^{15}\text{NSiH}_3$ were obtained by the heteronuclear double resonance

technique. The ^{15}N chemical shift " δ " of $(\text{SiH}_3)_3^{15}\text{N}$ was recently measured^{48b} (-79.9 ppm to low frequency of $\text{Me}_4^{15}\text{N}^+\text{I}^-$). The reaction of dichlorosilane with trisilylamine may be an exchange reaction and this may be considered an excellent method of preparing the monochloro-derivative of trisilylamine $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$ alone.

The formulations of the compounds as $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{N}\text{SiH}_3$ and $(\text{ClSiH}_2)_3\text{N}$ and their ^{15}N labelled compounds may be further proved by comparison of their observed vibrational spectra with the published infrared and Raman spectra of trisilylamine.⁴⁹

The Si-H and Si-Cl stretching modes appear in the expected regions (tables 18 and 19). The bands in the region $1002\text{-}700\text{ cm}^{-1}$ are due to SiH_3 and/or SiH_2 deformations and Si-N stretchings. But it is rather difficult to assign Si-N stretching modes until these chlorinated trisilylamines are labelled with ^{15}N isotope. The infrared spectra of these ^{15}N labelled chlorinated trisilylamines showed a remarkable difference in the region $1002\text{-}700\text{ cm}^{-1}$. The infrared band at 992 cm^{-1} in the monochloro species was shifted to 978 cm^{-1} . the band at 1002 cm^{-1} in dichloro species was shifted to 979 cm^{-1} and the band at 990.5 cm^{-1} in trichloro derivative of trisilylamine was shifted to 969.5 cm^{-1} . Hence these bands are assigned as (asymmetric) Si-N stretching modes, and the remaining bands in the region $950\text{-}700\text{ cm}^{-1}$, are all assigned as $-\text{SiH}_3$ and/or $-\text{SiH}_2$ deformations.

The bands near 480 cm^{-1} in infrared spectra were not shifted as expected; these are assigned as Si-N symmetric stretching modes in infrared and Raman spectra of all these chlorinated trisilylamines by comparison with the vibrational spectra published for $(\text{SiH}_3)_3\text{N}$. The shifts in these frequencies should be small if the mode is related

to $\nu_{\text{sym}}(\text{Si}_3\text{N})$ of $(\text{SiH}_3)_3\text{N}$. In that molecule $\nu_{\text{sym}}(\text{Si}_3\text{N})$ would not shift if ^{14}N is changed to ^{15}N , since the N does not move in the vibration.

The bands between 190 and 140 cm^{-1} in the Raman spectra for these chlorinated trisilylamines may be assigned due to ClSiN bending; the bands at 285 cm^{-1} in monochloro-, 358 cm^{-1} in dichloro-, and 322 cm^{-1} in trichloro- derivatives of trisilylamines may be due to SiNSi bending; and the bands at $230\text{ cm}^{-1}(\text{ClSiH}_2)_2\text{N SiH}_3$, 278 cm^{-1} in $(\text{ClSiH}_2)_3\text{N}$ may be assigned as asymmetric ClSiN bending modes. Only two modes due to Si-N stretching are observed in $(\text{SiH}_3)_3\text{N}$ because of the three-fold symmetry whereas three Si-N stretching modes are expected in the chlorinated trisilylamines, because of lower symmetry. In fact only two bands due to Si-N stretching modes are observed as in trisilylamine and their positions are exactly the same as in trisilylamine. This suggests that the effect of chlorine substituents on the stretching vibrations at Nitrogen is very small. A marked change is apparent however in the Raman spectrum in that the band near 1000 cm^{-1} , which is depolarised in trisilylamine, is strongly polarised in the unsymmetrically substituted molecules, $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$ and $(\text{ClSiH}_2)_2\text{NSiH}_3$. Thus chlorine substitution has a powerful effect on polarisation and hence does not show the effect of lower symmetry, possibly because chlorine is very polarisable. In the case of $(\text{ClSiH}_2)_3\text{N}$ the band at 1000 cm^{-1} is polarised and this may be due to the same reason mentioned above.

TABLE 12

Infrared Spectrum of the White Solid (Me₂SiCl.O.SnCl?) in Nujol

Infrared Frequency in cm ⁻¹	Infrared Intensity	Tentative Assignment
3000-2700	vs	Nujol + ν CH
1470-1350	s	Nujol + δ CH ₃ (asym)
1260	s	δ CH ₃ (sym)
1170-1150	sh	} ν Sn.O.Si?
1085	s	
1025	sh	} ρ CH ₃ + ν Si.O.Sn?
810	s	
735	sh	} Nujol + ν SiC
720	m	
560	w	ν SiCl
390	w, broad	ν SnCl

Where ν = very, s = strong, m = medium,

w = weak, and sh = shoulder

TABLE 13

Infrared spectrum of the White Solid ($\text{ClSiH}_2\text{.O.SnCl?}$) in Nujol

Infrared Frequency in cm^{-1}	Infrared Intensity	Tentative Assignment
3000-2700	vs	Nujol
2180-2140	w	v SiH
1470-1350	s	Nujol
1140	sh	} v Sn.O.Si?
1100	s, broad	
1070	s	
975	m	} δ SiH ₂
940	m	
920	w	
875	sh	} v Si.O.Sn?
830	s	
720	w	Nujol
520	w	v SiCl
410	w, broad	v SnCl

Where, v = very, s = strong, m = medium

w = weak, and sh = shoulder

TABLE 16

Infrared Spectra of Chlorinated Trisilylamines

$\text{ClSiH}_2^{14}\text{N}(\text{SiH}_3)_2$		$\text{ClSiH}_2^{15}\text{N}(\text{SiH}_3)_2$		$(\text{ClSiH}_2)_2^{14}\text{NSiH}_3$		$(\text{ClSiH}_2)_2^{15}\text{NSiH}_3$		$(\text{ClSiH}_2)_3^{14}\text{N}$		$(\text{ClSiH}_2)_3^{15}\text{N}$	
Vapour				Vapour				Vapour			
Frequency in cm^{-1}	Assignment	Frequency in cm^{-1}	Assignment	Frequency in cm^{-1}	Assignment	Frequency in cm^{-1}	Assignment	Frequency in cm^{-1}	Assignment	Frequency in cm^{-1}	Assignment
2195±1.0 m	} ν SiH	2195±1 m	} ν SiH	2200 s	} ν SiH	2200 s	} ν SiH	2210 s	ν SiH	2210 s	ν SiH
2170 s		2170 s		2178 sh		2170 sh					
1015.5 v	?										
992 s	ν Si ¹⁴ N(asym)	978 s	ν Si ¹⁵ N(asym)	1002 s	ν Si ¹⁴ N(asym)	979 s	ν Si ¹⁵ N(asym)	990.5s	ν Si ¹⁴ N(asym)	969.5 s	ν Si ¹⁵ N(asym)
941 vs	δ SiH ₃	949 sh	δ SiH ₃	946 vs	δ SiH ₃ and/ or SiH ₂	943 vs	δ SiH ₃ and/ or SiH ₂	949 s	δ SiH ₂	949 s	δ SiH ₂
887 s		δ SiH ₂		935 vs		880 vs		880 vs		876.5 vs	
740 v, broad	ρ SiH ₃	738 v, broad	ρ SiH ₃	742 v	ρ SiH ₃ and/ or SiH ₂	740±1 v	ρ SiH ₃ and/ or SiH ₂	741±1 v	ρ SiH ₂	741±1 v	ρ SiH ₂
				715 sh		572±1 sh		740±2 sh	572±1 sh	584 v	ν SiCl(asym)
550 v	ν SiCl	550 v	ν SiCl	542 m	ν SiCl(asym)	542 m	ν SiCl(asym)	548 m	ν SiCl(asym)	548 m	ν SiCl(asym)
488 vv	ν Si ¹⁴ N(sym)	480±1 vv	ν Si ¹⁵ N(sym)	483 vv	ν Si ¹⁴ N(sym)	483 vv	ν Si ¹⁵ N(sym)	498 vv	ν Si ¹⁴ N(sym)	498 vv	ν Si ¹⁵ N(sym)

Where v = very, s = strong, m = medium, v = weak and sh = shoulder

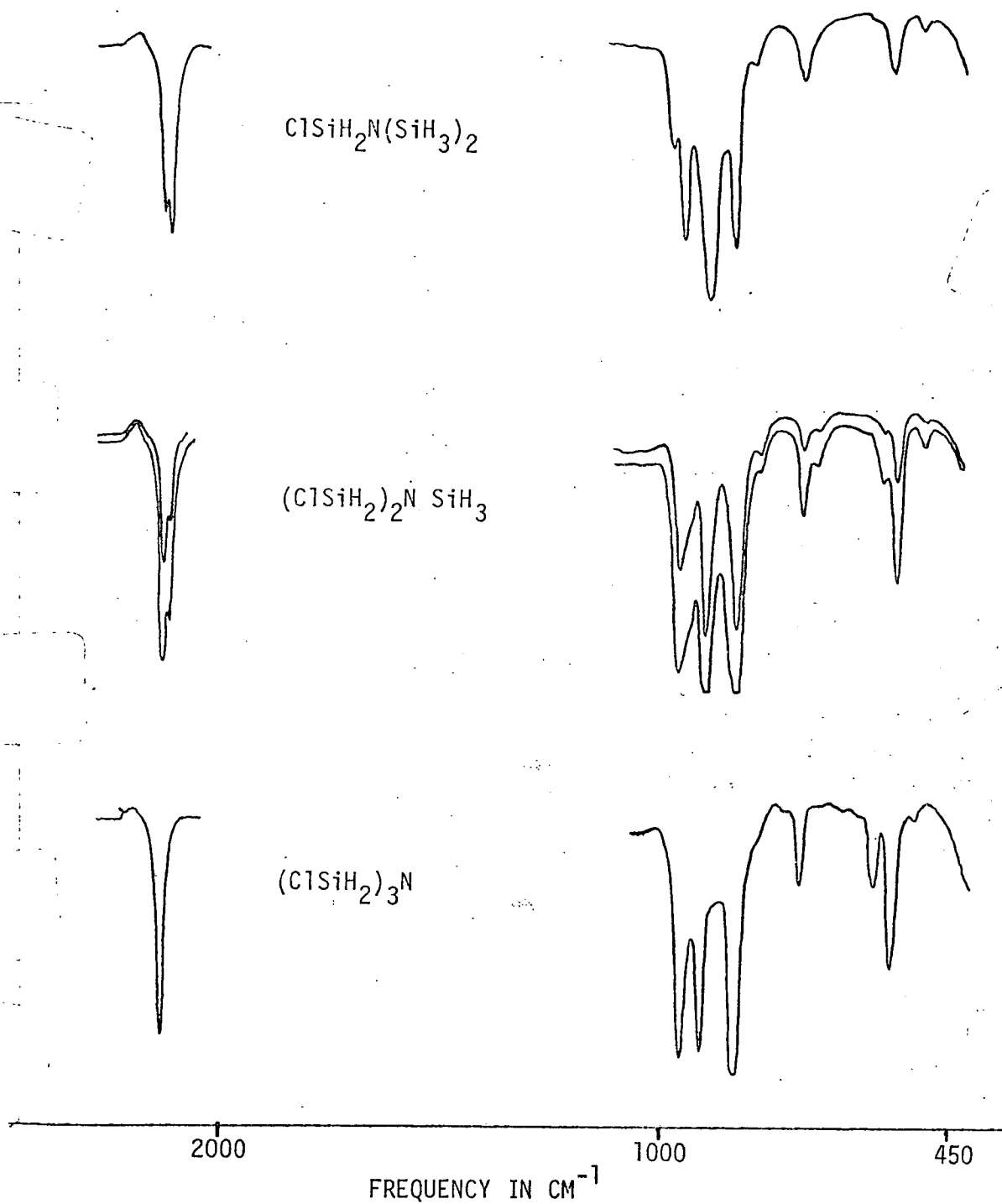


FIGURE 5: CORRELATION DIAGRAM OF THE INFRARED SPECTRA OF CHLORINATED TRISILYLAMINES

TABLE 19

Raman spectra of chlorinated trisilylamines (Liquid)

$\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$		$(\text{ClSiH}_2)_2\text{N SiH}_3$		$(\text{ClSiH}_2)_3\text{N}$		Assignment
Frequency in cm^{-1}	Pol. Ratio	Frequency in cm^{-1}	Pol. Ratio	Frequency in cm^{-1}	Pol. Ratio	
2180 vvs,br	p	2216+2 vs	p	2220 vs	p	ν SiH
998 s	p	996 w	p	1000 vw	dp	ν SiN(asym)
946 vs,br	dp	970 w	dp	945 w	dp?	} δ SiH ₃ and/or SiH ₂
		943 m	dp			
880 w	dp?	907 w	dp	878+2 w	dp?	
		870 vw,br	dp			
747+2 m	dp	745 s	dp	745 m	dp	} ρ SiH ₃ and/or SiH ₂
702 s	dp	628 vw	dp			
548 m	dp	580 s	p?	585 s	p	ν SiCl(asym)
		536 m	dp	550 m	dp	ν SiCl(sym)
490 vvs	p	480 vs	p	482 vs	p	ν SiN(sym)
285 m	p?	358 w	dp	322 s	dp	SiNSi bend?
		230 m	dp	278 m	dp	ClSiN bend (asym)
190 w,br	dp	160 s	p	140 s	p?	ClSiN bend (sym)

Where ν = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad
 p = polarised and dp = depolarised.

CHAPTER SIX

REACTION OF SILYL-TRANSITION-METAL-
-CARBONYL COMPOUNDS WITH
STANNIC CHLORIDE.

CHAPTER SIXReaction of silyl-transition-metal-carbonyl compounds with stannic chloride.6.1 INTRODUCTION

This chapter describes a study of reactions of stannic chloride with silylpentacarbonylmanganese and silyltetracarbonylcobalt. Aylett and Campbell studied the reaction of HCl with $\text{SiH}_3\text{Mn}(\text{CO})_5$ ⁵⁰ and $\text{SiH}_3\text{Co}(\text{CO})_5$ ⁵¹. A mixture of monochloro- and dichloro- derivatives was obtained by the reaction of $\text{SiH}_3\text{Mn}(\text{CO})_5$ with HCl at 75°C for 15 minutes and only $\text{Cl}_2\text{SiH.Mn}(\text{CO})_5$ was obtained under the same condition when the reaction was carried out for 30 minutes. The published infrared spectral data for $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$ in the region 1000 - 700 cm^{-1} was not correct due to the impossible fractionation of the monochloro-species from the dichloro-species. Pure $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$ was obtained by the reaction of SnCl_4 with $\text{SiH}_3\text{Mn}(\text{CO})_5$ and the partial characterisation of this compound is reported in this chapter.

The Si-Co bond in $\text{SiH}_3\text{Co}(\text{CO})_4$ was broken by SnCl_4 to give SiH_3Cl , SnCl_2 and $\text{ClCo}(\text{CO})_4$.

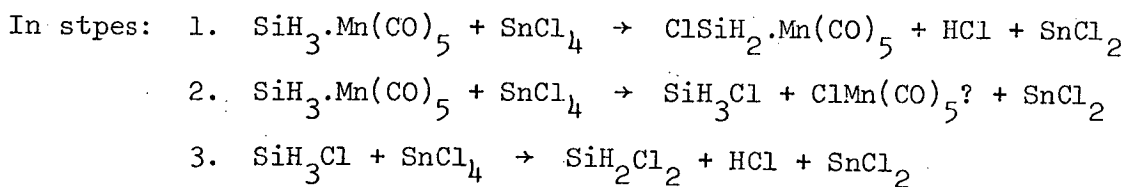
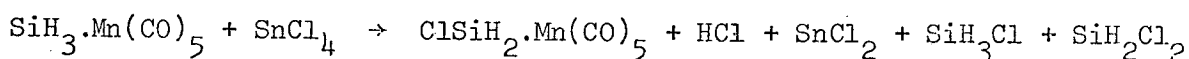
6.2:1 The reaction of silylpentacarbonylmanganese with stannic chloride.

Pure silylpentacarbonylmanganese (1m mole, 0.22 gm) and stannic chloride (1.06m moles, 0.28 gm) were condensed into a 45ml reaction ampoule and allowed to warm to room temperature. A white, thin film on the inner walls of the reaction ampoule began to form almost

immediately and the reaction appeared complete in 25 minutes at this temperature.

Trap-to-trap distillation of the remainder gave hydrogen chloride (1.04m moles) volatile at -130° , silyl chloride (0.1m mole) volatile at -120° , dichlorosilane (0.04m mole) volatile at -78° , and $\text{ClSiH}_2\text{Mn}(\text{CO})_5$ (0.82m mole, 0.213 gm) was left. $\text{HMn}(\text{CO})_5$ and $\text{Cl}_2\text{SiH.Mn}(\text{CO})_5$ were not detected among the products. The stannic chloride was quantitatively reduced to stannous chloride, an involatile white solid which remained in the reaction ampoule.

An increase in proportion of stannic chloride to a 1:3 ratio of reactants has no influence on the reaction, since neither $\text{Cl}_2\text{SiH.Mn}(\text{CO})_5$ nor any other products of decomposition were detected among the products. The reaction between silylpentacarbonylmanganese and stannic chloride may be expressed by the equation:



Steps 2 and 3 can be regarded as side reactions.

Although $\text{ClSiH}_2\text{Mn}(\text{CO})_5$ has been prepared by Aylett et al, an attempt will be made in this chapter to describe the characteristic of this molecule in more detail.

6.2:2 Nuclear magnetic resonance spectra.

Proton n.m.r. of $\text{ClSiH}_2\text{Mn}(\text{CO})_5$

TMS was used as solvent and reference standard.

Chemical shift: Singlet at 4.60 ± 0.01 T

$$^1J(\text{H}^{29}\text{Si}) = 215.0 \pm 2.0 \text{ Hz.}$$

6.2:3 Mass spectrum.

Exact mass of parent ions:

	Calculated	Measured	Error
$^{35}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{ } ^{55}\text{Mn}_1 (\text{C}^{16}\text{O})_5$	259.874102	259.874050	0.2 p.p.m.
$^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_1 \text{H}_2 \text{ } ^{55}\text{Mn}_1 (\text{C}^{16}\text{O})_5$	261.871152	261.871100	less than 0.2 p.p.m.

6.2:4 Infrared and Raman spectra.

The observed infrared and Raman spectra for $\text{ClSiH}_2\text{.Mn(CO)}_5$ may be found in Table 20. The assignments of these spectra have been justified in the discussion (6.4)

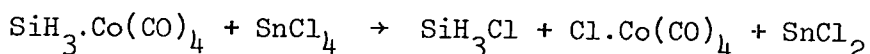
6.3 The reaction of silyltetracarbonylcobalt with stannic chloride.

Pure silyltetracarbonylcobalt (1.14m mole, 0.23 gm) and stannic chloride (1.2m moles, 0.313 gm) were condensed into a 45 ml reaction ampoule and allowed to warm to room temperature. A yellowish white solid began to form almost immediately and the reaction appeared complete in 5 minutes at this temperature.

Trap-to-trap distillation of the volatile product gave SiH_3Cl (1.14m moles) volatile at -78° and unreacted stannic chloride (0.04m mole) was left. The remaining unreacted stannic chloride was dissolved in grease of the vacuum line joints; no $\text{ClSiH}_2\text{.Co(CO)}_4$ nor HCo(CO)_4 was detected among the products. The involatile solid remained in the reaction ampoule.

C_6D_6 was added to the involatile yellowish white solid. SnCl_2 (insoluble in C_6D_6) was separated by filtration; the orange filtrate contained Cl.Co(CO)_4 , and the solvent C_6D_6 was removed by vacuum distillation to give an orange crystalline solid. The infrared spectrum of this solid in nujol was consistent with the published i.r. spectrum for Cl.Co(CO)_4 ; ⁵²

The reaction between silyltetracarbonylcobalt and stannic chloride may be expressed by the equation:



6.4 DISCUSSION

The reaction of stannic chloride with silylpentacarbonylmanganese gave only $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$ in contrast to the reaction of HCl with $\text{SiH}_3.\text{Mn}(\text{CO})_5$. This is in keeping with the behaviour of stannic chloride as a selective chlorinating agent. The HCl and SnCl_2 produced during the reaction have no influence on the chlorination at room temperature. Formation of a small quantity of SiH_3Cl may be due to the instability of Si-Mn bond in $\text{SiH}_3.\text{Mn}(\text{CO})_5$ towards cleavage by SnCl_4 giving SnCl_2 and $\text{ClMn}(\text{CO})_5$ in addition to SiH_3Cl , and the formation of very small quantity of SiH_2Cl_2 may be due to the chlorination of SiH_3Cl with the excess SnCl_4 present in the system. The attempted detection of $\text{ClMn}(\text{CO})_5$ among large excess of SnCl_2 produced during the reaction was unsuccessful.

The reaction of HCl with $\text{SiH}_3.\text{Co}(\text{CO})_4$ gave SiH_3Cl and $\text{HCo}(\text{CO})_4$. Similarly, with SnCl_4 , $\text{SiH}_3.\text{Co}(\text{CO})_4$ gave SiH_3Cl , $\text{ClCo}(\text{CO})_4$ and SnCl_2 . This may be due to the instability of Si-Co bond in $\text{SiH}_3.\text{Co}(\text{CO})_4$ towards HCl and SnCl_4 .

Although $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$ and $\text{Cl}_2\text{SiH}.\text{Mn}(\text{CO})_5$ were obtained by the reaction of HCl with $\text{SiH}_3.\text{Mn}(\text{CO})_5$ at 75° for 15 minutes, Aylett and Campbell were unable to isolate pure $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$. The i.r. bands given by them in the region $1000 - 700 \text{ cm}^{-1}$ were at 945m , 838 vs , 730 s which are not the same frequencies observed in this study.

For the first time, pure $\text{ClSiH}_2.\text{Mn}(\text{CO})_5$ was obtained by the

reaction of SnCl_4 with $\text{SiH}_3\cdot\text{Mn}(\text{CO})_5$. The measured exact mass for the parent ions was consistent with the calculated exact mass for the parent ions of $\text{ClSiH}_2\cdot\text{Mn}(\text{CO})_5$ within 0.2 p.p.m.

Nuclear magnetic resonance spectrum showed a singlet at 4.6 T with ^{29}Si satellites, and coupling constant $^1J(\text{H}^{29}\text{Si}) = 215$ Hz, which is typical of ClSiH_2 - compounds.

The compound $\text{ClSiH}_2\cdot\text{Mn}(\text{CO})_5$ is a liquid at room temperature with a very low vapour pressure. This colourless liquid changes to yellow at room temperature after a few minutes in light. Although it was possible to obtain a Raman spectrum the attempted Raman polarisation study was unsuccessful due to the change in colour of the sample in the laser beam. The observed Raman intensities are not significant, due to the absorption of blue laser by the yellow liquid.

The vibrational assignments for $\text{ClSiH}_2\cdot\text{Mn}(\text{CO})_5$ have been made by comparison with those published for $\text{SiH}_3\cdot\text{Mn}(\text{CO})_5$.

The Si-H (2130 cm^{-1} in i.r. and 2160 cm^{-1} in Raman), C-O ($2098, 2015$ and 1985 cm^{-1} in i.r. and $2070, 2040$ and 2020 cm^{-1} in Raman), and Si-Cl (512 cm^{-1} in i.r. and 540 cm^{-1} in Raman) stretching modes appear in the expected regions. The Mn-C stretching may also be readily assigned at 468 cm^{-1} in the i.r. and 460 cm^{-1} in the Raman spectra. The band at 302 cm^{-1} in the Raman spectrum may be assigned to the Si-Mn stretching mode. The Mn-CO deformation appears at 666 cm^{-1} in the case of $\text{SiH}_3\cdot\text{Mn}(\text{CO})_5$; the bands at 654 cm^{-1} in the infrared and 660 cm^{-1} in the Raman spectra of the chloro-compound may therefore be assigned as Mn-CO deformation. The remaining two bands at 948 and 835 cm^{-1} in the i.r. and 950 and 840 cm^{-1} in the Raman spectra are in the expected regions for SiH_2 -deformations.

TABLE 20

Infrared and Raman spectra of $\text{ClSiH}_2\text{Mn(CO)}_5$

Vapour		Liquid		
I.R. Frequency in cm^{-1}	Infrared Intensity	Raman Frequency in cm^{-1}	Raman Intensity	Tentative Assignments
2130	w	2160	s, broad	v SiH
2098	m	2070	vs, broad	} v CO
		2040	sh	
2015	vs	2020	sh	
1985	vw			
948	m	950	vw, broad	δ SiH ₂
835	m	840	vvw, broad	δ SiH ₂
654	s	660	w, broad	δ CO
512	w	540	vw, broad	v SiCl
468	vw	460	vvw, broad	v MnC
-	-	302	w	v SiMn

where s = strong, m = medium, w = weak

v = very and sh = shoulder

CHAPTER SEVEN

PREPARATION AND CHLORINATION
OF TRIMETHYLSILYLSILANE.

CHAPTER SEVENPreparation and chlorination of trimethylsilylsilane7.1 INTRODUCTION

This chapter describes a new method of preparing $\text{Me}_3\text{Si}\cdot\text{SiH}_3$ and its reactions with stannic chloride. The preparation of trimethylsilylsilane by a coupling reaction between SiH_3K and Me_3SiCl has been reported by Amberger et al⁵³; the yield was very low and the characterisation of this compound was not reported in detail. From the reaction of solid bis(trimethylsilyl)mercury with silyl bromide, a quite high yield of $\text{Me}_3\text{Si}\cdot\text{SiH}_3$ was obtained. The reaction of $\text{Me}_3\text{Si}\cdot\text{SiH}_3$ with stannic chloride gave the new compounds, $\text{Me}_3\text{Si}\cdot\text{SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si}\cdot\text{SiHCl}_2$. The partial characterisations of $\text{Me}_3\text{Si}\cdot\text{SiH}_3$, $\text{Me}_3\text{Si}\cdot\text{SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si}\cdot\text{SiHCl}_2$ are reported in this chapter.

7.2:1 The preparation of trimethylsilylsilane

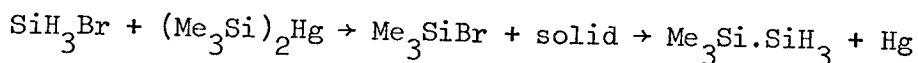
Silyl bromide (3m moles) was condensed in a 100ml reaction ampoule containing the yellow crystalline solid bis(trimethylsilyl)mercury ($\sim 10\text{m}$ moles, 3.5 gm) and allowed to warm to room temperature. The yellow solid immediately changed to yellowish-green. After 30 minutes at this temperature the reaction was stopped and all the volatile products were removed from the ampoule.

Trap-to-trap distillation of the volatile products gave SiH_4 (0.1m mole) volatile at -130° , Me_3SiH (0.05m mole) volatile at -120° , unreacted SiH_3Br (0.3m mole) volatile at -78° and Me_3SiBr (2.5m moles) involatile at -78° . The yellow residue with some mercury globules remained in the ampoule. After 18 hours at room

temperature this residue gave $\text{Me}_3\text{Si.SiH}_3$ (1m mole) involatile at -96° but volatile at -78° , Me_3SiBr (0.015m mole) and Me_3SiH (0.06m mole). More $\text{Me}_3\text{Si.SiH}_3$ (0.5m mole) was obtained from the same ampoule after 48 hours at room temperature. Thus the trimethylsilylsilane was evolved over a period of days from the yellow residue. The rate of formation of additional $\text{Me}_3\text{Si.SiH}_3$ decreased with an increase in time. The total quantity of $\text{Me}_3\text{Si.SiH}_3$ evolved from the yellow residue after 7 days

= 2.0 m moles.

The initial reaction products SiH_4 ⁵⁴, Me_3SiH ⁵⁵, and Me_3SiBr ⁵⁶ were identified by comparison of the observed and published infrared spectra. The reaction between silyl bromide and bis(trimethylsilyl) mercury may be expressed by the equation:



In steps:

1. $\text{SiH}_3\text{Br} + (\text{Me}_3\text{Si})_2\text{Hg} \rightarrow \text{Me}_3\text{SiBr} + \text{solid}$
2. $\text{Solid} \rightarrow \text{Me}_3\text{Si.SiH}_3 + \text{Hg}$

Since the detailed characterisation of $\text{Me}_3\text{Si.SiH}_3$ was not reported⁵³, an attempt will be made in this chapter to describe the characterisation of this molecule in more detail.

7.2:2 Nuclear magnetic resonance spectra.

Proton n.m.r. of $\text{Me}_3\text{Si.SiH}_3$

Benzene was used as solvent and reference standard.

¹H Chemical Shifts in ppm

T (SiH_3)	T (Me_3Si)
6.79(singlet)	9.93(singlet)

The ratio of integration = 1 : 3

Coupling Constants in Hz.

$$\begin{aligned}
 {}^1J(\text{H}^{29}\text{Si}) &= 182.0 & {}^2J(\text{HC}^{29}\text{Si}) &= 5.4 \\
 {}^2J(\text{HSi}^{29}\text{Si}) &= 6.0 & {}^3J(\text{HCSi}^{29}\text{Si}) &= 3.0 \\
 & & {}^1J(\text{H}^{13}\text{C}) &= 119.0 \pm 1
 \end{aligned}$$

^{29}Si and ^{13}C Chemical Shifts " δ " in ppm relative to Me_4Si (-ve to low frequency).

1. $\text{Me}_3^{28}\text{Si} \cdot {}^{29}\text{SiH}_3$ = -98.2
corrected ^{29}Si frequency = 19.865232 MHz.
2. $\text{Me}_3^{29}\text{Si} \cdot {}^{28}\text{SiH}_3$ = -17.42
corrected ^{29}Si frequency = 19.866837 MHz.
3. $(^{13}\text{CH}_3)_3\text{Si} \cdot \text{SiH}_3$ = +6.0
corrected ^{13}C frequency = 25.145146 MHz.

7.2:3 Mass spectrum

Exact mass of parent ions:

	Calculated	Measured	Error
$^{28}\text{Si}_2^{12}\text{C}_3\text{H}_{12}$	104.047753	104.047851	less than 1 ppm

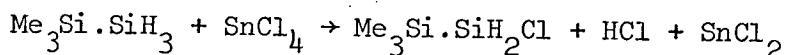
7.2:4 Infrared and Raman spectra.

The observed infrared and Raman spectra for $\text{Me}_3\text{Si} \cdot \text{SiH}_3$ may be found in table 21. The possible assignments of these spectra have been described in the discussion (7.5).

7.3:1 The reaction of trimethylsilylsilane with stannic chloride

Trimethylsilylsilane (1m mole) and stannic chloride (0.96m mole, 0.258 gm) were condensed in a 20ml reaction ampoule and allowed

to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form almost immediately and the reaction was complete in 5 minutes. Trap-to-trap distillation of the volatile products gave HCl (0.96m mole) volatile at -120° , unreacted $\text{Me}_3\text{Si.SiH}_3$ (0.04m mole) volatile at -78° , and $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ (0.96m mole) involatile at -78° . The stannous chloride (0.96m mole, 0.188 gm) produced during the reaction remained in the ampoule. The reaction between trimethylsilylsilane and stannic chloride may be expressed by the equation:



Since trimethylsilylchlorosilane ($\text{Me}_3\text{Si.SiH}_2\text{Cl}$) is a new compound, an attempt will be made in this chapter to describe the partial characterisation of this molecule in more detail.

7.3:2 Nuclear magnetic resonance spectra.

Proton n.m.r. of $\text{Me}_3\text{Si.SiH}_2\text{Cl}$

Benzene was used as solvent and reference standard.

^1H Chemical Shifts in ppm

T (SiH_2)	T (Me_3Si)
5.34(singlet)	9.98(singlet)

The ratio of integration = 1 : 4.5

Coupling Constants in Hz

$^1\text{J}(\text{H}^{29}\text{Si})$	= 204.0 \pm 1	$^2\text{J}(\text{HC}^{29}\text{Si})$	= 6.6
$^2\text{J}(\text{HSi}^{29}\text{Si})$	= 11.0	$^3\text{J}(\text{HCSi}^{29}\text{Si})$	= 3.8
		$^1\text{J}(\text{H}^{13}\text{C})$	= 120.0 \pm 1

^{29}Si and ^{13}C Chemical Shifts " δ " in ppm relative to Me_4Si (-ve to low frequency)

1	$\text{Me}_3^{28}\text{Si} \cdot ^{29}\text{SiH}_2\text{Cl}$	=	-30.75
	corrected ^{29}Si frequency	=	19.866572 MHz
2	$\text{Me}_3^{29}\text{Si} \cdot ^{28}\text{SiH}_2\text{Cl}$	=	-15.7
	corrected ^{29}Si frequency	=	19.866871 MHz
3	$(^{13}\text{CH}_3)_3\text{Si} \cdot \text{SiH}_2\text{Cl}$	=	-5.52
	corrected ^{13}C frequency	=	25.144856 MHz

7.3:3 Mass spectrum

Exact mass of parent ions:

	Calculated	Measured	Error
$^{35}\text{Cl}_1^{28}\text{Si}_2\text{C}_3\text{H}_{11}$	138.008782	138.008335	less than 3 ppm
$^{37}\text{Cl}_1^{28}\text{Si}_2\text{C}_3\text{H}_{11}$	140.005832	140.006094	less than 2 ppm

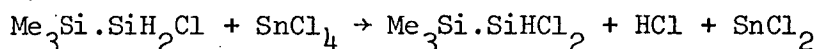
7.3:4 Infrared and Raman spectra

The observed infrared and Raman spectra for $\text{Me}_3\text{Si} \cdot \text{SiH}_2\text{Cl}$ may be found in table 22. The possible assignments of these spectra have been described in the discussion (7.5).

7.4:1 The reaction of trimethylsilylchlorosilane with stannic chloride.

Trimethylsilylchlorosilane (1m mole) and stannic chloride ($\sim 1.03\text{m}$ moles, 0.27 gm) were condensed in a 20 ml reaction ampoule and allowed to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form almost immediately and the reaction was complete in 18 hours. Trap-to-trap distillation of the volatile products gave HCl (1m mole) volatile at -78° ,

and $\text{Me}_3\text{Si.SiHCl}_2$ (1m mole) involatile at -78° . The stannous chloride (1m mole, 0.19 gm) produced during the reaction, remained in the ampoule. Since there was no recovery of SnCl_4 , the remaining might have been dissolved in the grease of the vacuum line joints. The reaction between trimethylsilylchlorosilane and stannic chloride may be expressed by the equation:



7.4:2 Nuclear magnetic resonance spectra

Proton n.m.r. of $\text{Me}_3\text{Si.SiHCl}_2$

Benzene was used as solvent and reference standard.

^1H Chemical Shift in ppm

T (SiH)	T (Me_3Si)
4.42(singlet)	10.01(singlet)

The ratio of integration = 1 : 9

Coupling Constants in Hz

$^1\text{J}(\text{H}^{29}\text{Si}) = 235.0 \pm 1$	$^2\text{J}(\text{HC}^{29}\text{Si}) = 7.0$
$^2\text{J}(\text{HSi}^{29}\text{Si}) = 18.8$	$^2\text{J}(\text{HCSi}^{29}\text{Si}) = 5.0$
	$^1\text{J}(\text{H}^{13}\text{C}) = 121.0 \pm 1$

^{29}Si and ^{13}C Chemical Shifts " δ " in ppm relative to Me_4Si (-ve to low frequency)

1 $\text{Me}_3^{28}\text{Si}^{29}\text{SiHCl}_2$	= +12.08
corrected ^{29}Si frequency	= 19.867422 MHz
2 $\text{Me}_3^{29}\text{Si}^{28}\text{SiHCl}_2$	= -6.54
corrected ^{29}Si frequency	= 19.867053 MHz

$$3 \text{ } (^{13}\text{CH}_3)_3\text{Si.SiHCl}_2 = -3.78$$

$$\text{corrected } ^{13}\text{C frequency} = 25.144900 \text{ MHz.}$$

7.4:3 Mass spectrum

Exact mass of parent ions

	Calculated	Measured	Error
$^{35}\text{Cl}_2 \text{ } ^{28}\text{Si}_2 \text{ } ^{12}\text{C}_3 \text{ } ^1\text{H}_{10}$	171.969810	171.969783	less than 1 ppm
$^{35}\text{Cl}_1 \text{ } ^{37}\text{Cl}_1 \text{ } ^{28}\text{Si}_2 \text{ } ^{12}\text{C}_3 \text{ } ^1\text{H}_{10}$	173.966854	173.966723	less than 1 ppm
$^{37}\text{Cl}_2 \text{ } ^{28}\text{Si}_2 \text{ } ^{12}\text{C}_3 \text{ } ^1\text{H}_{10}$	175.963910	175.964341	less than 3 ppm

7.4:4 Infrared and Raman spectra

The observed infrared and Raman spectra for $\text{Me}_3\text{Si.SiHCl}_2$ may be found in table 23. The possible assignments of these spectra have been described in the discussion (7.5)

7.5 DISCUSSION

During the reaction of silyl bromide with bis(trimethylsilyl) mercury (7.2:1), after 30 minutes at room temperature, a very small quantity of Si-H compounds was produced in addition to Me_3SiBr . But most of the Si-H compounds remained in the yellowish-green residue. The evolution of $\text{Me}_3\text{Si.SiH}_3$ (1m mole) from the yellowish-green residue and the occurrence of mercury (Hg) deposits at the bottom of the reaction ampoule after 18 hours at room temperature suggest that the reaction between $(\text{Me}_3\text{Si})_2\text{Hg}$ and SiH_3Br is through an intermediate compound, $\text{Me}_3\text{SiHgSiH}_3$. This residue further evolved $\text{Me}_3\text{Si.SiH}_3$ at room temperature over a period of days and this suggests that the intermediate compound, $\text{Me}_3\text{SiHgSiH}_3$ is fairly stable

in vacuum at room temperature. The evolution of $\text{Me}_3\text{Si.SiH}_3$ after 18 hours was not in large quantity. Therefore at room temperature, the quantity of evolution of $\text{Me}_3\text{Si.SiH}_3$ is dependent upon time. In other words, the rate of formation of $\text{Me}_3\text{Si.SiH}_3$ decreases with an increase in time. However, the above reaction is proved to be the best method of preparing $\text{Me}_3\text{Si.SiH}_3$ as the yield is quite high in contrast to the method reported by Amberger et al.⁵³

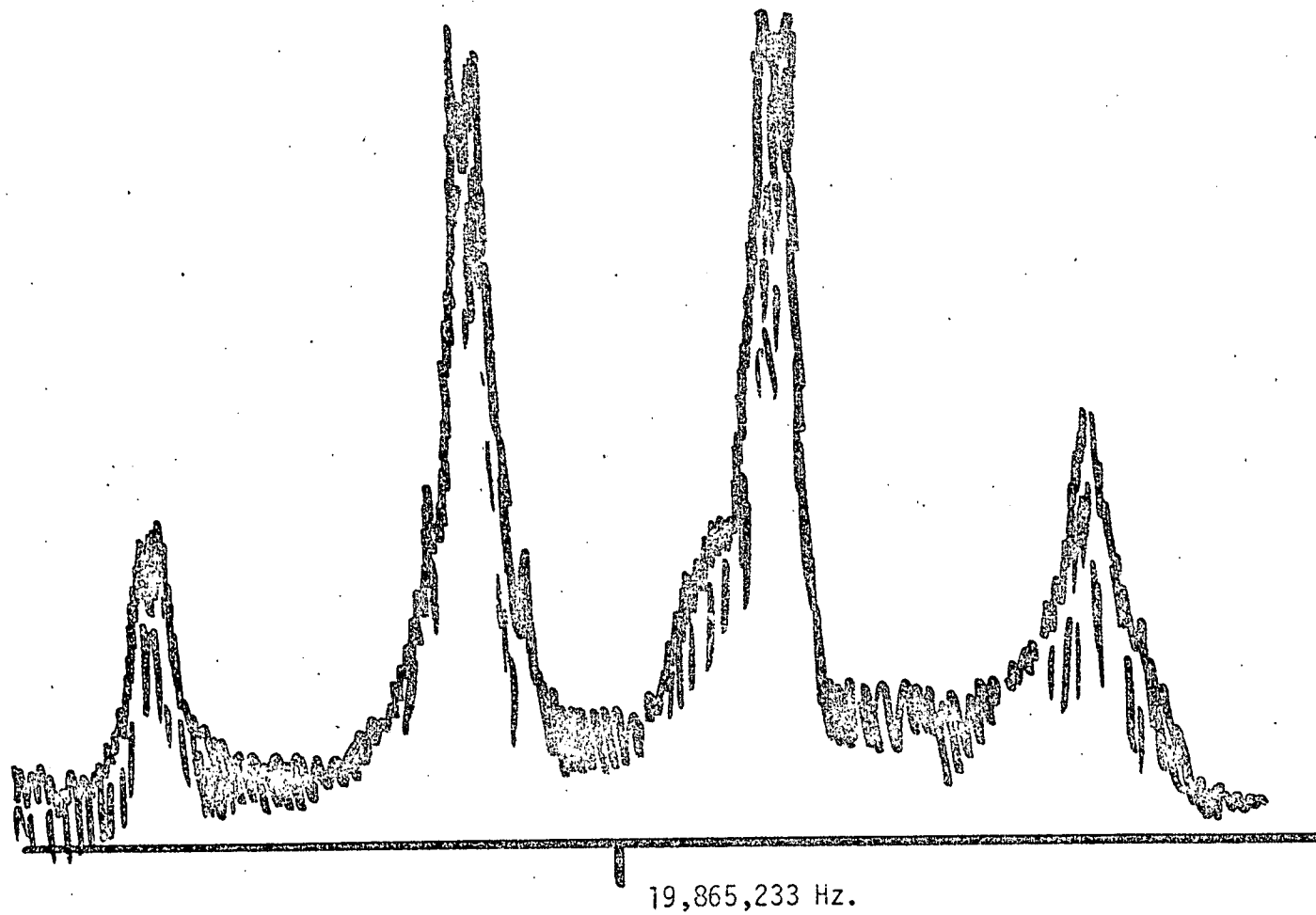
The existence of the above intermediate compound, $\text{Me}_3\text{SiHgSiH}_3$ was proved by its ^{199}Hg and ^{29}Si INDOR spectra which will be discussed in the second part of this thesis (chapter nine).

Although $\text{Me}_3\text{Si.SiH}_3$ has been prepared and identified by Amberger et al,⁵³ an attempt has been made here to describe the characterisation and chlorination of this molecule in more detail. From the reaction of trimethylsilylsilane with stannic chloride, the new compounds, $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si.SiHCl}_2$ were obtained. Each of these new compounds was characterised by proton n.m.r., hetero nuclear double resonance (for ^{29}Si and ^{13}C), mass, infrared and Raman spectroscopy.

The mass spectra showed exact masses of the parent ions of trimethylsilylsilane and the chlorinated trimethylsilylsilanes, which are consistent with the calculated masses, within the allowed error.

The proton n.m.r. spectra demonstrate the presence of two sets of protons in $\text{Me}_3\text{Si.SiH}_3$, $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si.SiHCl}_2$; coupling between SiH and CH protons was not detected. The ratio of integration indicates the relative number of protons in each set. The ^{29}Si INDOR spectrum of $\text{Me}_3\text{Si.SiH}_3$ (Fig 5.5) showed a quartet which proves the presence of one $-\text{SiH}_3$ group in the expected region published for other disilyl compounds.³³ The proton chemical shift and coupling

FIGURE 5.5 ^{29}Si INDOR SPECTRUM OF $\text{Me}_3\text{Si}\cdot^{29}\text{SiH}_3$



constants of $\text{Me}_3\text{Si}^{29}\text{SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si}^{29}\text{SiHCl}_2$ are in the expected regions published for other $-\text{SiH}_2\text{Cl}$ and $-\text{SiHCl}_2$ compounds.³³

The hetero nuclear double resonance technique (chapter eight) was used to obtain the ^{29}Si and ^{13}C chemical shifts for $\text{Me}_3\text{Si.SiH}_3$, $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si.SiHCl}_2$. The measured chemical shifts and coupling constants prove the presence of two types of Si atoms and one type of carbon atom in each of the above molecules. These results are consistent with the compounds being $\text{Me}_3\text{Si.SiH}_3$, $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si.SiHCl}_2$.

The formulations of the compounds as $\text{Me}_3\text{Si.SiH}_3$, $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si.SiHCl}_2$ is consistent with their observed vibrational spectra which have been assigned by comparison with the published vibrational spectra for other Me_3Si species.^{55,56,57}

The C-H, Si-H, Si-C, Si-Cl and Si-Si stretching modes and CH_3 deformations appear in the expected regions and most of these bands in the Raman spectra are polarised (tables 21, 22 and 23). The bands near 900 cm^{-1} in $\text{Me}_3\text{Si.SiH}_3$, near 875 cm^{-1} in $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and near 775 cm^{-1} in $\text{Me}_3\text{Si.SiHCl}_2$ may be due to CH_3 rocking. The bands in the region $990-930\text{ cm}^{-1}$ in $\text{Me}_3\text{Si.SiH}_3$ at 940 and 805 cm^{-1} in $\text{Me}_3\text{Si.SiH}_2\text{Cl}$ and in the region $915-850\text{ cm}^{-1}$ in $\text{Me}_3\text{Si.SiHCl}_2$ may be assigned as SiH_3 , SiH_2 and SiH deformations respectively. The bands in the region $380-150\text{ cm}^{-1}$ may be due to C_3Si and ClSiC bending modes.

TABLE 21.

Raman and Infrared spectra of $\text{Me}_3\text{Si.SiH}_3$

Liquid		Vapour	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignments
2965 _{±2} s	dp	2965 m	} v CH
2900 vs	p	2900 w	
2800 vvw	?		
2130 _{±2} vvs	p	2131 s	v SiH
1440 vw	?		} δ CH ₃ (asym)
1410 m	dp	1410 vw	
		1328 vvw	
		1262 m	} δ CH ₃ (sym)
1260 m	p?		
1250 _{±2} sh	p?		
		1078 vw	?
1055 vvw	p?		?
		993 w	} δ SiH ₃
990 vvw	dp?		
930 s	dp	931 m	
898 m	p?	900 m	} ρ CH ₃
830 m, br	dp?	840 vvs	
750 m	dp	760 m	ρ SiH ₃
698 vs	dp	695 m	v SiC
625 vvs	p	630 m	v SiC
498 _{±1} m	dp	492 m	?
475 s	p		?
410 vvs	p	410 w	v Si-Si
383 sh	p?	385 vw	} δ C ₃ Si
220 vvs	p?	-	
145 _{±2} vs	dp?	-	

where s = strong, m = medium, w = weak, sh = shoulder, br = broad
and v = very

TABLE 22

Raman and Infrared spectra of $\text{Me}_3\text{Si.SiH}_2\text{Cl}$

Liquid		Vapour	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignment
2970 s	dp	2958+1 m	} v CH
2910 s	p	2900 w 2860 vvw	
2140+2 vs	p	2138+1 s	v SiH
1410 w,br	dp	1410 w,br	} δCH_3 (asym) ?
		1325+ vvw	
1265 w	p?	1262 m	} δCH_3 (sym)
1252 w	dp		
940 m,br	dp	945+2 w,br	δSiH_2
870 sh			} ρCH_3
845 vw,br	dp	845 s,br	
805+2 vw	p?	802+2 vs	δSiH_2
755 vw	dp	743 w	$\rho \text{SiH}_2?$
702 s	dp	698 w	v SiC
630 vs	p	620 w	v SiC
525+2 m,br	dp?	530+1 m	v SiCl
478 m	p	490 vvw	?
418 vvs	p	405 vvw	v Si-Si
223 vs	dp	-	} $\delta \text{C}_3\text{Si}$
180 s	p?	-	
150 s	dp?	-	

where s = strong, m = medium, w = weak, sh = shoulder, br = broad
and v = very

TABLE 23

Raman and Infrared spectra of $\text{Me}_3\text{Si.SiHCl}_2$

Liquid		Vapour	
Raman Frequency in cm^{-1}	Raman Polarisation Ratio	Infrared Frequency in cm^{-1}	Possible Assignments
2965 m	dp	2968 \pm 2 w	} v CH
2902 s	p	2910 \pm 2 vw	
		2850 vvw	
2170 vs	p	2171 \pm 2 m	v SiH
1415 \pm 5 vw, br	dp	1405 vvw	δ CH ₃ (asym)
1250 \pm 5 vw, br	dp	1258 m	δ CH ₃ (sym)
1055 vvw	dp?		?
915 vvw, br	dp?		
		} 865 sh	δ SiH
850 \pm 5 vw, br	dp?		
775 w	dp	778 s	ρ CH ₃
738 m	dp	734 m	ρ SiH
702 w	dp	704 sh	v SiCl
625 vs	p	622 vw	v SiCl
542 sh	dp?	558 s	v SiCl(asym)
525m	p?	532 m	v SiCl(sym)
392 vvs	p	395 vvw	v Si-Si
258 m	dp?	-	?
215 s	dp?	-	} δ C ₃ Si
178 m	dp?	-	
152 s	dp?	-	
095? vw	p?	-	ClSiSi bend
			ClSiCl bend?

where s = strong, m = medium, w = weak, sh = shoulder, br = broad
and v = very

REFERENCES

1. T.N.Srivastava and M. Onyszchuk, Can. J. Chem., 40, 579 (1962).
K.M. Mackay and P.J. Roebuck, J. Chem. Soc., 1195 (1964).
2. F. Feher, P. Plichta and R. Guillery, Inorg. Chem., 10,
606 (1971).
3. L.M. Dennis and P.R. Judy, J. Amer. Chem. Soc., 51, 2321 (1929).
4. J.E. Drake and N. Goddard, Inorg. Nucl. Chem. Letters; 4,
385 (1968).
5. K.M. Mackay, P. Robinson, E.J. Spanier and A.G. MacDiarmid,
J. Inorg. Nucl. Chem., 28, 1377 (1966).
6. C. Riddle, Personal Communication.
7. J.E. Bentham, S. Cradock and E.A.V. Ebsworth, Inorg. Nucl. Chem.
Letters, 7, 1077 (1971).
8. N.S. Hosmane, S. Cradock and E.A.V. Ebsworth to be published.
9. G.W. Bethke and M.K. Wilson, J. Chem. Phys., 26, 1107 (1957).
10. D. Kummer and G. Fritz, Z. Anorg. Chem., 308, 105 (1961).
11. E.A.V. Ebsworth et al., Spectrochim. Acta, 13, 202 (1958).
12. E.A.V. Ebsworth and S. Cradock, J.C.S., 885 (1967).
13. D.W. Robinson and R.B. Reeves, J. Chem. Phys., 37, 2625 (1962).
14. D.W.W. Anderson, Ph.D. Thesis, Edinburgh 1973.
15. S.G. Frankiss, Spectrochim. Acta, 22(A), 295 (1966).
16. A.P. Hagen and P.J. Russo, Inorg. Nucl. Chem. Letters, 6, 507
(1970).
17. W.J. Savage, Personal Communication.
18. H.F. Angus, S. Cradock, E.A.V. Ebsworth and C. Glidewell,
Inorg. Nucl. Chem. Letters, 5, 717 (1969).

19. E. Amberger and H. Boeters, *Angew. Chemie. Int. Edit.*, 1, 52 (1962).
20. E.A.V. Ebsworth and C. Glidewell, *Spectrochim. Acta*, 22, 67, (1966).
21. J.C. Thompson, Ph.D. Thesis, Cambridge 1965.
22. B.J. Aylett and J.M. Campbell, *J.C.S. (A)*, 1916 (1969).
 ibid., page 1910
23. A.G. MacDiarmid; 'Preparative inorganic reactions' ed. W.L. Jolly (Wiley Interscience, New York, 1964).
24. E. Wiberg, O. Stecher, H.J. Andrascheck, L. Kreuzbichler and E. Staude, *Angew. Chem. Intern. Ed.* 2, 507 (1963)
25. J.M. Van den Berg, *Acta Cryst.*, 14, 1002 (1961).
 R.E. Rundle and D.H. Olson *Inorg. Chem.*, 3, 596 (1964).
26. M.C. Tobin, *J. Amer. Chem. Soc.*, 75, 1788 (1953).
27. A.L. Smith and N.C. Angelotti, *Spectrochim. Acta*, 15, 412 (1959).
28. E.A.V. Ebsworth, M. Onyszchuk and N. Sheppard, *J.C.S.*, 1453 (1958).
29. (a) C. Newman, J.K. O'Loane, S.R. Polo and M.K. Wilson, *J. Chem. Phys.*, 25, 855 (1956).
 (b) J.A. Hawkins and M.K. Wilson, *J. Chem. Phys.*, 21, 360 (1953).
30. R.P. Hollandsworth and M.A. Ring, *Inorg. Chem.*, 7, No.8, 1635 (1968).
31. S. Craddock, E.A.V. Ebsworth and A.G. Robiette, *Trans. Faraday Soc.*, 60, 1502 (1964).
32. E.G. Rochow, *Comprehensive Inorganic Chemistry*, Vol.1 (Pergamon Press, Oxford, 1973), p.1370.
33. B.J. Aylett, *Advances in Inorganic Chemistry and Radiochemistry* 11, 266 (1968).

34. C. Newman, J.K. O'Loane, S.R. Polo and M.K. Wilson, *J. Chem. Phys.*, 25, 855 (1956).
35. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p.318.
36. Badger and Zumwalt, *J. Chem. Phys.*, 6, 711 (1938).
37. C.J. Pouchert, *The Aldrich Library of Infrared Spectra* (Aldrich Chemical Co., Inc. 1970), page 50(F).
38. R.A. Whiteford, Ph.D. Thesis, Edinburgh (1973).
39. R.A. Whiteford, Ph.D. Thesis, Edinburgh (1973).
40. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, (D. Van Nostrand Co., New York 1945), p.364.
41. G.M. Kislyak, *Izvest. Akad. Nauk SSSR, Ser. Chim.*, 1133 (1960).
42. (a) E.A.V. Ebsworth, *Volatile Silicon Compounds*, Pergamon Press, London and Macmillan Co., N.Y. (1963).
(b) E.G. Rochow, *An Introduction to the Chemistry of the Silicones*, 2nd ed., Wiley, N.Y., (1951).
43. E.A.V. Ebsworth, S.G. Frankiss, and W.J. Jones, *J. Mol. Spectroscopy*, 13, 9 (1964).
44. D.W.W. Anderson, Ph.D. Thesis, Edinburgh (1973).
45. S.G. Frankiss, *Spectrochim. Acta*, 22, 295 (1966).
46. R.A. Whiteford, Personal Communication.
47. T.H. Chao and J. Laane, *Spectrochim. Acta*, 28A, 2443 (1972).

- 48 (a) W.J. Savage, B.Sc. Hons. Research Project, Edinburgh (1971).
(b) D.W.W. Anderson, J.E. Bentham and D.W.H. Rankin, J. Chem. Soc., Dalton, 1215 (1973).
49. E.A.V. Ebsworth, J.R. Hall, M.J. Mackillop, D.C. McKean, N. Sheppard and L.A. Woodward, Spectrochim. Acta, 13, 202 (1958).
50. B.J. Aylett and J.M. Campbell, J. Chem. Soc., (A), 1916 (1969).
51. B.J. Aylett and J.M. Campbell, J. Chem. Soc., (A), 1910 (1969).
52. M. Pankowski and M. Bigorgne, Compt. Rend., 264C, 1382 (1967).
53. E. Amberger and E. Mühlhofer, J. Organometal. Chem., 12, 55 (1968).
54. W.B. Steward and H.H. Nielsen, Phys. Rev., 47, 878 (1935).
55. D.F. Ball, P.L. Goggin, D.C. McKean and L.A. Woodward, Spectrochim. Acta, 16, 1358 (1960).
56. M.C. Tobin, J. Amer. Chem. Soc., 75, 1788 (1953).
57. H. Murata and K. Shimizu, J. Chem. Phys., 23, 1968 (1955).
C.C. Cerato, J.L. Lauer, and H.C. Beachell, J. Chem. Phys., 22, 1 (1954).

PART TWO

SOME NOVEL GROUP IV

DERIVATIVES OF MERCURY

CHAPTER EIGHT

INTRODUCTION

CHAPTER EIGHTINTRODUCTION

Organosilylmercury¹ and organogermerylmercury² compounds were first obtained in 1963, several types of such compounds being at present known.³ In comparison to organomercury compounds, R_2Hg , they are more reactive and thus are used for preparative work, especially for the synthesis of organosilicon and organogermanium compounds which are otherwise difficult to obtain. From this point of view the most interesting are the derivatives of the types $(R_3A)_2Hg$, where R = halogen, alkyl or aryl; A = Si, Ge. These are readily obtainable and thermally stable, but are highly reactive, necessitating their use in air-free conditions. Sufficient examples are now known to demonstrate the utility of these compounds for synthetic purposes. Although MacDiarmid et al⁴ suggested the possible formation of disilylmercury when they applied the Wurtz reaction to the synthesis of disilane and 1,2-dimethyldisilane, they were unable to prove the existence of disilylmercury. Up to the present, not a single $-HgSiH_3$ or $-HgGeH_3$ compound has been reported. With the intention of preparing trimethylsilylsilane, an excess of solid bis(trimethylsilyl)mercury was treated with silyl bromide; trimethylsilyl bromide was rapidly formed in almost quantitative yield as the only immediate volatile product. An involatile solid residue remained. Trimethylsilylsilane ($Me_3Si.SiH_3$) was evolved from that solid, over a period of days. This suggested the possible formation of an intermediate mercury compound, $Me_3SiHg.SiH_3$, and hence the mercury research was undertaken.

This part of the thesis describes the identification of trimethylsilylsilylmercury, disilylmercury, trimethylsilylgermylmercury, digermylmercury and trimethylsilylmethylmercury. Bis(trimethylsilyl)mercury was used as a starting material in the preparation of all these new mercury compounds. Although vibrational spectroscopy was used for partial characterisation of some of these species, ^{199}Hg and ^{29}Si inter nuclear double resonance (INDOR) spectroscopy was found to be the most useful technique in the identification of these new compounds. The n.m.r. parameters for the starting compound, $(\text{Me}_3\text{Si})_2\text{Hg}$ will also be given.

One of the disadvantages of double resonance methods for obtaining the details of the spectrum of a nucleus that is not observed directly is that they are rather time consuming. This difficulty is avoided to a considerable extent by the INDOR (Inter Nuclear Double Resonance) technique in which the height of a suitable line in the proton spectrum is monitored continuously, and variations are recorded as the second r.f. field is swept through the region of interest.⁵ The precise form of these variations will depend upon the amplitude of the irradiating field, the spacings in the irradiated spectrum, certain relaxation times, and other factors. However, if it is possible to have the second r.f. strong enough to give line splittings of several hertz without seriously affecting more than one line of the irradiated spectrum at a time, then the output of the recorder may resemble the "normal" spectrum of the irradiated nucleus quite closely. Difficulties tend to arise when the amplitude of the irradiating field is quite low, and the effects of spin population transfer may then predominate. In these circumstances the recorded

spectrum may have lines on either side of the baseline, and it is difficult to interpret the relative intensities satisfactorily. McFarlane et al⁶ showed these experimental difficulties with examples of ^{19}F INDOR spectra of difluoroacetic acid etc. The production of high-quality INDOR spectra places high demands upon the stability of the spectrometer, and an internal field-frequency locking system is almost essential. The second frequency may be driven through the required range either by mechanical or electrical means, and if the latter method is used a direct link to the recorder can then give pre-calibrated INDOR spectra. INDOR spectra are of greatest value when the nucleus of interest has a low magnetogyric ratio, for then the gain in sensitivity will be greatest. If the observed and irradiated nuclei are both coupled to other nuclei then several INDOR spectra will be obtained, according to which line is monitored. The complete spectrum is a superposition of these, although some care must be taken in assessing the relative intensities.

CHAPTER NINE

PREPARATION AND IDENTIFICATION

OF SOME NOVEL GROUP IV

DERIVATIVES OF MERCURY.

CHAPTER NINEPreparation and identification of some novel group IV derivatives of mercury.9.1 INTRODUCTION

This chapter describes a study of preparations of trimethylsilyl-silylmercury, disilylmercury, trimethylsilylgermylmercury, digermylmercury and trimethylsilylmethylmercury. These compounds were identified initially by their ^{199}Hg and ^{29}Si INDOR spectra. The infrared spectra of $\text{Me}_3\text{SiHgSiH}_3$, $\text{Me}_3\text{SiHgGeH}_3$ and $(\text{GeH}_3)_2\text{Hg}$, and the vibrational spectra for $\text{Me}_3\text{SiHgCH}_3$ are also reported in this chapter.

Although bis(trimethylsilyl)mercury has been used as a precursor for the synthesis of several organosilyl-compounds, a detailed n.m.r. study of this compound has not yet been reported; some n.m.r. parameters for $(\text{Me}_3\text{Si})_2\text{Hg}$ additional to those so far published⁷ are reported here.

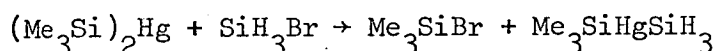
9.2:1 The preparation of trimethylsilylsilylmercury(a) Without solvent

Silyl bromide (1.1m moles) was condensed in a 30 ml reaction ampoule containing the yellow crystalline solid, bis(trimethylsilyl)mercury (\sim 1 m mole, 0.35 gm) and allowed to warm to room temperature. The yellow solid immediately changed to yellowish-green. After 45 minutes at this temperature the reaction was stopped by removal of all the volatile products, Me_3SiBr (\sim 1m mole) and SiH_3Br (0.1m mole), from the ampoule. The yellow residue, $\text{Me}_3\text{SiHgSiH}_3$ (\sim 1m mole, 0.3 gm), remained in the ampoule.

(b) With solvent

Silyl bromide (1m mole) was condensed in the ampoule containing

$(\text{Me}_3\text{Si})_2\text{Hg}$ (1m mole) in benzene and this yellow solution was heated to $50-60^\circ$. The yellow colour started fading. After 48 hours at $50-60^\circ$, all the volatile materials (Me_3SiBr and benzene) were removed from the ampoule by vacuum distillation. The yellow residue, $\text{Me}_3\text{SiHgSiH}_3$, remained in the ampoule. Me_3SiBr was identified by comparison of the observed and published infrared spectrum (7:2:1, ref.56) and this new compound ($\text{Me}_3\text{SiHgSiH}_3$) was identified by its ^1H n.m.r., ^{199}Hg INDOR, and the ^{29}Si INDOR (for $\text{Me}_3\text{SiHg}^{29}\text{SiH}_3$) spectroscopy (9.5:2). The observed infrared spectrum (table 26) was also used for the partial characterisation of this compound. The continual formation of a small quantity of mercury from $\text{Me}_3\text{SiHgSiH}_3$, and the very high reactivity of this compound towards traces of air and moisture made the analyses of mercury, carbon and hydrogen in the compound extremely difficult. The reaction between bis(trimethylsilyl)mercury and silyl bromide in 1:1 ratio of reactants may be expressed by the equation:



9.2:2 The preparation of disilylmercury

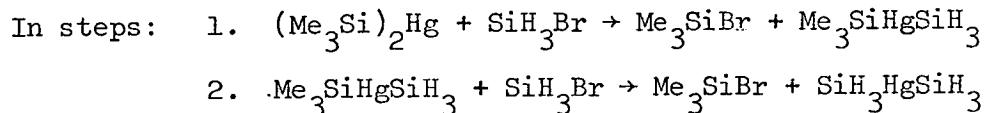
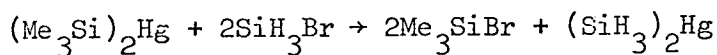
(a) Without solvent

Silyl bromide (1.2m moles) was condensed in a 30 ml reaction ampoule containing the yellow solid, $\text{Me}_3\text{SiHgSiH}_3$ (\sim 1m mole, 0.3 gm) and allowed to warm to room temperature. The yellow solid immediately changed to yellowish-green. After one hour at this temperature the reaction was stopped and the volatile products, Me_3SiBr (\sim 1m mole) and SiH_3Br (\sim 0.2m mole), were removed from the ampoule. The pale yellow residue, $(\text{SiH}_3)_2\text{Hg}$ (\sim 1m mole, 0.26 gm), remained in the ampoule.

(b) With solvent

Silyl bromide (1.2m moles) was condensed in the ampoule containing $\text{Me}_3\text{SiHgSiH}_3$ (\sim 1m mole) in benzene and this yellow solution was heated

to 50-60°. The yellow colour started fading. After 48 hours at 50-60°, all the volatile products (Me_3SiBr , very small quantity of SiH_3Br and benzene) were removed from the ampoule by vacuum distillation. The pale yellow residue, $(\text{SiH}_3)_2\text{Hg}$ ($\sim 1\text{m}$ mole, 0.26 gm), remained in the ampoule. This new compound was identified by its ^1H n.m.r., ^{199}Hg INDOR, and ^{29}Si INDOR spectroscopy (9.5:3). The attempts to obtain the infrared spectrum, and the analyses of Hg and H in the compound ($\text{SiH}_3\text{HgSiH}_3$) were unsuccessful due to the exceedingly reactive nature of this compound towards traces of air and moisture. The reaction between bis(trimethylsilyl)mercury and silyl bromide may be expressed by the equation:



9.2:3 The preparation of trimethylsilylgermylmercury

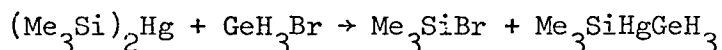
(a) Without solvent

Germyl bromide (2.1m moles) was condensed in a 20 ml reaction ampoule containing the yellow crystalline solid, bis(trimethylsilyl)mercury ($\sim 1.9\text{m}$ moles, 0.66 gm) and allowed to warm to room temperature. The yellow solid immediately changed to dark-yellow. After 15 minutes at this temperature the reaction was stopped and all the volatile products, Me_3SiBr ($\sim 1.9\text{m}$ moles) and GeH_3Br ($\sim 0.2\text{m}$ mole), were removed from the ampoule. The yellow residue, $\text{Me}_3\text{SiHgGeH}_3$ ($\sim 1.9\text{m}$ moles, 0.66 gm), remained in the ampoule.

(b) With solvent

Germyl bromide (1m mole) was condensed in the ampoule containing $(\text{Me}_3\text{Si})_2\text{Hg}$ (1m mole, 0.35 gm) in benzene and this yellow solution was warmed to room temperature. The yellow solution immediately changed to dark-yellow and then the colour started fading. After 40 minutes at

room temperature, all the volatile products (Me_3SiBr and benzene) were removed from the ampoule by vacuum distillation. The yellow residue, $\text{Me}_3\text{SiHgGeH}_3$ (1m mole, 0.35 gm), remained in the ampoule and this was identified by its ^1H n.m.r. and ^{199}Hg INDOR spectroscopy (9.5:4). The observed infrared spectrum (table 27) was also used for the partial characterisation of this compound. The attempts to analyse Hg, C and H in the compound ($\text{Me}_3\text{SiHgGeH}_3$) were unsuccessful due to the continual formation of a small quantity of mercury from the above mercury compound. The reaction between bis(trimethylsilyl)mercury and germyl bromide in 1:1 ratio of reactants may be expressed by the equation:



9.2:4 The preparation of digermylmercury

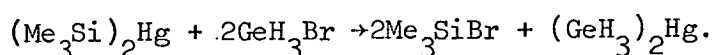
(a) With solvent

Germyl bromide (4.4m moles) was condensed in a 20 ml reaction ampoule containing $(\text{Me}_3\text{Si})_2\text{Hg}$ (\sim 2m moles, 0.7 gm) in benzene and this yellow solution was warmed to room temperature. The colour of the yellow solution immediately changed to dark-yellow and then started fading. After 3 hours at room temperature, all the volatile products (Me_3SiBr , unreacted GeH_3Br and benzene) were removed from the ampoule by vacuum distillation. The pale yellow residue, $(\text{GeH}_3)_2\text{Hg}$ (\sim 2m moles, 0.35 gm), remained in the ampoule.

(b) Without solvent

This digermylmercury was prepared by the other method; reacting solid bis(trimethylsilyl)mercury with excess GeH_3Br (1:2 ratio) at room temperature for one hour. Me_3SiBr was the only volatile product and the pale yellow solid, $(\text{GeH}_3)_2\text{Hg}$, remained in the ampoule. This new

compound $((\text{GeH}_3)_2\text{Hg})$ was identified by its ^1H n.m.r. and ^{199}Hg INDOR spectroscopy (9.5:5). The observed infrared spectrum (table 28) was also used for the partial characterisation of this compound. The attempts to analyse Hg and H in the above compound were unsuccessful due to the continual formation of a small quantity of mercury from $(\text{GeH}_3)_2\text{Hg}$. The reaction between bis(trimethylsilyl)mercury and germyl bromide may be expressed by the equation:



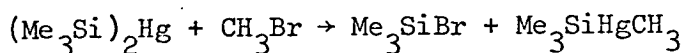
In steps:

1. $(\text{Me}_3\text{Si})_2\text{Hg} + \text{GeH}_3\text{Br} \rightarrow \text{Me}_3\text{SiBr} + \text{Me}_3\text{SiHgGeH}_3$
2. $\text{Me}_3\text{SiHgGeH}_3 + \text{GeH}_3\text{Br} \rightarrow \text{GeH}_3\text{HgGeH}_3 + \text{Me}_3\text{SiBr}$

9.2:5 The preparation of trimethylsilylmethylmercury

Methyl bromide (1m mole) was condensed in a 30 ml reaction ampoule containing the yellow crystalline solid, bis(trimethylsilyl)mercury (\sim 1m mole, 0.35 gm) and allowed to warm to room temperature. The yellow colour completely changed to colourless after a few hours. The reaction was stopped after 5 hours at this temperature and all the volatile products were removed from the ampoule by vacuum distillation.

Trap-to-trap distillation of the volatile products gave Me_3SiBr (1m mole) volatile at 0° , and the colourless liquid, $\text{Me}_3\text{SiHgCH}_3$ (\sim 1m mole, 0.29 gm) involatile at 0° . Nothing remained in the ampoule as an involatile residue. No trace of dimethylmercury (Me_2Hg) was detected among the products even when the excess CH_3Br was used. The new compound ($\text{Me}_3\text{SiHgCH}_3$) was identified by its proton n.m.r., ^{199}Hg n.m.r., infrared and Raman spectroscopy (9.5:6). The reaction between bis(trimethylsilyl)mercury and methyl bromide may be expressed by the equation:



9.3 Nuclear magnetic resonance spectra

Benzene was used as solvent and reference standard.

$(\text{Me}_3\text{Si})_2\text{Hg}$ in trimethylchlorosilane was transferred to a greaseless tap ampoule with an n.m.r. tube attached to its side arm (fig. 5.6), in a dry bag, containing dry nitrogen. The solvent trimethylchlorosilane was removed by vacuum distillation. The yellow crystals which remained in the ampoule were then reacted with SiH_3Br or GeH_3Br (the ratio of reactants is 1:1 for the preparations of $\text{Me}_3\text{SiHgSiH}_3$ and $\text{Me}_3\text{SiHgGeH}_3$; 1:2 for $(\text{SiH}_3)_2\text{Hg}$ and $(\text{GeH}_3)_2\text{Hg}$) at room temperature. After a few hours, all the volatile products were removed from the ampoule by vacuum distillation and the remaining yellow residue was dissolved in benzene. This yellow solution was then transferred to the side arm n.m.r. tube and sealed. Since $\text{Me}_3\text{SiHgCH}_3$ is volatile at room temperature, the above method was not used; instead $\text{Me}_3\text{SiHgCH}_3$ was condensed in an n.m.r. tube with benzene and sealed. The ^{199}Hg INDOR spectra were obtained for all these molecules but the ^{29}Si INDOR spectra were obtained for $\text{Me}_3\text{SiHg}^{29}\text{SiH}_3$ and $(\text{SiH}_3)_2\text{Hg}$. The heteronuclear double resonance technique was also used to obtain the chemical shifts of other nuclei. The ^{199}Hg , ^{29}Si and ^{13}C frequencies for the above group IV mercury compounds, in the field corresponding to a T.M.S. signal at exactly 100 MHz are given in table 24.

Recently Mitchell⁷ has published the proton n.m.r. spectrum with H-C-Si- ^{199}Hg coupling constant, of bis(trimethylsilyl)mercury. Mercury possesses two magnetic isotopes occurring at quite large abundances: ^{199}Hg which is 16.86 per cent abundant and has a spin of $\frac{1}{2}$ and ^{201}Hg which is 13.24 per cent abundant and has a spin of $\frac{3}{2}$. The large quadrupole moment of the latter isotope in general precludes its effect being observed in the proton spectrum. In this study, only the ^{199}Hg isotope was taken into consideration. The ^{29}Si (4.7% natural

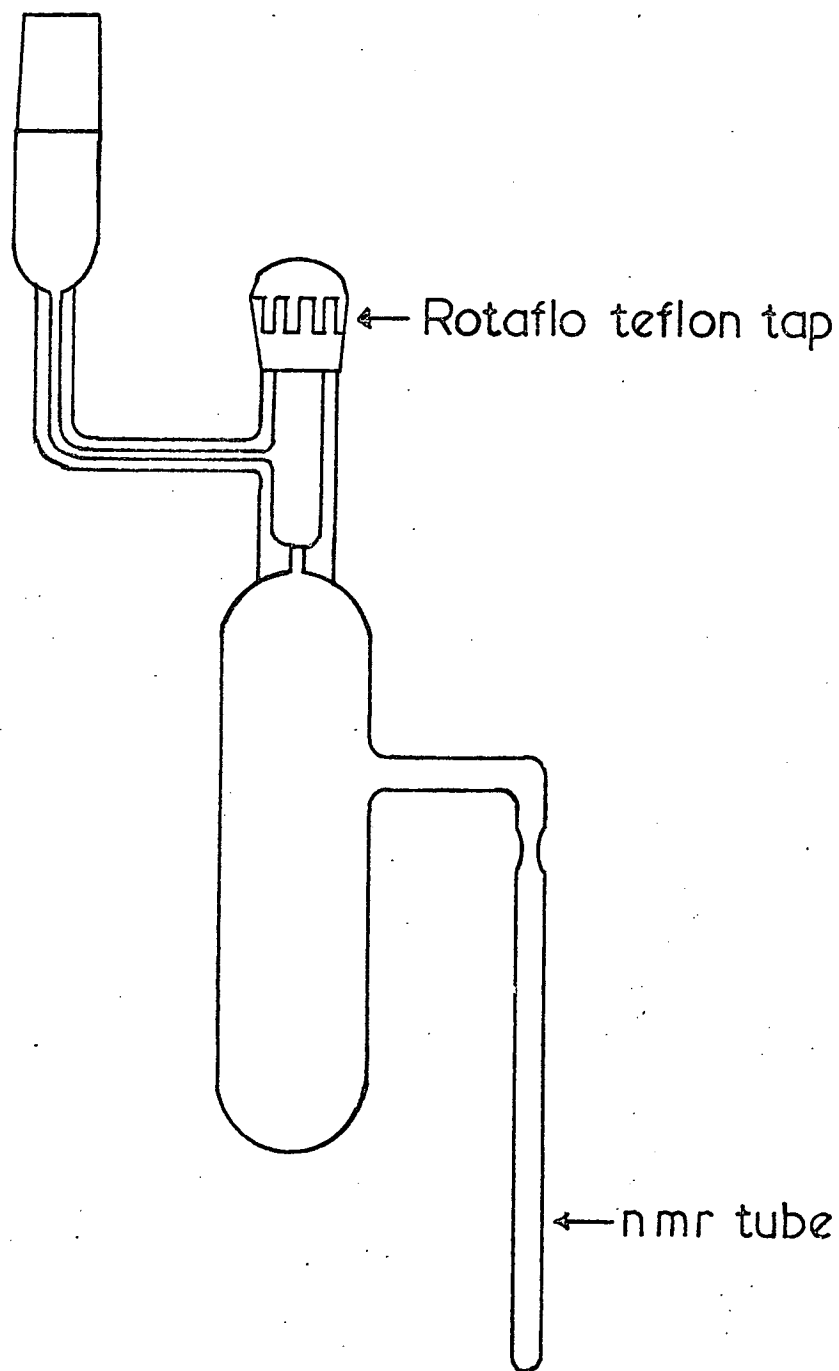
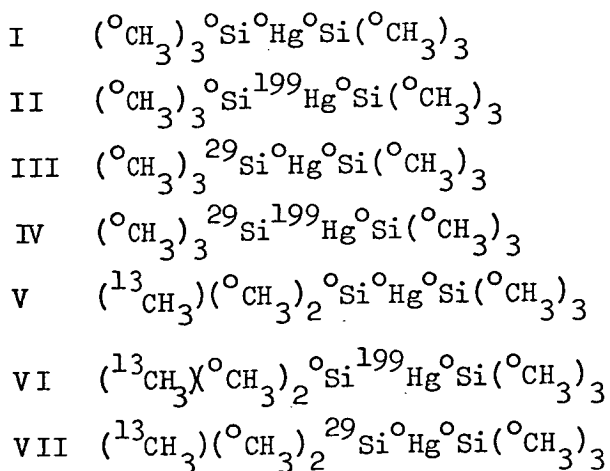


FIGURE 5.6

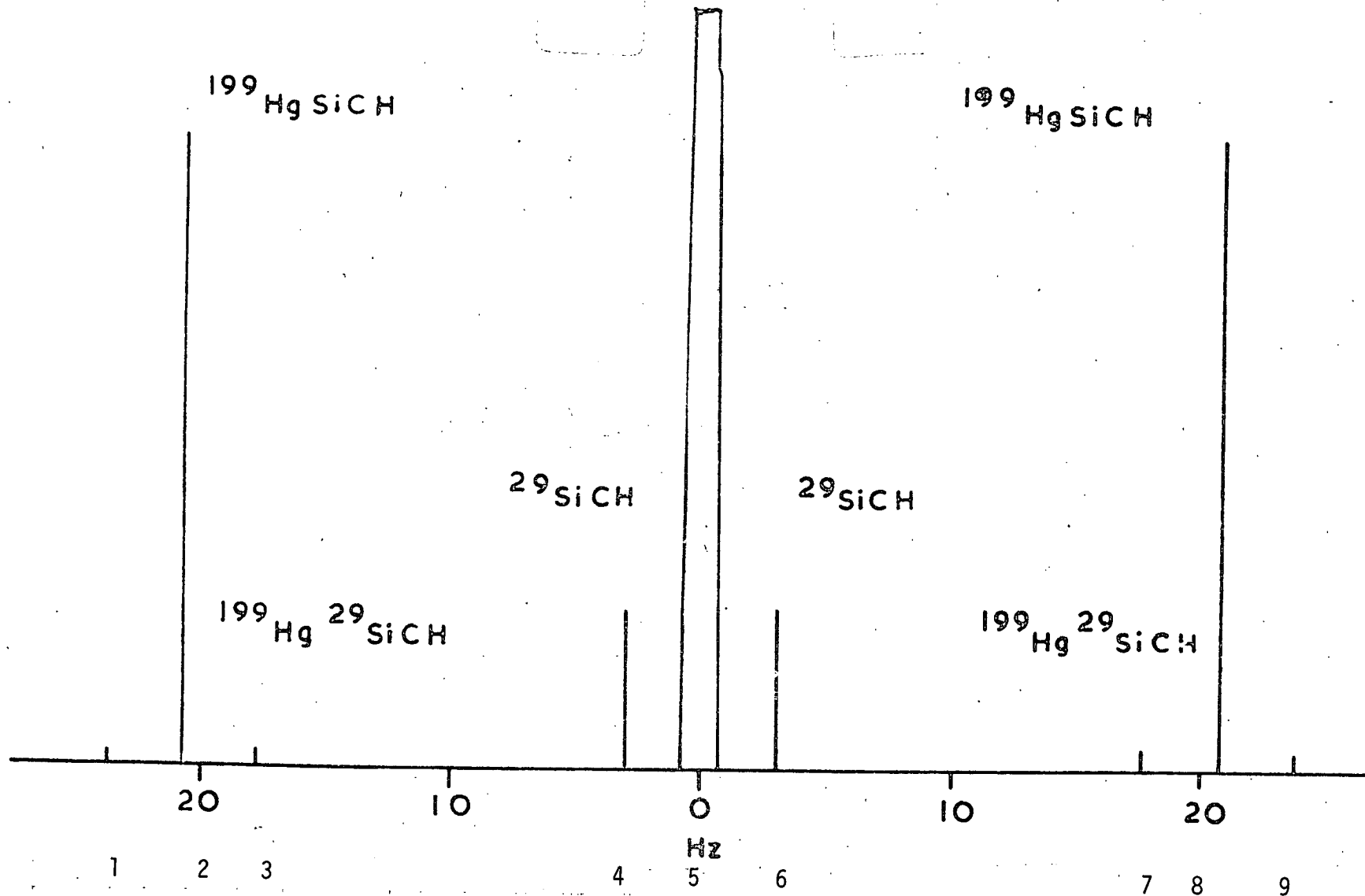
abundance) and ^{13}C (1.1% natural abundance) isotopes also have a spin of $\frac{1}{2}$. The ^1H , ^{199}Hg , ^{29}Si and ^{13}C spectra of bis(trimethylsilyl)mercury and other group IV derivatives of mercury are studied here. The proton spectra were observed directly whilst the ^{199}Hg and ^{29}Si spectra were measured indirectly by a double resonance method involving observation in the proton region (INDOR); ^{29}Si and ^{13}C proton decoupled spectra were also observed directly (only for $(\text{Me}_3\text{Si})_2\text{Hg}$) in an XL-100 spectrometer. The INDOR experiments were performed on a Varian HA100 spectrometer operating at a frequency of 100 MHz in the proton region and equipped with an external Schlumberger frequency supply unit for the decoupling experiments; a secondary recorder was used to obtain the INDOR spectra. The frequencies of the irradiating and observing fields were not phase-locked. The sample of $(\text{Me}_3\text{Si})_2\text{Hg}$ used in this investigation was dissolved in benzene to act as a reference standard and the tube sealed.

Absorption lines due to the following types (I - VI) of molecules were observed in the ^1H resonance spectrum and some of them (I - IV) are shown diagrammatically in the figure 6.



The superscript o denotes non-magnetic isotopes or magnetic isotopes whose effect cannot be detected in the spectra.

FIGURE 6; ^1H N.M.R. SPECTRUM OF $\text{Me}_3\text{SiHgSiMe}_3$



Line 5 is due to molecules (I); line 2 and 8 are due to molecules (II); line 4 and 6 are due to molecules (III); and lines 1,3,7 and 9 are due to molecule (IV).

The procedure used to locate the ^{199}Hg , ^{29}Si or ^{13}C absorption lines was to monitor in the frequency sweep mode one of the satellite lines in the ^1H spectrum and to vary the Schlumberger frequency in the ^{199}Hg or ^{29}Si or ^{13}C region until a perturbation of the monitored line indicated that a ^{199}Hg or ^{29}Si or ^{13}C transition with an energy level in common with the monitored line had been located. Only the ^{199}Hg INDOR spectrum of $(\text{Me}_3\text{Si})_2\text{Hg}$ was recorded and this is shown in figure 7. Only 13 lines were observed, although a 19-line pattern is expected for $(\text{Me}_3\text{Si})_2\text{Hg}$; in view of the relatively low intensities of the three outer lines on each side, it is not surprising that six lines escaped detection.

The lines 1,3,7 and 9 (fig. 6) are the ^{29}Si satellites of the ^{199}Hg satellites in molecule (IV). It was found that when the irradiating frequency was set in the Si region, at 19.868890 MHz lines 1 and 3 were decoupled and at 19.867910 MHz lines 7 and 9 were decoupled which proves that these lines are ^{29}Si satellites to ^{199}Hg satellites. When the irradiating frequency was set in the ^{199}Hg region at 17.918890 MHz lines 1 and 7 were decoupled and at 17.919870 MHz lines 3 and 9 were decoupled. The first pair of frequencies correspond to the central lines of the ^{199}Hg spectrum associated with the other ^{29}Si spin orientation, and the second pair with the lines associated with the other ^{29}Si orientation. This experiment gave the magnitudes of the ^{199}Hg -Si-C-H, ^{199}Hg - ^{29}Si coupling constants and shows that the sign of the ^{199}Hg - ^{29}Si coupling constant is opposite to the ^{29}Si -H coupling constant.

FIGURE 7

^{199}Hg INDOR Spectrum of $\text{Me}_3\text{Si.Hg.SiMe}_3$

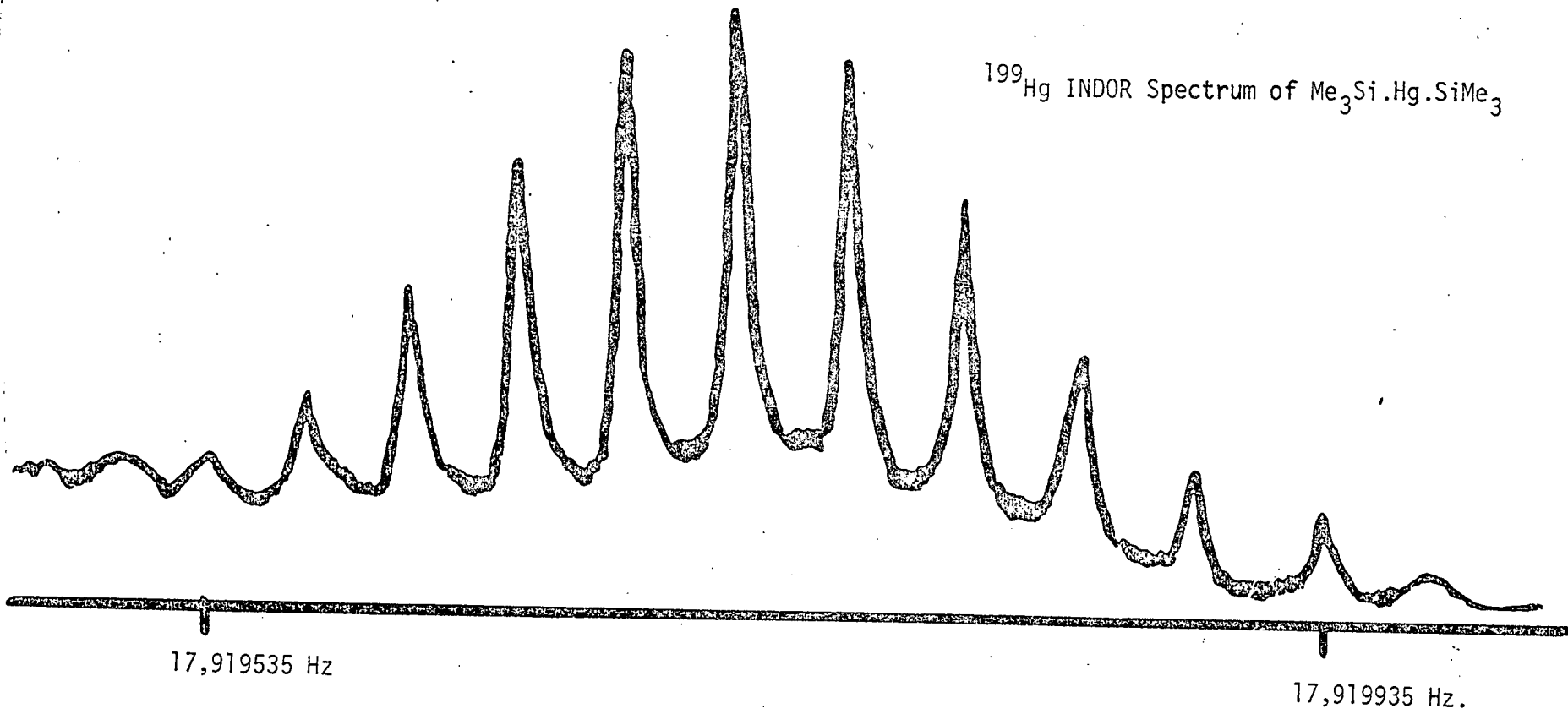


FIGURE 8

^{29}Si N.M.R. SPECTRUM OF $\text{Me}_3\text{SiHgSiMe}_3$

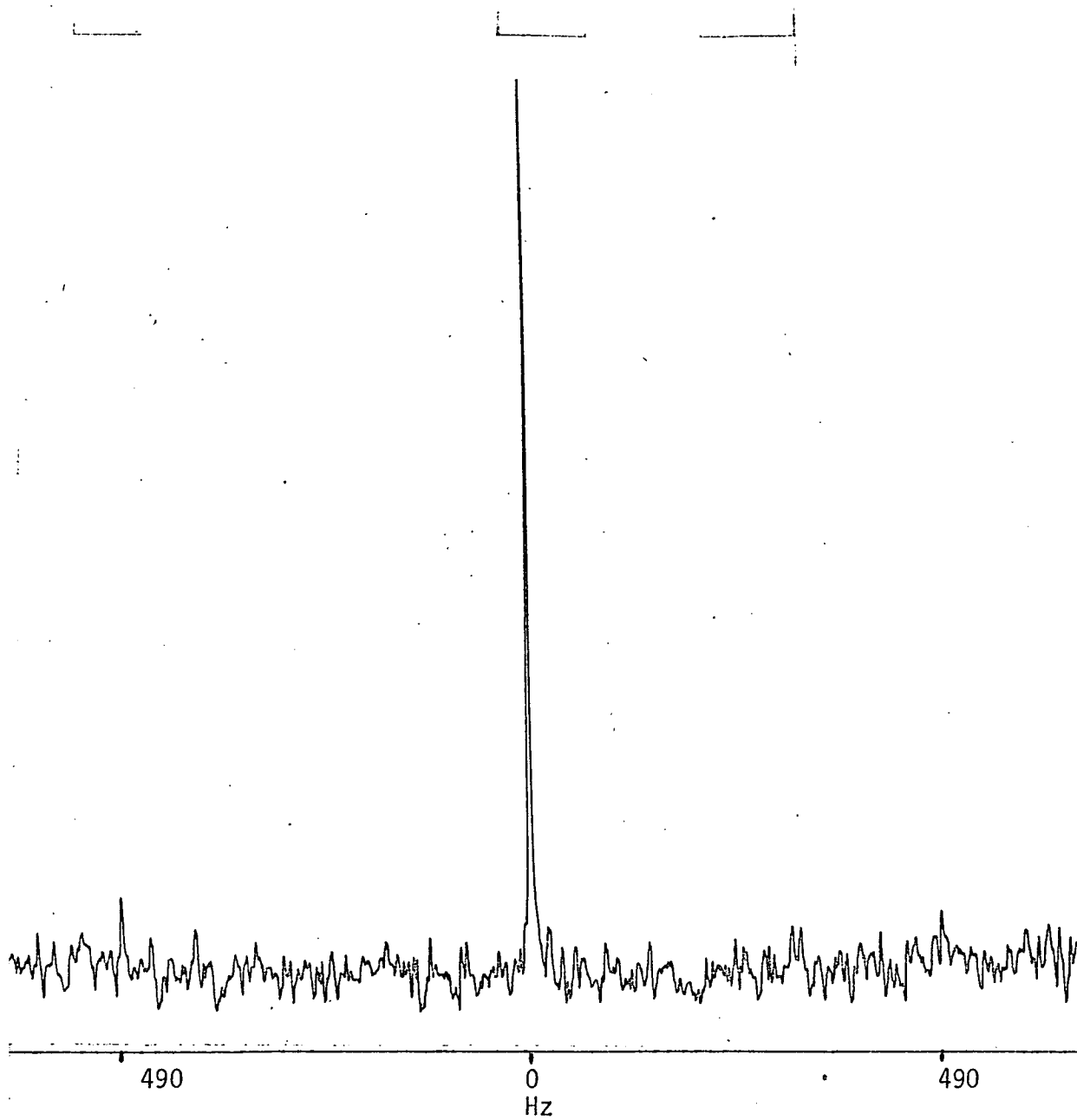
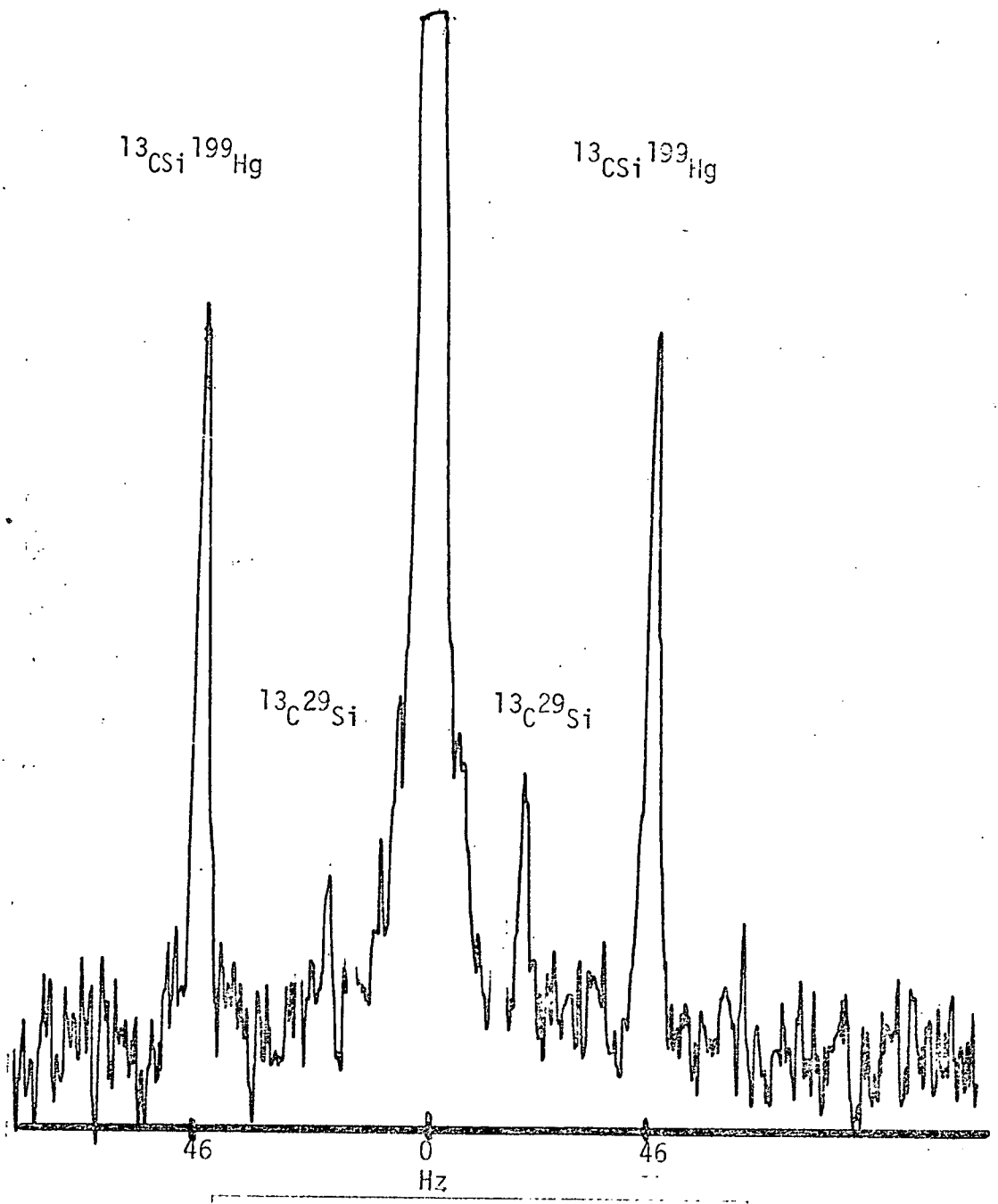


FIGURE 9

^{13}C N.M.R. SPECTRUM OF $\text{Me}_3\text{SiHgSiMe}_3$



The direct ^{29}Si n.m.r. spectrum (fig. 8) with proton decoupling showed a singlet with ^{199}Hg satellites of coupling constant $J(^{199}\text{Hg}-^{29}\text{Si}) = 983 \text{ Hz}$ which is consistent with the value obtained by the decoupling experiment (980 Hz). ^{13}C n.m.r. spectrum (fig. 9) with proton decoupling showed a singlet with ^{199}Hg and ^{29}Si satellites. These results are consistent with the compound being $(\text{Me}_3\text{Si})_2\text{Hg}$. It is also possible to identify the ^1H n.m.r. spectrum of $\text{Me}_3\text{SiHgSiH}_3$ in presence of $(\text{Me}_3\text{Si})_2\text{Hg}$ and this is shown in fig 10. The n.m.r. parameters for $(\text{Me}_3\text{Si})_2\text{Hg}$, $\text{Me}_3\text{SiHgSiH}_3$, $(\text{SiH}_3)_2\text{Hg}$, $\text{Me}_3\text{SiHgGeH}_3$, $(\text{GeH}_3)_2\text{Hg}$ and $\text{Me}_3\text{SiHgCH}_3$ are given in table 25 and the detailed study of these n.m.r. spectra has been described in the discussion (9.5).

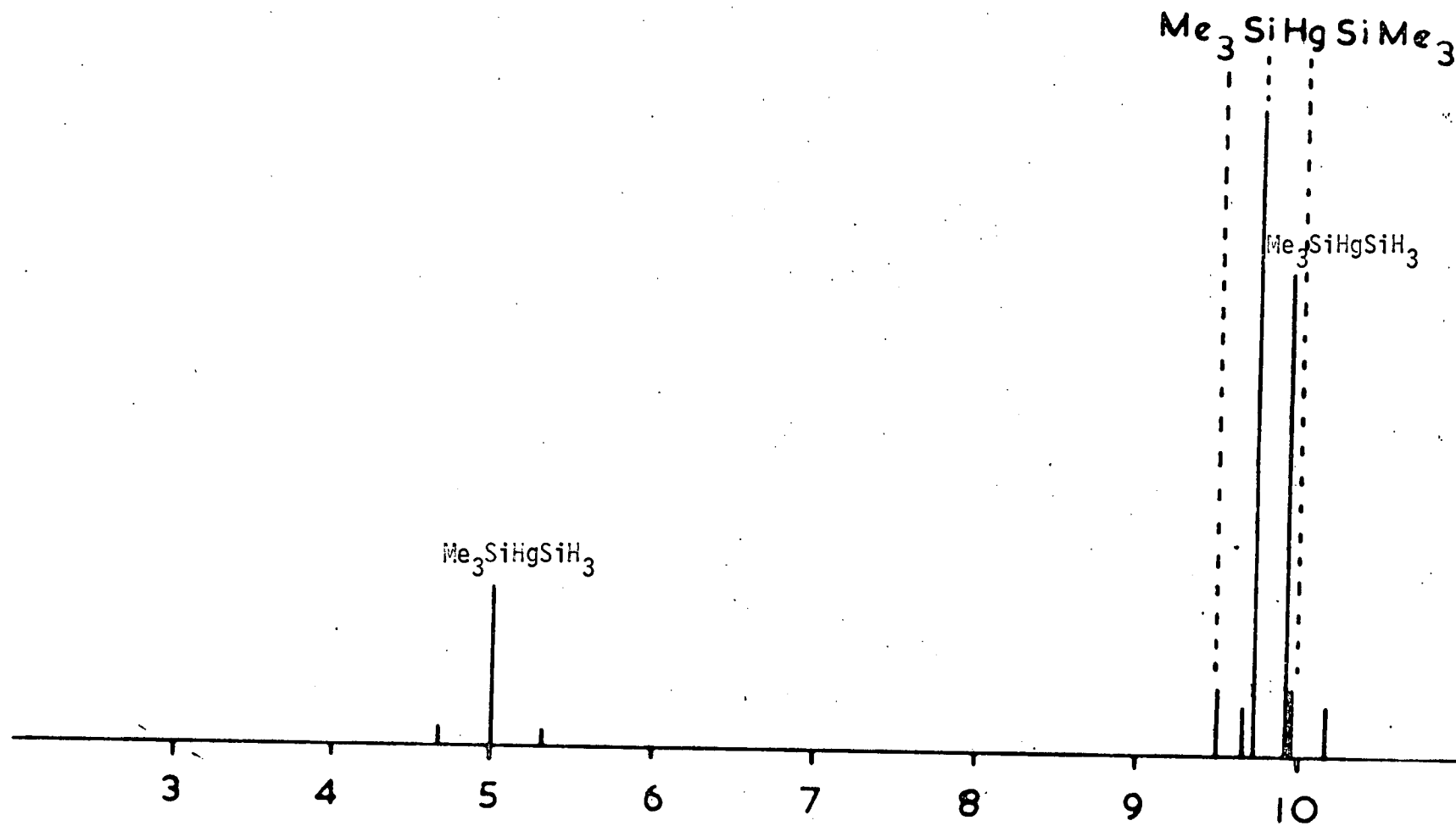
9.4 Infrared and Raman spectra

Since $(\text{SiH}_3)_2\text{Hg}$ is exceedingly reactive as a solid towards traces of air and moisture, attempts to obtain the infrared spectrum were unsuccessful. After several attempts the i.r. spectrum of $\text{Me}_3\text{SiHgSiH}_3$ was obtained (table 26). The infrared spectra of $\text{Me}_3\text{SiHgGeH}_3$ (table 27) and $(\text{GeH}_3)_2\text{Hg}$ (table 28) were obtained with less difficulty because, like other germyl compounds, these are less sensitive than silyl compounds to air and moisture. The attempts to obtain the Raman spectra of the above compounds were unsuccessful probably due to absorption of the exciting line. Both vibrational spectra were obtained only for $\text{Me}_3\text{SiHgCH}_3$ (table 29). The possible assignments of these spectra have been described in the discussion (9.5).

9.5 DISCUSSION

9.5:1 All these mercury compounds are soluble in benzene, and more stable in solutions than as solids, but less soluble in cyclopentane and Me_3SiBr . The $\text{Me}_3\text{SiHgSiH}_3$ is reactive as a solid towards traces of air

FIGURE 10 ^1H N.M.R. SPECTRUM



and moisture, whereas $(\text{SiH}_3)_2\text{Hg}$ is exceedingly reactive as a solid towards traces of air and moisture. The germyl-mercury compounds $(\text{Me}_3\text{SiHgGeH}_3$ and $(\text{GeH}_3)_2\text{Hg}$) can be handled in a dry bag containing dry nitrogen with less difficulty, because germyl compounds are generally less sensitive than silyl compounds to air and moisture. The solids, $\text{Me}_3\text{SiHgSiH}_3$, $(\text{SiH}_3)_2\text{Hg}$, $\text{Me}_3\text{SiHgGeH}_3$ and $(\text{GeH}_3)_2\text{Hg}$ are fairly stable for a few days in vacuum at room temperature, decomposing slowly to give $\text{Me}_3\text{Si.SiH}_3$, Si_2H_6 , $\text{Me}_3\text{Si.GeH}_3$ and Ge_2H_6 in addition to mercury globules. $\text{Me}_3\text{SiHgCH}_3$, a colourless liquid with a very low vapour pressure is quite stable at room temperature in vacuum but in daylight after several days the colour changes to yellow, and the compound disproportionates to give $(\text{Me}_3\text{Si})_2\text{Hg}$ and C_2H_6 . The decomposed products of the above mercury compounds, Si_2H_6^8 , $\text{Me}_3\text{Si.GeH}_3^9$, $\text{Ge}_2\text{H}_6^{10}$ and $\text{C}_2\text{H}_6^{11}$ were identified by comparison of their observed and published infrared spectra.

Thus it appears that an extensive range of silyl-mercury and germyl-mercury compounds can be prepared, and hence it opens a new field in silyl and germyl chemistry. All these silyl-mercury and germyl-mercury compounds may be useful precursors for the synthesis of silyl and germyl compounds.

9.5:2 The ^1H n.m.r. spectrum of $\text{Me}_3\text{SiHgSiH}_3$ in benzene showed peaks near 5 T (associated with $-\text{SiH}$) and 10 T (associated with Me_3Si -protons). Each peak had associated ^{199}Hg satellites, and both sets of satellites were collapsed by irradiation at the same ^{199}Hg frequency, showing that the two resonances were due to the same molecular species. The relative intensities of the SiH and the SiCH peaks were roughly 1:3. The ^{29}Si INDOR spectrum (fig.11) of $\text{Me}_3\text{SiHg}^{29}\text{SiH}_3$ showed a quartet by coupling with the three neighbouring protons and hence it proves the presence of one $-\text{SiH}_3$ group in the above molecule. The ^{29}Si chemical shift of $\text{Me}_3^{29}\text{SiHgSiH}_3$ was also obtained by "tickling"⁶ the ^{29}Si satellites of the Me_3Si -protons; the coupling constant, $^2\text{J}(\text{HC}^{29}\text{Si})$, is also in the expected range published for other Me_3Si -species¹² and helps to show the presence of one Me_3Si -group in the above mercury compound. Since the coupling constants, $^2\text{J}(\text{HSi}^{199}\text{Hg})$ and $^3\text{J}(\text{HCSi}^{199}\text{Hg})$, were measured in the ^1H n.m.r. spectrum, it was possible to predict the expected ^{199}Hg INDOR spectrum. The calculated ^{199}Hg INDOR spectrum showed a 40-line pattern due to coupling ($^2\text{JH}^{199}\text{Hg} = 66.0 \text{ Hz}$) with the 3 equivalent protons of this SiH_3 -group and the 9 equivalent protons of the Me_3Si -group ($^3\text{JH}^{199}\text{Hg} = 54.0 \text{ Hz}$). The pattern is complicated because the magnitudes of the two-bond and the three-bond couplings are comparable, a common feature where heavy nuclei like ^{199}Hg are involved. Although resolution of the observed ^{199}Hg INDOR spectrum was not very good, the splittings of the lines and the spaces between the lines are in close agreement with the calculated ^{199}Hg INDOR spectrum. Both observed and calculated ^{199}Hg INDOR spectra for $\text{Me}_3\text{SiHgSiH}_3$ are shown in figure 12. Thus all these results, and

FIGURE 11

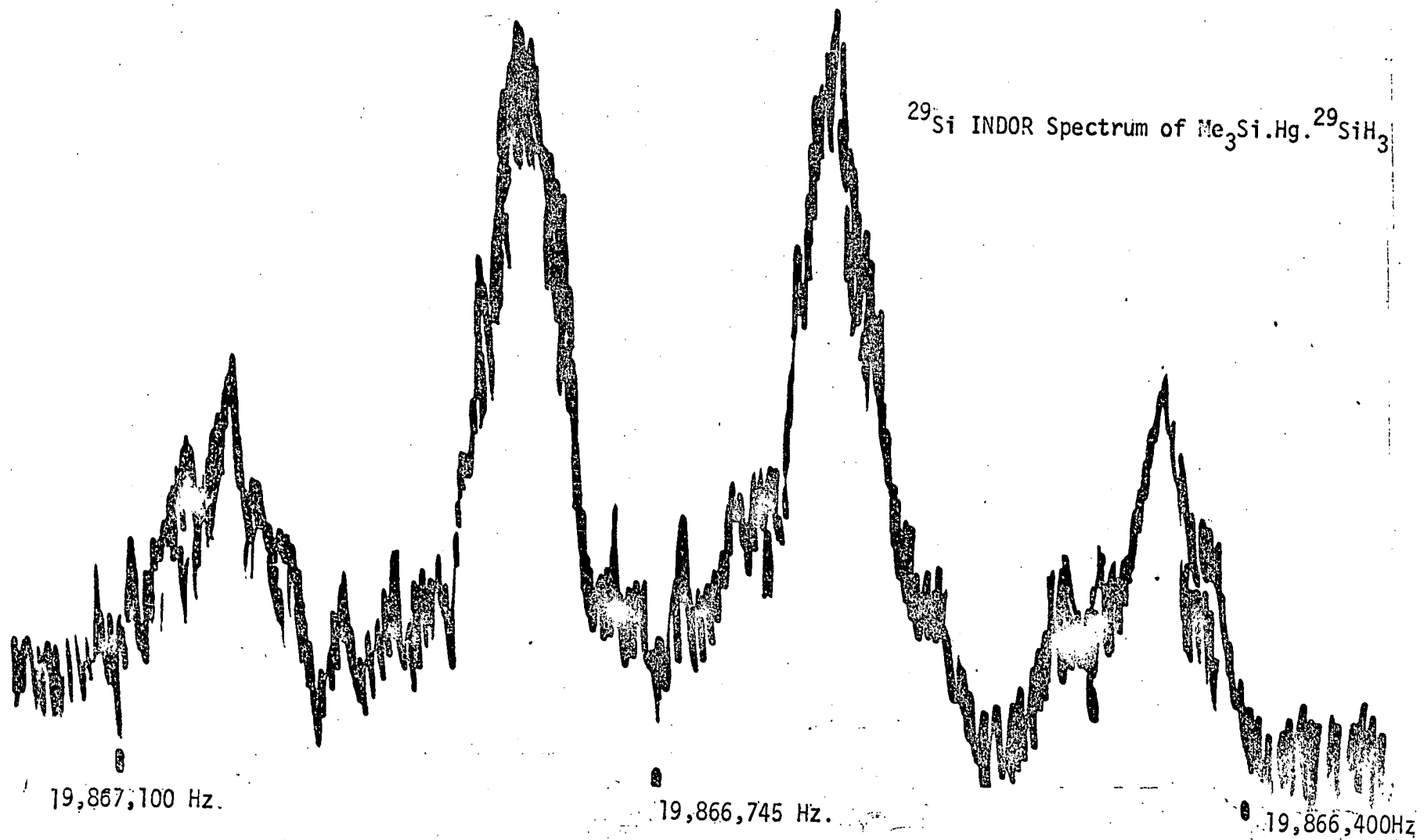
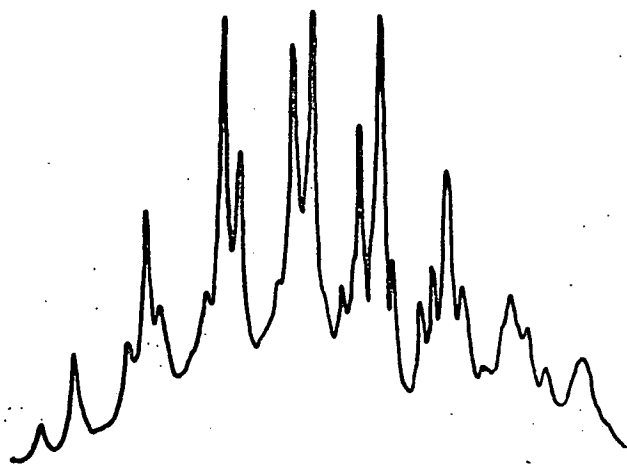
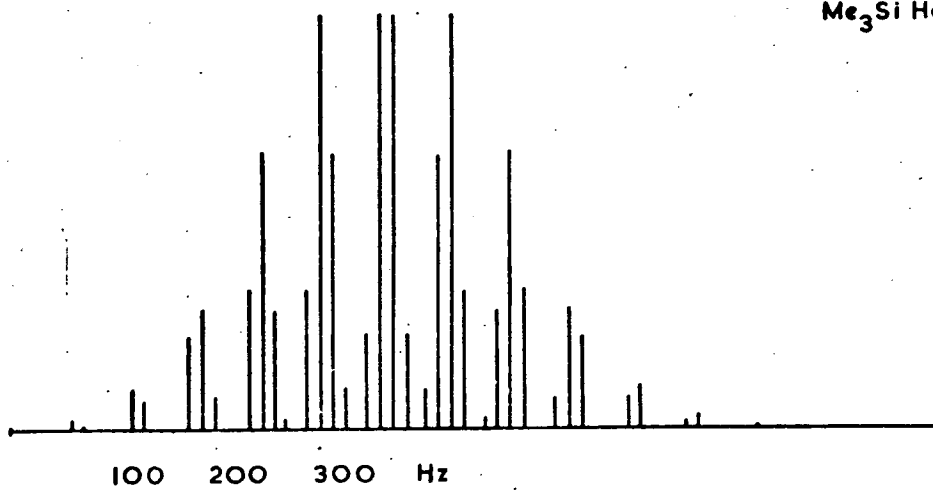


FIGURE 12



^{199}Hg INDOR Spectrum
of



particularly the ^{199}Hg INDOR spectrum, establish the identification of the compound as $\text{Me}_3\text{SiHgSiH}_3$.

9.5:3 The ^1H n.m.r. spectrum of $(\text{SiH}_3)_2\text{Hg}$ showed a resonance near 5 T with ^{29}Si and ^{199}Hg satellites. The ^{29}Si INDOR spectrum (fig.14) showed the quartet expected for SiH_3 -groups. The 7-line pattern of the ^{199}Hg INDOR spectrum (fig. 13) established the identity of the compound as $(\text{SiH}_3)_2\text{Hg}$.

9.5:4 The ^1H n.m.r. spectrum of $\text{Me}_3\text{SiHgGeH}_3$ in benzene showed peaks near 4.5 T (associated with $-\text{GeH}$) and 10 T (associated with Me_3Si -protons). Each peak had associated ^{199}Hg satellites, and both sets of satellites were collapsed by irradiation at the same ^{199}Hg frequency, showing that the two resonances were due to the same molecular species. The relative intensities of the GeH and the SiCH peaks were roughly in the ratio 1:3. Since the coupling constants, $^2\text{J}(\text{HGe}^{199}\text{Hg})$ and $^3\text{J}(\text{HCSi}^{199}\text{Hg})$, were measured in the ^1H n.m.r. spectrum, it was possible to predict the expected ^{199}Hg INDOR spectrum assuming the presence of three protons in the region of GeH resonance. Since germanium has no convenient isotope with nuclear spin $\frac{1}{2}$, the presence of GeH_3 -groups could not be proved by INDOR spectroscopy. The calculated ^{199}Hg INDOR spectrum showed a 40-line pattern by the superposition of two ^{199}Hg INDOR spectra, as for $\text{Me}_3\text{SiHgSiH}_3$. The observed ^{199}Hg INDOR spectrum showed most of the 40 lines expected, and is in close agreement with the calculated spectrum. Both observed and calculated ^{199}Hg INDOR spectra for $\text{Me}_3\text{SiHgGeH}_3$ are shown in figure 15. The ^{29}Si chemical shift of $\text{Me}_3\text{SiHgGeH}_3$ was obtained by "tickling" the ^{29}Si satellites

FIGURE 13

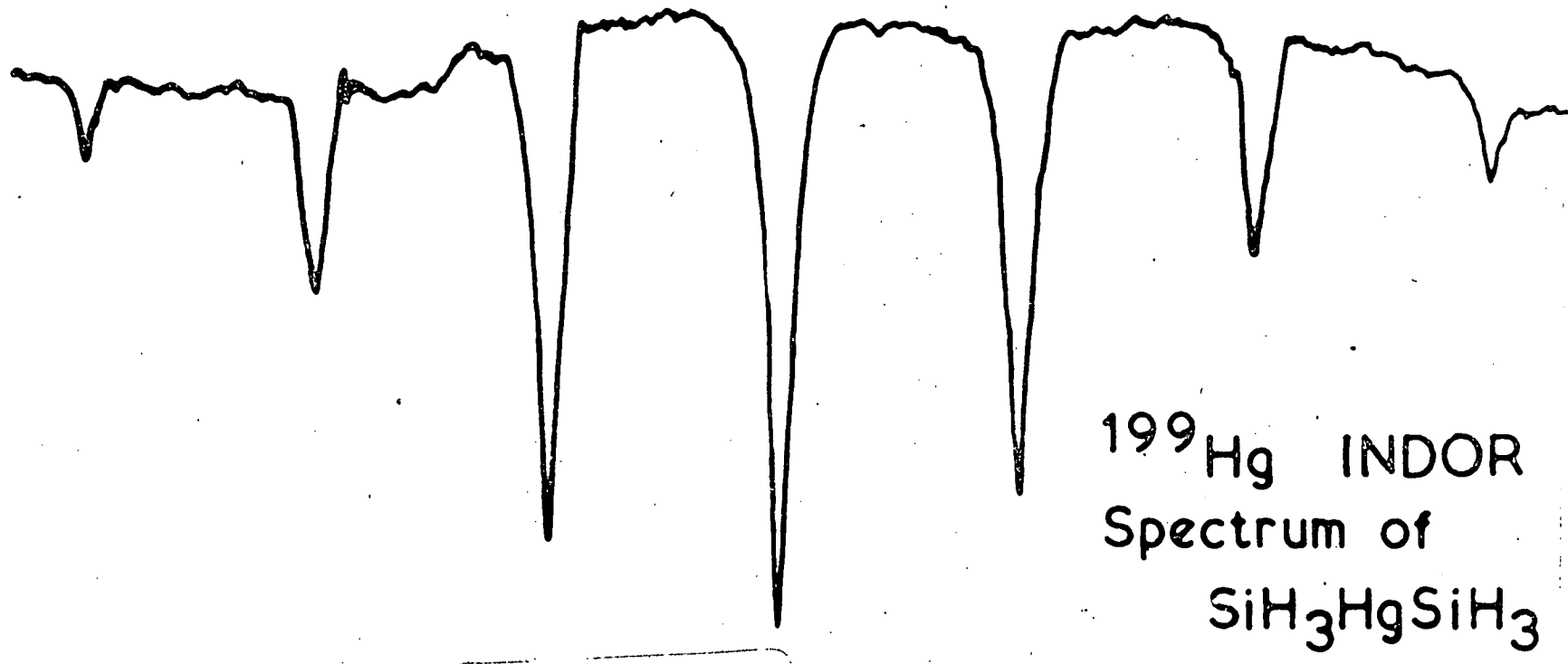
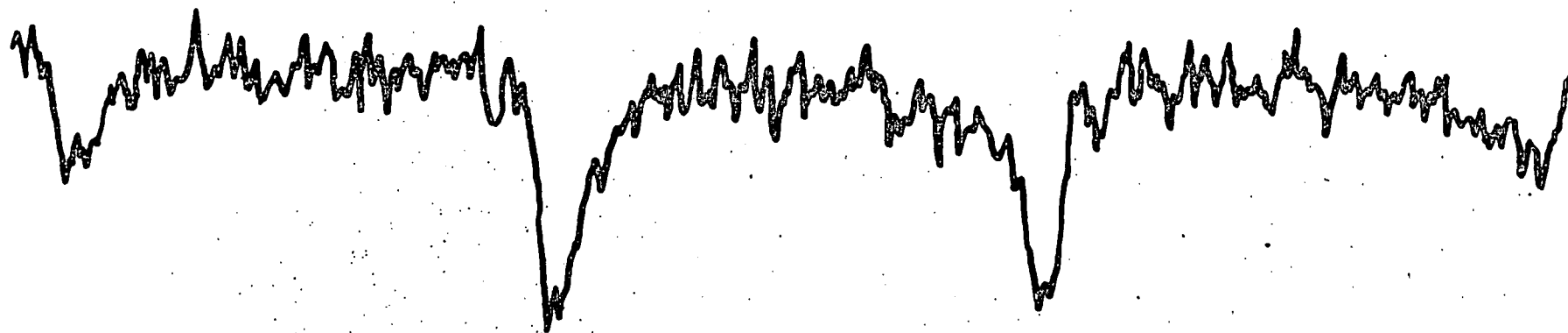


FIGURE 14 ^{29}Si INDOR SPECTRUM OF $\text{SiH}_3\text{HgSiH}_3$



of the Me_3Si -protons in the region of ^{29}Si frequency; the coupling constant, $^2J(\text{HC}^{29}\text{Si})$, is in the expected range for other Me_3Si -species and hence it proves the presence of one Me_3Si -group in the above mercury compound. Thus all these results are consistent with the compound being $\text{Me}_3\text{SiHgGeH}_3$.

- 9.5:5 The ^1H n.m.r. spectrum of $(\text{GeH}_3)_2\text{Hg}$ showed a resonance near 5.5 T (in the region of GeH resonance) with ^{199}Hg satellites. The ^{199}Hg INDOR spectrum (fig. 16) showed the 7-line pattern (coupling with six equivalent protons in the GeH region), expected for $(\text{GeH}_3)_2\text{Hg}$.
- 9.5:6 The ^1H n.m.r. spectrum of $\text{Me}_3\text{SiHgCH}_3$ in benzene showed the peaks near 9.8 T (associated with $-\text{HgCH}$) and 10 T (associated with Me_3Si -protons). Each peak has associated ^{199}Hg satellites, and both sets of satellites were collapsed by irradiation at the same ^{199}Hg frequency, showing that the two resonances were due to the same molecular species. The relative intensities of the CH and the SiCH peaks were roughly in the ratio 1:3. As in the previous cases (9.5:2 and 9.5:4), the predicted 40-line pattern of the ^{199}Hg INDOR spectrum of $\text{Me}_3\text{SiHgCH}_3$ was calculated, but the observed ^{199}Hg INDOR spectrum showed a distorted 10-line pattern. This may be due to some other factors which are mentioned earlier (chapter eight). Although the observed ^{199}Hg INDOR spectrum is not in complete agreement with its calculated spectrum, the identity of the compound as $\text{Me}_3\text{SiHgCH}_3$ may be established by the observed infrared and Raman spectra (table 29).

FIGURE 15

^{199}Hg INDOR spectrum
of

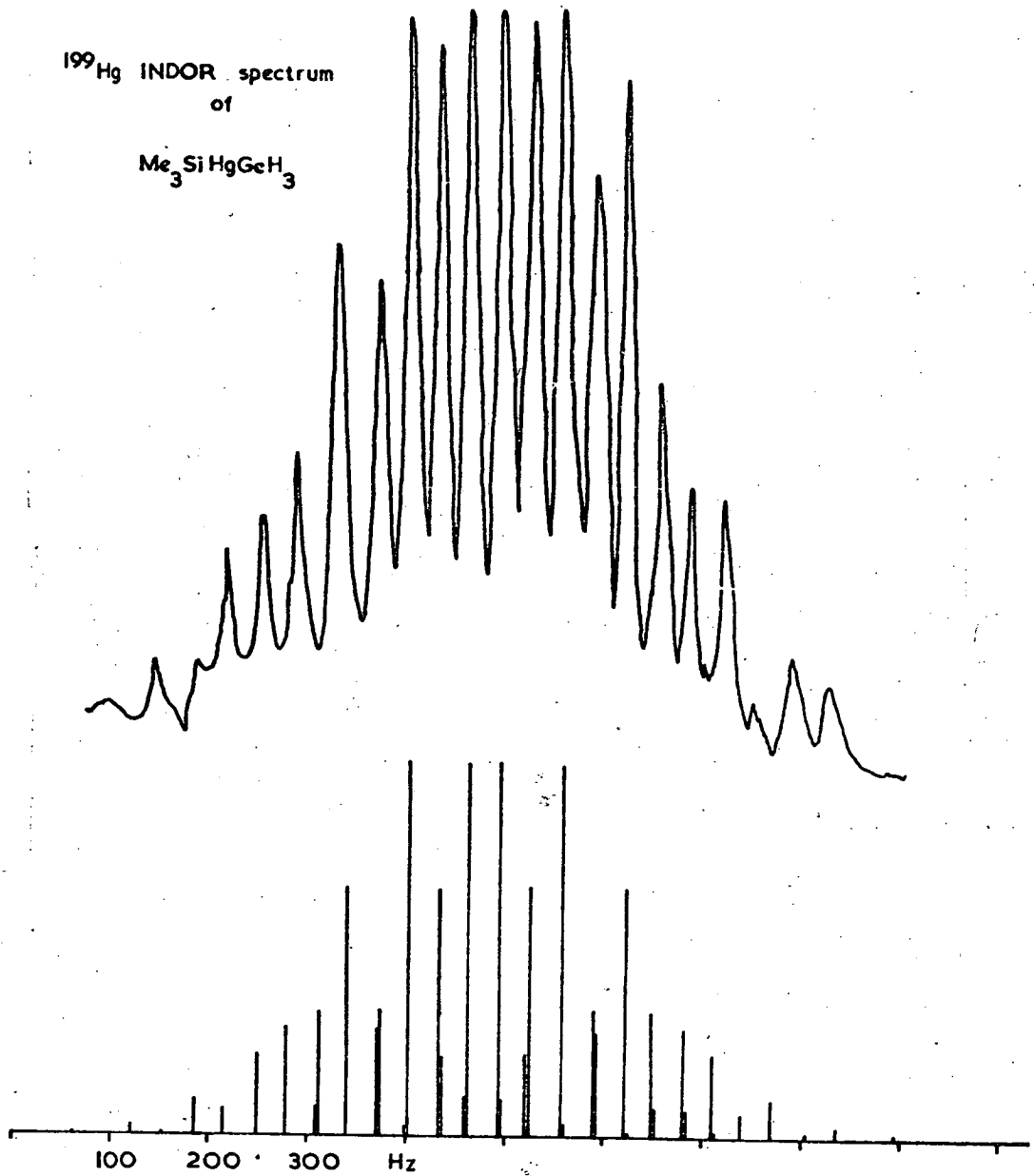
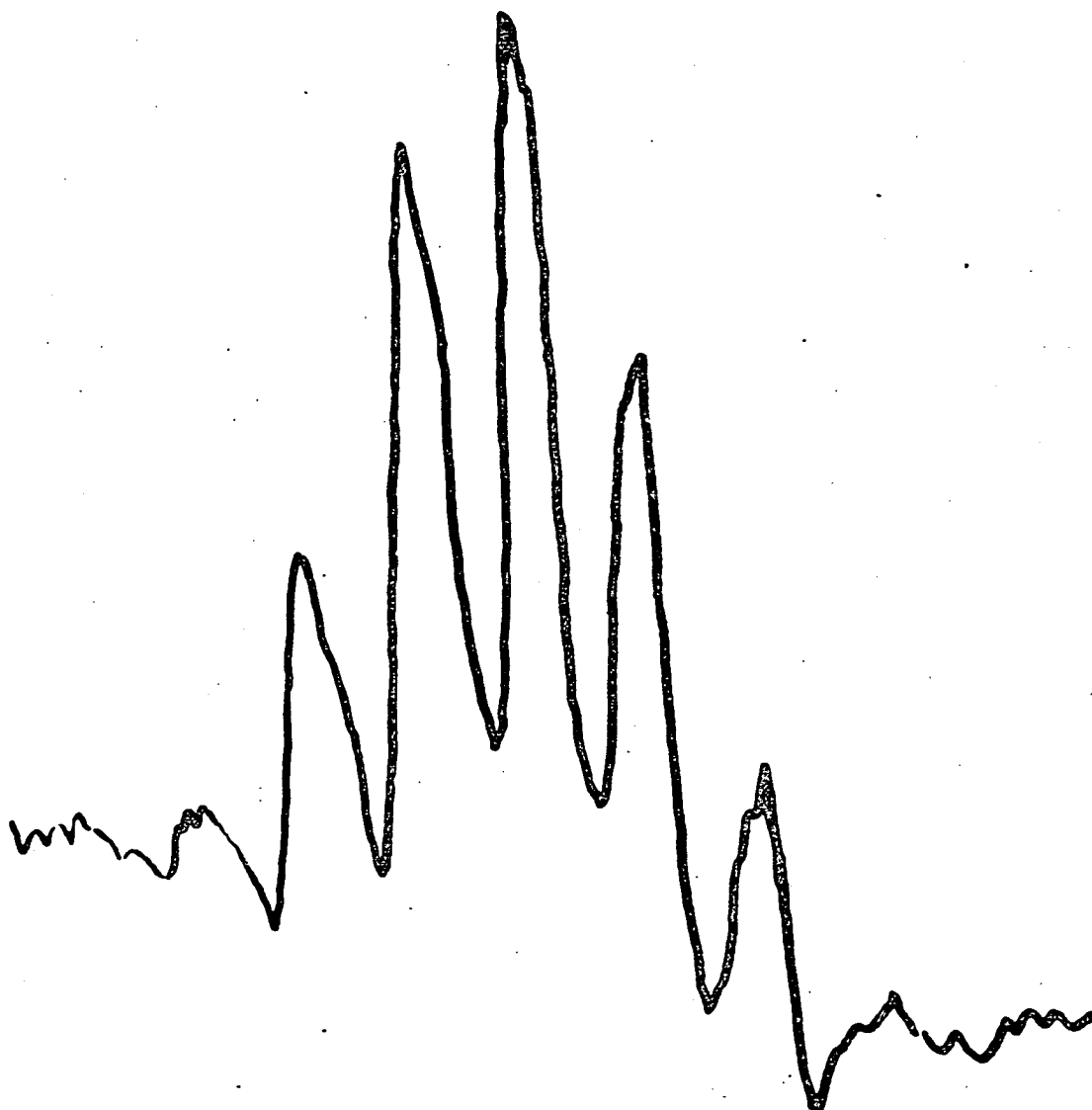
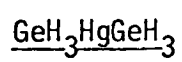


FIGURE 16

^{199}Hg INDOR SPECTRUM OF



9.5:7 The infrared spectra of $\text{Me}_3\text{SiHgSiH}_3$, $\text{Me}_3\text{SiHgGeH}_3$ and $(\text{GeH}_3)_2\text{Hg}$ were obtained using nujol as a mulling agent. Both infrared and Raman spectra were obtained for $\text{Me}_3\text{SiHgCH}_3$ as a vapour (IR) or liquid (Raman).

a) $\text{Me}_3\text{SiHgMH}_3$ (M = Si or Ge) and $(\text{GeH}_3)_2\text{Hg}$

The Si-H and Ge-H stretching modes, and CH_3 deformations appear in the expected regions.^{8,9,10} The GeH_3 deformations and GeH_3 rock in the observed i.r. spectrum of digermylmercury may be readily assigned by comparison of the observed frequencies with the published infrared spectrum for digermane.¹⁰ The bands in the region $1000\text{--}600\text{ cm}^{-1}$ for $\text{Me}_3\text{SiHgSiH}_3$ and $\text{Me}_3\text{SiHgGeH}_3$ are due to SiH_3 or GeH_3 deformations, CH_3 rocking and Si-C stretching modes. After a few minutes of oxidation of $\text{Me}_3\text{SiHgSiH}_3$, the bands at 915 and 970 cm^{-1} were disappeared and new bands appear at 945 and 980 cm^{-1} respectively; the bands at 610 cm^{-1} completely disappeared and hence the bands at 915 and 970 may be assigned as SiH_3 deformations and the band at 610 cm^{-1} may be due to the SiH_3 rocking modes of $\text{Me}_3\text{SiHgSiH}_3$. The very strong band in the spectrum of this compound at 840 cm^{-1} may be due to the CH_3 rocking modes and the bands at 690 and 750 cm^{-1} are probably due to Si-C stretching modes. Similarly in $\text{Me}_3\text{SiHgGeH}_3$, the bands at 898 and 780 cm^{-1} may be assigned as GeH_3 deformations, and the band at 550 cm^{-1} may be the GeH_3 rock; the very strong band at 825 cm^{-1} may be assigned as the CH_3 rock. The remaining two bands at 730 and 675 cm^{-1} are probably due to Si-C stretching modes. In the case of $\text{Me}_3\text{SiHgSiH}_3$, two more bands are observed, one at 461 cm^{-1} and the other at 263 cm^{-1} . Since the reported¹ infrared active Si-Hg stretching mode in $(\text{Me}_3\text{Si})_2\text{Hg}$ is at 318 cm^{-1} , the band at

263 cm^{-1} may be one of the Si-Hg stretching modes. The i.r. spectrum of $(\text{GeH}_3)_2\text{Hg}$ shows one very weak band at 218 cm^{-1} . This may well be due to the antisymmetric Ge-Hg stretching mode.

b) $\text{Me}_3\text{SiHgCH}_3$

The infrared and the Raman spectra of $\text{Me}_3\text{SiHgCH}_3$ show the C-H and Si-C stretching modes, CH_3 deformations, and CH_3 rocking modes in the expected regions. The strongly polarised band in the Raman spectrum at 500 cm^{-1} may be assigned as the C-Hg stretching modes by comparison of the observed and published C-Hg stretching frequencies in the vibrational spectra for Me_2Hg ¹³. The band at 325 cm^{-1} which is polarised in the Raman spectrum may be due to the Si-Hg stretching mode. The bands at 232 and 175 cm^{-1} may be assigned to C_3Si deformations and the band at 108 cm^{-1} may be due to SiHgC bend.

TABLE 24Corrected Frequencies in MHz

		<u>^{199}Hg</u>	<u>^{29}Si</u>	<u>^{13}C</u>
(1)	$\text{Me}_3\text{SiHgSiMe}_3$	17.919760	19.868454	25.145167
(2)	(i) $\text{Me}_3\text{SiHgSiH}_3$	17.917000	-	-
	(ii) $\text{Me}_3^{28}\text{SiHg}^{29}\text{SiH}_3$	-	19.866744	-
	(iii) $\text{Me}_3^{29}\text{SiHg}^{28}\text{SiH}_3$	-	19.868449	-
(3)	$\text{SiH}_3\text{HgSiH}_3$	17.914654	19.866978	-
(4)	$\text{Me}_3\text{SiHgGeH}_3$	17.913989	19.868000	-
(5)	$\text{GeH}_3\text{HgGeH}_3$	17.908501	-	-
(6)	$\text{Me}_3\text{SiHgCH}_3$	17.912974	-	-

TABLE 25

The n.m.r. parameters for the group IV mercury compounds

	$(\text{Me}_3\text{Si})_2\text{Hg}$	$\text{Me}_3\text{SiHgSiH}_3$	$(\text{SiH}_3)_2\text{Hg}$	$\text{Me}_3\text{SiHgGeH}_3$	$(\text{GeH}_3)_2\text{Hg}$	$\text{Me}_3\text{SiHgCH}_3$
$T(\text{SiH}_3/\text{GeH}_3)$, ppm	-	4.98	5.46	4.54	5.16	-
$T(\text{HgCH}_3)$, ppm	-	-	-	-	-	9.78
$T(\text{Me}_3\text{Si})$, ppm	9.73	9.90	-	9.86	-	9.91
$\delta(^{199}\text{Hg})^a$, ppm	+481.0	+327.1	+196.0	+159.0	-147.45	+102.28
$\delta(^{29}\text{Si})^b$, ppm- Me_3Si	+64.0	+63.7	-	+41.1	-	n.m.
H_3Si	-	-22.1	-10.3	-	-	-
$\delta(^{13}\text{C})^b$, ppm	+6.84	n.m.	-	n.m.	-	n.m.
$^1J(\text{H}^{29}\text{Si})$, Hz	-	178.0	185.0	-	-	-
$^2J(\text{HC}^{29}\text{Si})$, Hz	6.2	6.0	-	6.8	-	n.m.
$^2J(\text{H}^{199}\text{Hg})$, Hz	-	66.0	84.0	92.0	147.0	74.5
$^3J(\text{HCSi}^{199}\text{Hg})$, Hz	40.9	54.0	-	62.0	-	51.0
$^1J(\text{H}^{13}\text{C})$, Hz	120.0	n.m.	-	n.m.	-	n.m.
$^1J(^{29}\text{Si}^{199}\text{Hg})$, hz	983.0	n.m.	n.m.	n.m.	-	n.m.
$^1J(^{13}\text{C}^{29}\text{Si})$, Hz	39.3	n.m.	-	n.m.	-	n.m.
$^2J(^{13}\text{CSi}^{199}\text{Hg})$, Hz	92.3	n.m.	-	n.m.	-	n.m.

^aIn ppm relative to Me_2Hg (+ve to high frequency). ^bIn ppm relative to Me_4Si (+ve to high frequency). n.m. = not measured.

TABLE 26

Infrared spectrum of $\text{Me}_3\text{SiHgSiH}_3$ in nujol ($4000\text{-}200\text{ cm}^{-1}$)

Frequency in cm^{-1}	Intensity	Possible Assignment
2960 - 2830	s	v CH + nujol
2130	s, broad	v SiH
1455	m	} nujol
1375	m	
1315	vw	} $\delta\text{ CH}_3$
1253	s	
1070	vw, broad	Si-O-Si impurity?
975	vw	} $\delta\text{ SiH}_3$
915	m	
840	vs, broad	$\rho\text{ CH}_3$
750	w	v SiC
690	m	v SiC
610	m, broad	$\rho\text{ SiH}_3$
461 \pm 1	vw	?
263	w	v Si-Hg

where s = strong, m = medium, w = weak and v = very

TABLE 27

Infrared spectrum of $\text{Me}_3\text{SiHgGeH}_3$ in nujol ($4000\text{-}200\text{ cm}^{-1}$)

Frequency in cm^{-1}	Intensity	Possible Assignment
2940 - 2830	s	ν CH = nujol
2012	w	ν GeH
1455	m	} nujol
1375	m	
1238	m	δ CH_3
896	m	δ GeH_3
825	s	ρ CH_3
775	m	δ GeH_3
730	m	ν SiC
672	m	ν SiC
601	m	?
550	m	ρ GeH_3 ?
450	w	?

where s = strong, m = medium and w = weak

TABLE 28

Infrared spectrum of $(\text{GeH}_3)_2\text{Hg}$ in nujol ($4000\text{-}50\text{ cm}^{-1}$)

Frequency in cm^{-1}	Intensity	Possible Assignment
2040	w	ν GeH
843	m	} δ GeH_3
775	m,broad	
470	w,broad	ρ GeH_3
218	vw	ν Ge-Hg?

Where m = medium, w = weak, and v = very

TABLE 29

Raman and Infrared spectra of Me₃SiHgCH₃

Liquid		Vapour	
Raman Frequency in cm ⁻¹	Raman Polarisation Ratio	Infrared Frequency in cm ⁻¹	Possible Assignment
2960 ± 2 vw	-	2950 ± 5 w	} ν CH
2905 ± 2 vw	-	2900 ± 5 vw	
1440 vvw	-		
1420 vw	-	1405 vw	} δ CH ₃
1250 vvw	-	1259 m	
1160 w	-	-	δ CH ₃
850 w, broad	-	853 s	} ρ CH ₃
		840 sh	
740 ± 5 vvw	-	760 vw	ν SiC
690 ± 2 w	-	685 vw	ν SiC
630 w	-	622 vw	?
500 s	p	500 m	ν C-Hg
325 m	p	-	ν Si-Hg?
232 w	dp?	-	} δ C ₃ Si
175 m	dp?	-	
108 ± 2 m	dp?	-	

Where s = strong, m = medium, w = weak, sh = shoulder, v = very, p = polarised and dp = depolarised.

REFERENCES

1. E. Wiberg, O. Stecher, H.J. Andraschek, L. Kreuzbichler and E. Staude, *Angew. Chem.*, 75 516 (1963); *Angew Chem., Int. Ed. Engl.*, 2, 507 (1963).
2. N.S. Vyazankin, G.A. Razuvaev and E.N. Gladyshev, *Dokl. Akad. Nauk SSSR*, 151, 1326 (1963).
3. N.S. Vyazankin, G.A. Razuvaev and O.A. Kruglaya, *Organometal. Chem. Syn.*, 1, 205 (1971).
D. Seyferth, *J. Organometal. Chem.*, 62, 136 (1973).
4. A.D. Craig and A.G. MacDiarmid, *J. Inorg. Nucl. Chem.*, 24, 161 (1962).
5. E.B. Baker, *J. Chem. Phys.*, 37, 911 (1962).
6. W. McFarlane and R.F.M. White, *Techniques of High Resolution N.M.R. Spectroscopy* (Butterworths, London 1972), p.96.
7. T.N. Mitchell, *J. Organometal. Chem.*, 38, 17 (1972).
8. G.W. Bethke and M.K. Wilson, *J. Chem. Phys.*, 26, 1107 (1957).
9. E. Amberger and E. Muhlhofer, *J. Organometal. Chem.*, 12, 55 (1968).
10. V.A. Crawford, K.H. Rhee and M.K. Wilson, *J. Chem. Phys.*, 37, 2377 (1962).
11. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., N.Y., 1945), p.344.
12. M.L. Maddox, S.L. Stafford and H.D. Kaesz, *Adv. Organomet. Chem.*, 3, 1 (1965)
13. A.M.W. Bakke, *J. Mol. Spec.*, 41,1(1972)

APPENDIX ONEDetermination of chemical shifts and correction of observed frequenciesA. Correction of observed frequencies

The values given in the table 24, relative to T.M.S. at exactly 100 MHz were obtained by using the following relationship:

1. Frequency correction for the n.m.r. spectrometer (HA100)

$$= (100 - \text{observed frequency}) = X \text{ in Hz.}$$

2. Total correction

= (X - manual oscillator frequency) + chemical shift in Hz relative to T.M.S. of the reference compound used to supply the locking signal (e.g. Benzene, T.M.S. and Cyclopentane etc.)

$$= + Y \text{ in Hz.}$$

3. Correction factor =

$$\frac{100.0 + Y}{100.0} = Z$$

4. The frequency correction for the observed ^{199}Hg or ^{29}Si or ^{13}C frequency

$$= \text{observed frequency in MHz} \times Z = \text{Corrected frequency in MHz}$$

B. Determination of chemical shifts " δ " in ppm relative to the standard.

$$\frac{\text{corrected frequency} - \text{frequency of the standard}}{\text{Frequency of the standard}} \quad \text{in MHz}$$

$$= + "Q" \text{ in ppm relative to the standard.}$$

ABSTRACT OF THESIS

Name of CandidateMR. NARAYAN SADASHIV HOSMANE.....
AddressDEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH, EH9 3JJ.....
DegreePh.D..... Date27th August, 1974.....
Title of ThesisSOME REACTIONS OF STANNIC CHLORIDE WITH SILICON HYDRIDES AND SOME.....
.....NOVEL GROUP IV DERIVATIVES OF MERCURY.....

The first part of the thesis describes a study of reactions of silane, disilane, alkyl substituted monosilanes, monohalo-substituted monosilanes, SiH_3 -derivatives of different types of unsaturated carbon compounds, SiH_3 -derivatives of elements of groups V and VI, SiH_3 -transitionmetal-carbonyl compounds, and trimethylsilylsilane with stannic chloride. The new compounds, (SiH_2ClF , $\text{ClSiH}_2\cdot\text{C}\equiv\text{CH}$, $\text{ClSiH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CF}_3$, $\text{ClSiH}_2\cdot\text{CH}=\text{CH}_2$, $\text{Cl}_2\text{HSiCH}=\text{CH}_2$, $\text{ClSiH}_2\text{CH}_2\text{-CH}=\text{CH}_2$, $\text{ClSiH}(\text{C}_4\text{H}_6)$, $\text{ClSiH}_2\text{N}(\text{SiH}_3)_2$, $(\text{ClSiH}_2)_2\text{NSiH}_3$, $(\text{ClSiH}_2)_3\text{N}$, $\text{Me}_3\text{Si}\cdot\text{SiH}_2\text{Cl}$ and $\text{Me}_3\text{Si}\cdot\text{SiHCl}_2$) obtained during this study were partially characterised by n.m.r., mass, infrared and Raman spectroscopy. In addition to the chlorination reactions, a new method of preparing $\text{Me}_3\text{Si}\cdot\text{SiH}_3$ is also described.

The preparation and identification of some novel group IV derivatives of mercury ($\text{Me}_3\text{SiHgSiH}_3$, $(\text{SiH}_3)_2\text{Hg}$, $\text{Me}_3\text{SiHgGeH}_3$, $(\text{GeH}_3)_2\text{Hg}$ and $\text{Me}_3\text{SiHgCH}_3$) have been studied in the second part of the thesis. Although ^{199}Hg and ^{29}Si INDOR spectroscopy was the major tool for the identification of these compounds, vibrational spectroscopy was used to confirm this identification.