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SYNTHESIS AND CHARACTERIZATION OF STANNOLES

*The University of Oklahoma*

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GRADUATE COLLEGE

SYNTHESIS AND CHARACTERIZATION

OF STANNOLES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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degree of

DOCTOR OF PHILOSOPHY

BY

WAYNE A. GUSTAVSON

Norman, Oklahoma

1980

SYNTHESIS AND CHARACTERIZATION  
OF STANNOLES

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TO LAURA,  
FOR HER LOVE, PATIENCE, SACRIFICE,  
AND UNDERSTANDING

It was the best of times, it was the worst of times,  
it was the age of wisdom, it was the age of foolishness,  
it was the epoch of belief, it was the epoch of incredulity,  
it was the season of Light, it was the season of Darkness,  
it was the spring of hope, it was the winter of despair,  
we had everything before us, we had nothing before us,  
we were all going to Heaven, we were all going direct the other way-

Charles Dickens

## ACKNOWLEDGEMENTS

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Lastly, I would like to thank Laura who moved 1700 miles in order to make this degree possible.

## FOREWARD

This work was undertaken to synthesize 1,1-disubstituted-2,3,4,5-tetraphenylstannoles. The starting material for this study was 1,1-diiodo-2,3,4,5-tetraphenylstannole. This compound is of value for the organometallic chemist due to its utility as an intermediate in the preparation of many other five-membered heterocyclic tin compounds and to investigate the stereochemistry of hexa- and penta-coordinate complexes of stannoles. The products of these reactions were identified through tin-119m Mössbauer, infrared, proton, and mass spectroscopies.

1,1-Diiodo-2,3,4,5-tetraphenylstannole was prepared in good yield from phenyltin cleavage of hexaphenylstannole by elemental iodine and was found to be thermally stable. Analogous halogenation by elemental chlorine resulted in cleavage of the stannole ring. The great reactivity of iodine attached to tin makes the diiodostannole a highly versatile starting material for the preparation of 1,1-diazido-2,3,4,5-tetraphenylstannole, 1,1-dicyanato-2,3,4,5-tetraphenylstannole, 1,1-diacetato-2,3,4,5-tetraphenylstannole, 1,1-bis(diphenylphosphino)-2,3,4,5-tetraphenylstannole, 1,1-bis(dimethylamino)-2,3,4,5-tetraphenylstannole, 1-fluoro-1-iodo-2,3,4,5-tetraphenylstannole, moreover, the adducts that are formed with pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine indicate the ability to form penta- and hexa-coordinated complexes, all having trans-iodine structures.

Treatment of the diiodotetraphenylstannole with excess lithium



cyclopentadiene results in lithium 1,1-dicyclopentadienyl-1-iodo-2,3,4,5-tetraphenylstannole which, along with its bromine analog, are the only lithium salts of five-coordinate  $[R_4SnX]^-$  compounds. This compound contains pseudorotating axial- and equitorial-fluxional monohapto-cyclopentadienyl groups. Conductivity measurements gave  $\Lambda_o = 133 \text{ ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$ , characteristic of a 1:1 electrolyte. The temperature dependent nuclear magnetic resonance spectrum showed non-equivalent resonances of two cyclopentadienyl groups. These two resonances merge into a singlet peak at  $100^\circ\text{C}$ , indicating that conformers of the axially-most-electronegative type and in which the stannole ring spans one axial- and one equitorial-position can interconvert by a pseudorotation which may go through a tetragonal pyramid.

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# SYNTHESIS AND CHARACTERIZATION OF STANNOLES

## CHAPTER I

### INTRODUCTION

#### 1.1 ORGANOTIN COMPOUNDS

Within the group of compounds known as organotins, i.e., compounds containing at least one tin-carbon bond, there exists a wide spectrum of structures, reactivity and industrial applications. As such, this group constitutes one of the most extensively researched areas of organometallic chemistry, and is the subject of many books<sup>(1,2)</sup> and reviews<sup>(3,4)</sup>.

The first organotin compound was prepared in 1849 by Frankland<sup>(5)</sup> when diethyltin diiodide was produced from the reaction of ethyl iodide with tin metal. In 1852 Löwig<sup>(6)</sup> isolated triethyltin iodide and hexaethylditin from the reaction of ethyl iodide and a tin-sodium alloy. These first recorded preparations of organotin compounds mark the beginnings of organotin chemistry.

Tin, atomic number 50, has four valence shell electrons, and hence a dominating oxidation state of +4. However, the stability of the divalent state increases going down Group IV B, and while tin(II)

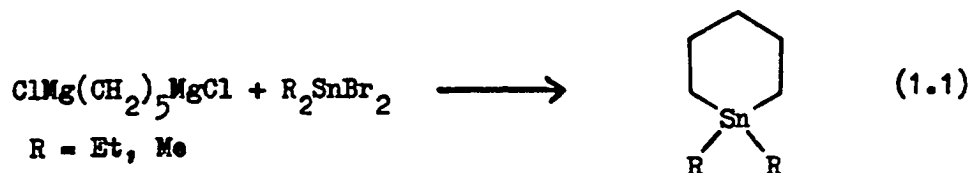
is unstable with respect to tin(IV), the converse is true for lead. As a result, the investigation of organotin(IV) compounds is extensive compared to that of organotin(II) compounds, although over the last twenty years, improved manipulation techniques have brought about a resurgence of interest in this field.

Basic studies in organotin chemistry are stimulated by the success with which a large number of physical techniques can be applied to organotin compounds. For example, tin has two spin of one-half nuclides, tin-117 and tin-119, which are used in nuclear magnetic resonance studies<sup>(7)</sup>; tin has ten stable isotopes which allow for easy identification of tin-containing fragments in the mass spectrometer<sup>(8)</sup>; tin-119m is one of the easiest to observe Mössbauer resonances<sup>(9)</sup>; and easily assignable tin-carbon stretching frequencies are found in the Raman and infrared<sup>(10)</sup>.

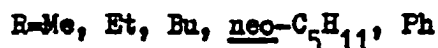
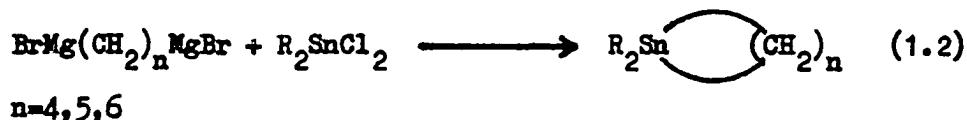
Organotin compounds are generally classified according to the number of tin-carbon bonds present and have the general formula  $R_4\text{Sn}$ ,  $R_3\text{SnX}$ ,  $R_2\text{SnX}_2$ , and  $\text{RSnX}_3$  where R is an organic substituent. The subject of this study was the preparation of heterocyclic compounds containing tin.

## 1.2 RINGS AND STANNOLES

The first tin-containing heterocycle was prepared in 1917 by Grüttner and Krause<sup>(11)</sup> when they synthesized 1,1-diethyl and 1,1-dimethyl derivatives of stannacyclohexane:

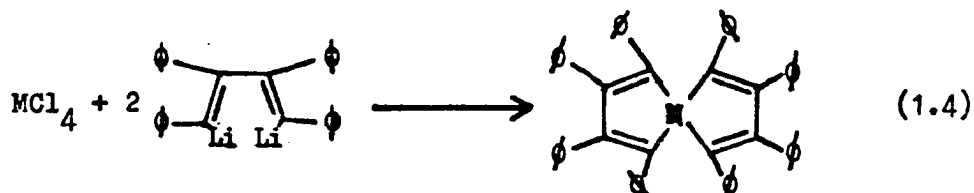
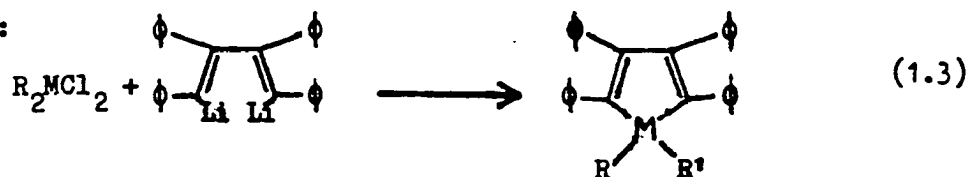


Blewett and Zimmer<sup>(12)</sup> synthesized stannacyclopentanes, -cyclohexanes and -cycloheptanes using Grignard reactions:



The first metallole, 1-metalcyclopentadiene, was prepared in 1959 by Braye and Hubel<sup>(13)</sup> when they reacted diphenyldichlorosilane with a diphenylacetylene-iron complex to form hexaphenylsilole. The study of the metalloles was facilitated through the work of Smith and Hoehn<sup>(14)</sup> who found that diphenylacetylene could be dimerized in the presence of lithium metal in diethylether to form 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-cis, cis-butadiene. By the careful addition of a suspension of the dilithium reagent to a solution of a di-, tri-, or tetrahalide, heterocyclopentadienes containing elements of the fourth group, both monocyclic ( $\text{M}=\text{Si}$ ,  $\text{R}, \text{R}'=\text{CH}_3$ ,  $\text{CH}_2\text{CH}$ ,  $\text{C}_6\text{H}_5$ <sup>(15,16)</sup>;  $\text{R}=\text{Cl}$ ,  $\text{R}'=\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ <sup>(17)</sup>;  $\text{M}=\text{Ge}$ ,  $\text{R}, \text{R}'=\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ <sup>(15,16)</sup>,  $\text{Cl}$ <sup>(17)</sup>;  $\text{R}=\text{Cl}$ ,  $\text{R}'=\text{C}_6\text{H}_5$ <sup>(17)</sup>;  $\text{M}=\text{Sn}$ ,  $\text{R}, \text{R}'=\text{C}_6\text{H}_5$ <sup>(18)</sup>,  $\text{R}, \text{R}'=\text{CH}_3$ <sup>(15,16)</sup>,  $\text{R}, \text{R}'=\text{CH}_2\text{CH}$ <sup>(19)</sup>;  $\text{M}=\text{Pb}$ ,  $\text{R}, \text{R}'=\text{Me}$ <sup>(20)</sup>) and spiro ( $\text{M}=\text{Ge}$ ,  $\text{Sn}$ <sup>(15,16)</sup>) compounds have been

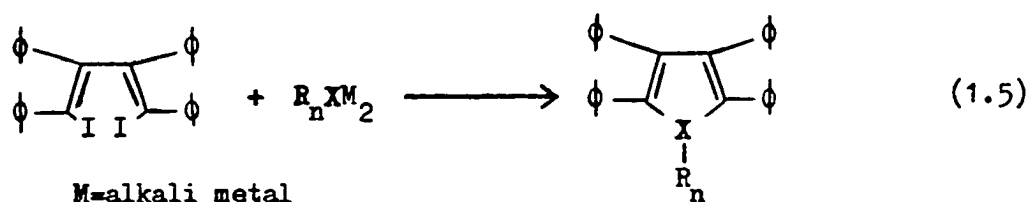
prepared:



The reverse addition has been used to obtain additional monocyclic ( $M=Si$ ,  $R, R'=C_6H_5$ <sup>(18)</sup>,  $CH_3$ ;  $R=H$ ,  $R'=C_6H_5$ ,  $CH_3$ <sup>(21)</sup>;  $R=CH_3$ ,  $R'=Cl$ ,  $C_6H_5$ ,  $Me_2N$ <sup>(21,22)</sup>;  $M=Sn$ ,  $R'=C_6H_5$ <sup>(18)</sup>) and spiro ( $M=Ge$ ,  $Sn$ <sup>(18)</sup>) compounds from the di-, tri-, and tetrahalides, respectively.

Unsubstituted and partially substituted metalloles have been prepared using different reaction sequences. Goubeau, Kalmar and Hoffman<sup>(23)</sup> and Nefedov and Manakov<sup>(24)</sup> prepared 1,1-dimethylsilole from the dehydrogenation of 1,1-dimethyl-1-silacyclopentane<sup>(23)</sup> and 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane<sup>(24)</sup>. Dehydrogenation of 1,1,3,4-tetrachloro-1-silacyclopentane was reported to yield 1,1-dichlorosilole<sup>(25,26,27,28)</sup>, but was later disclaimed<sup>(29)</sup>. Siloles containing a variety of organic groups have been prepared by the dehydrohalogenation of the corresponding 3,4-dichloro-1-silacyclopentanes<sup>(30,31)</sup>.

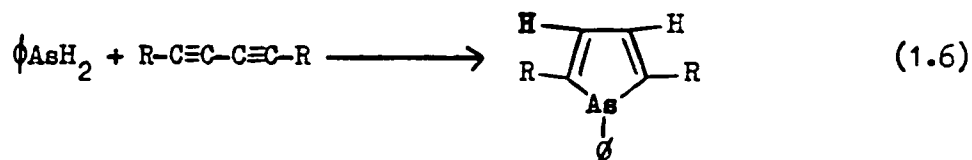
1,4-Diiodotetraphenylbutadiene also leads to the formation of heterocyclopentadienes<sup>(18)</sup> as:



This reaction proceeds slowly and requires higher temperatures than the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene which usually reacts rapidly even at low temperatures. The compounds  $R_n X M_2$  are known where  $X$  is a member of Group IV, V, or VI<sup>(18)</sup>. Tetraphenylmercurocyclopentadiene has been prepared from 1,4-diiodotetraphenylbutadiene and sodium amalgam at room temperature<sup>(18)</sup>.

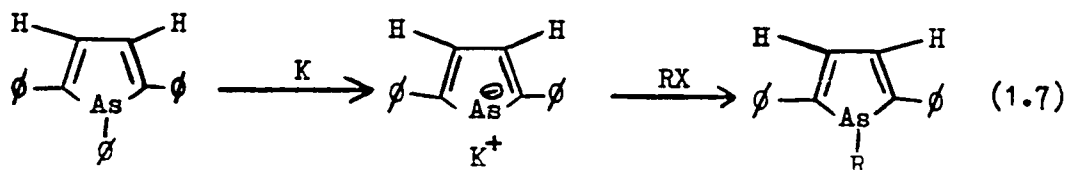
Markl and Hauptman<sup>(32)</sup> have synthesized a series of arsenoles

by the reaction of phenylarsine with substituted 1,3-butadiynes in benzene with catalytic amounts of *n*-butyllithium:



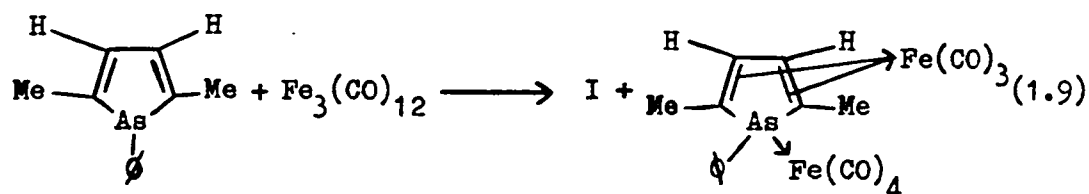
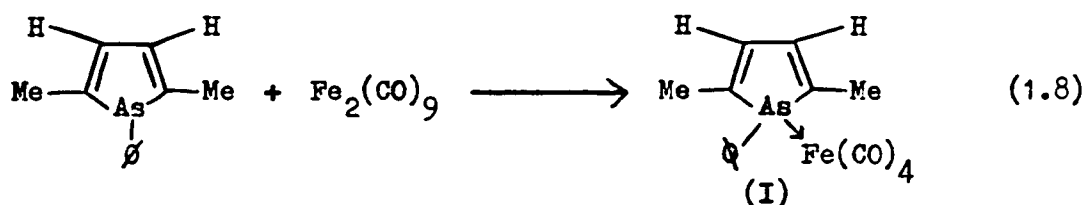
where  $\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{CH}_3, \text{C}_6\text{H}_4\text{Cl}, \text{CH}_3$

This reaction was extended in order to substitute the ring at the 1-position:

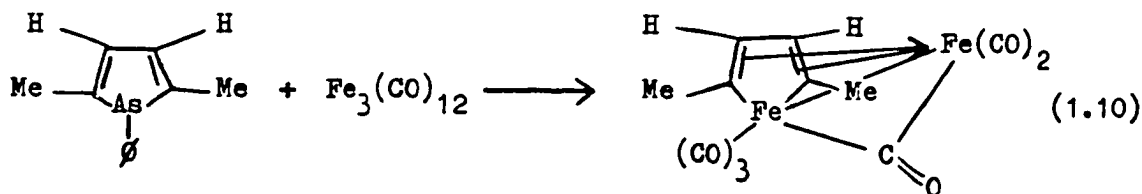


where  $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{OCH}_3$  (32).

Thiollet and Mathey<sup>(33)</sup> have prepared iron carbonyl complexes of 1-phenyl-2,5-dimethylarsenole. Reaction with  $\text{Fe}_2(\text{CO})_9$  resulted in a  $\text{Fe}(\text{CO})_4$  complex, while reaction with  $\text{Fe}_3(\text{CO})_{12}$  in toluene gave  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}_2(\text{CO})_7$  complexes:



At higher temperatures, however, a ferrole complex is formed by an original  $\text{As} \rightarrow \text{Fe}$  exchange:

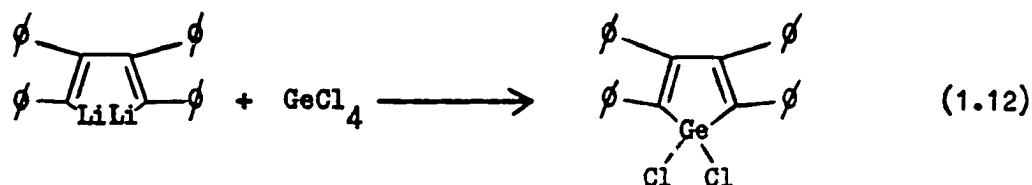
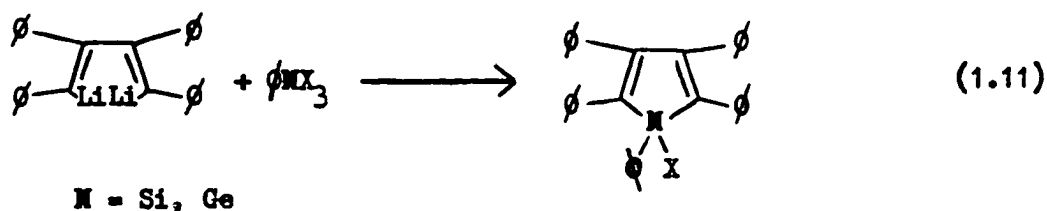


Freedman<sup>(34)</sup> studied 1,1-dimethyl-2,3,4,5-tetraphenylstannole for possible ring aromaticity and concluded that if ring stability toward electrophiles is a reliable indication of resonance stabilization then there is little doubt that the stannole possessed little, if any, such stability. Chemical reduction and stability of siloles and germales containing hydrogen have been studied by electron spin resonance. In one study<sup>(17)</sup>, it was found that, with n-butyllithium as the reducing agent and with removal of the proton from the metal, the reduced species was a conjugated lithium derivative, while in another study<sup>(35)</sup> radical anions and dianions were formed when potassium or sodium was used as the reducing agent with the proton or protons being removed from the carbon atoms of the metallole ring.

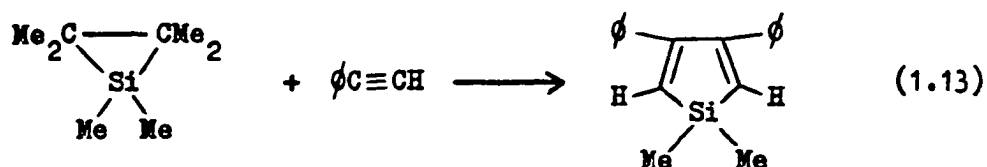
In early work with metalloles<sup>(15,16)</sup> it was assumed that the tin and germanium dihalide derivatives did exist in the course of the formation of the spiro-compounds. Isolation of these compounds was attempted, but the reactivity of the intermediate made isolation difficult. 1-Chloro-2,3,4,5-tetraphenylarsenole, however, was prepared from the reaction of arsenic trichloride and an equimolar amount of 1,4-dilithio-2,3,4,5-tetraphenylbutadiene.

Braye, Hubel, and Caplier<sup>(18)</sup> prepared 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene by the addition of carbon tetrabromide to a suspension of 1,4-dilithio-2,3,4,5-tetraphenylbutadiene.

In 1969 Curtis<sup>(36)</sup> described the synthesis of a series of halogen-substituted sila- and germacyclopentadienes. The addition of the dilithium reagent to the halides  $\text{RMX}_3$  or  $\text{MX}_4$ , which was previously called the reverse addition, gave the halogen-substituted derivatives:

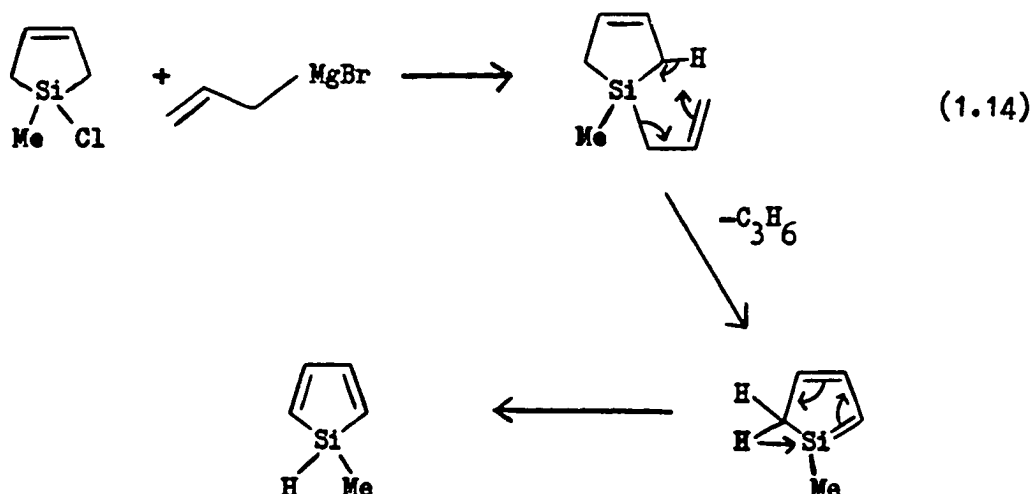


Additional methods have been used to prepare various siloles. The reaction of hexamethylsilirane with 9 molar equivalents of phenylacetylene was carried out in the presence of 1 mole %  $(\phi_3\text{P})_2\text{PdCl}_2$  to give 1,1-dimethyl-3,4-diphenylsilole<sup>(37)</sup>:

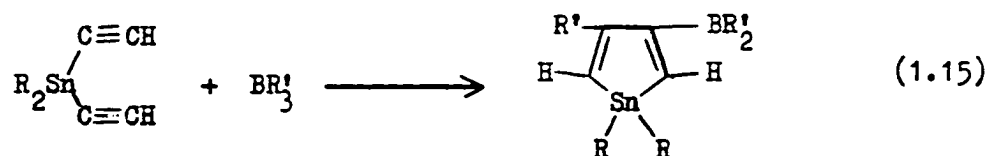


Recently, T.J. Barton<sup>(38)</sup> synthesized dimers of 1-methylsilole. This was achieved by flow pyrolysis of 4-allyl-4-methyl-4-silacyclopentane which yielded the Diels-Alder dimers of 1-methylsilole via the extrusion of propene followed by 1,5-hydrogen migration to silicon and dimerization. It was possible to trap 1-methylsilole monomer by the addition of maleic anhydride:

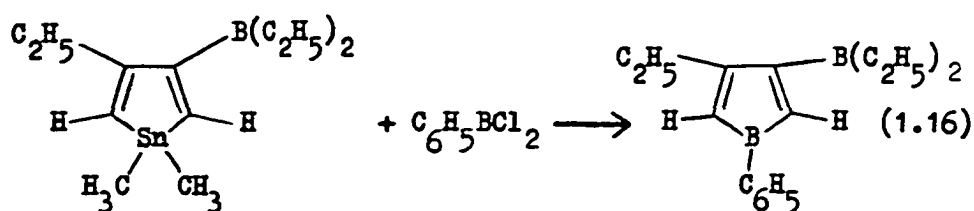




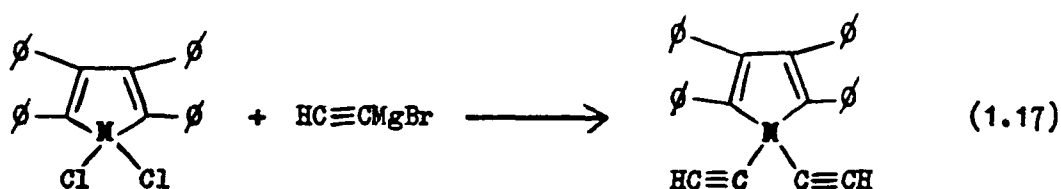
Dialkyl[diethynylstannanes of the type  $R_2Sn(C\equiv CH)_2$  are known to react with trialkylboranes,  $BR'_3$ , to give substituted stannoles<sup>(39)</sup>:



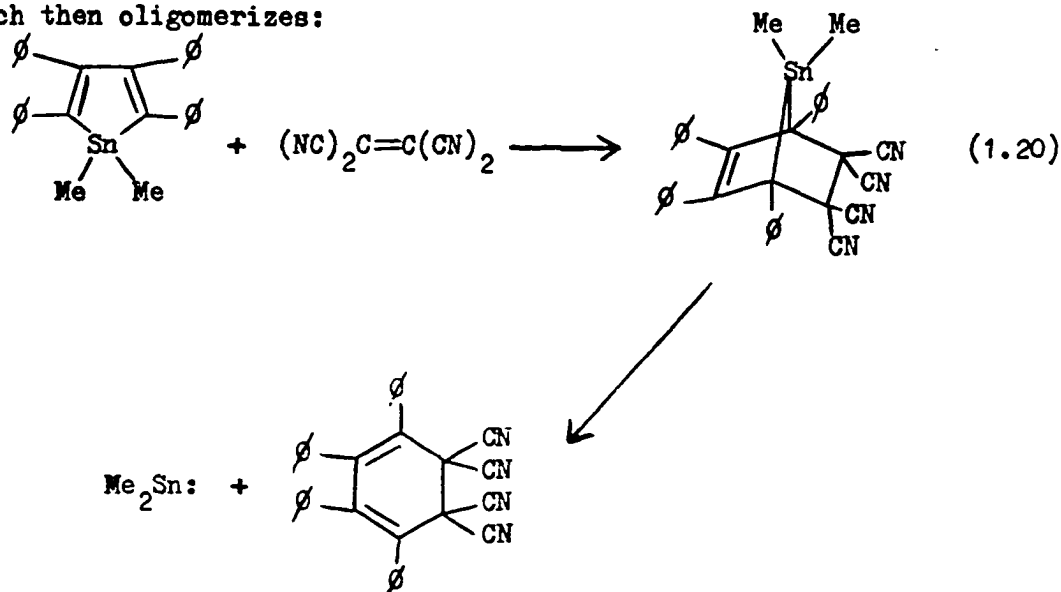
where  $R = CH_3$ ,  $C_2H_5$  and  $R' = C_2H_5$ ,  $i-C_3H_7$ ,  $n-C_4H_9$ . The resulting stannoles were then converted into their borole analogues by reaction with phenylboron dichloride:



Relatively little chemistry has been performed with the metalloles of the main group elements. 1,1-Diethynyl-2,3,4,5-tetra-phenylsilole and its germanium analogue, however, have been prepared by the reaction of the halosilole or halogermole with ethynylmagnesium-bromide<sup>(40)</sup>:

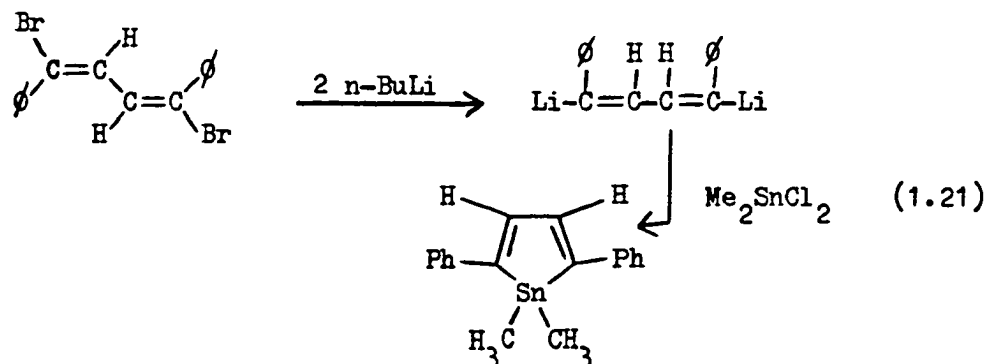


Reaction of 1,1-dimethyltetraphenylstannole with tetracyanoethylene results in the formation of 5,5,6,6-tetracyano-7,7-dimethyl-1,2,3,4-tetraphenyl-7-stannanobornene<sup>(43)</sup>. This compound is stable at  $-30^{\circ}\text{C}$ . for several weeks, but decomposes above  $-20^{\circ}\text{C}$ . to give 5,5,6,6-tetracyano-1,2,3,4-tetraphenyl-1,3-cyclohexadiene and dimethyltin(II), which then oligomerizes:



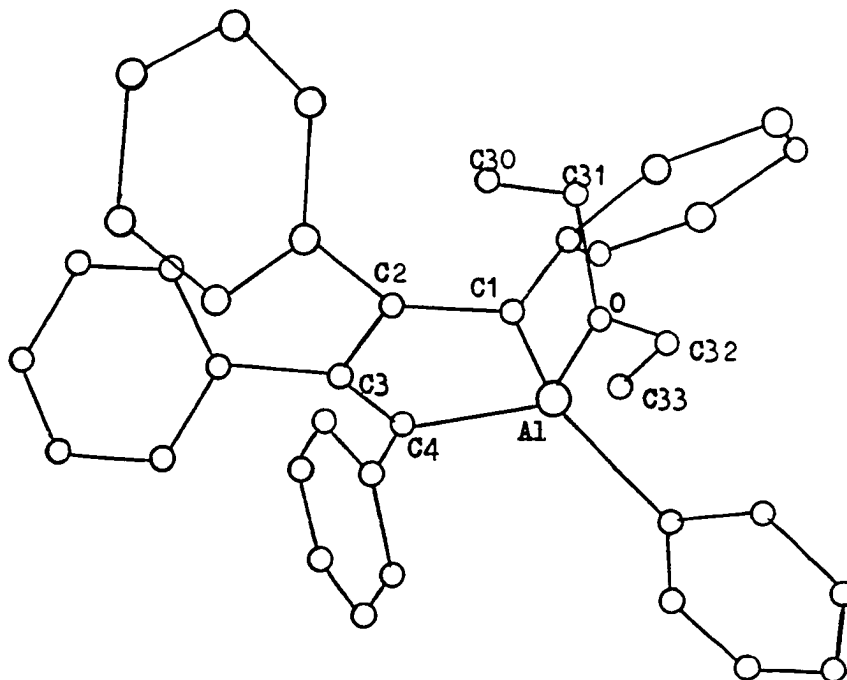
The analogous reaction takes place with 1,1-dimethyltetraphenylstannole and phenylacetylene or dimethylacetylenedicarboxylate<sup>(44)</sup>.

Only one stannole has been prepared to date that contains substituents other than phenyl groups attached to the carbon atoms of the cyclopentadiene ring. 1,1-Dimethyl-2,5-diphenylstannole was prepared by Gilman in 1967<sup>(31)</sup> by the action of *n*-butyllithium on 1,4-dibromo-1,4-diphenyl-1,3-trans, trans-butadiene followed by reaction of the resulting dilithium reagent with dimethyltin dichloride:



The resulting stannole upon irradiation suffered cleavage of the bonds from the tin to the vinylic carbons in the ring<sup>(45)</sup>.

Only one X-ray crystal structure has been reported for a metallole of a main group element<sup>(46)</sup>. The cyclopentadiene ring in pentaphenylaluminole is completely planar with the aluminum atom showing the greatest out-of-plane deviation. The aluminum bonds to the butadiene moiety in a symmetrical manner. Furthermore, it is linked with a phenyl group and, to complete its coordination sphere, with one molecule of diethyl ether.



### 1.3 VIBRATIONAL SPECTROSCOPY

The frequencies of bands in both infrared (IR) and Raman spectra are important analytically and for the structural information they provide, and several papers have reported observed Sn-X (X = halogen, O, C, S, N) stretching frequencies<sup>(10,47,48,49)</sup>.

The position of  $\nu(\text{Sn-C})$  bands are generally in the region  $600\text{--}470\text{ cm}^{-1}$ , and appear to be relatively insensitive to changes in coordination at tin. The number of observed bands, however, can be important. Monoalkyltin(IV) compounds exhibit one Sn-C stretching vibration as expected, but for four-coordinated di- and triorganotin compounds, two bands are predicted:  $\nu_{\text{as}}(\text{Sn-C})$  in the region  $600\text{--}500\text{ cm}^{-1}$ , and  $\nu_{\text{s}}(\text{Sn-C})$  in the  $500\text{--}470\text{ cm}^{-1}$  region<sup>(48)</sup>. The situation is more complex for longer chain alkyl groups.

Two Sn-C stretches are observed in the spectrum of  $n\text{-BuSnCl}_3$  corresponding to gauche- and trans- conformers of the alkyl chain, the higher frequency vibration being the one assigned to the trans- conformation<sup>(50)</sup>. Liquid or solution spectra, where both conformers are often present, are generally more complex than solid state spectra, where a particular conformation is usually favored.

Trigonal bipyramidal five-coordinated structures that contain a planar  $\text{C}_3\text{Sn}$  moiety, can be identified by the absence of the  $\nu_{\text{s}}(\text{Sn-C})$  stretch which is present for tetrahedrally coordinated species<sup>(51)</sup>.

Assignments of the tin-methyl rocking mode,  $\rho(\text{CH}_3\text{-Sn})$ , in the region  $791\text{--}770\text{ cm}^{-1}$ , have been made for methyltin compounds having tetrahedral<sup>(52)</sup>, trigonal bipyramidal<sup>(53,54)</sup>, and octahedral geometries<sup>(55)</sup>.

Tin-phenyl stretches are more difficult to assign owing to

coupling with ring vibrations.

Table 1.1 lists frequencies of the tin-halide stretching vibrations. The ranges for the tin halides are  $\nu(\text{Sn-Cl})$  385-315  $\text{cm}^{-1}$ ,  $\nu(\text{Sn-Br})$  264-222  $\text{cm}^{-1}$ , and  $\nu(\text{Sn-I})$  207-170  $\text{cm}^{-1}$ . Less information is available for the fluorides where the frequencies probably lie in the range 372-328  $\text{cm}^{-1}$ . The fluorides differ considerably from the other halides owing to their highly associated, bridged structures in the solid state.

As with the corresponding alkyl derivatives, one band is expected for monophenyltin derivatives (ca. 250-236  $\text{cm}^{-1}$ ) and two bands for four-coordinated di- and triphenyltin derivatives [ $\nu_{\text{as}}(\text{Sn-}\phi)$  280-260  $\text{cm}^{-1}$  and  $\nu_{\text{g}}(\text{Sn-}\phi)$  240-225  $\text{cm}^{-1}$ ]<sup>(56)</sup>.

While the frequency of the tin-carbon stretches are usually independent of coordination number, they are affected by electro-negative substituents attached to the tin. In general, the greater the electronegativity of or the greater the number of electronegative substituents, the higher the frequency of  $\nu(\text{Sn-C})$ <sup>(48)</sup>.

Tin-chlorine stretches, on the other hand, are sensitive to change in coordination number at tin. Changing the coordination number from four to six causes the frequency of  $\nu(\text{Sn-Cl})$  to be lowered by as much as 100  $\text{cm}^{-1}$ <sup>(48)</sup>. This effect decreases for the heavier halogens.

TABLE 1.1

TIN-HALIDE STRETCHING FREQUENCIES<sup>a</sup> (cm<sup>-1</sup>)

COMPOUND	Cl		Br		I	
	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$
$R\text{SnX}_3$	385-364	369-358	264-256	253-225	200	170
$R_2\text{SnX}_2$	361-349	345-338	260-248	242-238	204-196	186-176
$R_3\text{SnX}$	336-318		234-222		189-182	
$R\text{SnX}_3 \cdot L_2$	299-267		201-170			
$R_2\text{SnX}_2 \cdot L_2$	252-215		169-140			

a) data taken from references 10 and 57.

#### 1.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A review on the subject of n.m.r. of organometallic compounds appeared in 1965 and contained a section on organotin compounds<sup>(58)</sup>. The applications of this spectroscopic technique to the study of organotins has been discussed by Poller<sup>(59)</sup>, Smith<sup>(7)</sup>, Kennedy<sup>(60)</sup>, and Petrosyan<sup>(61)</sup>.

Of the ten isotopes of tin, three have nuclear spin quantum number,  $I = 1/2$ . Of these,  $^{115}\text{Sn}$  has an abundance (0.34%) too low to make n.m.r. measurements possible.  $^{117}\text{Sn}$  (7.54%) and  $^{119}\text{Sn}$  (8.62%) nuclei are of interest. The magnetic resonance effects of these nuclei, along with  $^1\text{H}$  and  $^{13}\text{C}$ , provide useful structural information to the organotin chemist.

Although numerous  $^1\text{H}$  chemical shifts ( $\tau$ ) have been reported, and factors affecting their frequencies discussed, most of the structural evidence derived from  $^1\text{H}$  n.m.r. concerns the magnitude of the indirect two-bond tin-proton coupling constants,  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ . Since  $|^1J(^{119}\text{Sn}-^{13}\text{C})|$  and  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$  are linearly related<sup>(62)</sup>, changes in the nature of the tin-carbon bond will be reflected in the two bond tin-proton coupling constants.

Table 1.2 shows the values of  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$  for a series of methyltin(IV) compounds, along with the structure they adopt.

Solvent studies of methyltin(IV) chlorides<sup>(63,64)</sup> indicate a correlation between % s-orbital character in the Sn-C bond, and hence structure, and the magnitude of  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ . Dilute trimethyltin chloride solutions exhibit similar coupling constants to tetramethyltin (both in  $\text{CCl}_4$ ), and hence similar structures. If a coordinating



TABLE 1.2

 $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$  VALUES FOR METHYLTIN COMPOUNDS

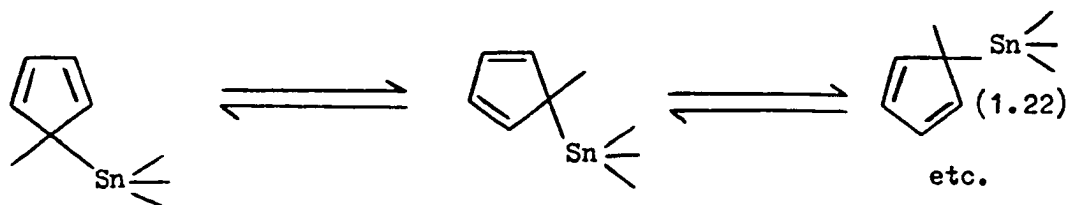
COMPOUND	SOLVENT	$ ^2J(^{119}\text{Sn}-\text{C}-^1\text{H}) $	GEOMETRY	REFERENCE
$\text{Me}_4\text{Sn}$	$\text{CCl}_4$	54 Hz	Tetrahedral	18,19
$\text{Me}_3\text{SnCl}$	$\text{CCl}_4$	58.2	Tetrahedral	19
	$\text{CH}_3\text{CN}$	64.7	Intermediate	19
	$\text{C}_5\text{H}_5\text{N}$	68.0	Trigonal Bipyramid	19
$\text{Me}_2\text{SnCl}_2$	Neat	71.0	Trigonal Bipyramid	18
	$\text{CCl}_4$	69.7	Trigonal Bipyramid	18
$\text{Me}_2\text{Sn}(\text{salen})$	$\text{CDCl}_3$	99.3	<u>trans</u> -Octahedral	21
	$\text{CDCl}_3$	83	<u>trans</u> -Octahedral	21

Salen is the N,N'-ethylenebis(salicylaldiminato) anion

solvent is used, e.g., pyridine, the geometry at the tin increases to trigonal bipyramidal<sup>(64,65)</sup>, and the magnitude of the coupling constant increases. As a result, increase in % s-orbital character from 25% ( $sp^3$  hybrid bonds) to 33.3% ( $sp^2$  hybrid bonds) is accompanied by an increase in the value of  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ . On this basis, the structure of trimethyltin chloride in weakly coordinating acetonitrile is postulated as intermediate between tetrahedral and trigonal bipyramidal<sup>(64)</sup>. A study of dimethyltin dichloride in various solvents has produced similar results<sup>(64)</sup>. The overall implications are that increases in  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$  correlate with a greater planarity of a  $\text{C}_3\text{Sn}$  moiety and a greater linearity of a  $\text{C}_2\text{Sn}$  moiety.

This latter postulate is borne out by  $^1\text{H}$  n.m.r. studies of  $\text{Me}_2\text{Sn}(\text{salen})$ <sup>(66)</sup>, which has two distinct  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$  values corresponding to two isomeric octahedral structures. One structure probably has cis-methyl groups (83 Hz) while the other structure has trans-methyl groups (99.3 Hz).

Variable-temperature  $^1\text{H}$  n.m.r. has been used to determine the bonding in some cyclopentadienyltin(IV) compounds<sup>(67)</sup>. At  $-60^\circ\text{C}$ ., only one proton resonance is observed, owing to a metallotropic rearrangement, or ring "whizzing", but at ca.  $-150^\circ\text{C}$ ., the spectrum due to the nonfluxional system can be observed, by line broadening.



### 1.5 MASS SPECTROMETRY

In the last few years, mass spectrometry has been extensively applied to structural elucidation of organotin compounds. An excellent review was published by Glockling in 1968<sup>(68)</sup>.

Tin has ten stable isotopes which allow for easy identification of tin-containing fragments in the mass spectrometer. Tin isotope masses and abundances are given in Table 1.3.

Bond dissociation energies for tin compounds are low when compared to the analogous values for Ge and Si<sup>(70)</sup>. As a result, it is not surprising that organotin molecules show extensive fragmentation in the mass spectrometer. For example, the most abundant ion from the cyclic  $\text{Sn}_6\phi_{12}$  compound is that fragment associated with two tin atoms<sup>(71)</sup>.

Smaller organotin molecules, however, often show the molecular ion peak as well as a characteristic fragmentation pattern. Fragmentation rules have been derived for trialkyltin halides<sup>(72)</sup>.

As tin has ten naturally occurring isotopes, each ion appears in the mass spectrum as a series of peaks close to one another. This can make interpretation of spectra difficult, especially when two fragments differ by only one or two mass units.

### 1.6 MÖSSBAUER SPECTROSCOPY

The study of the recoilless nuclear resonant fluorescent absorption of  $\gamma$ -rays is more commonly known as Mössbauer spectroscopy, after its discoverer, Rudolf Mössbauer. The Mössbauer effect enables measurement of some of the relatively weak interactions between a nucleus and its surrounding electrons, hence the chemical environment

TABLE 1.3

## TIN ISOTOPE MASSES AND ABUNDANCES

ISOTOPE	MASS	ABUNDANCE (%)
$^{112}\text{Sn}$	111.90494	0.95
$^{114}\text{Sn}$	113.90296	0.65
$^{115}\text{Sn}$	114.90353	0.34
$^{116}\text{Sn}$	115.90211	14.24
$^{117}\text{Sn}$	116.90306	7.57
$^{118}\text{Sn}$	117.90179	24.01
$^{119}\text{Sn}$	118.90339	8.58
$^{120}\text{Sn}$	119.90213	32.97
$^{122}\text{Sn}$	121.90341	4.71
$^{124}\text{Sn}$	123.90524	5.98

of the nucleus, and its application principally to  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$  nuclei make it a technique of fundamental importance to the iron and tin organometallic chemist. As such, the technique has been the subject of numerous reviews<sup>(73,74,75,76,77,9)</sup> monographs<sup>(78,79)</sup> and books<sup>(80,81)</sup>.

The resonance condition required for  $^{119}\text{Sn}$  and the methods used for observing this resonance are discussed in detail in the above texts. However, a more detailed discussion of the two major parameters to which this resonance gives rise, Isomer Shift (IS) and Quadrupole Splitting (QS), is necessary. Figure 1.1 shows the transitions required to produce these parameters.

Experimentally, the IS is the displacement of the resonance from zero relative velocity, i.e., the mismatch between the sets of nuclear energy levels of the source and the absorber.

Mathematically, the I.S. may be represented by the expression:

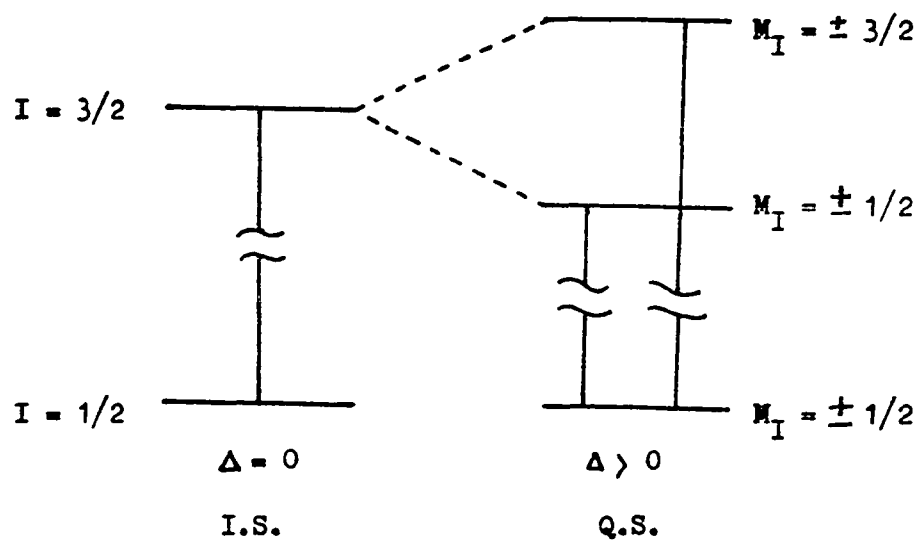
$$\text{I.S.} = \frac{K \Delta R}{R} \left[ (\psi_{5s}(0))_a^2 - (\psi_{5s}(0))_s^2 \right] \quad (1.23)$$

where  $K$  = constant,  $R$  = nuclear radius,  $\Delta R$  = the change in nuclear radius from excited to ground state,  $(\psi_{5s}(0)) = 5s$  electron density at the nucleus, and the subscripts  $a$  and  $s$  denote the absorber and the source, respectively. Since the ratio  $\Delta R/R$  is now accepted as positive<sup>(82)</sup> an increase in the I.S. represents an increase in the  $s$  electron density at the nucleus.

The degeneracy of the excited state,  $I = 3/2$ , is partially lifted in the presence of a non-zero electric field gradient, and

FIGURE 1.1

MÖSSBAUER ENERGY TRANSITIONS



consideration of the selection rule,  $\Delta m_I = 0, \pm 1$ , shows that two transitions will be allowed. The separation of the two peaks in the spectrum is proportional to the energy separation of the two excited states,  $\Delta E_Q$ , and is the Q.S. In this case the centroid of the two peaks is the I.S.

The I.S. is a measure of the electron density at the nucleus, which in turn is related to the electron density in the valence shell of the tin atom, and should thus vary with the changing polarity of the bonds to tin. Oxidation state, coordination number, geometry, and stereochemistry at and around the tin atom also contribute to the value of the I.S.<sup>(77)</sup>, and will be discussed later.

Comparison of the s-p and s-p-d hybrid orbitals needed for bonding in tin(II) and tin(IV) compounds, shows a theoretical decrease in the s electron density at the tin when the oxidation state is increased. As a result, the I.S. values for tin(IV) compounds will be less than the I.S. values for tin(II) compounds. The I.S. for  $\beta$ -tin, 2.56 mm/s, is taken as the dividing line for the two oxidation states<sup>(9)</sup>.

If a series of compounds of similar structure is considered, the value of the I.S. will reflect the nature of the bonds to tin. As the electronegativity of the ligands increase, the electron density at the tin decreases, so the I.S. also decreases.

For the isostructural series  $[\text{SnX}_4\text{Y}_2]^{2-}$  (X, Y = Cl, Br, I), linear relationships have been found between I.S. and (i) the sum of the Pauling electronegativities<sup>(83)</sup> and (ii) Mulliken electronegativities<sup>(84)</sup>. For the series  $\text{R}_n\text{SnX}_{4-n}$ , I.S. should increase regularly

with increasing  $n$ , if there is no change in structure, although for  $X = \text{halogen}$  a maximum is found at  $n = 2$ <sup>(77)</sup>.

Stereochemical changes may contribute to this, although the most significant factor is thought to be polarization of the tin-carbon bonds by the electronegative groups making them more covalent, the effect maximizing at  $n = 2$ <sup>(85)</sup>.

Increase in coordination number is usually associated with a decrease in I.S. As a result, I.S. for a series of tin halides follows the trend  $\text{SnX}_4 > \text{SnX}_5^- > \text{SnX}_6^{2-}$ <sup>(86)</sup>. The situation for organotin(IV) derivatives is not entirely clear, and no changes in I.S. have been reported which can be attributed solely to a change in coordination number<sup>(73)</sup>.

Stereochemical factors have been used to explain changes in I.S. for a series of cis- and trans-  $\text{R}_2\text{SnX}_4$  species, where it is found that, for similar ligands  $X$ , the isomer shifts are greater in the trans case. Bond polarities offer only partial explanation of this phenomenon. An increase in the C-Sn-C angle, corresponding in a hybridization treatment to an increasing  $s$ -character of the Sn-C bonds, seems to be responsible<sup>(87)</sup>.

The value of the Q.S. is directly related to the electric field gradient (E.F.G.) at the Mössbauer nucleus. Initial arguments for tin suggested that direct bonding interactions producing a non-cubic distribution of electrons, were due to non-uniformity in the  $\pi$ -framework about the tin<sup>(88)</sup>. Later reports, however, show that the primary contribution to the E.F.G. is an imbalance in the polarity of the sigma bonds from the ligands to the tin, supplemented in some



instances by structural effects, with distortions in the  $\pi$ -framework being secondary factors<sup>(89)</sup>.

Many theories have been suggested to correlate the Q.S. values with structure. The use of the  $\rho$  factor<sup>(90)</sup>, the ratio of Q.S. to I.S. met with some early success. Five- or six-coordination was expected for  $\rho > 2.1$ , and four-coordination was expected for  $\rho < 1.8$ . More recent work has shown that this approach is not reliable<sup>(91)</sup>.

A more widely reviewed theory is the "point-charge" approximation<sup>(92,93,94)</sup>, where each ligand is considered to be a point charge, and makes a contribution, denoted by  $[L]$ , to the electric field gradient. The tensor  $[L]$  is known as the partial field gradient. The quadrupole splitting can be represented by the equation:

$$\text{Q.S.} = 1/2 e^2 q Q (1 + n^2/3)^{1/2} \quad (1.24)$$

where  $Q$  is the quadrupole moment of the nucleus,  $e$  is the protonic charge, and  $q$  ( $=V_{zz}$ ) and  $n$ , an asymmetry parameter, are functions of the electric field gradient at the nucleus. The electric field gradient is the negative gradient of the potential,  $V$ , and is given by the expression:

$$\text{E.F.G.} = - \begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix} \quad (1.25)$$

Careful choice of axes can reduce this tensor to a combination of the components  $V_{xx}$ ,  $V_{yy}$ , and  $V_{zz}$  where:

$$V_{xx} + V_{yy} + V_{zz} = 1 \quad (1.26)$$

As a result, only two parameters must be considered,  $V_{zz}$  and  $n$ , where:

$$n = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (1.27)$$

Contributions to the electric field gradient can come from substituents bonded directly to the tin in the first coordination sphere ( $q_{val}$ ) and those more removed in the lattice ( $q_{latt}$ ). Since  $q_{val} \gg q_{latt}$ <sup>(78)</sup> only the former must be considered.

Insertion of the calculated partial field gradient values into the proper point charge expression<sup>(73)</sup>, some of which are shown in Figure 1.2, in conjunction with the preceeding expression for the quadrupole splitting, allows the calculation of quadrupole splitting values for various geometries. Correlation between the predicted and the observed quadrupole splitting values has been good<sup>(93,94,95)</sup>, and the model has been widely used to predict structure<sup>(96,97,98)</sup>. This is especially true for octahedral compounds with formula  $R_2SnX_4$ . The point charge model predicts  $Q.S._{trans} = 2[Q.S._{cis}]$ , and work by Fitzsimmons<sup>(99)</sup> has shown that this prediction is valid. As a result those compounds with Q.S. ca. 2mm/s are cis- and those with Q.S. ca. 4 mm/s are trans-octahedral structures.

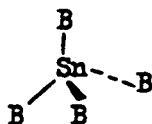
For the cis- and trans- isomers of octahedral  $R_2SnX_4$  complexes, a breakdown of the point charge model has been observed. So while the sign of the quadrupole splitting in the two cases should differ, both are experimentally determined to be negative<sup>(100,101)</sup>. In the presence of strongly chelating ligands, distortions from regular octahedral geometries are observed, e.g., in  $Me_2Sn(oxin)_2$ <sup>(102)</sup> the C-Sn-C angle

FIGURE 1.2

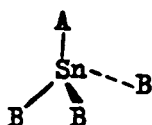
POINT CHARGE EXPRESSIONS FOR SOME COMMON STRUCTURES

STRUCTURE

COMPONENTS OF ELECTRIC FIELD GRADIENT



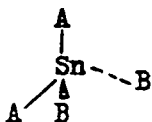
$$V_{zz} = V_{xx} = V_{yy} = 0$$



$$V_{zz} = (2[A] - 2[B])e$$

$$V_{xx} = V_{yy} = (-[B] + [A])e$$

$$n = 0$$

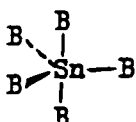


$$V_{zz} = (2[A] - 2[B])e$$

$$V_{yy} = (2[B] - 2[A])e$$

$$V_{xx} = 0$$

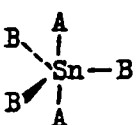
$$n = 1$$



$$V_{zz} = (4[B]^a - 3[B]^e)e$$

$$V_{xx} = V_{yy} = (3/2[B]^e - 2[B]^a)e$$

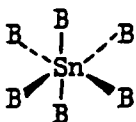
$$n = 0$$



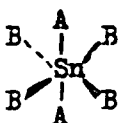
$$V_{zz} = (4[A]^a - 3[B]^e)e$$

$$V_{xx} = V_{yy} = (-2[A]^a + 3/2[B]^e)e$$

$$n = 0$$



$$V_{zz} = V_{xx} = V_{yy} = 0$$



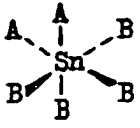
$$V_{zz} = (4[A] - 4[B])e$$

$$V_{xx} = V_{yy} = (2[B] - 2[A])e$$

$$n = 0$$

FIGURE 1.2

POINT CHARGE EXPRESSIONS FOR SOME COMMON STRUCTURES

STRUCTURE	COMPONENTS OF ELECTRIC FIELD GRADIENT
	$V_{zz} = (2[B] - 2[A])e$ $V_{xx} = V_{yy} = ([A] - [B])e$ $n = 0$

Expressions in this table are taken from reference 9.

is  $111^\circ$  rather than the  $90^\circ$  expected for cis-methyl groups. Recalculation of the sign of the quadrupole splitting on the basis of a distorted cis-structure achieves the observed experimental result<sup>(77)</sup>.

Bancroft<sup>(90)</sup> has used quadrupole splitting values to distinguish the three isomers of a trigonal bipyramidal  $R_3SnX_2$  structure. Observed quadrupole splitting values fall in the ranges cis- $R_3SnX_2$ , 1.7-2.3 mm/s, trans- $R_3SnX_2$ , 3.0-3.9 mm/s, and mer- $R_3SnX_2$ , 3.5-4.1 mm/s.

Since its first observation in 1957<sup>(103)</sup>, the Mössbauer effect has become a very important method for research into solid state chemistry. Information obtained from measurement of the I.S. and Q.S. measured at 77K is often sufficient for investigations of molecular structure. However, from these experiments, little or no correlation with lattice structure can be gained.

The strength of the Mössbauer resonance is dependent on the magnitude of the recoilless resonant interaction, which is related to the strength of the binding of the Mössbauer nucleus within the solid lattice. On a qualitative basis, a Mössbauer resonance at room temperature indicates the presence of a polymeric lattice<sup>(73,76)</sup>. A recent publication by G.M. Bancroft<sup>(104)</sup>, however, has demonstrated that there are exceptions to this rule. More conclusive results, however, have been gained from experiments studying the rate of decay of the Mössbauer resonance. Harrison<sup>(105)</sup> has shown that the rates of decay of the Mössbauer resonances of polymeric and non-polymeric lattices are very different and that the slope of the straight line obtained by plotting  $\log A$  against temperature gives a reliable guide to the relative strength of the intermolecular interactions in the

solid state.

By combining the results of variable temperature Mössbauer experiments with data from laser Raman spectra of the lattice mode region ( $20\text{--}100\text{ cm}^{-1}$ ), which gives additional information concerning the lattice vibration modes in the solid, it is possible to derive an effective vibrating mass. This is an effective mass associated with the thermally excited motion of the Mössbauer atom, and as a result localized associations within the lattice network can be detected<sup>(106)</sup>.

While it is possible, in practice, to measure the recoil-free fraction of the absorbing nucleus,  $f$ , it is more convenient to measure the area under the resonance curve obtained in the spectra. If a thin absorber is used, the area ( $A$ ) and the recoil-free fraction are related by:

$$A = \pi/2 \ f \Gamma \mathcal{E} \quad (1.28)$$

where  $\Gamma$  is the half-height line width and  $\mathcal{E}$  is an absorption term.

The recoil-free fraction is given by:

$$f = \exp \left[ \frac{-E_\gamma^2 \langle x^2 \rangle}{h^2 c^2} \right] \quad (1.29)$$

where  $E_\gamma$  is the energy of the  $\gamma$ -radiation,  $\langle x^2 \rangle$  is the component of the mean square amplitude of vibration of the emitting atom in the direction of the  $\gamma$ -ray,  $h$  is Plank's constant, and  $c$  is the speed of light.

By equating expressions (1.28) and (1.29) it can be seen that the slower the decay of the area with increasing temperature, the smaller the increase in atomic displacement of the Mössbauer atom, and hence, the stronger the binding within the lattice.

The temperature dependence of the recoil-free fraction derived from the Debye model of solids is given by the expression:

$$f(T) = \exp \frac{-3E_R}{2K \theta_D} \left[ 1 + \frac{4T^2}{\theta_D^2} \int_0^{\theta/T} \left( \frac{x}{e^x - 1} \right) dx \right] \quad (1.30)$$

where  $K$  is a constant,  $E_R$  is the recoil energy,  $\theta_D$  is the Debye temperature.

In the high temperature limit, the integral in expression (1.30) becomes  $\theta_D/T$  so that:

$$\ln f = \frac{-6E_R T}{K \theta_D^2} \quad (1.31)$$

The recoil energy,  $E_R$ , can be calculated by considering the law of conservation of momentum<sup>(107)</sup>:

$$E_R = \frac{E_\gamma^2}{2M_{\text{eff}} c^2} \quad (1.32)$$

where  $M_{\text{eff}}$  is the effective recoiling mass containing the Mössbauer atom. When expression (1.32) is substituted into expression (1.31), the following results:

$$\ln f = \frac{-3E_\gamma^2 T}{K \theta_D^2 M_{\text{eff}} c^2} \quad (1.33)$$

As a result, a plot of  $\ln f$  vs.  $T$  will give a straight line with slope,  $S$ , where:

$$S = \frac{-3 E_\gamma^2}{K \theta_D^2 M_{\text{eff}} c^2} \quad (1.34)$$

From equation (1.28), however, it can be seen that  $A$  and  $f$  are linearly related, so a plot of  $\ln A$  vs.  $T$  will also have a slope  $S$ .

In order to determine the effective vibrating mass,  $M_{\text{eff}}$ , a value for the Debye temperature,  $\theta_D$ , must be known. This can be obtained from laser Raman data. For molecular solids it is assumed that the intra- and intermolecular motions do not couple, and that the lattice can be thought of as a series of hard spheres that are held together by Van der Waals forces.

The intra-cell intermolecular vibrations of these spheres against each other occur in the  $200\text{--}20\text{ cm}^{-1}$  region in the Raman spectrum of the solid. If one vibration mode in this region corresponds to the intra-unit cell vibration of two molecules against each other, then this vibration mode,  $w_L$ , and the Debye temperature are related by:

$$\theta_D = \frac{h w_L}{K} \quad (1.35)$$

As a result:

$$-\ln A = \frac{3 E_y^2 K T}{M_{\text{eff}} c^2 h^2 w_L^2} \quad (1.36)$$

This expression allows for the experimental determination of the effective vibrating mass, which in turn allows for the distinguishing of a solid as monomeric, dimeric, trimeric, etc. When a polymeric lattice is being considered, the effective vibrating mass corresponds to part of the polymeric chain; the formula weight or an integral multiple of the formula weight. This has been successfully illustrated by P.G. Harrison<sup>(108)</sup>.

Resonance area data has been collected for various organotin compounds, and semilogarithmic plots of the resonance area (normalized to 77K) vs. temperature were found to be linear<sup>(105)</sup>. From these data



and known crystal structures the following generalizations can be made: (i) compounds which have a lattice composed of discrete, monomeric molecules have temperature coefficients (slope of the line in a graph of  $\ln A$  vs.  $T$ ) of ca.  $-1.8 \times 10^{-2} \text{ K}^{-1}$  regardless of the coordination number at tin; (ii) weak intermolecular interactions, such as the hydrogen-bonding that occurs between adjacent molecules, have temperature coefficients of ca.  $-1.71 \times 10^{-2} \text{ K}^{-1}$ ; (iii) a more extensive system of hydrogen-bonding causes a further reduction in the temperature coefficient to a value of ca.  $-1.27 \times 10^{-2} \text{ K}^{-1}$ , reflecting the increase in the rigidity of the lattice; (iv) strongly hydrogen-bonded systems and one-, two-, and three-dimensional polymeric lattices exhibit temperature coefficients of ca.  $-9.0 \times 10^{-3} \text{ K}^{-1}$ ; and (v) compounds that have a strongly packed ionic lattice have temperature coefficients of ca.  $-2.3 \times 10^{-3} \text{ K}^{-1}$ . Examples of these five compound types are shown in Table 1.4.

TABLE 1.4

## TEMPERATURE COEFFICIENTS OF ORGANOTIN COMPOUNDS

COMPOUND	TEMP. COEFF. ( $\times 10^2/K^{-1}$ )	STRUCTURE
$\text{Me}_3\text{SnONPhCOPh}$	1.74	Monomeric molecules <sup>a</sup>
$\text{Ph}_3\text{SnONPhCOPh}$	1.85	Monomeric molecules <sup>b</sup>
$\text{Me}_3\text{SnO}_3\text{SPh}\cdot\text{H}_2\text{O}$	1.71	Weak H-bonded, 1-D lattice <sup>c</sup>
$\text{Me}_3\text{SnO}_2\text{CC}_5\text{H}_4\text{N}\cdot 2\cdot\text{H}_2\text{O}$	1.27	3-D network with H-bonds <sup>d</sup>
$\text{Me}_2\text{Sn}(\text{ONHCOMe})_2$	0.92	Strong H-bonds <sup>e</sup>
$\text{Me}_3\text{SnOC}_6\text{H}_{10}$	0.97	1-D polymer <sup>f</sup>
$\text{Sn}(\text{O}_2\text{CH})_2$	0.84	2-D polymer <sup>g</sup>
$\text{Me}_2\text{SnO}$	0.87	Polymeric lattice <sup>h</sup>
$\text{SnO}$	0.23	Ionic lattice

a) Harrison, P.G.; Molloy, K.C.; Thornton, E.W., *Inorg. Chim. Acta* (1979), 33, 137.

b) Harrison, P.G.; King, T.J.; *J. Chem. Soc. Dalton*, (1974), 2298.

c) Harrison, P.G.; Phillips, R.C.; Richards, J.A., *J. Organometal. Chem.*, (1976), 114, 47.

d) Harrison, P.G.; Phillips, R.C.; Thornton, E.W., *J. Chem. Soc. Chem. Comm.*, (1977), 603.

e) Harrison, P.G.; King, T.J.; Phillips, R.C., *J. Chem. Soc. Dalton*, (1976), 2317.

f) Ewings, P.F.R.; Harrison, P.G.; King, T.J.; Phillips, R.C.; Richards, J.A., *J. Chem. Soc. Dalton*, (1975), 1950.

g) Harrison, P.G.; Thornton, E.W., *J. Chem. Soc. Dalton*, (1978), 1274.

h) Moore, W.J.; Pauling, L., *J. Am. Chem. Soc.* (1941), 63, 1392.

## CHAPTER II

### 1,1 - DIHALO - 2,3,4,5 - TETRAPHENYLSTANNOLE

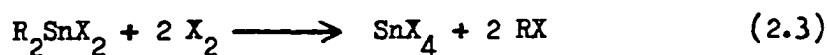
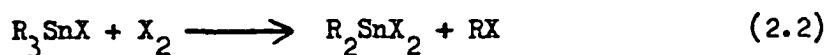
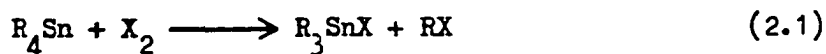
#### 2.1 INTRODUCTION

Organotin halides form an important class of organotin derivatives and were among the first organotin compounds to be isolated<sup>(6)</sup>. Organotin halides are of great utility to the organo-metallic chemist because they are intermediates in the preparation of other organotin compounds.

Organotin halides have the formula  $R_3SnX$ ,  $R_2SnX_2$ , or  $RSnX_3$ , where R is an organic group such that a direct Sn-C bond is involved, and X is a halogen or pseudo-halogen.

Organotin halides are prepared by halogenation of the fully-substituted compounds,  $R_4Sn$ , exchange reactions between the fully-substituted compound and a tin(IV) halide,  $SnX_4$ <sup>(109)</sup>, or by various reactions starting from metallic tin or its inorganic compounds<sup>(110)</sup>.

Elemental halogens cleave  $R_4Sn$  compounds to  $R_3SnX$ ,  $R_2SnX_2$ , or  $SnX_4$ , depending on the conditions and molar ratios of materials employed<sup>(111,112,113,114,115,116)</sup>.



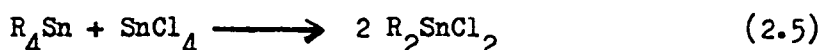
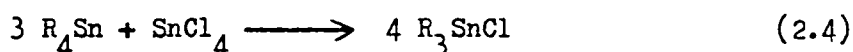
In these reactions the first two groups are cleaved stepwise, but the

two remaining groups are then cleaved simultaneously<sup>(117)</sup>. As a result,  $R_3SnX$  and  $R_2SnX_2$  compounds are prepared in this manner, but not  $RSnX_3$  compounds. A number of studies have determined the relative ease of cleavage of various organic groups from tin<sup>(112,115,117,118,119)</sup>.

The groups, arranged in order of decreasing ease of cleavage are:

o-tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > i-butyl > n-butyl > i-amyl > amyl > hexyl > heptyl > octyl.

Rearrangement reactions between tin(IV) halides,  $SnX_4$ , and tetra-aryls or -alkyls,  $R_4Sn$ , are the most widely used method of preparing organotin halides. A particular halide might be obtained by taking  $R_4Sn$  and  $SnX_4$  in proper proportions<sup>(109)</sup>:

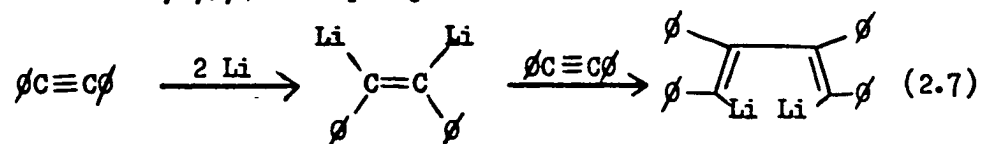


## 2.2 DIMERIZATION OF DIPHENYLACETYLENE WITH LITHIUM

This reaction was first reported by Bergmann and Schlenk<sup>(120)</sup> in 1928 and was followed by a detailed investigation by Smith and Hoehn<sup>(14)</sup> in 1941. Two major products were isolated from this reaction. The first product is the desired cis-1,4-dilithio-tetra-phenylbutadiene. The second material, upon quenching, produces 1,2,3-triphenylnaphthalene. The relative amounts of each product can be varied by adjusting the reaction conditions<sup>(14)</sup>. If a 1:1 molar ratio of diphenylacetylene to lithium metal is employed, the final product is cis-1,4-dilithio-1,2,3,4-tetraphenylbutadiene. 1,2,3-Tri-phenylnaphthalene becomes the predominant product when a 2-fold excess

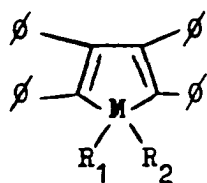
of metal is used.

Leavitt, Manuel, and Johnson<sup>(15,16)</sup> reported that ring closure to form the substituted naphthalene derivative occurred even though diphenylacetylene and lithium were reacted in a 1:1 molar ratio. Their dimerizations resulted in yields of ca. 60% of the cis-1,4-dilithio-1,2,3,4-tetraphenylbutadiene:

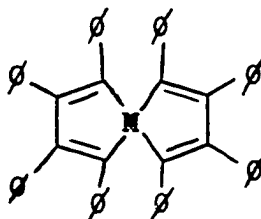


### 2.3 RING FORMATION OF cis-1,4-DILITHIO-1,2,3,4-TETRAPHENYL-1,3-BUTADIENE WITH ORGANOMETALLIC HALIDES

The reaction of the organolithium compound, cis-1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, with organometal halides leads to the preparation of heterocyclopentadienes with the general structure I, as mentioned in Chapter I. A 2:1 molar ratio of dilithiotetraphenylbutadiene with tetrahalides leads to the formation of spiro-compounds with structure II, where M is Ge or Sn<sup>(15,16)</sup>:



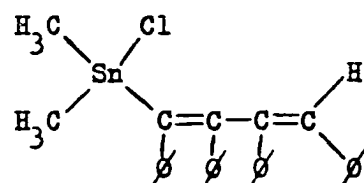
I



II

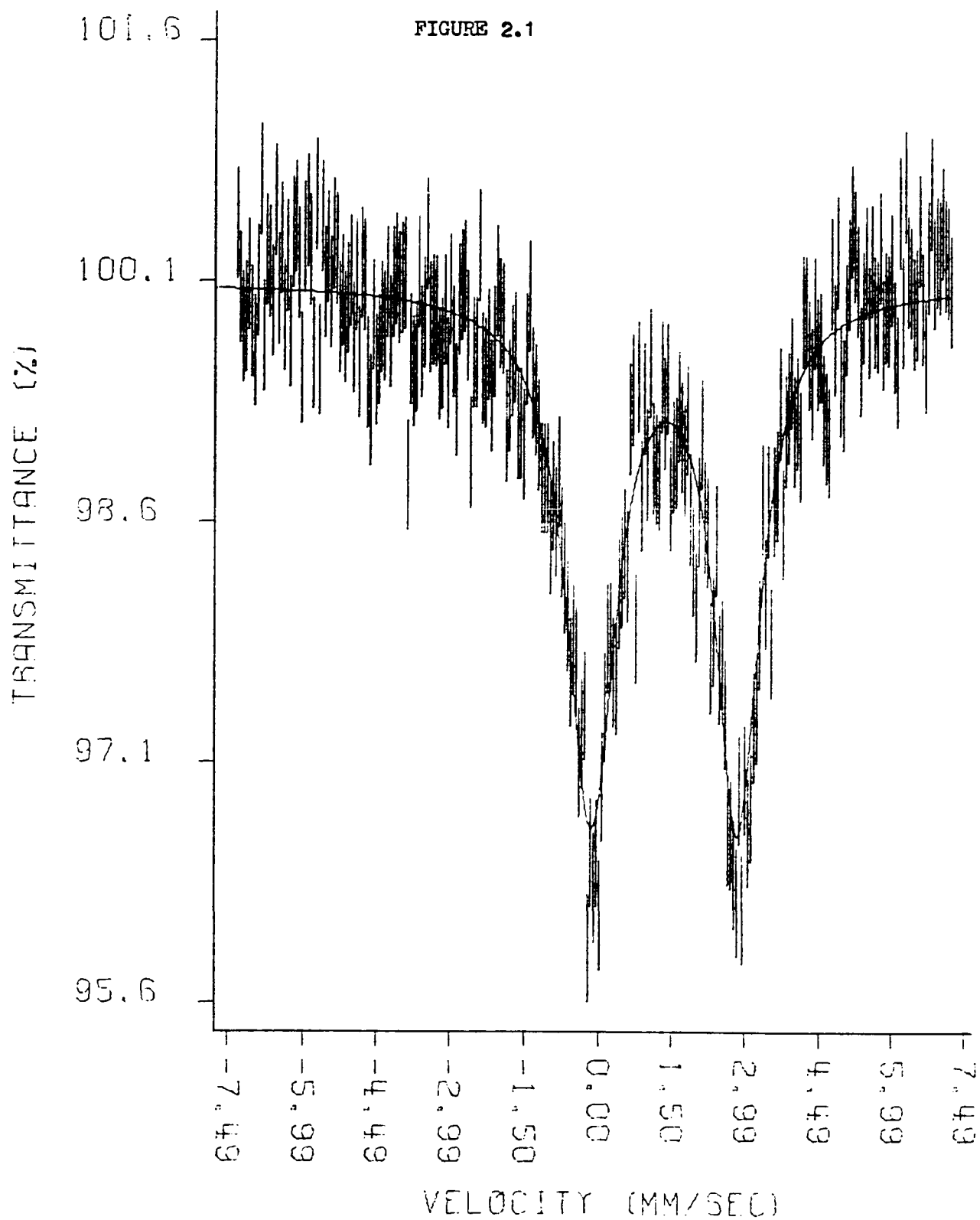
Analogous condensation reactions lead to hydrocarbon cyclopentadienes. When benzal dichloride and dibromomethane were substituted for the metal dihalides, pentaphenylcyclopentadiene and tetraphenylcyclopentadiene, respectively, were produced<sup>(15,16)</sup>.

However, spiro-products are often produced from the reaction of the dilithium reagent and metal dihalides. Zavistoski and Zuckerman<sup>(19)</sup> have reported that the production of spiro-compounds depends on the molar ratio of the two reactants and on the sequence of addition of one reactant to the other. When the dilithium reagent is added to the metal dihalide, the latter is always in excess, and the expected heterocyclopentadienes are formed<sup>(15,16,25,26,27,28,29)</sup>. In the reverse addition, where the metal dihalide is added to the dilithium reagent, the spiro-compound is formed. The reverse addition of dimethyltin dichloride produced a white solid which has been identified as 1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyldimethyltin chloride<sup>(19)</sup>, having the structure:

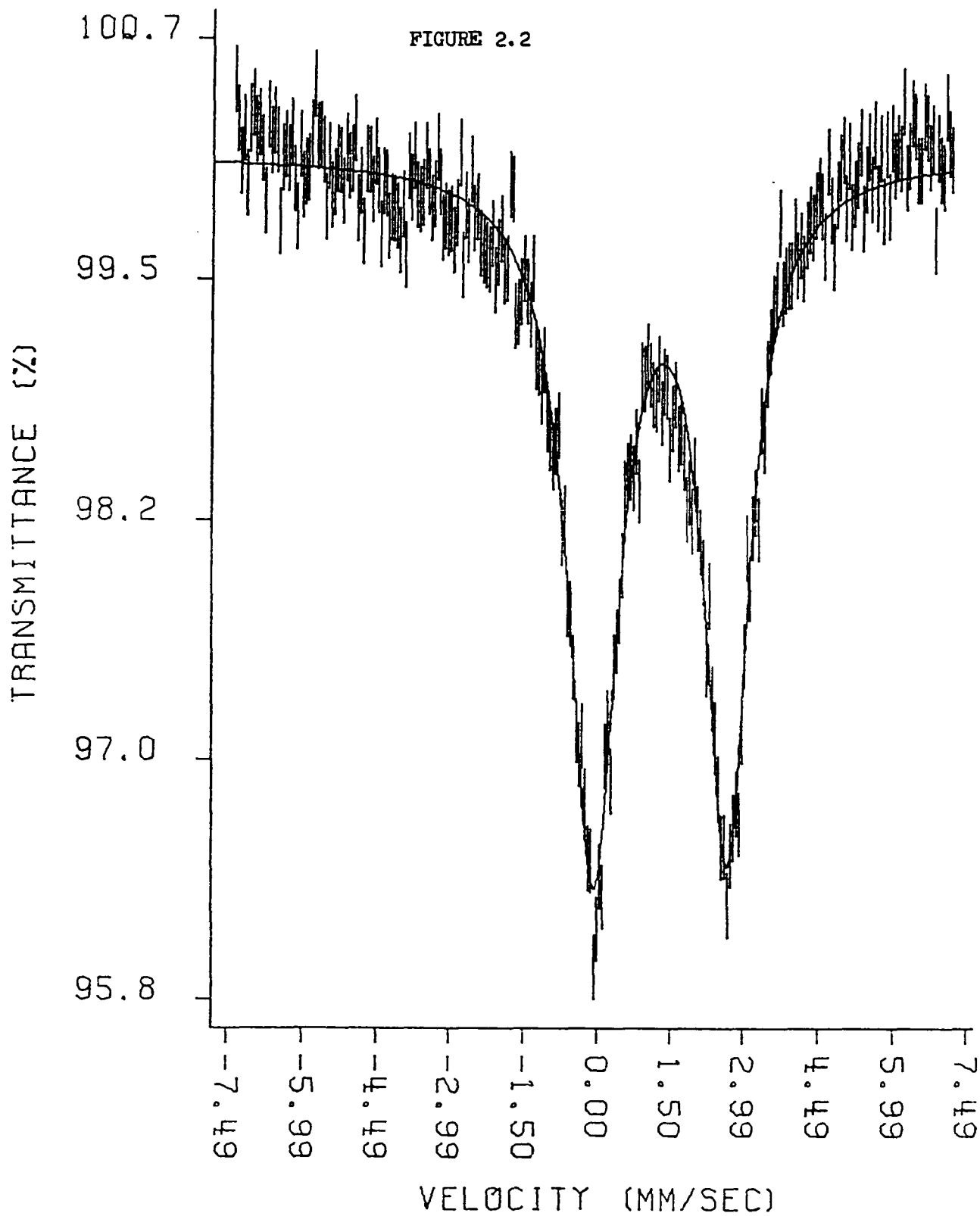


1,2,3,4-Tetraphenyl-cis, cis-1,3-butadienyldiphenyltin chloride has been isolated as a product of the reaction of the dilithium reagent with diphenyltin dichloride. The presence of well-defined quadrupole splittings in the  $^{119}\text{mSn}$  Mössbauer spectra of these compounds (Figures 2.1 and 2.2) clearly rules out the expected dimethyl- or hexaphenylstannole (Figure 2.3) structures.

The isolation of these monochlorotin compounds gives convincing evidence that the reactions proceed stepwise with the intermediate replacement of one tin-chlorine bond. In an excess of the organotin reagent cyclization proceeds through the loss of lithium



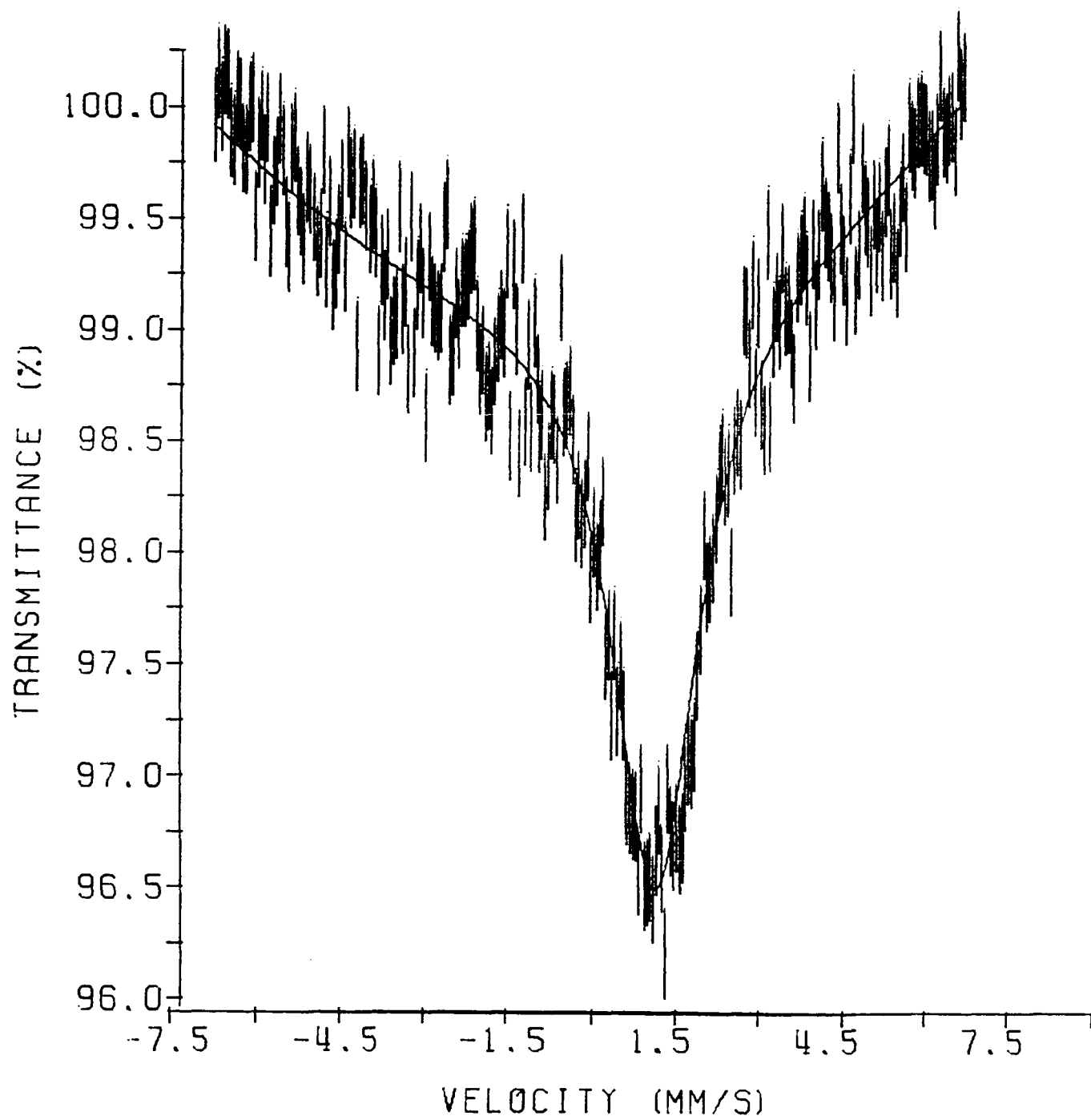
DIMETHYL (TETRAPHENYL-1,3-BUTADIENE-1-YL)TIN CHLORIDE



1,2,3,4-TETRAPHENYL-cis,cis-1,3-BUTADIENYLDIPHENYLTIN CHLORIDE

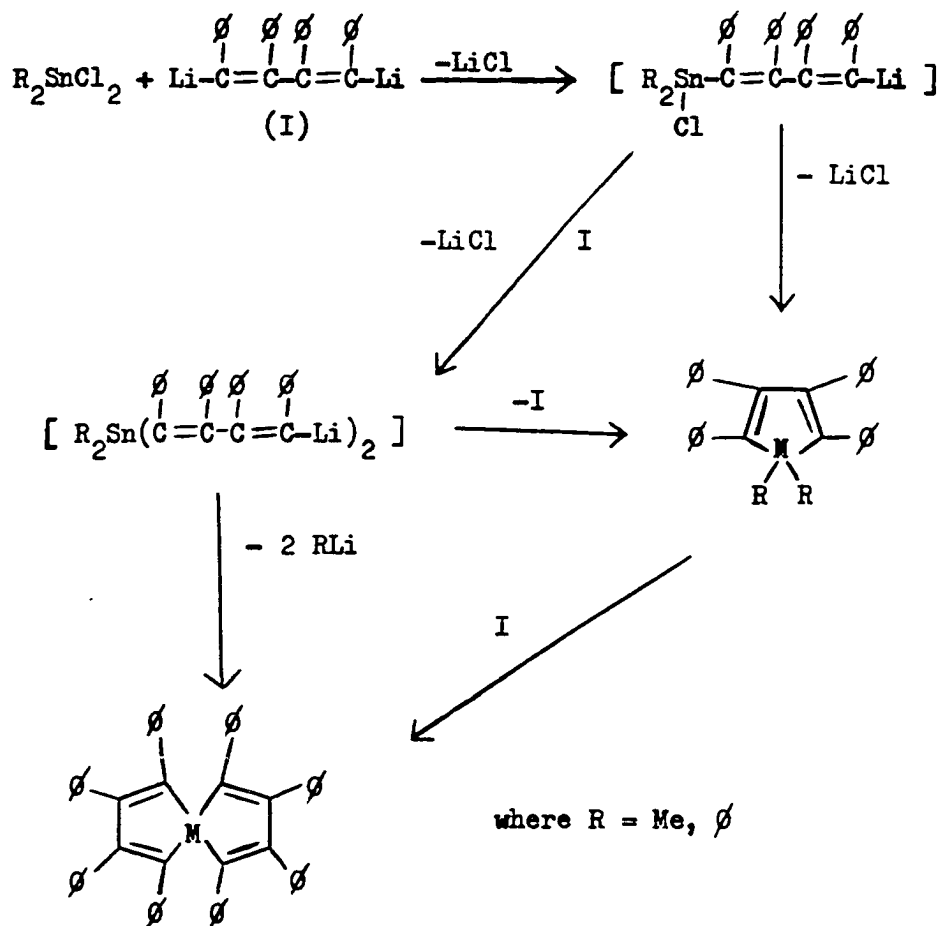


FIGURE 2.3



00 208 HEXAPHENYLSTANNOLE

chloride to form the stannole ring. In the presence of excess lithium reagent, however, there is competition for the second chlorine on the tin by another molecule of the lithium reagent which can lead to the formation of a diorganotin moiety substituted by two butadiene groups, each with an active organolithium site for subsequent ring closure with elimination of RLi. These results indicate that the stannole ring is produced and then can undergo a cleavage in the presence of excess organolithium reagent to form the spiro-compound.



REACTION SCHEME I

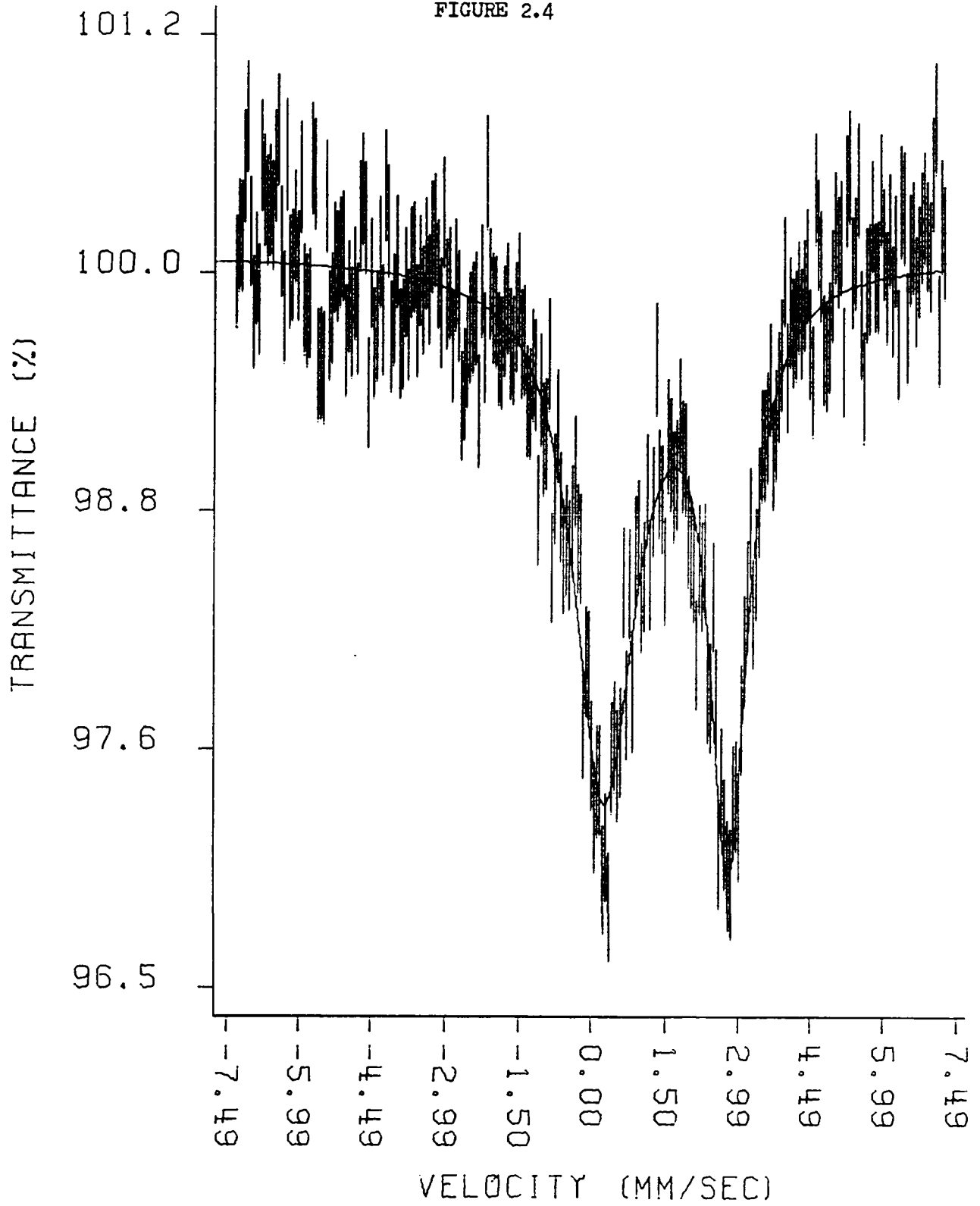
It should be pointed out, however, that in some instances the order of addition of the reactants has no apparent effect on the formation of products. Dimethyldichlorosilane, dimethyldichlorogermane, and diphenyllead dichloride give only the metalloles<sup>(19)</sup>, regardless of the sequence of addition.

#### 2.4 1,1-DIIDO-2,3,4,5-TETRAPHENYLSTANNOLE

As stated previously, cis-1,4-dilithio-1,2,3,4-tetraphenylbutadiene has been used in an apparently general reaction to form a wide variety of metalloles. In this study the method of Van Beelen, Wolters, and Van der Gen<sup>(20)</sup> was used. This is a slight modification of the method used by Leavitt, et al.,<sup>(15,16)</sup> and Braye, Hubel, and Caplier<sup>(18)</sup>. Hexaphenylstannole is prepared in good yields by the addition of an ethereal suspension of the dilithium reagent to a solution of diphenyltin dichloride under nitrogen. The stannole obtained on recrystallization from methylene chloride-ethanol (1:1) had a melting point slightly lower than that recorded in the literature (obs. 172-173°, lit.<sup>(15,16)</sup> 173-174°). The infrared spectrum was identical to that of the literature<sup>(18)</sup>.

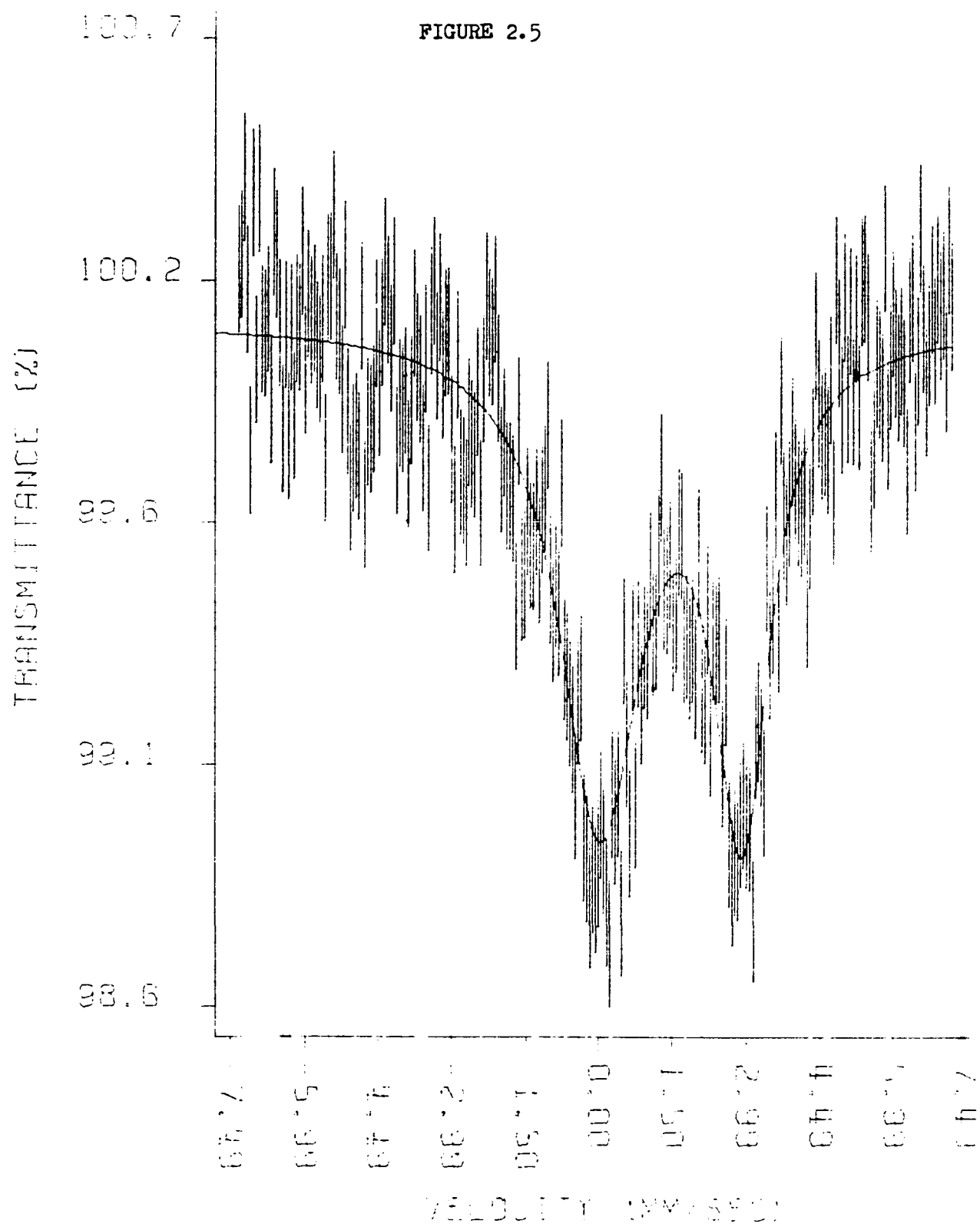
It is evident that hexaphenylstannole reacts as a normal tin compound. Thus, cleavage with elemental bromine<sup>(121)</sup> or iodine, at low temperature, occurs preferentially at the phenyl-tin bond rather than at the olefinic carbon-tin bond. Freedman<sup>(34)</sup> found that cleavage with elemental bromine of 1,1-dimethyl-2,3,4,5-tetraphenylstannole occurred at the olefinic carbon-tin bond instead of the methyl-tin bond. This reflects an ease of cleavage which increases in the order: phenyl > vinyl > methyl.

FIGURE 2.4



DI-iodostannole

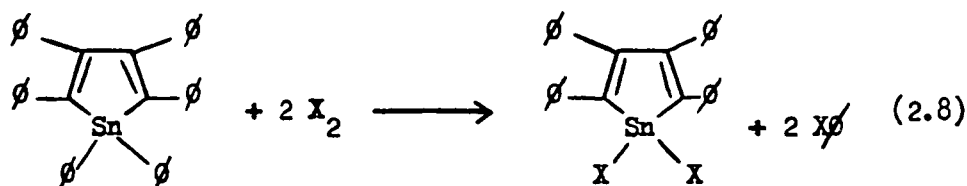
100.7



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The reaction of hexaphenylstannole with elemental chlorine, contrary to the analogous reactions with bromine and iodine, results in the cleavage of the olefinic carbon-tin bond rather than at the tin-phenyl bond.

The halogenation of hexaphenylstannole results in the formation of 1,1-dihalo-2,3,4,5-tetraphenylstannole and halobenzene:



where  $X = \text{Br}, \text{I}$ .

The infrared spectrum of the diiodostannole was consistent with the structure given above by being very similar to that of hexaphenylstannole<sup>(18)</sup> and dibromostannole<sup>(122)</sup> (Fig 2.5). The far-infrared spectrum contains bands at 184 and 80  $\text{cm}^{-1}$  which can be identified as the asymmetric and symmetric tin-iodine stretching vibrations, respectively. In dialkyltin dihalides the positions of these bands have been assigned as  $\nu_{\text{as}}(\text{Sn-I})$  205–180  $\text{cm}^{-1}$  and  $\nu_{\text{s}}(\text{Sn-I})$  85–75  $\text{cm}^{-1}$ <sup>(123)</sup>. The Mössbauer spectrum (Figure 2.4) is a doublet with I.S.  $1.61 \pm 0.01$  mm/s and Q.S.  $2.32 \pm 0.02$  mm/s, consistent with four-coordinated, tetrahedral tin. The Mössbauer parameters for other  $\text{R}_2\text{SnX}_2$  compounds are compared in Table 2.1.

The mass spectrum of this compound contained no peak in the vicinity of the parent peak (calc.  $M/e = 729$ ). An abundant fragment appeared at  $M/e = 356$ , but containing no tin, has been assigned as:

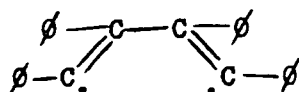


TABLE 2.1

 $^{119}\text{m}\text{Sn}$  MÖSSBAUER PARAMETERS (mm/s)

COMPOUND	I.S.	Q.S.	REFERENCE
$\text{Me}_2\text{SnBr}_2$	$1.59 \pm 0.09$	$3.41 \pm 0.09$	9
$\text{Et}_2\text{SnBr}_2$	$1.68 \pm 0.06$	$3.37 \pm 0.12$	9
$\text{Et}_2\text{SnI}_2$	$1.72 \pm 0.05$	$2.97 \pm 0.10$	9
$(\text{n-Bu})_2\text{SnBr}_2$	$1.70 \pm 0.15$	$3.15 \pm 0.50$	9
$(\text{n-Bu})_2\text{SnI}_2$	$1.80 \pm 0.07$	$2.90 \pm 0.21$	9
$\text{Ph}_2\text{SnBr}_2$	$1.43 \pm 0.03$	$2.54 \pm 0.06$	9
$\text{Ph}_2\text{SnI}_2$	$1.51 \pm 0.04$	$2.38 \pm 0.08$	9
Dibromostannole	$1.51 \pm 0.06$	$2.51 \pm 0.12$	122
Diiodostannole	$1.61 \pm 0.01$	$2.32 \pm 0.02$	this study

As stated previously, there are ten stable isotopes of tin (112, 114, 115, 116, 117, 118, 119, 120, 122, 124) whose natural abundances are given in Table 1.3. This produces a very characteristic pattern for every tin-containing fragment. The most abundant isotope of tin has a mass of 120, so the most abundant tin-containing peaks are found centered at  $M/e = 120$ , 247, and 374. These peaks correspond to Sn, SnI, and SnI<sub>2</sub> fragments, respectively. Surrounding each of these peaks is the characteristic tin splitting pattern. Iodine does not add to the complexity of this pattern because iodine has only one stable isotope ( $M/e = 127$ ). The relative intensities of the tin-containing peaks are shown in Figure 2.6.

No tin-containing fragments were observed that also contained organic substituents.

Variable temperature Mössbauer spectroscopy was discussed in Chapter I, so the theory of the experiment will not be discussed here. The plot of  $\ln(A_T/A_{77})$  (normalized to the area under the resonance curves at 77K) vs. temperature for dibromostannole between 77 and 95K, which is shown in Figure 2.7, has a slope of  $-2.23 \times 10^{-2} \text{ K}^{-1}$ . This rather steep slope is evidence for the monomeric, tetrahedral structure of dibromostannole.

Leavitt<sup>(15,16)</sup> presumed that in the course of preparations of the spiro-compound that the stannole or germole dihalide derivatives would exist:



FIGURE 2.6

RELATIVE INTENSITIES OF PEAKS CONTAINING THE SnI FRAGMENT

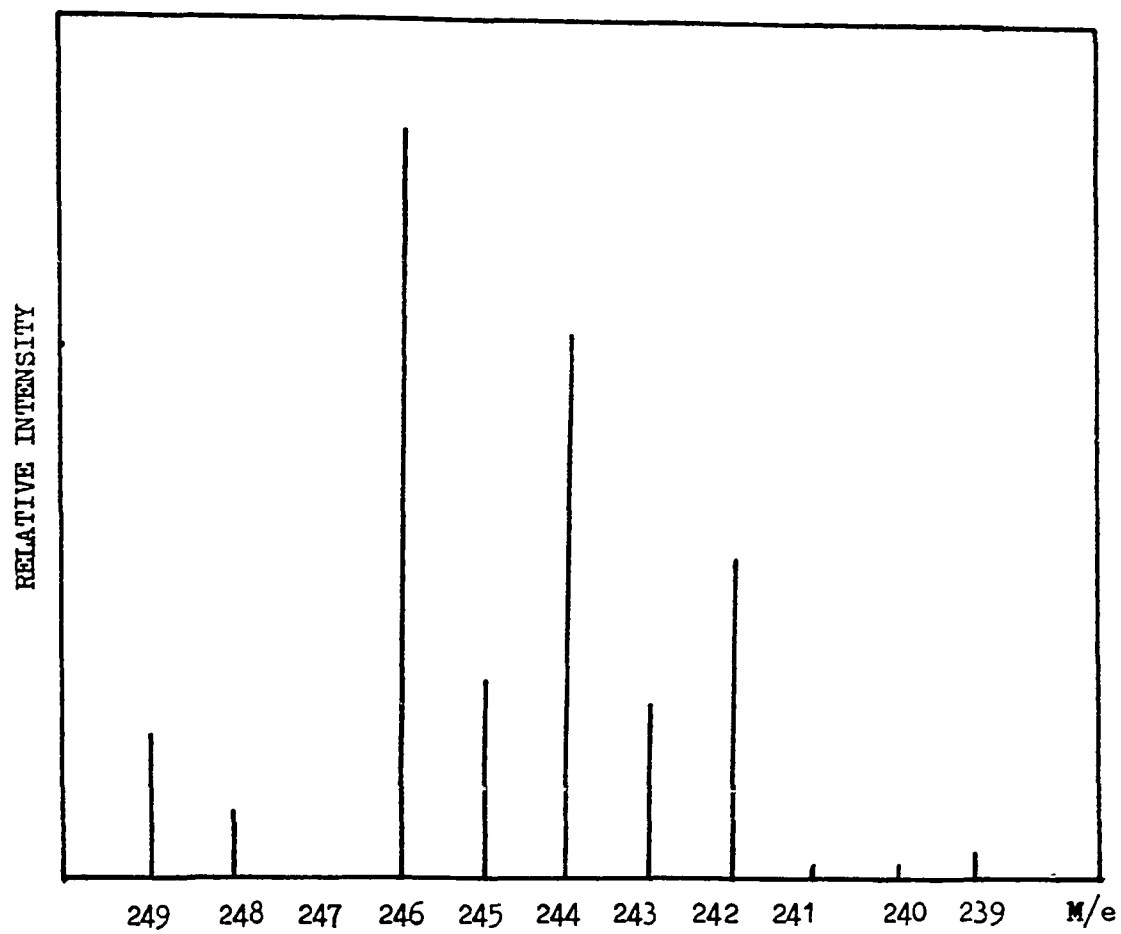
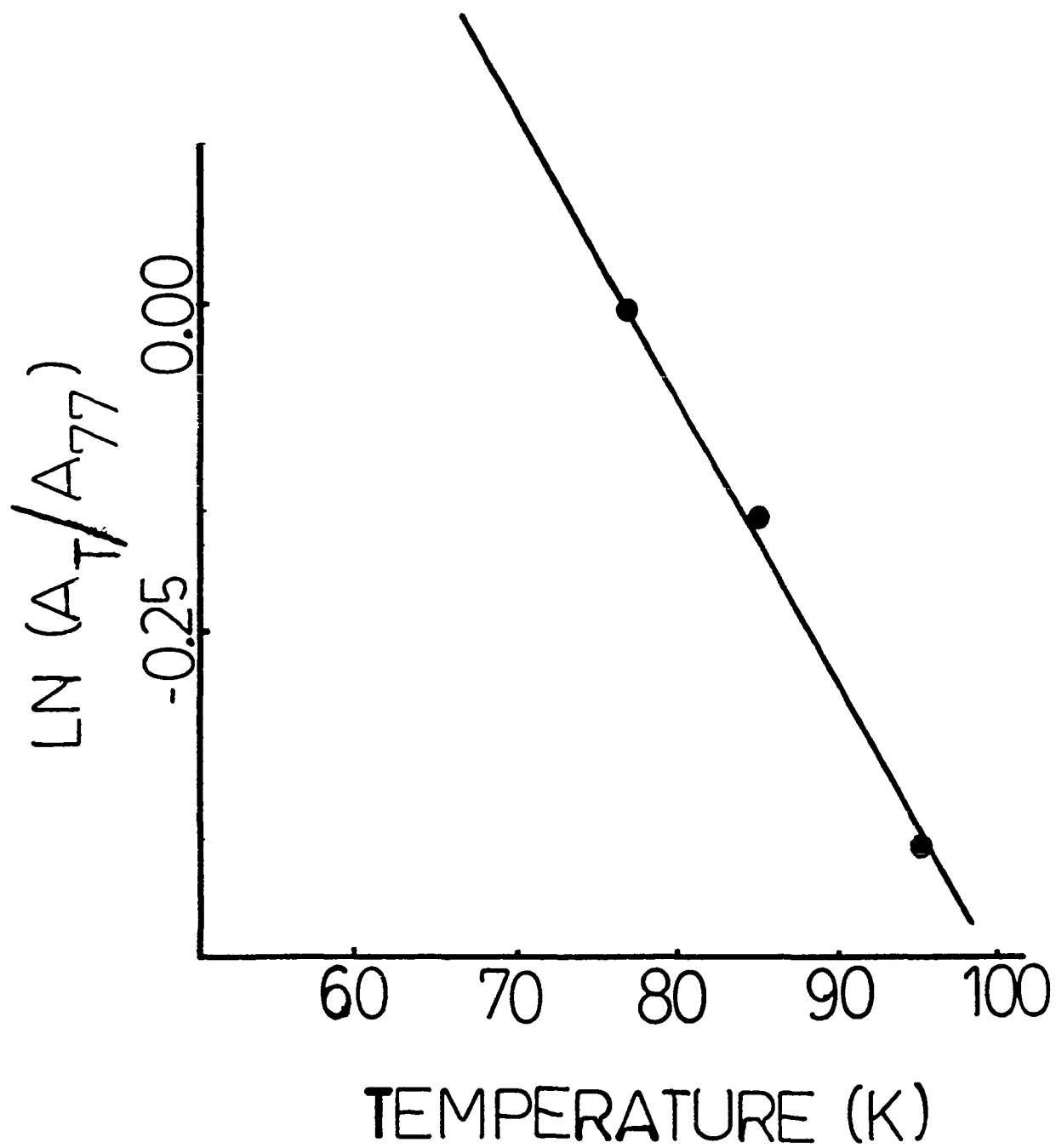
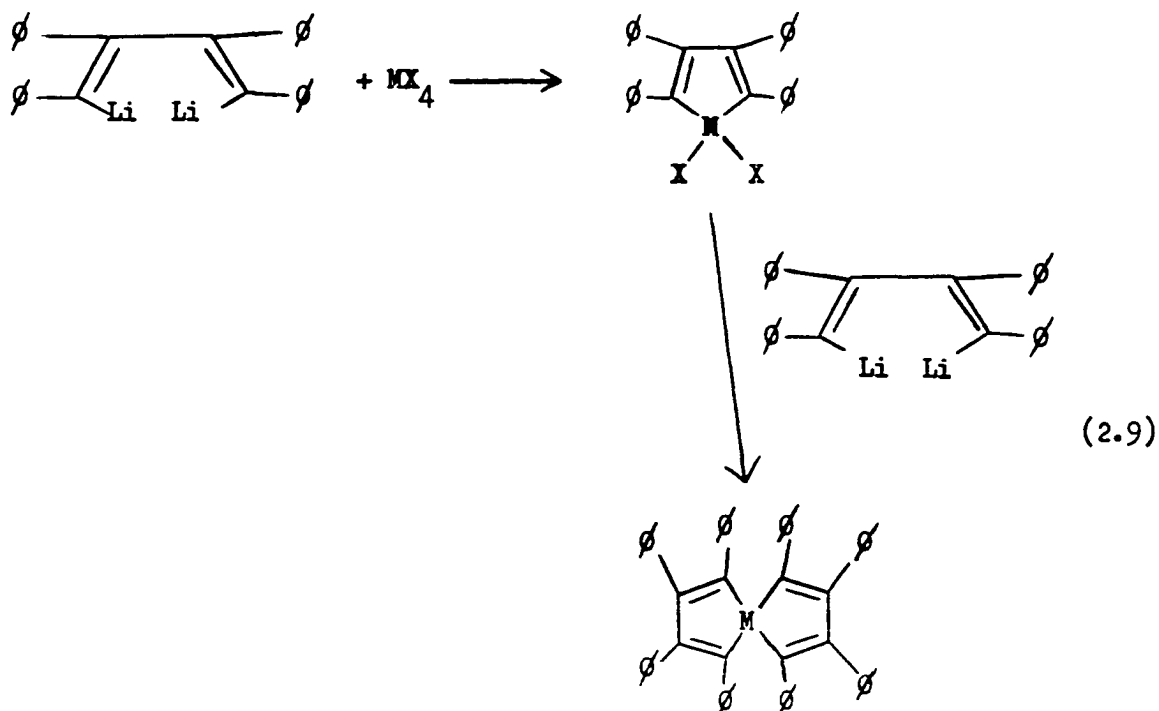


FIGURE 2.7

VARIABLE TEMPERATURE MÖSSBAUER SPECTRUM OF DIBROMOSTANNOLE





where  $M = \text{Ge}, \text{Sn}$ .

However, 1:1 molar ratios of the dilithiobutadiene with tin(IV) chloride, bromide, and iodide provided octaphenyl-1,1'-spirobis-stannole having a melting point  $274-276^\circ$  vs. lit.<sup>(18)</sup>  $270-280^\circ\text{C}$ . The infrared spectra were consistent with this formulation<sup>(18)</sup>. No additional tin-containing species were isolated from these reactions.

## CHAPTER III

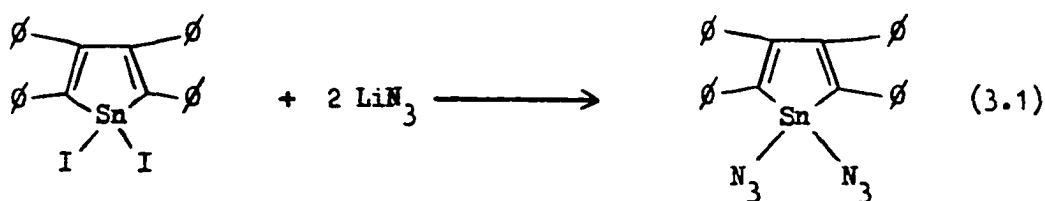
### DERIVATIVES OF 1,1-DIHALO-2,3,4,5-TETRAPHENYLSTANNOLE

#### 3.1 INTRODUCTION

As stated in Chapter II, the organotin halides occupy a key position in the chemistry of the organic compounds of tin. Organotin halides derive most of their importance through their use as starting materials for the synthesis of many series of other organotin compounds. A number of derivatives of 1,1-dibromo- and 1,1-diiodo-2,3,4,5-tetraphenylstannole have been prepared and studied by I.R., N.M.R., and tin-119m Mössbauer spectroscopies.

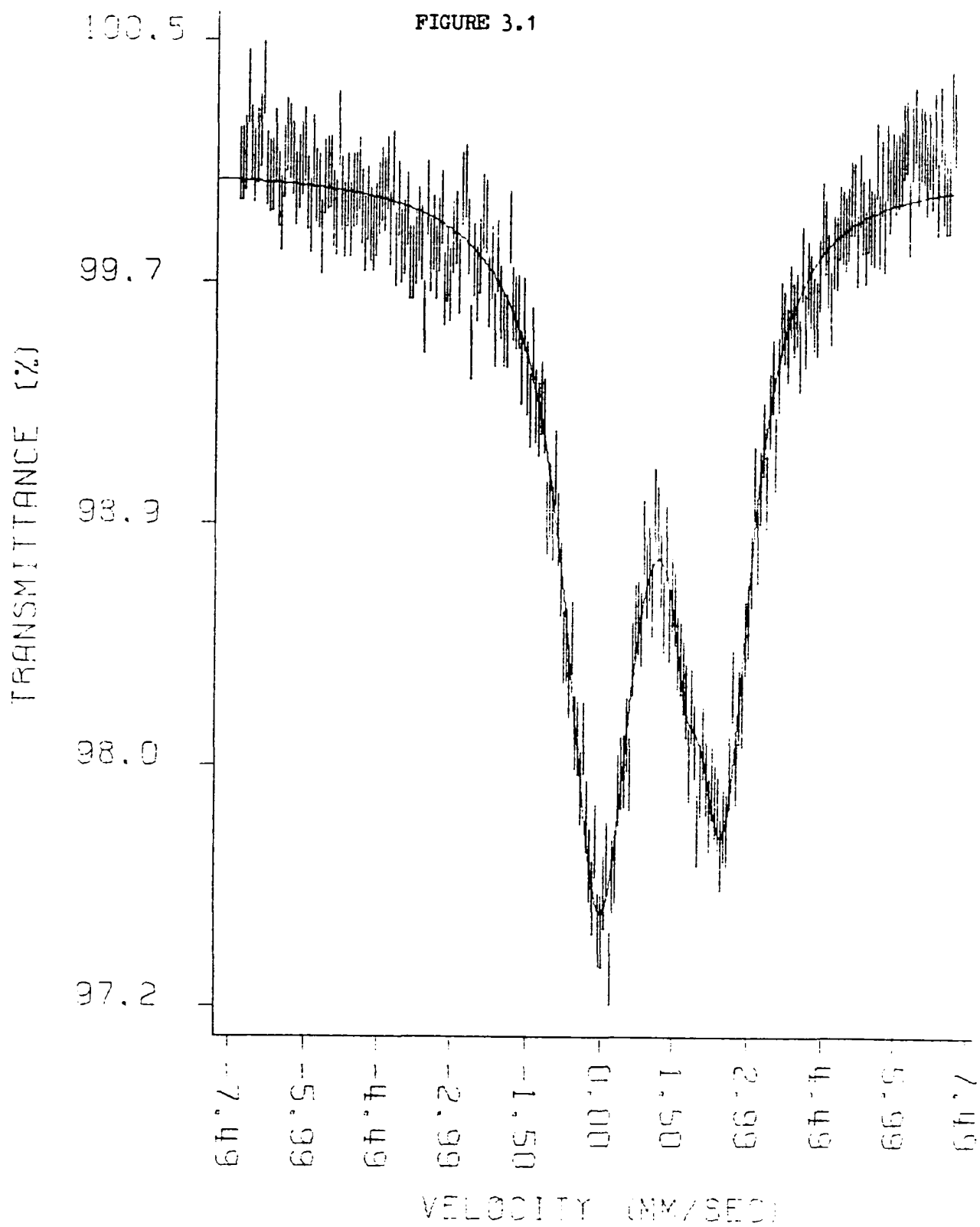
#### 3.2 1,1-DIAZIDO-2,3,4,5-TETRAPHENYLSTANNOLE

The 1,1-diazido-2,3,4,5-tetraphenylstannole was prepared from the reaction of lithium azide with the stannole diiodide:



The infrared spectrum of this compound contains bands at 2090 and 1275  $\text{cm}^{-1}$  which are assigned to the asymmetric and symmetric azide stretches, respectively<sup>(124)</sup>. A sharp band was also found at 690  $\text{cm}^{-1}$  which is the azide bending mode. The infrared spectrum also contains a band at 472  $\text{cm}^{-1}$  which is assigned as the intramolecular

FIGURE 3.1



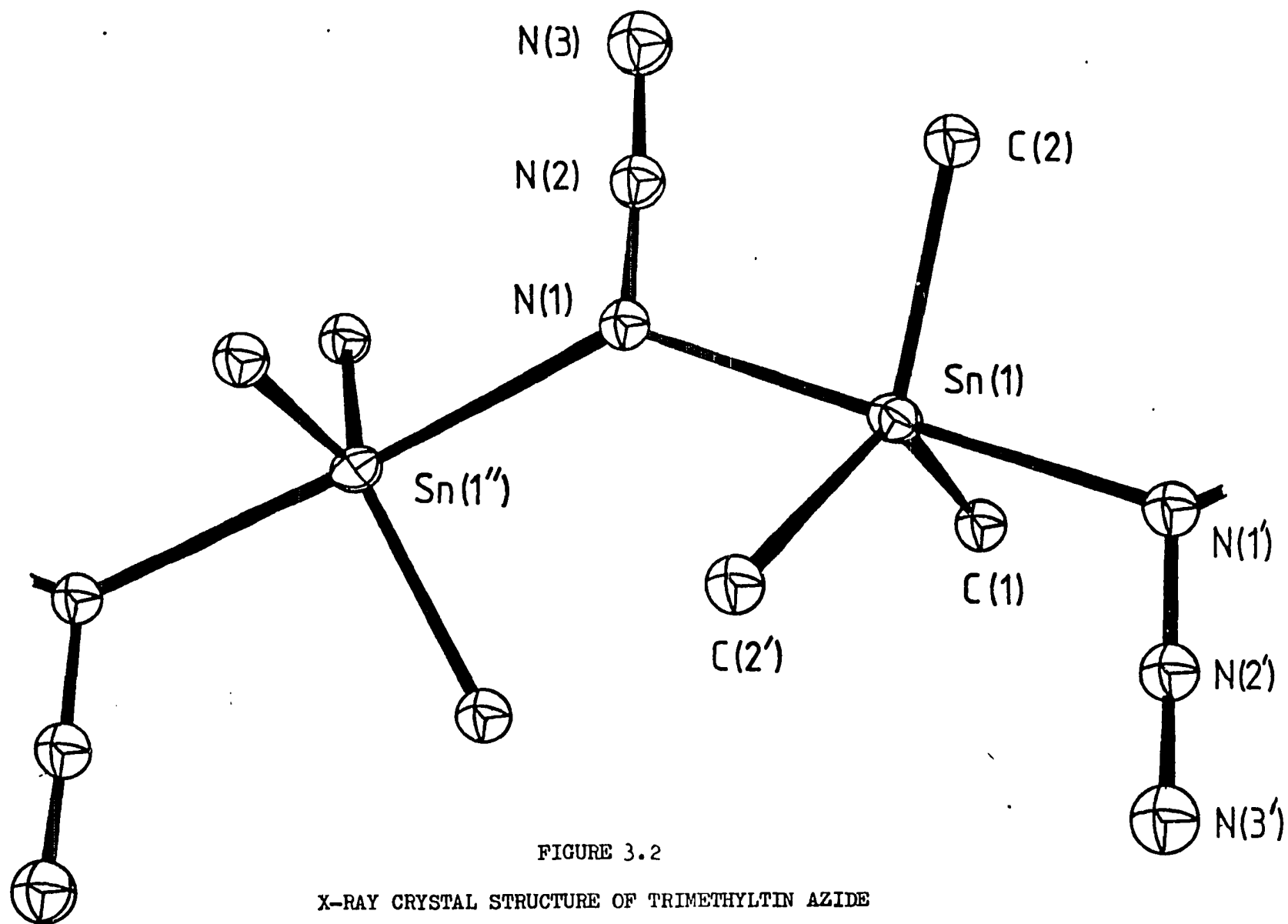


TABLE 3.0

MÖSSBAUER PARAMETERS FOR DISUBSTITUTED STANNOLES (mm/s)

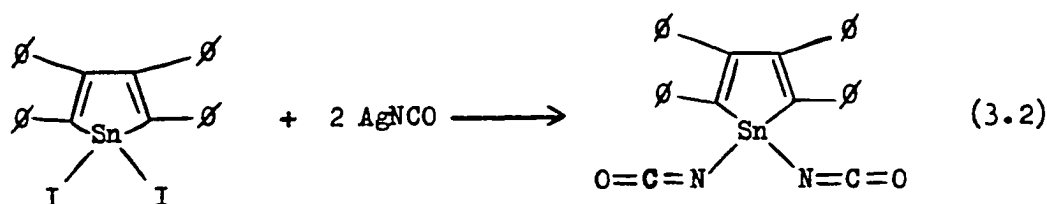
COMPOUND	I.S.	Q.S.	$\Gamma$
Diazidostannole	$1.18 \pm 0.01$	$2.44 \pm 0.02$	$1.53 \pm 0.03$
Dicyanatostannole	$1.05 \pm 0.01$	$2.47 \pm 0.02$	$1.16 \pm 0.02$
Diacetatostannole	$1.09 \pm 0.02$	$2.87 \pm 0.04$	$1.36 \pm 0.05$

$\Gamma$  is the half-height peak width

Sn-N stretch. An additional band is also found at  $270\text{ cm}^{-1}$ , and is assigned to an intermolecular Sn-N stretch<sup>(125)</sup>. The presence of an intermolecular Sn-N stretch indicates that the tin atoms are bridged in an unsymmetrical manner by azide groups. The question of how the azide bridging actually occurs remains uncertain. It has been suggested that azide bridging can occur through both the  $\alpha$ - and  $\gamma$ -nitrogens<sup>(126)</sup>, but there is no X-ray crystallographic data to support this suggestion. The more common type of azide-bridging occurs through the  $\alpha$ -nitrogen, as found for trimethyltin azide, whose crystal structure has recently been completed<sup>(126a)</sup> (Figure 3.2). The Mössbauer spectrum (Figure 3.1 and Table 3.0) agrees with the concept of azide bridges.

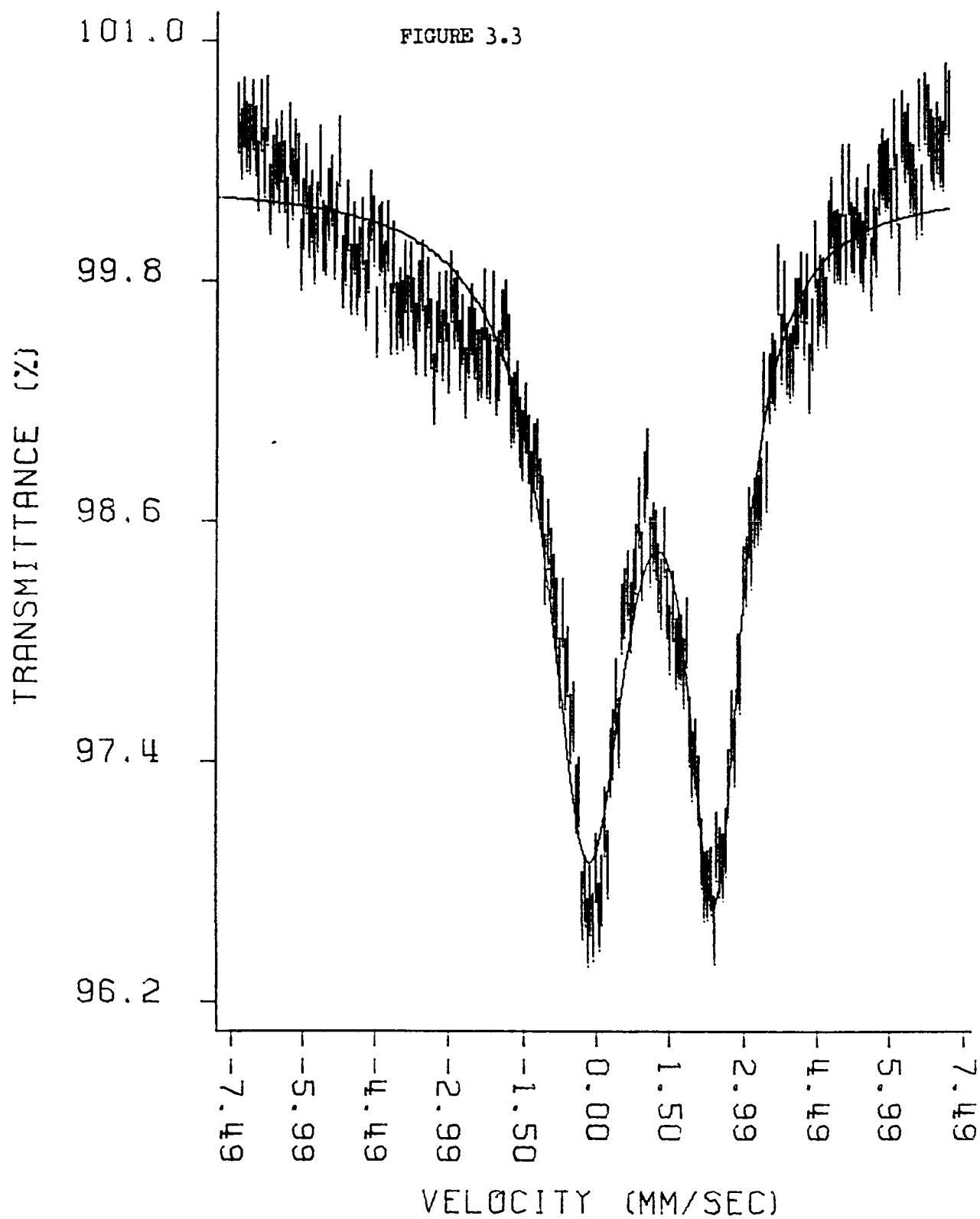
### 3.3 1,1-DICYANATO-2,3,4,5-TETRAPHENYLSTANNOLE

The 1,1-dicyanato-2,3,4,5-tetraphenylstannole was prepared from the reaction of stannole diiodide with silver(I) cyanate:



Complexes of (iso)cyanates with metals have been extensively investigated in order to solve the interesting problem of whether the NCO group is bonded to the metal through the oxygen atom, M-OCN (cyanate), or through the nitrogen atom, M-NCO (isocyanate)<sup>(127,128)</sup>. The criterion that has been adopted to establish the bond type is that the cyanato complexes exhibit very sharp C-O stretching absorptions below  $1200\text{ cm}^{-1}$ , whereas the isocyanate complexes exhibit broad, more intense bands above  $1200\text{ cm}^{-1}$ <sup>(129)</sup>. The infrared spectrum of this compound



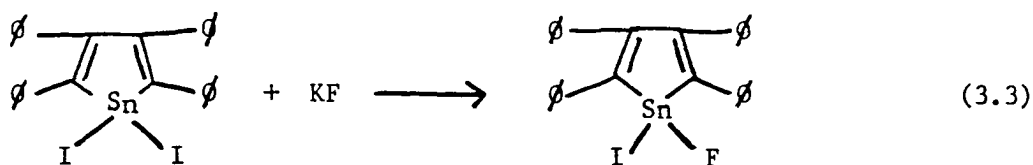


DICYANATOOSTANNOLE

shows the strong NCO bands at  $2210$  and  $1350\text{ cm}^{-1}$ , both of which are absent in the starting material. The band at  $1350\text{ cm}^{-1}$  indicates that the NCO is bonded to the tin through the nitrogen and is thus an isocyanate. The infrared spectrum also contains bands at  $610\text{ cm}^{-1}$ , which is assigned to the NCO bend, and  $385\text{ cm}^{-1}$  which is the Sn-N stretch<sup>(125)</sup>. The Mössbauer spectrum (Fig. 3.3 and Table 3.0) is consistent with bridging isocyanate groups.

#### 3.4 1-FLUORO-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE

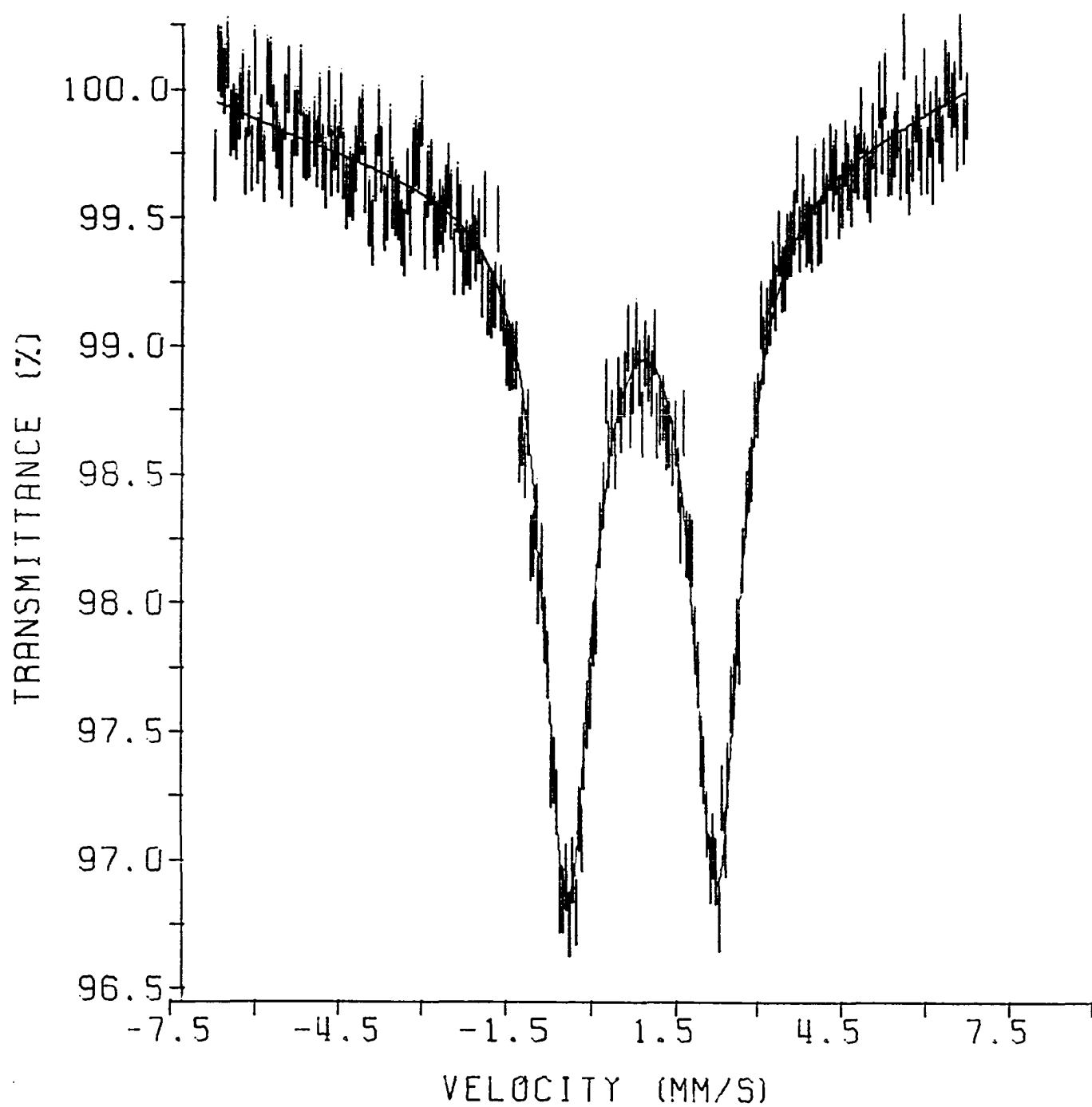
The 1-fluoro-1-iodotetraphenylstannole has been prepared from the reaction of 1,1-diiodostannole with potassium fluoride in a mixture of tetrahydrofuran and ethanol:



Organotin monofluorides have some special structural characteristics<sup>(130)</sup>. The structure of the trigonal bipyramidal trimethyltin fluoride has not been satisfactorily solved due to disorder. This compound appears to contain trimethyltin groups and fluorine atoms arranged alternately along an infinite chain axis. The two possible structures arise because of anomalies in the electron density projections that result from the disorder of the fluorine atoms within each chain and disorder of the chains with respect to one another. Disorder is also present in the crystals of tri-n-butyltin fluoride, for which an incomplete structure is available<sup>(131)</sup>.

The infrared spectrum of the fluoro-iodostannole shows the strong Sn-F stretching absorption band at  $560\text{ cm}^{-1}$  and a broad band at  $350\text{ cm}^{-1}$

FIGURE 3.4



00 208 FLUORO-IODOSTANNOLE

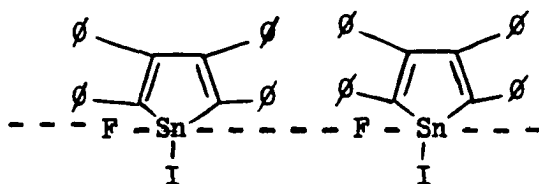
TABLE 3.1

MÖSSBAUER PARAMETERS FOR FLUORO-HALOSTANNOLES (mm/s)

COMPOUND	I.S.	Q.S.	REFERENCE
Fluoro-bromo-stannole	$1.17 \pm 0.06$	$2.82 \pm 0.12$	122
Fluoro-iodo-stannole	$1.22 \pm 0.02$	$2.74 \pm 0.03$	this work
	$\Gamma = 1.08 \pm 0.02$		

$\Gamma$  is the half-height peak width

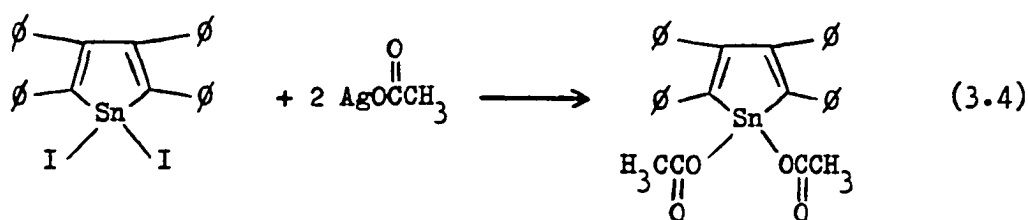
suggesting the bridging of tin atoms by fluorine atoms<sup>(132)</sup>. The most reasonable structure proposed on the basis of the infrared spectrum is that the stannole groups are bridged by the fluorine atoms forming a nonlinear, unsymmetrical F-Sn-F bond:



This formulation is in agreement with the structure proposed for 1-fluoro-1-bromo-tetraphenylstannole<sup>(122)</sup>. The Mössbauer parameters for the two compounds are also in good agreement (Table 3.1 and Figure 3.4).

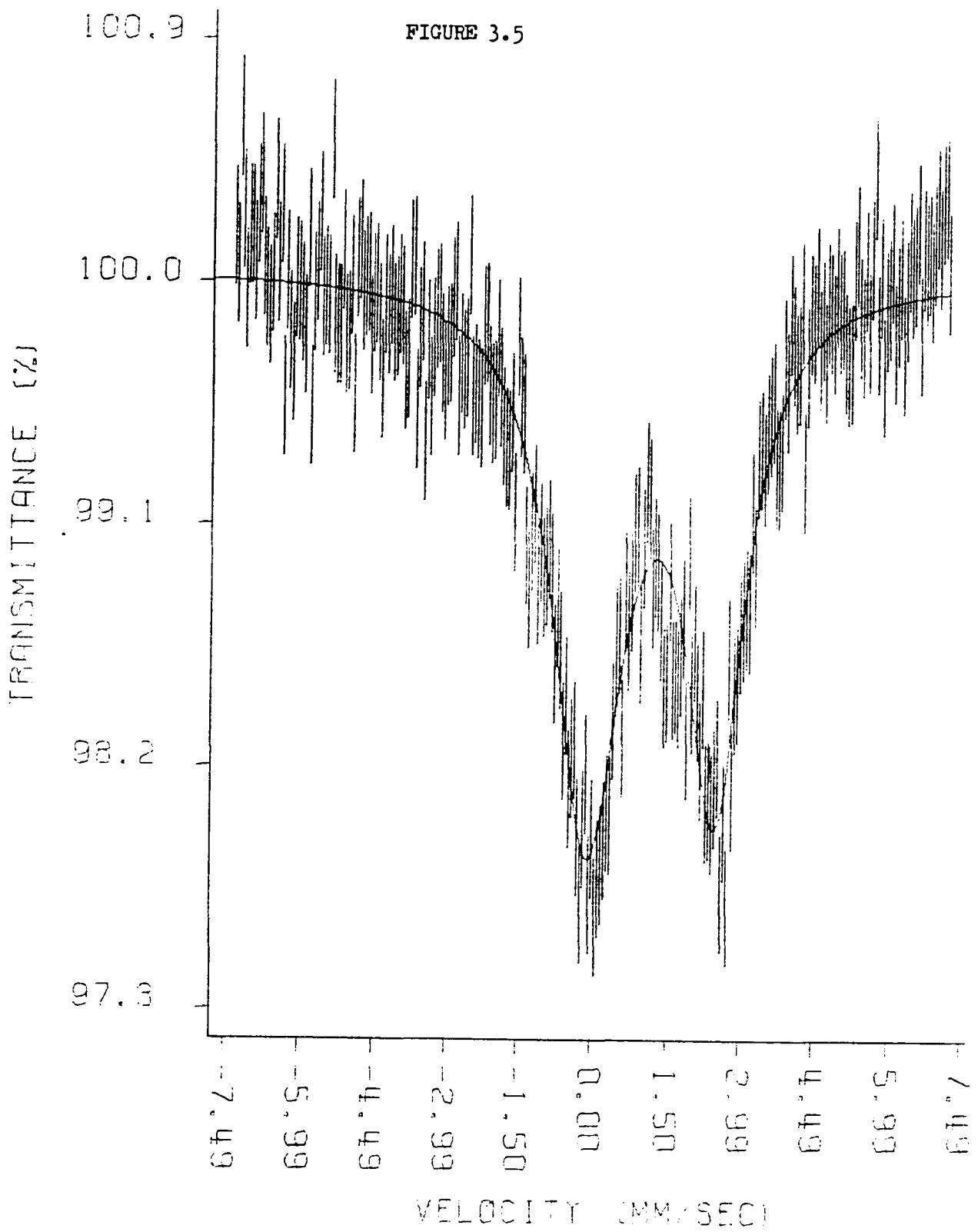
### 3.5 1,1-DIACETATO-2,3,4,5-TETRAPHENYLSTANNOLE

The 1,1-diacetato-2,3,4,5-tetraphenylstannole has been prepared from the reaction of 1,1-diiodo-2,3,4,5-tetraphenylstannole with silver(I) acetate:



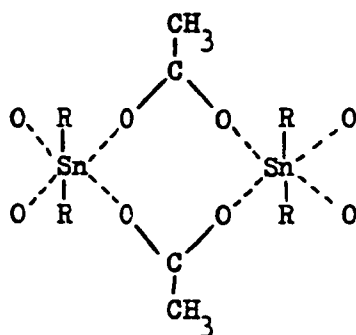
The infrared spectrum of this compound contains prominent bands at 1567 and 1323  $\text{cm}^{-1}$  which are assigned as the carboxylate asymmetric and symmetric stretches, respectively<sup>(1,133)</sup>. Other bands associated with the carboxylate group are the  $\text{CO}_2$  scissor vibration which is a strong band at 760  $\text{cm}^{-1}$ , the  $\text{CO}_2$  out-of-plane deformation which is a medium band at 615  $\text{cm}^{-1}$ , and the in-plane  $\text{CO}_2$  deformation which is a weak band at 490  $\text{cm}^{-1}$ . A medium band that occurs at 295  $\text{cm}^{-1}$  has been

FIGURE 3.5



assigned to the  $\nu(\text{Sn-O})$  mode.

No X-ray crystal data is available for diorganotin diacetates, but in the solid state there has been speculation on the existence of bridging acetoxy groups<sup>(134)</sup>:

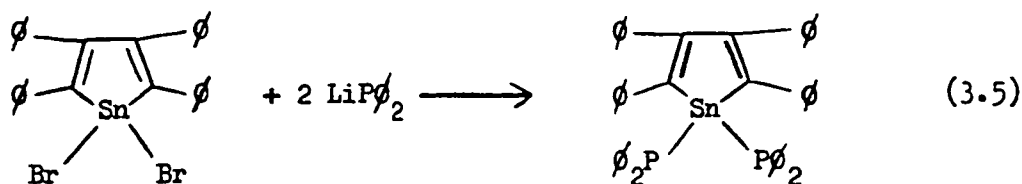


The Mössbauer spectrum (Figure 3.5 and Table 3.0) of this compound (I.S.  $1.09 \pm 0.02$ , Q.S.  $2.87 \pm 0.04$  mm/s) is in good agreement with a structure containing tin atoms with greater than four-coordination ( $\rho = 2.63$ ).

The n.m.r. spectrum in  $\text{CDCl}_3$  contains a single resonance at 2.18 ppm (relative to TMS) in addition to the phenyl group multiplet.

### 3.6 BIS(DIPHENYLPHOSPHINO)-TETRAPHENYLSTANNOLE

1,1-Bis(diphenylphosphino)-2,3,4,5-tetraphenylstannole has been prepared by the reaction of lithium diphenylphosphine and dibromo-tetraphenylstannole:



The infrared spectrum of this compound contains bands at 1437 and  $998\text{ cm}^{-1}$  which are attributed to the asymmetric and symmetric phosphorus-phenyl stretches, respectively<sup>(135)</sup>. An additional band of

medium intensity that occurs at  $354\text{ cm}^{-1}$  has been assigned to the  $\nu(\text{Sn-P})$  mode.

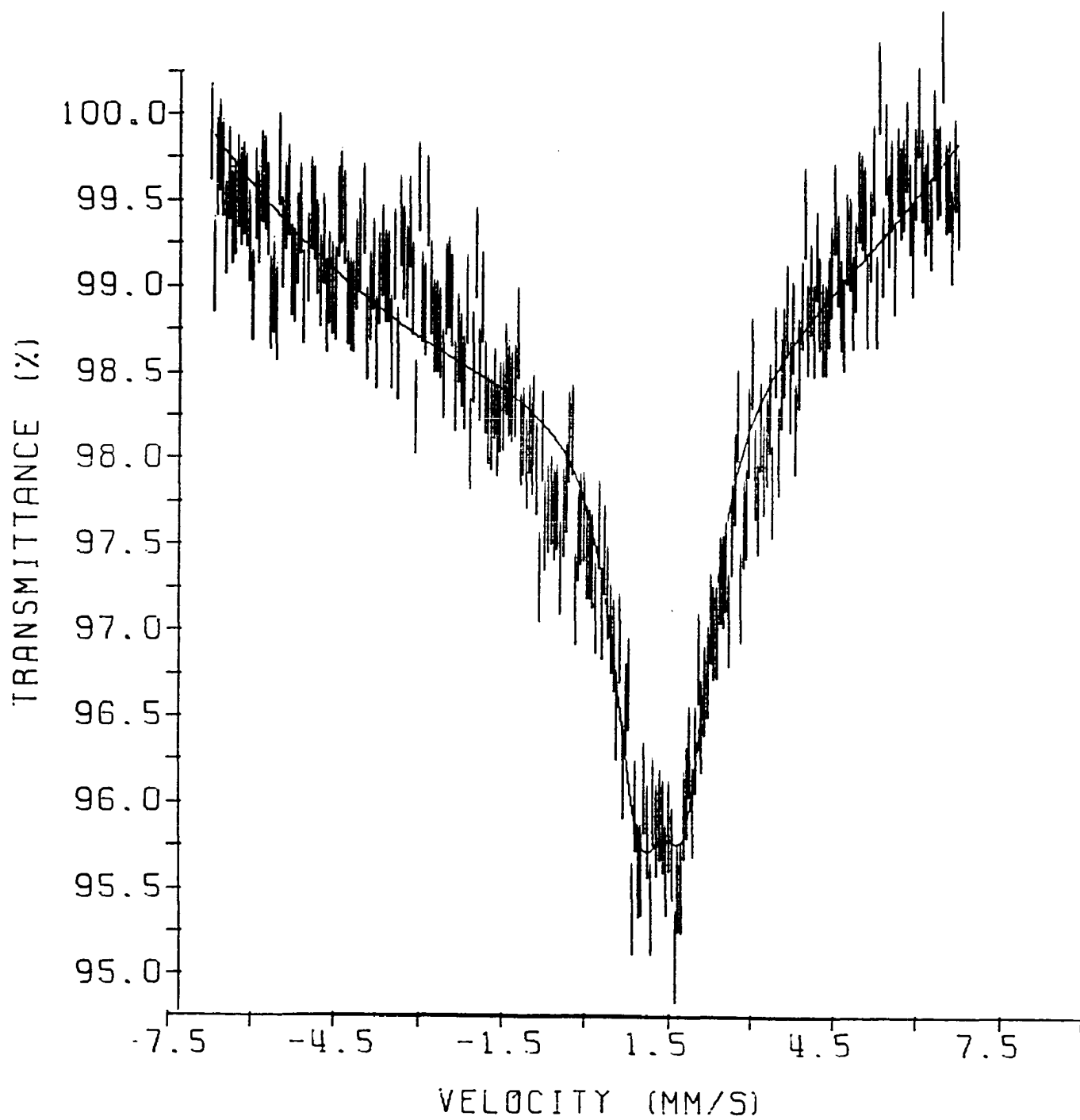
The Mössbauer spectrum (Figure 3.6) contains a narrow doublet, I.S.  $1.51 \pm 0.01$  and Q.S.  $0.83 \pm 0.03\text{ mm/s}$ . The small value for the Q.S. is in excellent agreement with the results of Schumann and Zuckerman<sup>(136)</sup> concerning organotin complexes of Group V elements. Table 3.2 lists the Mössbauer parameters for organotin-phosphines. The small Q.S. values observed for the phosphines could arise from electronegativity differences between the two kinds of attached groups, or from  $(p \rightarrow d)-\pi$  interactions between the tin and the phosphorus. Schumann and Zuckerman<sup>(136)</sup> reported that the Q.S. values for tin-phosphines are enhanced by coordination with transition metal carbonyls. Strong  $(p \rightarrow d)-\pi$  bonding in these tin-phosphines would delocalize the lone pair on phosphorus and preclude further coordination in transition metal complexes.

If  $(p \rightarrow d)-\pi$  interactions were responsible for the small Q.S. values which could be derived by fitting as doublets the broadened  $^{119}\text{mSn}$  Mössbauer resonances recorded for the phosphorus ligands, then the singlet lines should sharpen when the complex is formed. Instead, the Q.S. is increased. This is best interpreted in terms of an increase in polarity of the tin-phosphorus  $\sigma$ -bond on coordination. The higher effective electronegativity of the coordinated phosphorus atom then perturbs the electron distribution about the attached tin atom, giving rise to an enhanced electric field gradient and the resolvable Q.S.

On the basis of these results, it is concluded that the small resolvable Q.S. in this phosphine is also due to the small difference



FIGURE 3.6



DU 250 DBS PLUS DIPHENYLPHOSPHINOLITHIUM

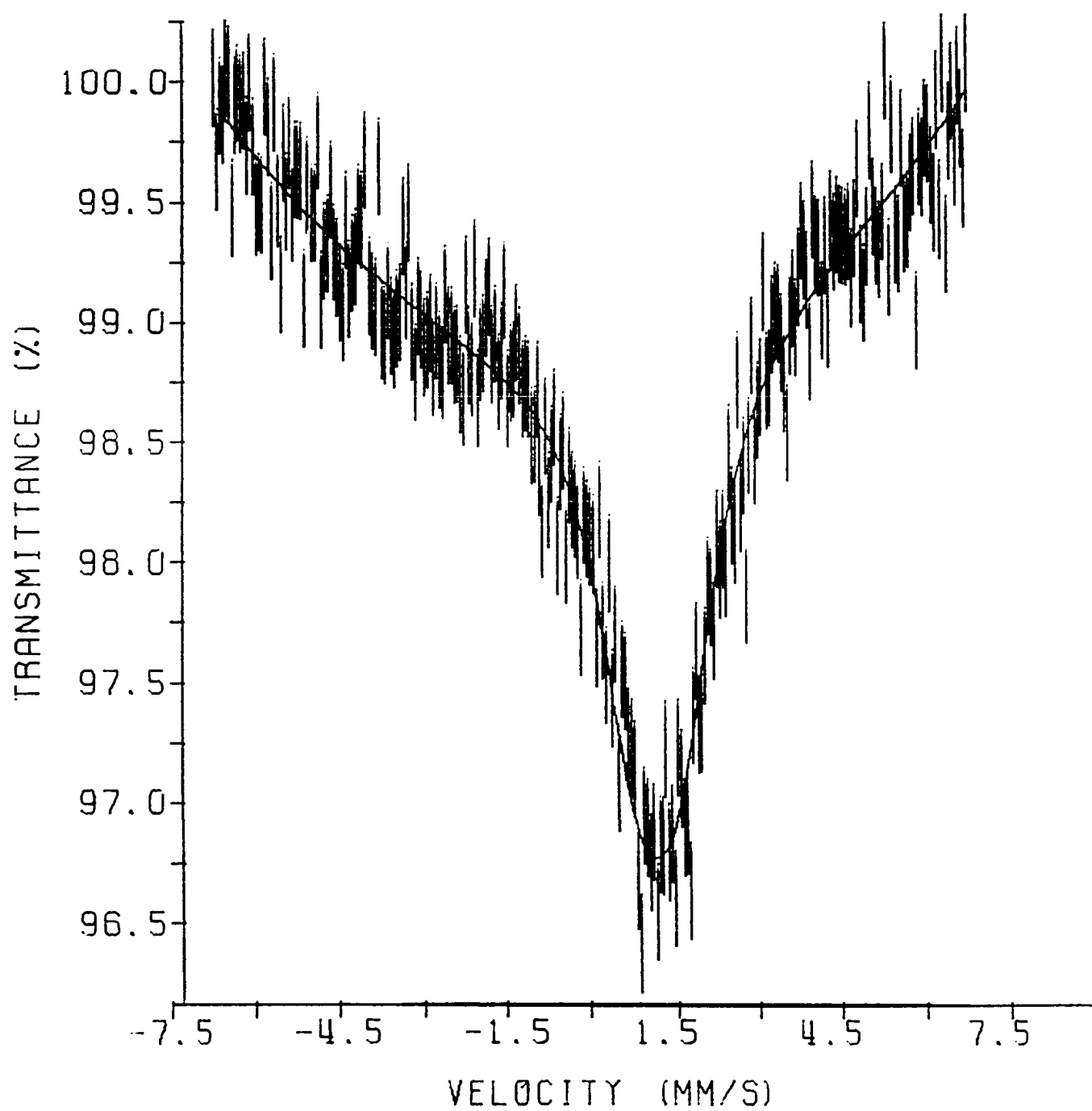
TABLE 3.2

TIN-119m <sup>119</sup>MÖSSBAUER DATA FOR TIN-PHOSPHINES (mm/s)

COMPOUND	I.S.	Q.S.	REFERENCE
$[(CH_3)_3Sn]_3P$	$1.32 \pm 0.06$	-	136
$[(CH_3)_3Sn]_2PC(CH_3)_3$	$1.36 \pm 0.06$	-	136
$(CH_3)_3SnP(C_6H_5)_2$	$1.34 \pm 0.06$	$0.86 \pm 0.12$	136
Bis(diphenylphosphino)stannole	$1.51 \pm 0.01$	$0.83 \pm 0.03$	this work
	$\Gamma = 1.20 \pm 0.08$		

 $\Gamma$  is the half-height peak width

FIGURE 3.7

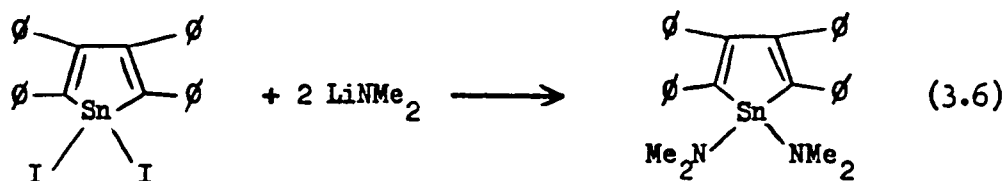


00 242 BIS(DIMETHYLAMINO) STANNOLE

in electronegativity between tin and phosphorus.

### 3.7 BIS(DIMETHYLAMINO)TETRAPHENYLSTANNOLE

1,1-Bis(dimethylamino)-2,3,4,5-tetraphenylstannole has been prepared by the reaction of lithium dimethylamine and diiodostannole:



The infrared spectrum of this compound contains a band of medium intensity at  $950 \text{ cm}^{-1}$  which is assigned as the symmetric  $\text{N}-\text{C}_2$  stretch<sup>(137)</sup>. Another band at  $530 \text{ cm}^{-1}$  has been assigned to the tin-nitrogen stretch<sup>(137)</sup>.

The Mössbauer spectrum (Figure 3.7) consists of a narrow doublet (I.S.  $1.25 \pm 0.02$ , Q.S.  $0.72 \pm 0.08$ ,  $\Gamma = 1.66 \pm 0.13 \text{ mm/s}$ ). These parameters are in agreement with those found for the bis(diphenylphosphino)-stannole and other diorganotin diamines reported by Harrison and Zuckerman<sup>(138)</sup>.

The proton n.m.r. spectrum in  $\text{CDCl}_3$  contained a single resonance at 2.38 ppm (relative to TMS) in addition to the phenyl multiplet.

## CHAPTER IV

### FORMATION OF ADDUCTS OF 1,1-DIIDO-2,3,4,5-TETRAPHENYLSTANNOLE

#### 4.1 INTRODUCTION

Many organotin compounds are known in which the coordination number of tin is greater than four. The situation with regard to organotin complexes can be summarized under five general headings.

#### 4.2 AXIAL-MOST-ELECTRONEGATIVE, TRIGONAL BIPYRAMIDAL STRUCTURES

In the trigonal bipyramidal arrangements of five-coordinated complexes, the most electronegative atom or group tends to occupy the axial-positions in an axial-most-electronegative arrangement. This view is corroborated by the X-ray crystallographic analysis that the complex,  $\text{Me}_3\text{SnCl}\cdot\text{py}$ , which contains monomeric trigonal bipyramidal molecules where the pyridine and the chlorine atom are located in the axial-positions<sup>(65)</sup>. The X-ray structure of  $\text{Me}_3\text{SnNO}_3\cdot\text{H}_2\text{O}$  also shows a trigonal bipyramidal structure with axial water and nitrate groups<sup>(139)</sup>. These are only two of many examples of complexes of organotin compounds where the molecule assumes a trigonal bipyramidal structure in which the most electronegative groups or atoms are in the axial-positions<sup>(131)</sup>.

#### 4.3 TIN AS A HARD ACID

It is widely accepted that tin(IV) is a Class A acceptor<sup>(140)</sup>, or a hard acid<sup>(141)</sup>. The substitution of organic groups at tin confers some softness<sup>(142)</sup>, with this change sometimes being sufficient to

cause the compounds to show characteristics of Class B acceptors toward certain ligands<sup>(143)</sup>. Measurements of the enthalpies of formation, for example, show that trimethyltin chloride forms more stable adducts of oxygen or nitrogen donors than it does with the corresponding sulfur or phosphorus ligands<sup>(144,145,146)</sup>.

#### 4.4 ELECTRONEGATIVITY OF SUBSTITUENTS

The electronegativity of substituents at tin determines the ability of tin compounds to form complexes. Thus the acceptor strengths of the tin(IV) halides are in the order;  $\text{SnI}_4 < \text{SnBr}_4 < \text{SnCl}_4 < \text{SnF}_4$ , when the bases are those containing nitrogen or oxygen<sup>(143)</sup>. When organic groups replace the chlorine atoms of tin(IV) chloride, the acceptor strength of the tin decreases as indicated by the sequences;  $\text{SnCl}_4 > \text{RSnCl}_3 > \text{R}_2\text{SnCl}_2 > \text{R}_3\text{SnCl}$ <sup>(147)</sup>, and  $\text{PhSnCl}_3 > \text{MeSnCl}_3 > \text{BuSnCl}_3$ <sup>(148,149)</sup>. The stability and range of the addition compounds that are formed appears to decrease as the number of organic groups increases. No addition compounds with the formula  $\text{R}_4\text{SnL}$ , where R is an organic group, are known to be stable. It has been demonstrated by X-ray crystallography that the intramolecular coordination to the tin atom is destroyed when the bromine at tin is replaced by a proton as in (4-halo-1,2,3,4-tetraphenyl-cis,cis-1,3-butadienyl)dimethyltin<sup>(150)</sup> (see Figure 4.1). Numerous unsuccessful attempts were made in an effort to prepare pyridine adducts of hexaphenylstannole and dimethyl-tetraphenylstannole. No pyridine complexes were ever observed in either of these reactions.

#### 4.5 ANIONIC, CATIONIC AND NEUTRAL COMPLEXES

The complexes of organotin halides with Lewis bases can be

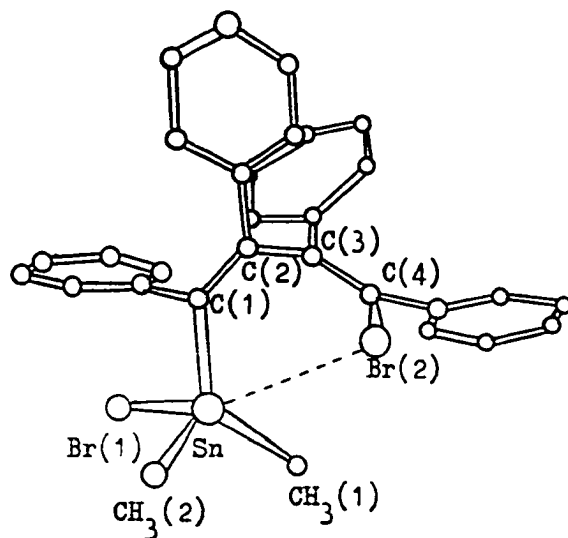


FIGURE 4.1

Molecular conformation of (4-bromo-1,2,3,4-tetraphenyl-cis,cis-1,3-butadienyl)dimethyltin bromide. The intramolecular Sn-Br(2) interaction is shown by the dotted line.

neutral, cationic, or anionic species. The most important class of Lewis bases are those derived from nitrogen-containing bases. The majority have the composition  $R_nSnX_{4-n} \cdot 2L$ , where L is a monodentate nitrogen base and  $n = 1, 2$ , or 3.

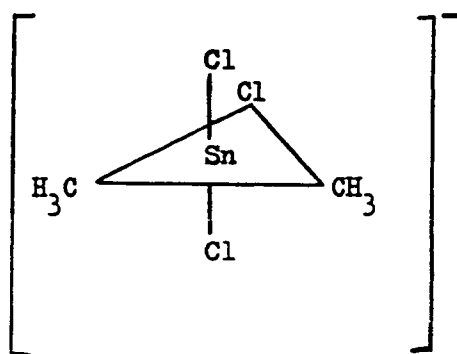
Clark<sup>(151)</sup> reported that infrared evidence suggests trigonal bipyramidal structures for both the 1:1 and the 1:2 ammonia adducts of trimethyltin bromide and chloride,  $R_3Sn(NH_3)X$  and  $[R_3Sn(NH_3)_2]X$ , respectively. Clark also concluded that complex formation by triorganotin halides with monodentate nitrogen bases appears to be highly influenced by the tendency to adopt a five-coordinated geometry.

X-ray crystal structures of diorganotin dihalide complexes with nitrogen bases are quite rare<sup>(152)</sup>. The structures of only four such compounds,  $Me_2SnCl_2 \cdot 2py$ <sup>(153)</sup>,  $Me_2SnBr_2 \cdot 2py$ <sup>(154)</sup>,  $Ph_2SnCl_2 \cdot bipy$ <sup>(155)</sup>, and  $Me_2SnCl_2 \cdot terpy$ <sup>(156)</sup> have been published to date. The first three compounds all assume octahedral configurations as would be expected.  $Me_2SnCl_2 \cdot 2py$  and  $Me_2SnBr_2 \cdot 2py$  are isostructural with all trans-configurations.  $Ph_2SnCl_2 \cdot bipy$ , on the other hand, has trans-phenyl groups, and cis, cis-chlorine and bipy groups, attributable to the inability of the bipyridine to bridge trans-positions. The terpyridine adduct of  $Me_2SnCl_2$  forms a double salt which is formulated as  $[Me_2SnCl, terpy]^+$  and  $[Me_2SnCl_3]^-$ . The tin environment in the cations is distorted octahedral with methyl groups in trans relation and approximately normal to the mean plane of the terpyridyl group. In the anions, there is a trigonal bipyramidal tin environment with both methyl groups occupying equatorial-positions.

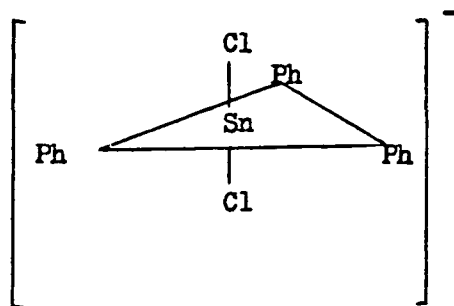
Penta-coordinated complexes, such as  $M^+[Me_2SnX_3]^-$ , and hexa-



coordinated complexes,  $M^+ [Me_2SnX_4]^{2-}$ , where  $X = Br$  or  $Cl$  and  $M^+ = Cs^+$ ,  $Me_4N^+$ , or  $Et_4N^+$ , have been reported by Clark and Wilkins<sup>(154)</sup>. From infrared evidence the doubly negative charged complexes appear to have trans-Me groups in an octahedral structure. The trigonal bipyramidal complex,  $M^+ [Me_2SnX_3]^-$ , exhibits two Sn-C and two Sn-X stretching absorptions in the infrared spectrum which confirms the structure:



Triphenyltin halide complexes with  $Me_4NCl$ <sup>(155)</sup> have structures which contain a penta-coordinated anion in which the phenyl groups are equatorial and the chlorine atoms axial in a trigonal bipyramidal geometry:



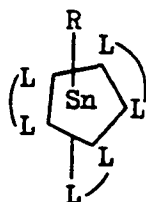
The system  $R_{4-n}SnCl_n + R_4NCl$  ( $R = Ph, Bu; n = 1, 2, 3; R = Me, Et; n = 2, 3$ ) has been studied both potentiometrically<sup>(157)</sup> and conductometrically<sup>(155)</sup> in acetonitrile to show that the ability to form complexes decreases in the following sequence for the penta-coordinated

anionic complexes:  $\text{PhSnCl}_4^- > \text{EtSnCl}_4^- > \text{BuSnCl}_4^- > \text{Ph}_2\text{SnCl}_3^- > \text{Me}_2\text{SnCl}_3^- > \text{Et}_2\text{SnCl}_3^- > \text{Pr}_2\text{SnCl}_3^- > \text{Ph}_3\text{SnCl}_2^- > \text{Bu}_3\text{SnCl}_2^-$ . Thus, the anionic complexes become less stable as the number of organic groups attached to the metal atom increases. The decrease in stability  $\text{Ph} > \text{Me} > \text{Et}$  is apparently associated with the decreasing electronegativity of these groups, and not with steric factors. This agrees with the series of formation constants for  $\text{Me}_2\text{SnX}_n^{2-n}$ <sup>(157)</sup>, where  $n = 1, 2, 3$ , or  $4$ , and  $\text{MeSnX}_n^{3-n}$ <sup>(158)</sup>, where  $n = 1, 2, 3, 4$ , or  $5$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , or  $\text{I}$  which confirms the tendency for complex formation,  $\text{F}^- \gg \text{Cl}^- > \text{Br}^- > \text{I}^-$ <sup>(159)</sup>.

The difference in stability in solution may be attributed both to variation in the solvation ability of the medium and to the reactivity of the anion ligand. Chloride complexes have been found to be less stable in water than they are in acetonitrile<sup>(160)</sup>. Water is more efficient at competing with the anions than is the weakly solvating acetonitrile. Thus, the stability constants of the anionic complexes,  $\text{R}_{4-n}\text{SnCl}_{n+1}^-$ , in acetonitrile increase. It becomes possible to measure the stability constants of bromo- and iodo-complexes when a solvent such as acetone is employed<sup>(161)</sup>.

#### 4.6 HIGHER COORDINATION

Monoorganotin compounds with three chelating groups can exist in seven-coordinated structures which are pentagonal bipyramids and involve oxygen, sulfur, and nitrogen atoms bonded to the tin as shown:



Examples of this coordination are methyltin trinitrate<sup>(162)</sup>, where the methyl group occupies an apical-position, and the methyl- and butyltin-tris(N,N-diethyldithiocarbamates)<sup>(131)</sup>.

There have been no X-ray crystal structures published to date that contain an eight-coordinated organotin compound<sup>(131)</sup>.

#### 4.7 NEUTRAL ADDUCTS OF STANNOLES WITH PYRIDINE, 2,2'-BIPYRIDINE, 1,10-PHENANTHROLINE, AND 2,2',2''-TERPYRIDINE

1,1-Diiodo-2,3,4,5-tetraphenylstannole (I) was reacted with several Lewis bases to form donor-acceptor adducts of five- or six-coordinated tin. Complexes were formed with pyridine (II), 2,2'-bipyridine (III), 1,10-phenanthroline (IV), and 2,2',2''-terpyridine (V). The 2,2',2''-terpyridine adduct of 1-fluoro-1-iodo-2,3,4,5-tetraphenylstannole (VI) was also formed. The structural assignments of these adducts are based upon infrared and tin-119m Mössbauer data and by analogy with the adducts formed with 1,1-dibromo-2,3,4,5-tetraphenylstannole<sup>(122)</sup>.

##### 4.7a INFRARED SPECTRA OF THE ADDUCTS

In comparison of infrared spectra of the adducts with their respective ligands and diiodostannole, there are a number of changes in band positions and the appearance of new bands (Table 4.1) which indicate that true complexation occurs.

TABLE 4.1

## INFRARED BAND POSITIONS OF COMPLEXES OF STANNOLES

I	I <sup>a</sup>	py	II	II <sup>a</sup>	bipy	III	III <sup>a</sup>
1600w	1600m						
		1582s	1592m	1589m		1590m	
1574w	1575w		1575s	1579m	1579s		1579m
						1565w	
1490w	1485m	1482m	1480w	1464s			
1442m	1445s		1440m		1451s	1440w	1449s
		1439s	1430m	1439s	1415m		
				1376m	1377s		
					1252m		1258m
		1213w	1218s	1213m			
		1145w	1140m	1148m	1140m		1150m
					1085m		
		1068w	1070s	1065m		1065m	1065m
		1030m			1042m		
				1024m		1020m	1018m
			1010s				
990w	995m	990m	996s	998m	993m	990w	
			913s	912m		905w	
					894m		880m
			805s	800m		780m	
762m	763m	746s			755s	755m	755s
731s	732s						
		702s	722s	725s		723s	723s
695s	692s		690s	695s	652s	690s	688s
		600m			619s		615m
565m	576s						
548s	553s		534m	545m		534m	552s
513m	525s						
444m	445m		440s	443m		435w	442m

a) signifies adducts of 1,1-dibromo-2,3,4,5-tetraphenylstannole<sup>(122)</sup>

TABLE 4.1 (continued)

## INFRARED BAND POSITIONS OF COMPLEXES OF STANNOLES

I	I <sup>a</sup>	phen	IV	IV <sup>a</sup>	terpy	V	V <sup>a</sup>
1600w	1600m		1595m			1595m	1595m
		1587m					
1574w	1575w				1580m	1570w	1572m
1490w	1485m	1459s	1478w	1459s			1465s
					1452s	1445w	1440s
1442m	1445s		1440w	1429s	1422s	1431w	1429s
		1421s	1428w				
		1377m		1377m			
			1210m		1260m	1258w	1263m
							1168w,d
					1101m		1105m
		1091m					
						1065m	
						1020m	1020m
990w	995m					990w	997m
			910w	854m			872w
		851s		841m			
			785s		830m		800m
762m	763m		755m		767s	780w	780m
731s	732s	737s	721s	727s		720s	730s
695s	692s		690s	695s	653m	688s	690s
		622m			630m		620w
565m	576s						574m
548s	553s		558w	556m		555w	550s
513m	525s						520m
444m	445m			447m			440m

a) signifies adducts of 1,1-dibromo-2,3,4,5-tetraphenylstannole<sup>(122)</sup>

### PYRIDINE ADDUCT

The bands at 1600 (stretching mode of a conjugated C=C), 762 and 731  $\text{cm}^{-1}$  (out-of-plane deformation of benzene) in I are completely absent in the complex. The band at 548 (Sn-C stretching) is lowered to 534  $\text{cm}^{-1}$ . Changes are also observed in the ligand bands. The band at 746 is lowered to 722  $\text{cm}^{-1}$ , and the band at 702 is lowered to 690  $\text{cm}^{-1}$ . This shift to lower energy in the pyridine spectrum has also been observed by Greenwood and Wade<sup>(163)</sup> who reported that a band at 705  $\text{cm}^{-1}$  (the C-H out-of-plane deformation) is shifted about 25  $\text{cm}^{-1}$  in the complexes pyridinium chloride, pyridinium tetrachloroborate, and boron trichloride-pyridine.

### BIPYRIDINE ADDUCT

The stannole band at 762  $\text{cm}^{-1}$  is either not observed or else it is lowered enough to be obscured by the ligand band at 755  $\text{cm}^{-1}$ . The band at 731 is lowered to 723  $\text{cm}^{-1}$ , and the band at 695 is lowered to 690  $\text{cm}^{-1}$ . The bipyridine bands at 1415 and 619  $\text{cm}^{-1}$  are not observed in the complex.

### PHENANTHROLINE ADDUCT

The stannole band at 695 is lowered in energy to 690  $\text{cm}^{-1}$ , the band at 762 is lowered to 755  $\text{cm}^{-1}$ , and the band at 731 is lowered to 721  $\text{cm}^{-1}$ . The phenanthroline band at 851 is not observed, and a new band appears in the complex at 1210  $\text{cm}^{-1}$ .

### TERPYRIDINE ADDUCT

The stannole bands at 1600 and 1574 are lowered to 1595 and 1570  $\text{cm}^{-1}$ , respectively. The band at 763  $\text{cm}^{-1}$  is not observed in the complex. The terpyridine band at 1422 is raised to 1431  $\text{cm}^{-1}$ , and the

band at 1260 which is associated with the C-N-C (unsaturated) stretching frequency is lowered to 1258  $\text{cm}^{-1}$ . The bands at 830 and 630  $\text{cm}^{-1}$  are not observed in the complex.

The infrared stretching frequencies for Sn-I bonds occur at 200-160 and 85-75  $\text{cm}^{-1}$  for the bond stretches and bends, respectively<sup>(123)</sup>. These frequencies are below the range of the infrared spectrometer used in this study. As a result, it is not possible to assign structures to the adducts of diiodotetraphenylstannole by observation of the appearance or disappearance of the symmetric Sn-I stretches in the infrared spectra of the complexes. For this reason, structural assignments are based upon tin-119m Mössbauer data and by analogy with the complexes formed with dibromotetraphenylstannole. The Mössbauer parameters for the parent compounds and their adducts are listed in Table 4.2.

#### 4.7b MÖSSBAUER SPECTRA OF ADDUCTS AND COORDINATION NUMBER OF TIN

The question of the coordination number of tin in the complexes is difficult to settle. Beattie and McQuillan<sup>(164)</sup> have suggested that the adducts of  $\text{Me}_2\text{SnCl}_2$  and  $\text{MeSnCl}_3$  with nitrogen bases are generally six-coordinated. Six-coordination has also been proposed for  $\text{Me}_2\text{SnCl}_2 \cdot 2\text{py}$  by Tanaka<sup>(165)</sup>, and this compound has also been shown to have an octahedral structure by X-ray diffraction<sup>(65)</sup>. A coordination number of six has also been assigned to complexes of bipyridine and phenanthroline with alkyltin halides<sup>(166)</sup>.

Three geometrical isomers are possible for the pyridine adducts of diiodotetraphenylstannole:

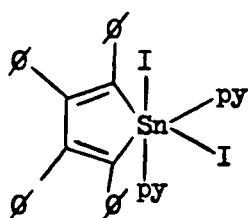
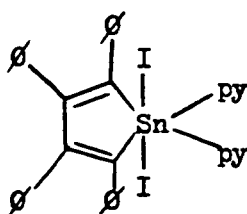
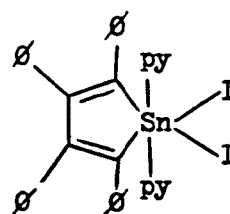
TABLE 4.2  
 $^{119}\text{mSn}$  Mössbauer Parameters (mm/s)

COMPOUND	I.S.	Q.S.	$\rho^a$	ASSIGNMENTS FROM MÖ SPECTRA
1,1-diiodo-2,3, 4,5-tetraphenyl- stannole	$1.61 \pm 0.02$ ( $1.03 \pm 0.04$ )	$2.32 \pm 0.04$	1.44	
1,1-dibromo-2,3, 4,5-tetraphenyl- stannole	$1.57 \pm 0.06$	$2.35 \pm 0.12$	1.50	
diiodostannole- 2py	$1.19 \pm 0.01$ ( $1.15 \pm 0.02$ )	$2.55 \pm 0.01$	2.14	<u>cis</u> -py groups
dibromostannole- 2py	$1.05 \pm 0.06$	$2.36 \pm 0.12$	2.25	<u>cis</u> -py groups
diiodostannole- bipy	$1.21 \pm 0.01$ ( $1.15 \pm 0.04$ )	$2.49 \pm 0.02$	2.06	<u>cis</u> -bipy group
dibromostannole- bipy	$1.09 \pm 0.06$	$2.62 \pm 0.12$	2.40	<u>cis</u> -bipy group
diiodostannole- phen	$1.14 \pm 0.01$ ( $1.29 \pm 0.04$ )	$2.61 \pm 0.02$	2.29	<u>cis</u> -phen group
dibromostannole- phen	$1.05 \pm 0.06$	$2.53 \pm 0.12$	2.41	<u>cis</u> -phen group
diiodostannole- terpy	$1.49 \pm 0.02$ ( $1.21 \pm 0.06$ )	$2.49 \pm 0.03$	1.67	
dibromostannole- terpy	$1.48 \pm 0.06$	$2.58 \pm 0.12$	1.74	

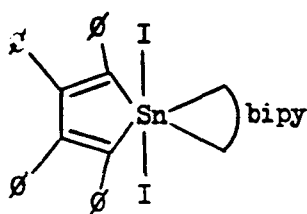
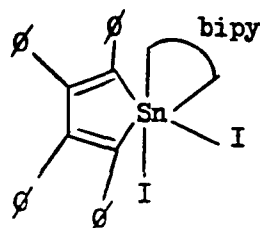
The values listed in parentheses are those for the half-height peak widths.

a)  $\rho = \text{Q.S.}/\text{I.S.}$

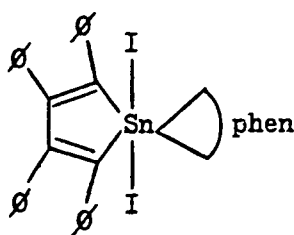
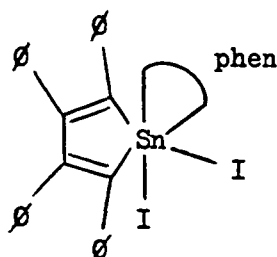


cis-Icis-pytrans-Icis-pycis-Itrans-py

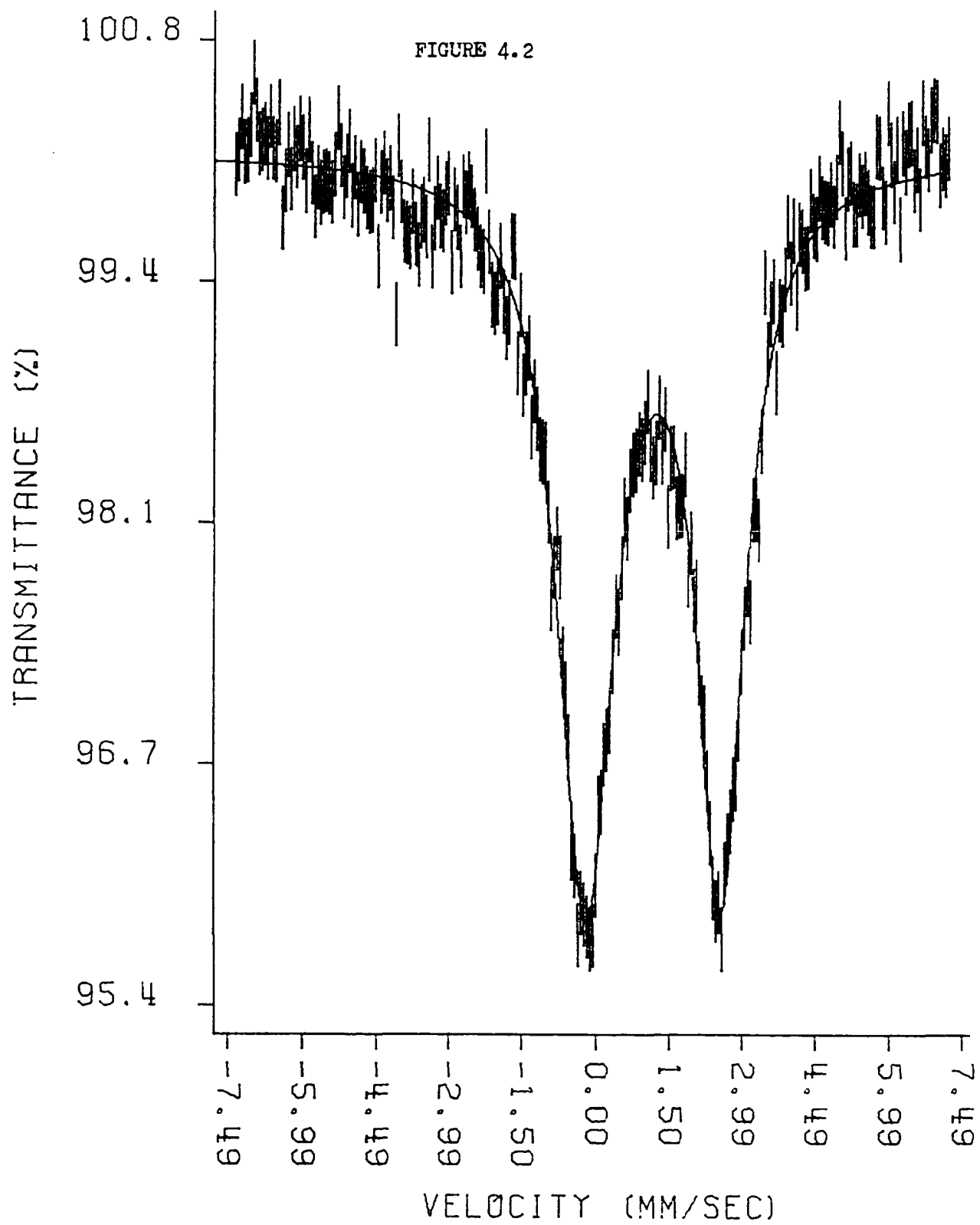
There are two distinct geometrical isomers for the bipyridine adduct of diiodostannole:

trans-Icis-bipycis-Icis-bipy

For the phenanthroline adduct, there are again two possible geometric isomers:

trans-Icis-phencis-Icis-phen

The Mössbauer parameters for the complexes are given in Table 4.2. All give well-defined doublet spectra (Figures 4.2 - 4.4). The isomer shift (I.S.) values of the complexes fall below 2.56 mm/s, indicating the presence of tin(IV). The ratio of the quadrupole



PYRIDINE ADDUCT OF DIIODOSTANNOLE

FIGURE 4.3

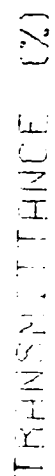
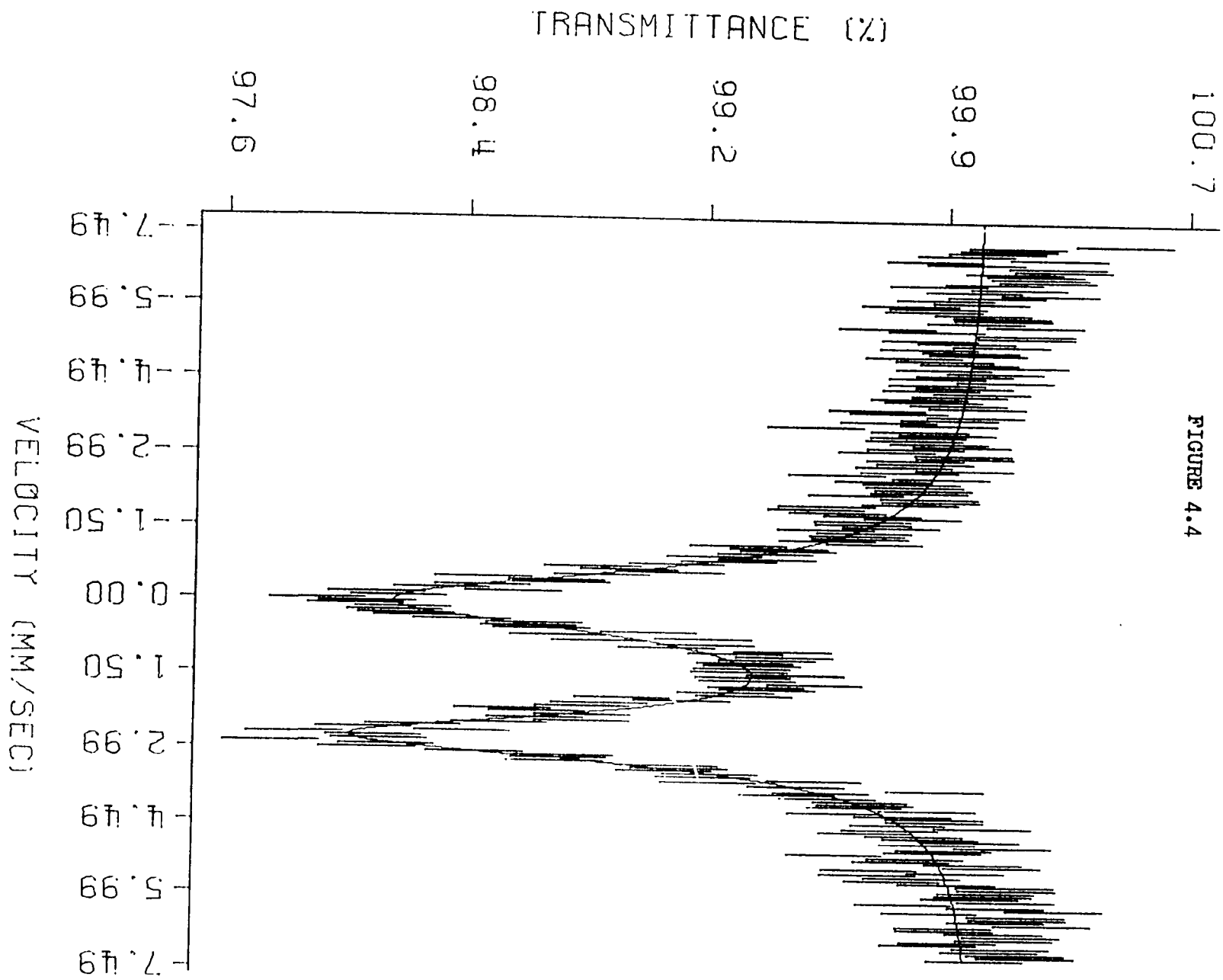


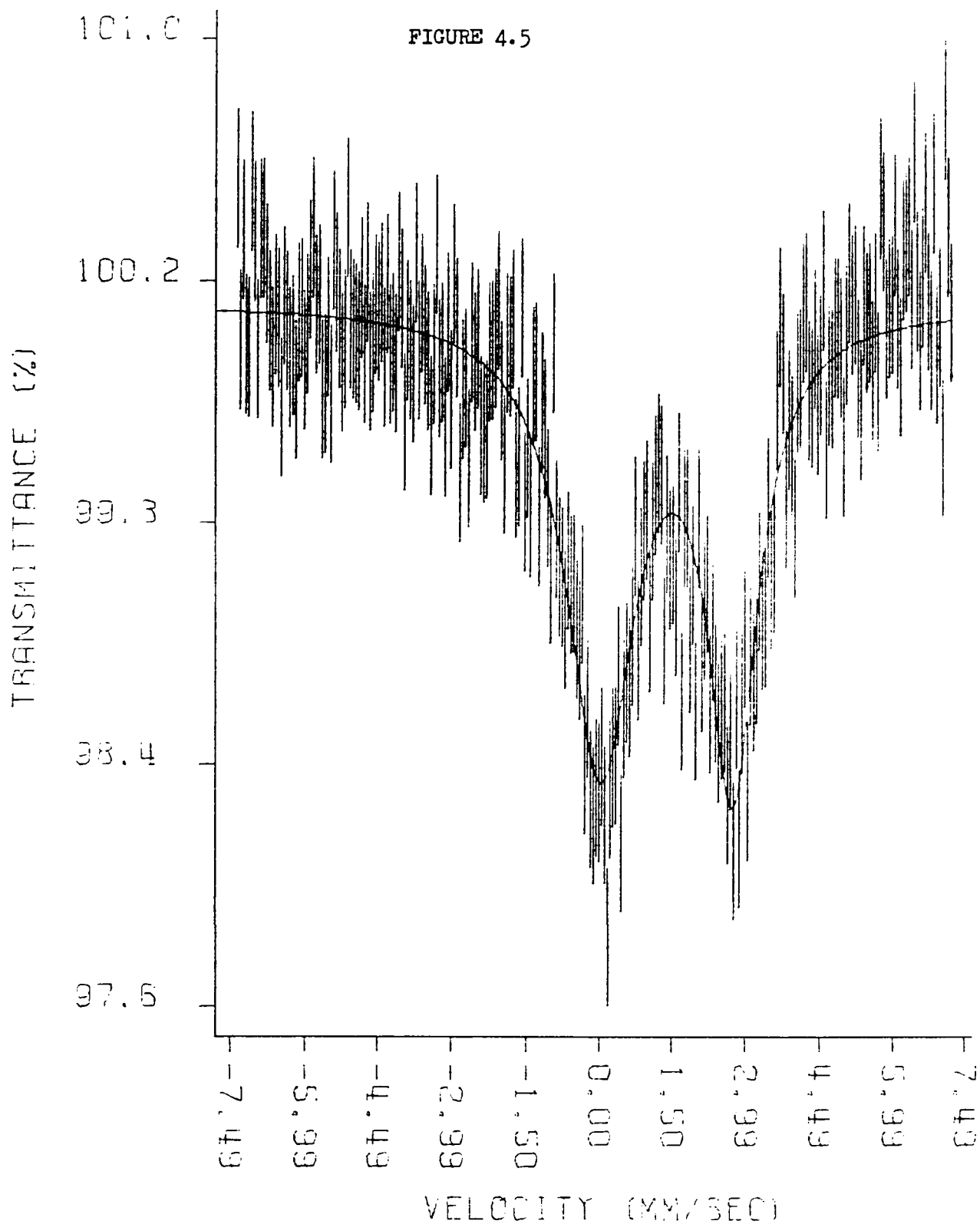
FIGURE 4.4



PHEN PRODUCT OF DI-1000STANNOLE

splitting (Q.S.) to the isomer shift, the  $\rho$ -value, is often used to gain information on the coordination number of tin(IV) compounds. Values  $> 2.1$  are generally associated with coordination numbers greater than four, and values  $\leq 1.8$  with four-coordination. This rule may be used with a reasonable degree of assurance, even though it is not absolute and a number of exceptions are known<sup>(9)</sup>. Its application to the data in Table 4.2 indicates that the adducts, with the exception of the terpyridine adducts, have coordination higher than four.

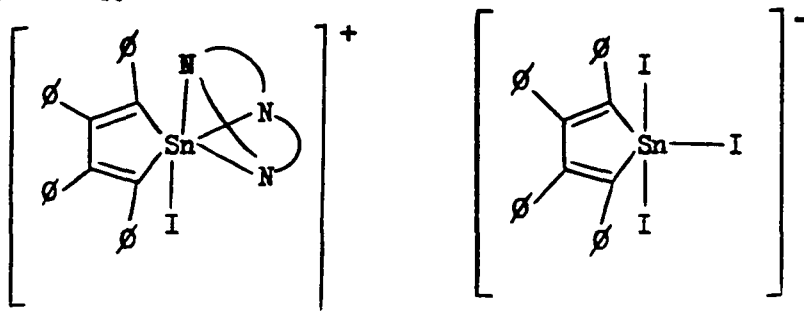
The quadrupole splitting (Q.S.) values are included in the data summarized in Table 4.2. It should be noted, as mentioned in Chapter I, that the magnitude of the Q.S. parameter makes it possible to distinguish between the cis- and trans-configurations of Sn-C groups in these adducts. Fitzsimmons<sup>(99,167)</sup> and Debye<sup>(168)</sup> in extensions of earlier work on  $^{57}\text{Fe}$  Mössbauer spectra, concluded that for compounds of the type  $\text{R}_2\text{SnX}_4$  ( $\text{X}=\text{Cl}, \text{O}$ , or  $\text{N}$ ) ( $\text{R}=\text{alkyl}$  or  $\text{aryl}$ ), the Q.S. value for the cis-isomer was half the Q.S. value for the trans-isomer, and further, that the Q.S. trans- had a value of 4 mm/s. A similar interpretation has been suggested by Greenwood and Ruddick<sup>(88)</sup> for the compound  $\text{Me}_2\text{Sn}[(\text{Ph}_2\text{PO})_2\text{N}]_2$  (Q.S. = 4.18 mm/s) to which they assign a  $\text{D}_{2h}$  symmetry. Recently, Beattie<sup>(170)</sup> reported trans- $\text{Ph}_2\text{SnCl}_2 \cdot \text{bipy}$  and trans- $\text{Ph}_2\text{SnCl}_2 \cdot \text{phen}$ , having Q.S. = 3.90 and 3.70 mm/s, respectively, and cis- $\text{Ph}_2\text{Sn} \cdot \text{oxin}_2$  and cis- $\text{Pr}_2\text{Sn} \cdot \text{oxin}_2$ , having Q.S. = 1.78 and 2.20 mm/s, respectively, where oxin is the 8-oxyquinoline anion. On these bases and by comparison with the adducts of dibromostannole, whose structures were assigned by the lack of a symmetric



2,2',2''-TERPHENYL PRODUCT OF 01-1000STAINOLE

Sn-Br stretch in the infrared spectra of the adducts<sup>(122)</sup>, the complexes of pyridine, 2,2'-bipyridine, and 1,10-phenanthroline are all assigned the structures containing two cis-Sn-C groups and trans-iodine groups in the octahedral structures.

The most probable structure for the complex formed with 2,2',2''-terpyridine is (65):



Zuckerman, et al.,<sup>(171)</sup> have reported the tin-119m Mössbauer parameters of 2,2',2''-terpyridine adducts of  $\text{Me}_2\text{SnCl}_2$ ,  $\text{Ph}_2\text{SnCl}_2$ ,  $n\text{-Bu}_2\text{SnCl}_2$ ,  $\text{Me}_3\text{SnCl}$ , and  $\text{SnCl}_4$ . All of the spectra, except that of  $\text{SnCl}_4$ , are well defined doublets, and that both types of tin atoms in the adduct (the five-coordinate anion and the six-coordinate cation) give rise to I.S. and Q.S. values sufficiently similar to allow their respective resonances to fall within the envelope of the same doublet. The observed Mössbauer spectrum (Figure 4.5) gives parameters for the 2,2',2''-terpyridine adduct of diiodostannole that are in agreement with previous reports, as shown in Table 4.3.

#### 4.8 1-FLUORO-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE ADDUCT OF 2,2',2''-TERPYRIDINE

As discussed previously, the structure of the terpyridine adducts of diiodo- and dibromostannole most likely are:

TABLE 4.3

## NEUTRAL COMPOUNDS AND CHARGED COMPLEXES OF ORGANOTIN HALIDES

COMPOUND	I.S. (d)	Q.S. (d)
$\text{Me}_2\text{SnCl}_2^{(a)}$	$1.54 \pm 0.06$	$3.33 \pm 0.12$
$[\text{Me}_2\text{SnCl} \cdot \text{terpy}]^{+(a)}$	$1.46 \pm 0.06$	$3.58 \pm 0.12$
$[\text{Me}_2\text{SnCl}_3]^{-(a)}$	$1.40 \pm 0.06$	$3.30 \pm 0.12$
$[\text{Me}_2\text{SnCl} \cdot \text{terpy}]^+ [\text{Me}_2\text{SnCl}_3]^{-(a)}$	$1.38 \pm 0.06$	$3.31 \pm 0.12$
$\text{BuSnCl}_3^{(a)}$	$1.31 \pm 0.06$	$1.83 \pm 0.12$
$[\text{BuSnCl}_2 \cdot \text{terpy}]^{+(a)}$	$1.09 \pm 0.06$	$1.76 \pm 0.12$
$[\text{BuSnCl}_5]^{2-(a)}$	$1.07 \pm 0.06$	$1.86 \pm 0.12$
$[\text{BuSnCl}_2 \cdot \text{terpy}]^+ [\text{BuSnCl}_5]^{2-(a)}$	$1.07 \pm 0.06$	$1.94 \pm 0.12$
$\text{Ph}_2\text{SnCl}_2^{(a)}$	$1.38 \pm 0.06$	$2.75 \pm 0.12$
$[\text{Ph}_2\text{SnCl} \cdot \text{terpy}]^{+(a)}$	$1.20 \pm 0.06$	$3.24 \pm 0.12$
$[\text{Ph}_2\text{SnCl}_3]^{-(a)}$	$1.25 \pm 0.06$	$2.62 \pm 0.12$
$[\text{Ph}_2\text{SnCl} \cdot \text{terpy}]^+ [\text{Ph}_2\text{SnCl}_3]^{-(a)}$	$1.17 \pm 0.06$	$2.88 \pm 0.12$
dibromostannole <sup>(b)</sup>	$1.57 \pm 0.06$	$2.35 \pm 0.12$
dibromostannole $\cdot$ terpy <sup>(b)</sup>	$1.48 \pm 0.06$	$2.58 \pm 0.12$
diiodostannole <sup>(c)</sup>	$1.61 \pm 0.02$ ( $1.03 \pm 0.04$ )	$2.32 \pm 0.04$
diiodostannole $\cdot$ terpy <sup>(c)</sup>	$1.49 \pm 0.02$ ( $1.21 \pm 0.06$ )	$2.49 \pm 0.03$

a) taken from reference 171

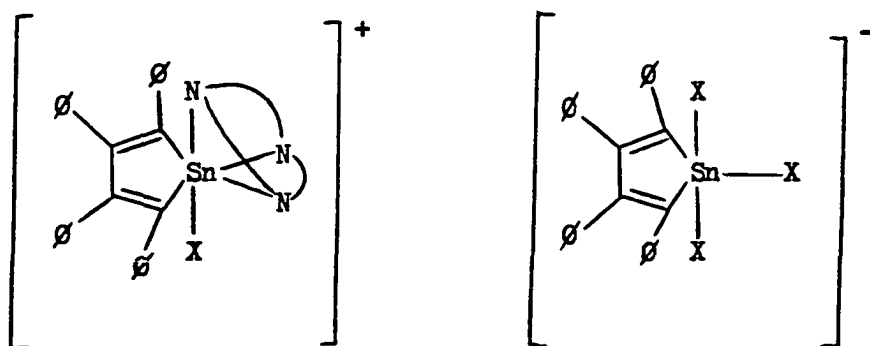
b) taken from reference 122

c) this work

d) mm/s

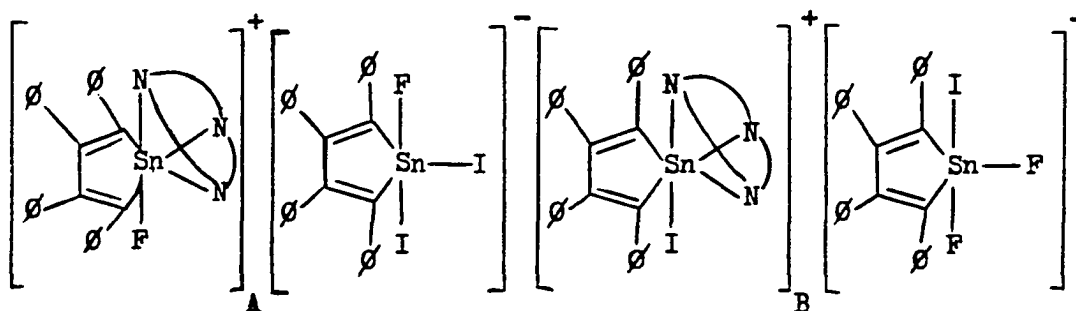
Values in parentheses are those for the half-height peak widths





All of the terpyridine adducts of diorganotin dihalides, however, have been synthesized from starting materials where both of the halides were the same element. If the halide groups are different, two possible sets of double salts can be produced by the transfer of one halide from what becomes the cation to the anion.

The terpyridine complex of 1-fluoro-1-iodo-2,3,4,5-tetra-phenylstannole was thus prepared in an effort to determine which halide ion would be transferred. The two possible products are:



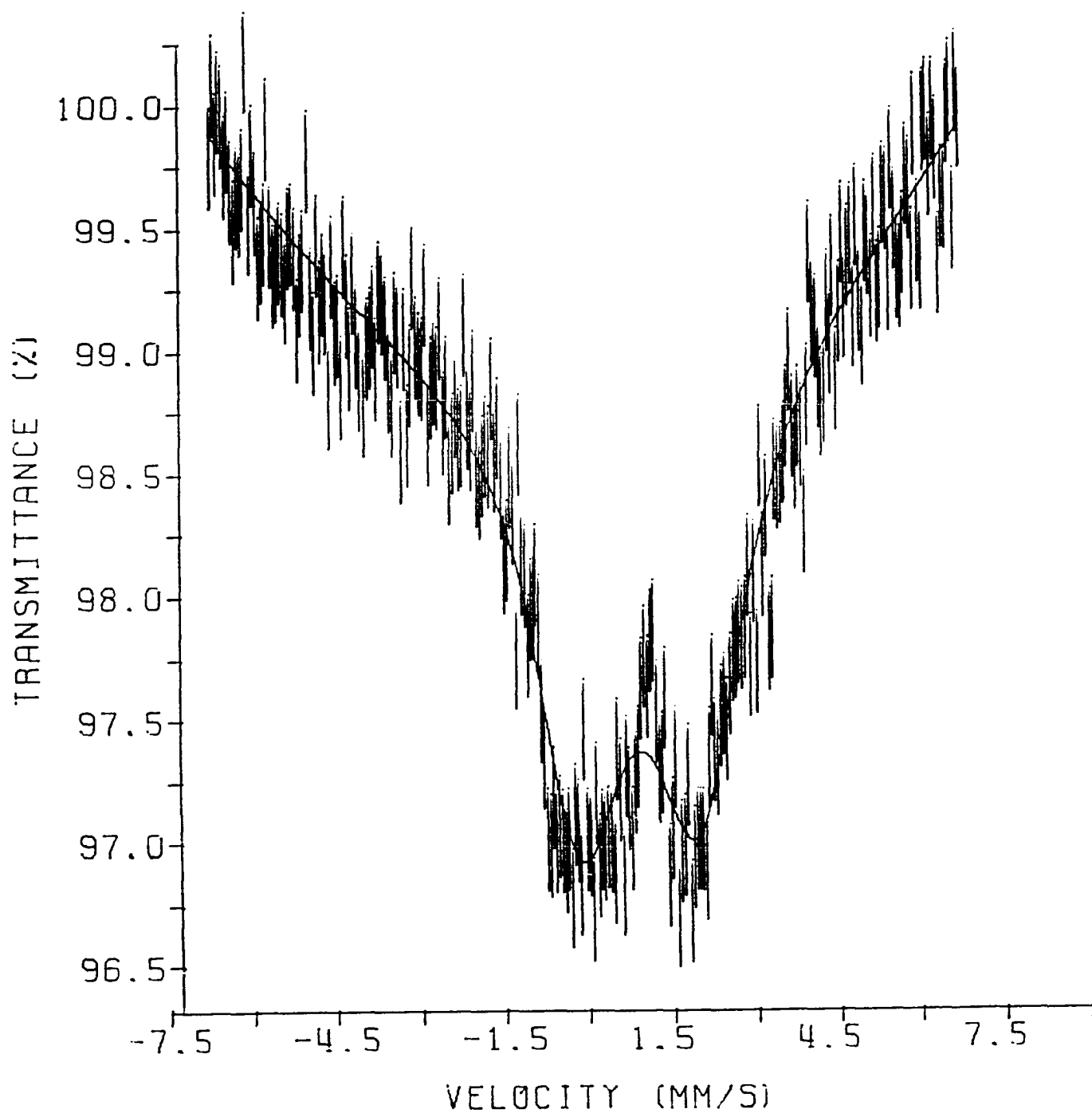
A comparison of the infrared spectral data of the adduct, terpyridine, and the fluoro-iodostannole is given in Table 4.4.

The stannole bands at 1595 (stretching mode of a conjugated C=C) and 1575  $\text{cm}^{-1}$  are lowered to 1590 and 1568  $\text{cm}^{-1}$  respectively. The band at 550  $\text{cm}^{-1}$  (Sn-C stretch) is lowered to 545  $\text{cm}^{-1}$ . The terpyridine band at 1422  $\text{cm}^{-1}$  is raised to 1430  $\text{cm}^{-1}$ , and the band

TABLE 4.4  
INFRARED SPECTRAL DATA ( $\text{cm}^{-1}$ )

FLUOROIODOSTANNOLE	TERPYRIDINE	ADDUCT
1595m		1590w
1575w	1580m	1658w
	1562s	1540w
		1485w
1440w	1452s	1445w
	1422s	1430m
	1260m	1250m
1178m		
1150w		1140m
	1101m	1108s
1066m		1072m
1035m		1022s
1000w		998s
930m		
913s		
		872s
	830m	
		805s
786m		781s
762s	767s	768m
735s		737s
		695s
	653m	653s
611s	630m	617s
570s		568s
550s		545s
520m		520s
449s		443s
350m	391m	
315m		

FIGURE 4.6



at  $1260\text{ cm}^{-1}$  (C-N-C stretch) is lowered to  $1250\text{ cm}^{-1}$ . The bands at  $830$  and  $630\text{ cm}^{-1}$  are not observed in the complex. The Sn-F stretch of the stannole,  $570\text{ cm}^{-1}$ , is lowered to  $568\text{ cm}^{-1}$  in the complex. The bridging Sn-F stretch observed in the stannole,  $350\text{ cm}^{-1}$ , is not observed in the adduct, thus indicating that complexation breaks up the intermolecular association of the stannole.

Infrared spectroscopy, however, is unable to determine whether isomer A or B is the product of the complexation reaction, but it is reasonable to assume that isomer A should be the product. In the formation of isomer A, an iodine is transferred to the anion and is replaced at the cation by a terpyridine group. In the formation of isomer B, a fluorine is transferred. In order for these transfers to occur, the Sn-halide bond must be broken. The tin-fluorine bond has a much higher dissociation energy ( $112\text{ kcal/mole}$ )<sup>(2)</sup> than the tin-iodine bond ( $62\text{ kcal/mole}$ )<sup>(2)</sup>. This difference in bond dissociation energies strongly favors the formation of isomer A.

The Mössbauer spectrum of the complex, I.S. =  $1.20 \pm 0.04$ , Q.S. =  $2.84 \pm 0.08\text{ mm/s}$ , (Figure 4.6) does not shed any light on which isomer is formed. It does, however, show that the chemical environments of the two tin sites in the complex are sufficiently similar that they give rise to only one doublet (half-height peak width is  $1.65 \pm 0.06\text{ mm/s}$ ).

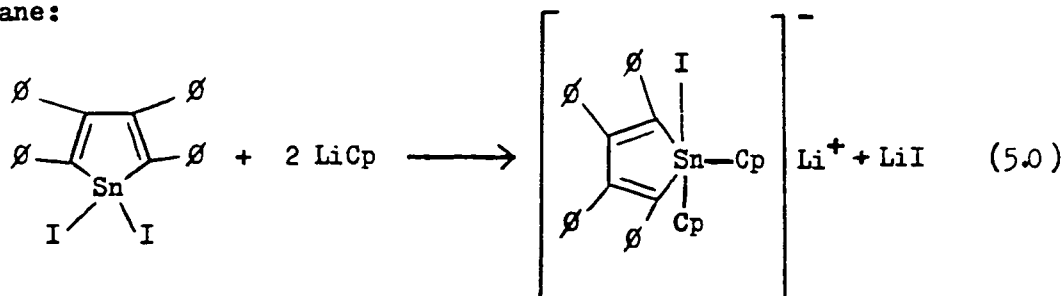
Additional investigations must be carried out in order to determine which isomer is formed in this reaction.

## CHAPTER V

### LITHIUM 1,1-DICYCLOPENTADIENYL-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE

#### 5.1 INTRODUCTION

Lithium 1,1-dicyclopentadienyl-1-iodo-2,3,4,5-tetraphenylstannole was prepared from the reaction of 1,1-diiodo-2,3,4,5-tetraphenylstannole and lithium cyclopentadiene in a 1:2 molar ratio in hexane:



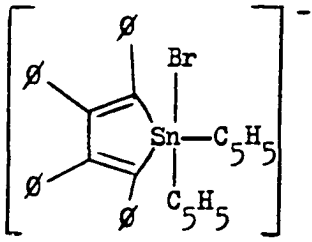
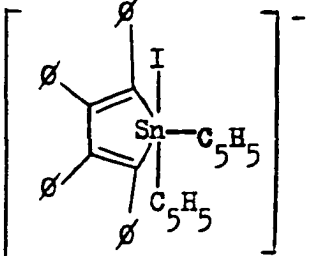
Structural information for this compound was obtained by infrared, proton nuclear magnetic resonance, and tin-119m Mössbauer spectroscopies.

It is assumed that an intermediate in this reaction is 1,1-bis( $\eta^1$ -cyclopentadienyl)tetraphenylstannole, and that this intermediate is a sufficiently strong Lewis acid to take up iodide ion during its formation from lithium cyclopentadiene and give the  $[\text{R}_4\text{SnI}]^-$  anion rather than precipitating lithium iodide.

#### 5.2 NUCLEAR MAGNETIC RESONANCE STUDY

The proton n.m.r. spectrum of the compound at room temperature contains two resonances, other than the phenyl multiplet, that can be assigned to the tin-cyclopentadienyl system [5.79 and 5.46 ppm

TABLE 5.1  
NUCLEAR MAGNETIC RESONANCE PARAMETERS FOR  
CYCLOPENTADIENYLTIN HALIDES

COMPOUND	$ ^2J(^{119}\text{Sn}-\text{C}-^1\text{H}) $ (Hz)	REFERENCE
$(\underline{\text{h}}^1-\text{C}_5\text{H}_5)_2\text{SnCl}_2$	41.8	172
$(\underline{\text{h}}^1-\text{C}_5\text{H}_5)_2\text{SnBr}_2$	40.5	172
$(\underline{\text{h}}^1-\text{C}_5\text{H}_5)_2\text{SnI}_2$	37.0	172
$(\underline{\text{h}}^1-\text{C}_5\text{H}_5)_3\text{SnCl}$	33.5	173
$(\underline{\text{h}}^1-\text{C}_5\text{H}_5)\text{SnCl}_3$	59.8	173
	$\text{M}^+$ 25.4 (M = Li) 26.0 (M = Tl)	122 122
	$\text{Li}^+$ 23.2	this work

relative to TMS) in  $\text{CDCl}_3$ ,  $\left| J(^{117,119}\text{Sn}-^1\text{H}) \right| = 23.2 \text{ Hz}$ . The integration ratio (2.2:1 calculated; 2.4:1 found) reveals two cyclopentadienyl groups per stannole ring. Table 5.1 lists nmr data for related cyclopentadienyl tin halides. It is evident from Table 5.1 that the nmr data are consistent with those for analogous  $^1\text{H}$ -cyclopentadienyltin derivatives.

As shown in Figure 5.1 the two equal intensity resonances exhibited at  $25^\circ\text{C}$  merge into a single, upshifted peak at  $100^\circ\text{C}$ . From the slope of the Arrhenius plot (Figure 5.2), the value for  $\Delta E^\ddagger = 11.4 \text{ kcal/mole}$  for the process. The formula<sup>(174)</sup>:

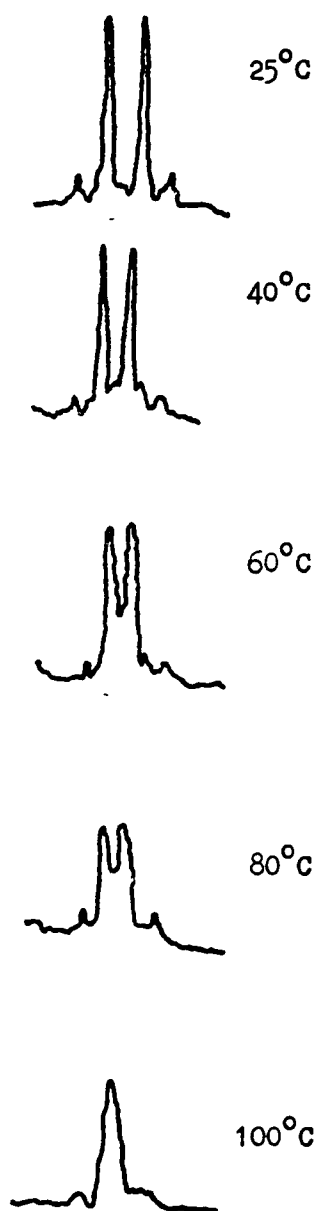
$$\tau\delta\nu = \pm \frac{1}{\pi\sqrt{2}} \sqrt{r \pm (r^2 - 1)^{\frac{1}{2}}} \quad (5.1)$$

was used to calculate  $\tau$ , where  $r = \frac{\text{maximum doublet intensity}}{\text{minimum doublet intensity}}$ , and

$\delta\nu$  = chemical shift difference in the absence of rotational averaging i.e., the doublet separation is much greater than the line width at one-half maximum intensity of the doublet components (this occurs at the lowest temperature). The rate of internal rotation is given by  $k = \frac{1}{2}\tau$ , where  $k = k_0 e^{-E_a/RT}$ , and thus a plot of  $\log(\frac{1}{2}\tau)$  vs.  $1/T$  will give a straight line with slope  $-E_a/RT$ . From this slope the barrier restricting rotation,  $E_a$ , can be calculated<sup>(174)</sup>. The tin-proton couplings associated with the two resonances remain relatively unchanged over the temperature range studied. Table 5.2 gives a comparison of the data obtained from the Arrhenius plots for this compound with the data from the analogous bromo compound<sup>(122)</sup>.

Preservation of the couplings through the high-temperature region specifies that an intramolecular process is occurring, and the

FIGURE 5.1



N.M.R. SPECTRUM OF LITHIUM 1,1-DICYCLOPENTADIENYL-1-iodo-2,3,4,5-  
TETRAPHENYLSTANNOLE AT SEVERAL TEMPERATURES



FIGURE 5.2

ARRHENIUS PLOT FOR PSEUDO-ROTATION FOR

LITHIUM 1,1-DICYCLOPENTADIENYL-1-IODOTETRAPHENYLSTANNOLE

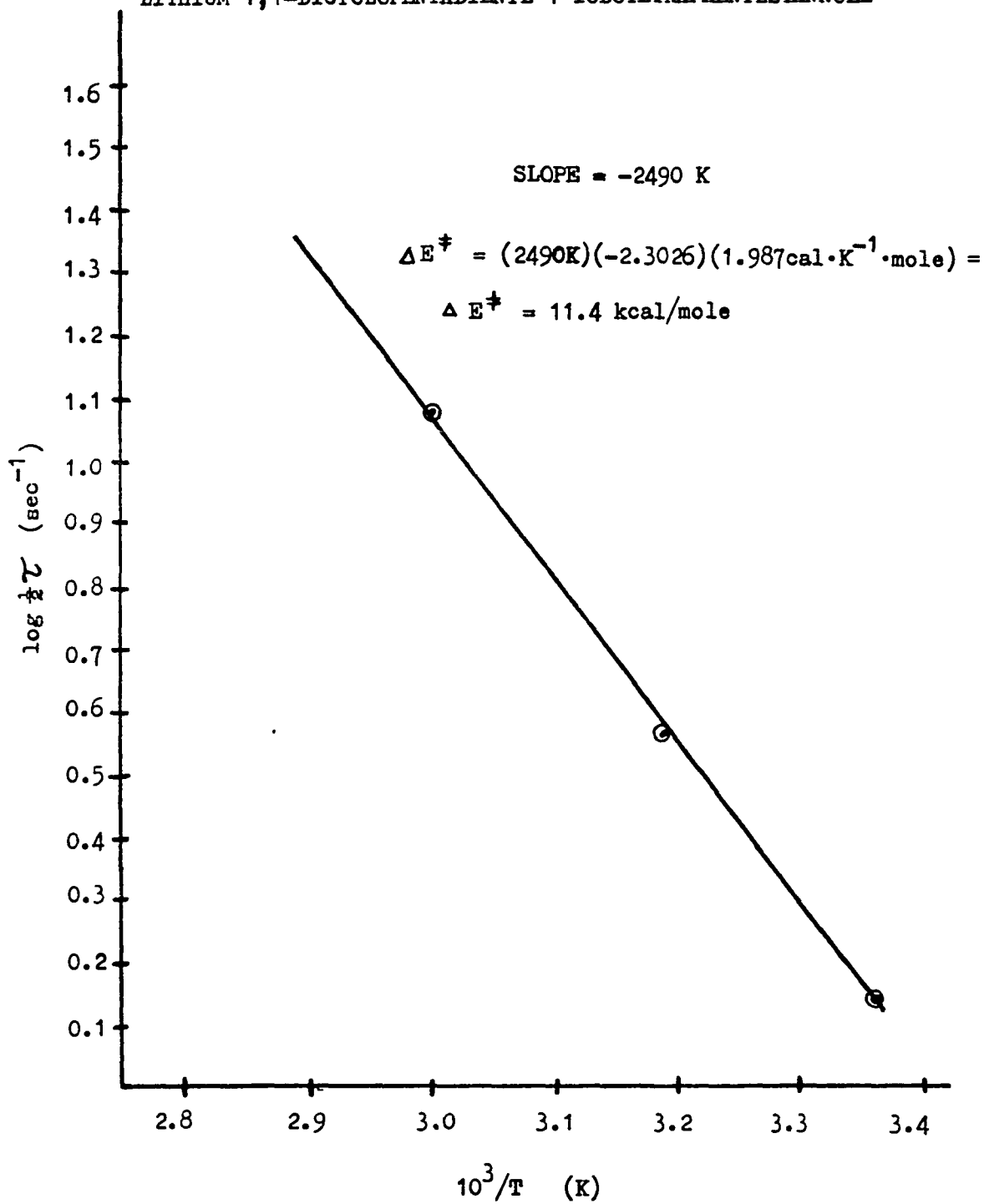
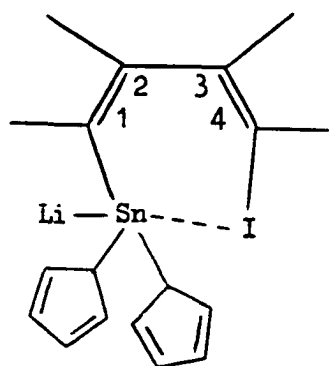
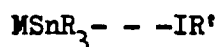


TABLE 5.2

## ARRHENIUS DATA FOR DICYCLOPENTADIENYLSTANNOLES

PARAMETER	DICYCLOPENTADIENYL- IODOSTANNOLE	DICYCLOPENTADIENYL- BROMOSTANNOLE
Barrier to internal rotation	11.4 kcal/mole	12.2 kcal/mole
Slope of Arrhenius curve	-2490 K	-2660 K
Reference	This work	122

lack of a shift upon changing temperature eliminates the possibility of a monomer-dimer equilibrium. The origin of the cyclopentadienyl group nonequivalence may lie in a hindered diene rotation in a  $\text{LiSnR}_3\text{-IR}$  system arising from intramolecular Sn-I coordination of the type studied by Boer<sup>(175,176,177)</sup>:



- a) hindered rotation about  
 $\text{C}_2 - \text{C}_3$ , diene dissymmetry
- b) 2 rotamers of equal population

This compound, however, exhibits none of the properties of the triorganotin lithium compounds described in the literature<sup>(178)</sup>.

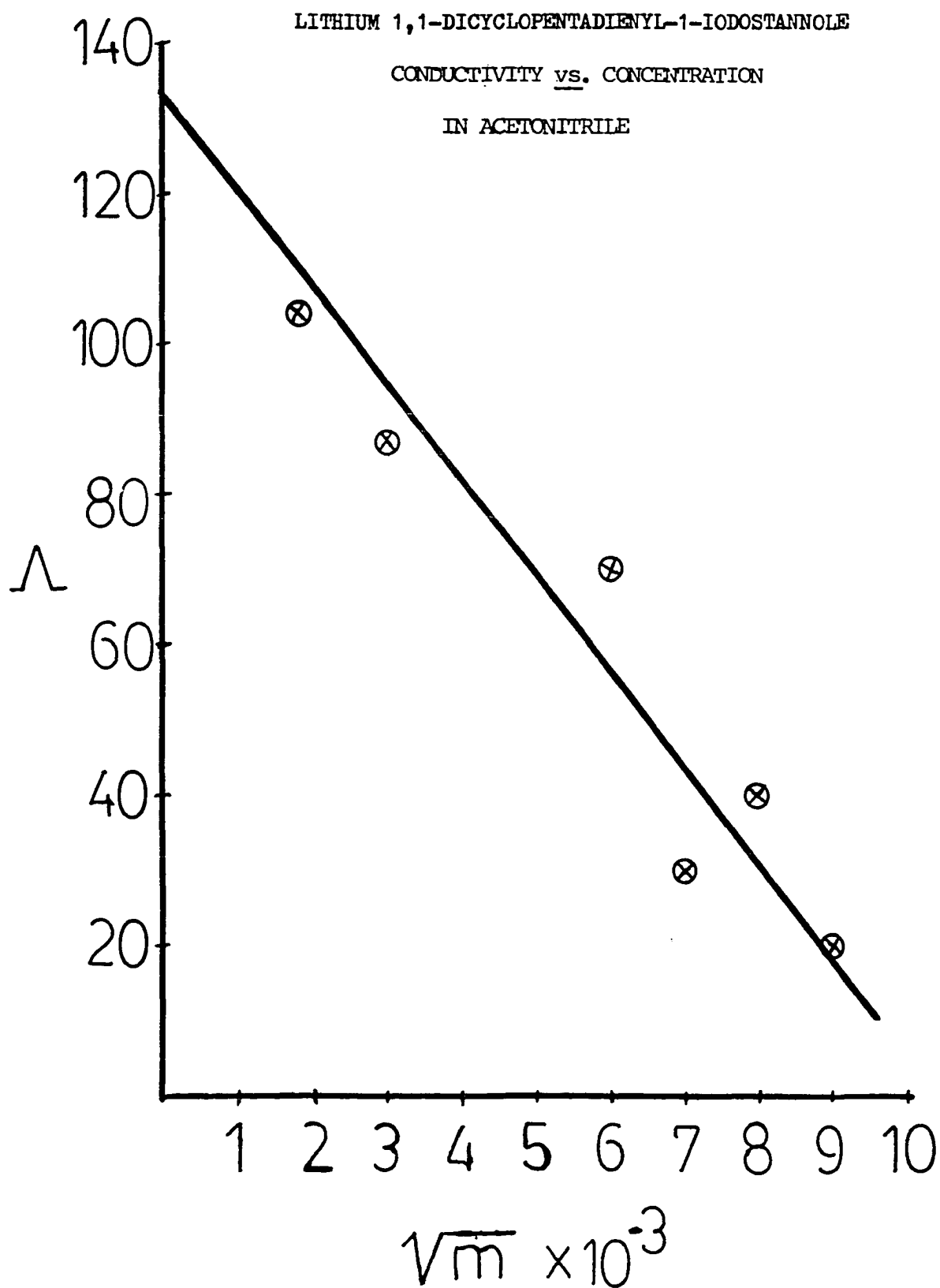
### 5.3 CONDUCTIVITY MEASUREMENTS

The measurement of conductivity provides a valuable method of studying electrolytic solutions. It is usually assumed that the free ions in solution obey the limiting equation developed by Onsager<sup>(179)</sup> and that their equivalent conductance ( $\Lambda$ ) in dilute solution may be written:

$$\Lambda = \alpha[\Lambda_0 - b(\alpha m)^{\frac{1}{2}}] \quad (5.2)$$

where  $\alpha$  is the fraction of free ions at a concentration,  $m$ ,  $b$  is the Onsager slope, and  $\Lambda_0$  is the equivalent conductance at infinite dilution. For a weakly ionized substance,  $\Lambda$  varies with the concen-

FIGURE 5.3



tration because the degree of ionization varies with the concentration. The equivalent conductance, however, must approach a constant, finite value at infinite dilution. This value can be calculated from extrapolation of a graph of  $\Lambda$  vs.  $m^{\frac{1}{2}}$  to zero concentration. This value at infinite dilution is then characteristic of the ratio of the electrolytes in the solution.

Conductivity measurements were taken for lithium 1,1-dicyclopentadienyl-1-iodo-2,3,4,5-tetraphenylstannole over the concentration range  $1.8 \times 10^{-6}$  to  $8 \times 10^{-5}$  M and gave  $\Lambda_0$  (y-intercept) of  $133 \text{ ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$  at infinite dilution in acetonitrile, characteristic of a 1:1 electrolyte (Figure 5.3). The acetonitrile used in the above-mentioned experiment was distilled from phosphorus pentoxide, under nitrogen, and stored over molecular sieves. The water content of the solvent, however, was unknown. Only negligible conductivity was shown for the acetonitrile itself.

Table 5.3 gives a comparison of the conductivity data for this compound and the analogous bromo compound.

#### 5.4 PSEUDOROTATION MECHANISM

As a result of the conductivity measurements, ionic formulations  $[\text{R}_4\text{SnI}]^-\text{Li}^+$  (Figure 5.4) based upon the conventional trigonal bipyramidal arrangement of ligands about tin must be considered<sup>(180)</sup>.

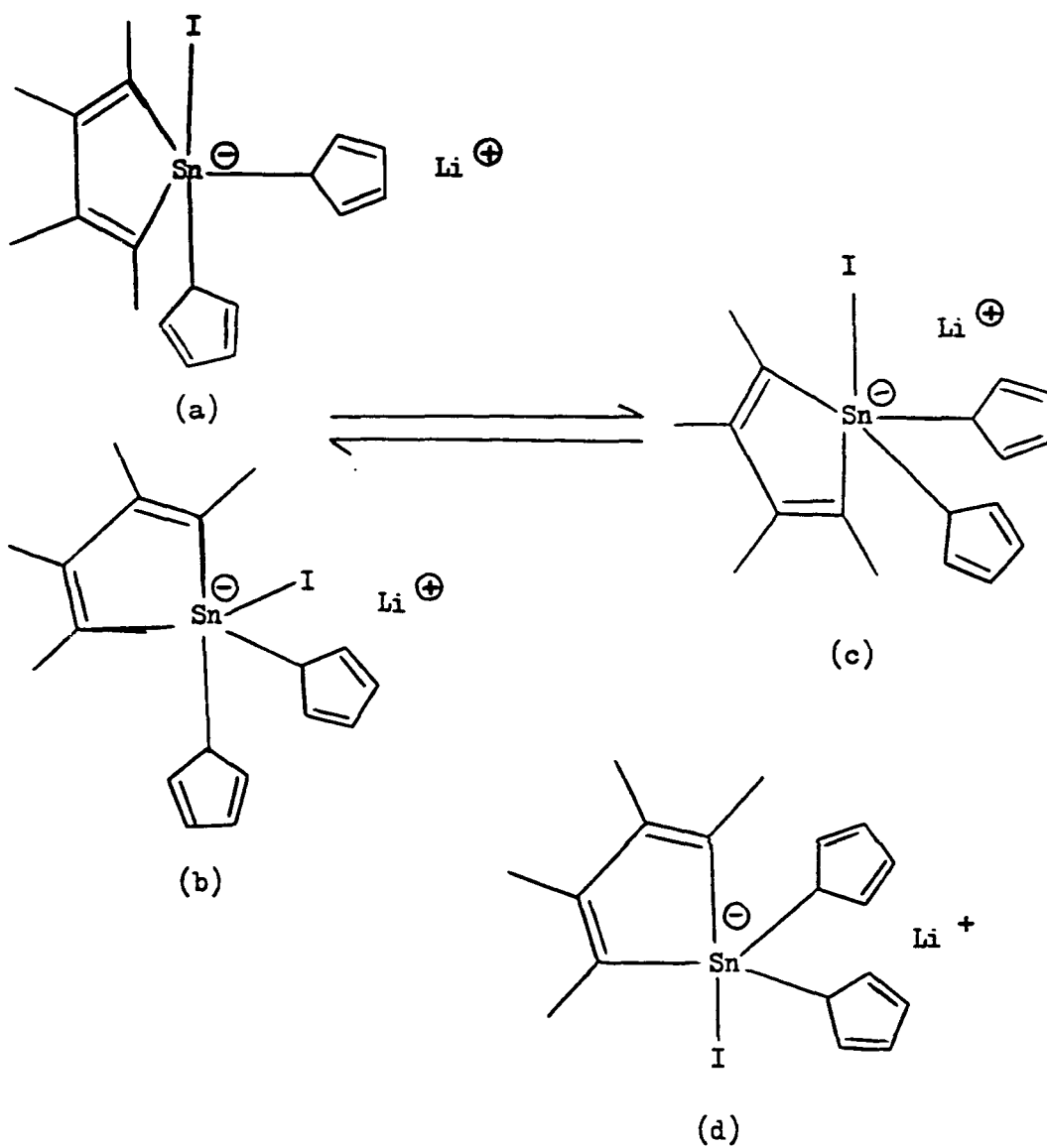
Conformers of the axially-most-electronegative type (a) and in which the stannole ring spans one equatorial- and one axial-position (b) may interconvert through a pseudorotation mechanism which may go through a tetragonal pyramid (c) as shown in Figure 5.4.

TABLE 5.3

## CONDUCTIVITY DATA FOR DICYCLOPENTADIENYLSTANNOLES

PARAMETER	DICYCLOPENTADIENYL- IODOSTANNOLE	DICYCLOPENTADIENYL- BROMOSTANNOLE
Concentration range(M)	$1.8 \times 10^{-6}$ to $8 \times 10^{-5}$	$1.8 \times 10^{-6}$ to $9 \times 10^{-6}$
$\Lambda_o$ (ohm <sup>-1</sup> mole <sup>-1</sup> cm <sup>2</sup> )	133	123
Electrolyte type	1:1	1:1

FIGURE 5.4  
 IONIC FORMULATIONS FOR  $[R_4SnI]^- Li^+$



Pseudorotation about either of the tin attachments to the stannole ring would place the ring in a diequatorial position with a stannole C-Sn-C angle of  $120^\circ$ . Such an expansion of the ring angle at tin would be accompanied by considerable strain. Square pyramidal intermediates have been proposed to rationalize the temperature-dependent proton n.m.r. of 2-biphenyl-bis(4,4-bitolyl)-antimony whose singlet methyl resonance collapses to a quartet at  $-60^\circ\text{C}$  ( $\Delta E^\ddagger = 11.6 \text{ kcal/mole}$ )<sup>(181,182)</sup>. Pentaphenylantimony has a square pyramidal structure in the solid state<sup>(183,184,185)</sup>.

Structure d, combining both the axial-iodine and the stannole ring spanning axial- and equatorial-positions, of the tetragonal pyramid (c) could give rise to the observed cyclopentadienyl group non-equivalence through a stannole ring nonplanarity. Such non-equivalence arising from a preferred dissymmetric diene conformation is proposed for the related (4-bromo-1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyl)dimethyltin bromide<sup>(175,176,177)</sup>, but is less likely for this compound.

As a result, the pseudorotation of structure a to form structure b provides the best explanation for the observed cyclopentadienyl group non-equivalence.

## 5.5 INFRARED DATA

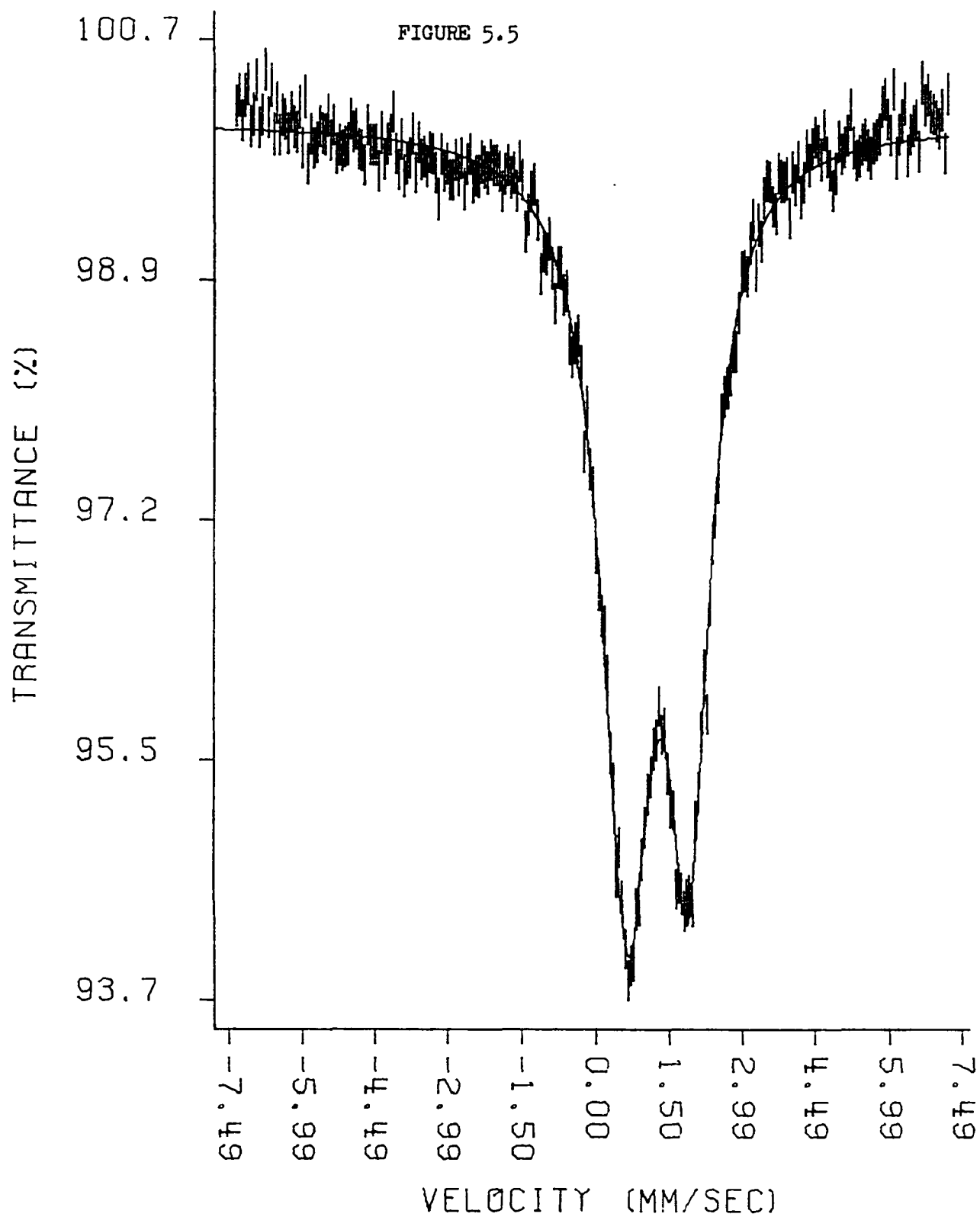
The infrared spectrum of this compound contains prominent bands at  $1425$  and  $1027 \text{ cm}^{-1}$  which arise from the C-C stretching mode and ring breathing mode of the  $\sigma$ -bonded cyclopentadienyl ring, respectively<sup>(186)</sup>. The new bands at  $332$  and  $328 \text{ cm}^{-1}$  can be assigned to the  $\nu_{\text{asym}}(\text{Sn-C}_5\text{H}_5)$  and  $\nu_{\text{sym}}(\text{Sn-C}_5\text{H}_5)$ , respectively, as found in



$(C_5H_5)_4Sn^{(187)}$ , as well as in mixed cyclopentadienyltin methyl and phenyl derivatives<sup>(188)</sup>. Other absorptions above 3000 and between 1595 and 695  $cm^{-1}$  specify the diene nature of the  $C_5H_5$  ligands<sup>(187,189)</sup>. The rest of the spectrum resembles that of the diiodostannole.

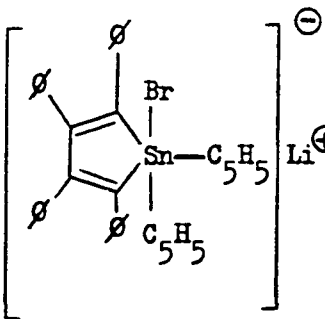
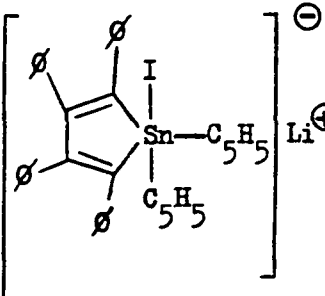
#### 5.6 MÖSSBAUER DATA

The Mössbauer spectrum (Figure 5.5) contains a doublet with I.S.  $1.49 \pm 0.03$  and Q.S.  $0.96 \pm 0.05$  mm/s, which is consistent with other cyclopentadienyltin(IV) halides, as shown in Table 5.4.



LITHIUM 1,1-DICYCLOPENTADIENYL-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE

TABLE 5.4  
MÖSSBAUER PARAMETERS (mm/s) FOR  
CYCLOPENTADIENYLTIN(IV) HALIDES

COMPOUND	I.S.	Q.S.	REFERENCE
$(\underline{h}^1\text{-C}_5\text{H}_5)_2\text{SnCl}_2$	$1.51 \pm 0.06$	$1.83 \pm 0.12$	172
$(\underline{h}^1\text{-C}_5\text{H}_5)_2\text{SnBr}_2$	$1.58 \pm 0.06$	$1.67 \pm 0.12$	172
$(\underline{h}^1\text{-C}_5\text{H}_5)_2\text{SnI}_2$	$1.68 \pm 0.06$	$1.43 \pm 0.12$	172
	$1.41 \pm 0.06$	$1.03 \pm 0.12$	122
	$1.49 \pm 0.03$ ( $1.05 \pm 0.04$ )	$0.96 \pm 0.05$	this work

Value in parenthesis is that for the half-height peak width.

## CHAPTER VI

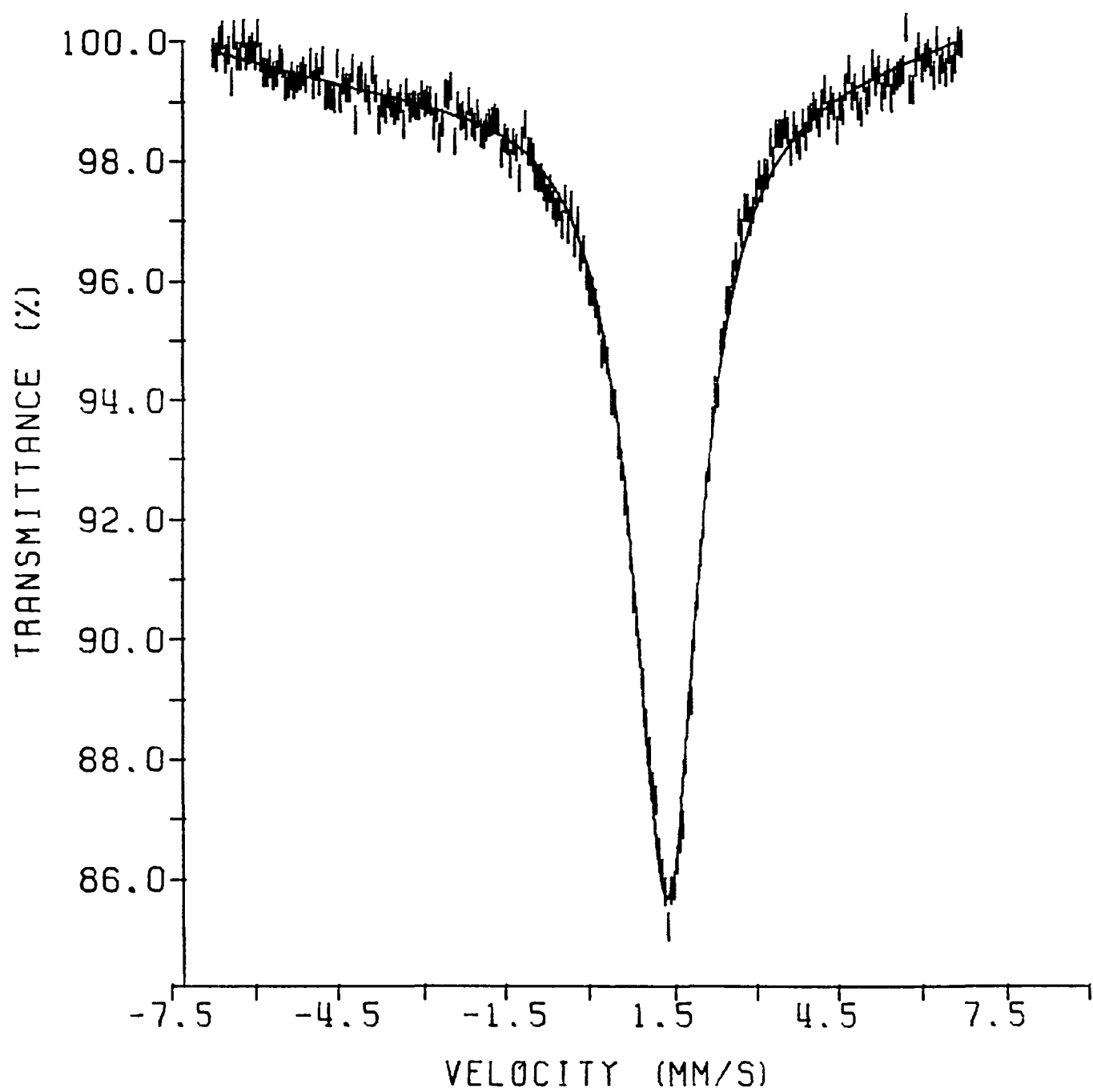
### ATTEMPTED STANNOLE PREPARATIONS

#### 6.1 REACTION OF DICYCLOPENTADIENYLTIN DICHLORIDE WITH 1,4-DILITHIO-1,2,3,4-TETRAPHENYLBUTADIENE

The reaction of dicyclopentadienyltin dichloride and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was performed in an attempt to synthesize 1,1-dicyclopentadienyltetraphenylstannole. Dicyclopentadienyltin dichloride was prepared by a modification of the method of Tomaja and Zuckerman<sup>(190)</sup>. Tetrakis(cyclopentadienyl)tin(IV) was prepared via the action of lithium cyclopentadiene on tin(IV) chloride. Tetrakis(cyclopentadienyl)tin(IV) is a light yellow colored solid (m.p. 70-71° vs. lit. 71-73°C) that is pyrophoric in air. The compound gives a single, sharp resonance in the Mössbauer spectrum (Figure 6.1) (I.S. =  $1.48 \pm 0.01$  mm/s). Although tetrakis(cyclopentadienyl)tin(IV) has been known since 1957<sup>(191)</sup> its Mössbauer spectrum has never been reported<sup>(9,192)</sup>, but is in good agreement with other cyclopentadienyltin(IV) compounds (Table 6.1).

Dicyclopentadienyltin dichloride was then prepared by an exchange reaction of freshly prepared tetrakis(cyclopentadienyl)tin(IV) and tin(IV) chloride. The light yellow product was identified by comparison of the melting point and Mössbauer spectrum (Figure 6.2) with the literature values (m.p. 39-40° vs. 38-40°C; I.S. =  $1.44 \pm 0.01$ ,

FIGURE 6.1



00 208 TETRACYCLOPENTADIENYLTIN

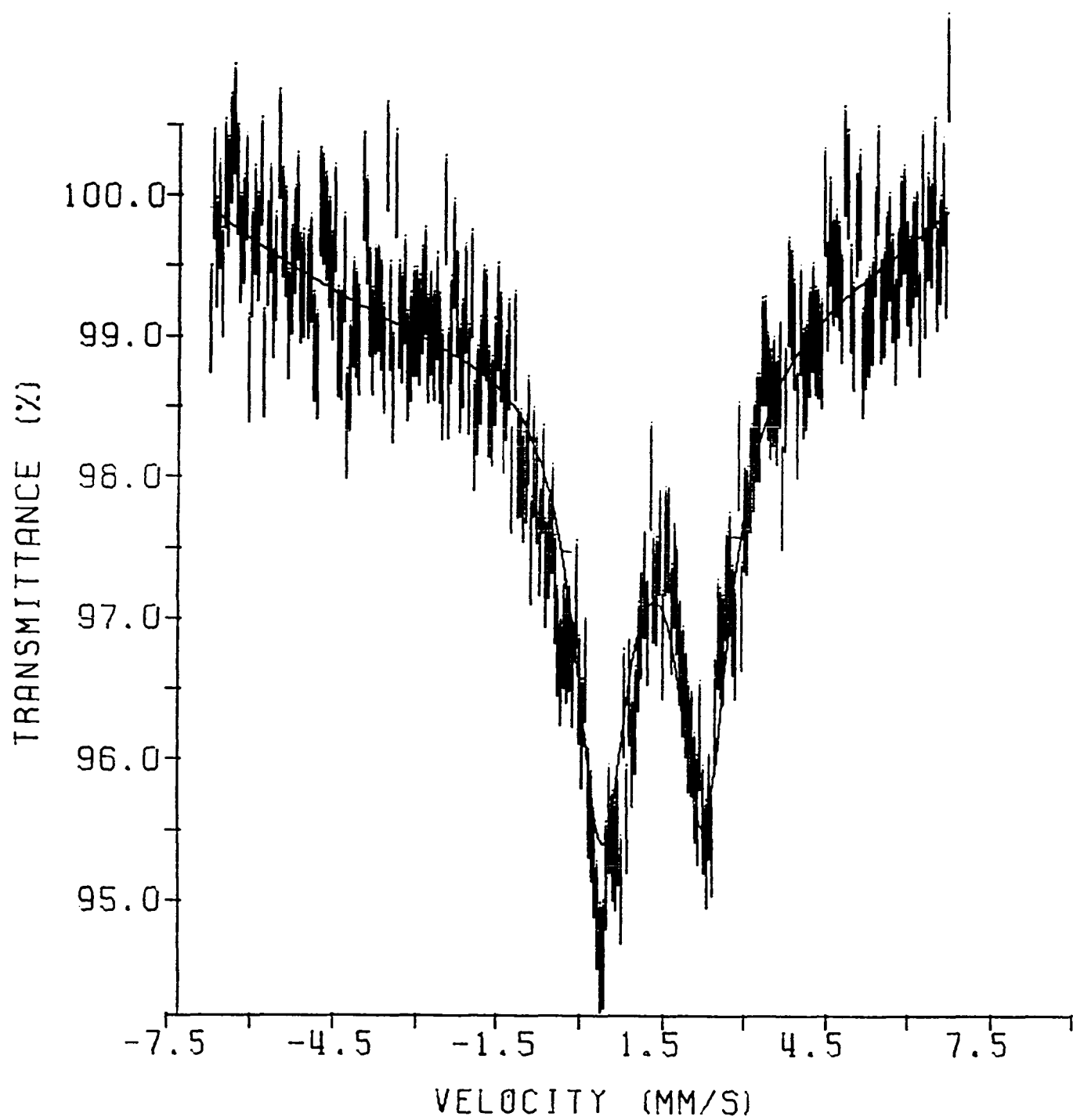
TABLE 6.1

 $^{119}\text{m}\text{Sn}$  NÖSSBAUER PARAMETERS FOR CYCLOPENTADIENYLTIN COMPOUNDS (mm/s)

COMPOUND	I.S.	Q.S.	REFERENCE
$(\underline{\text{h}}^1\text{-C}_5\text{H}_5)_4\text{Sn}$	$1.48 \pm 0.01$ ( $1.30 \pm 0.05$ )	-	this work
$(\underline{\text{h}}^1\text{-C}_5\text{H}_5)_2\text{SnCl}_2$	$1.51 \pm 0.06$	$1.83 \pm 0.12$	190
$(\underline{\text{h}}^1\text{-C}_5\text{H}_5)_2\text{SnBr}_2$	$1.58 \pm 0.06$	$1.67 \pm 0.12$	190
$(\underline{\text{h}}^1\text{-C}_5\text{H}_5)_2\text{SnI}_2$	$1.68 \pm 0.06$	$1.43 \pm 0.12$	190
$(\underline{\text{h}}^1\text{-C}_5\text{H}_5)_2\text{SnCl}_2$	$1.44 \pm 0.01$ ( $1.55 \pm 0.05$ )	$1.88 \pm 0.02$	this work

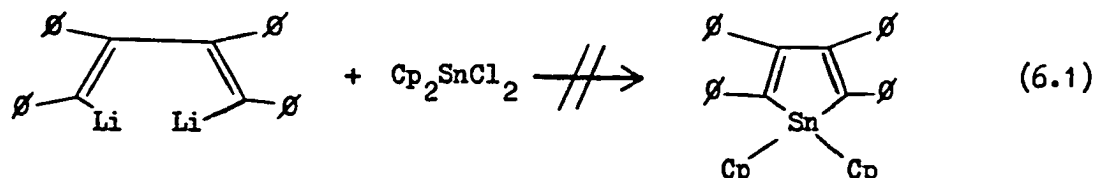
Values in parentheses are those for the half-height peak widths.

FIGURE 6.2



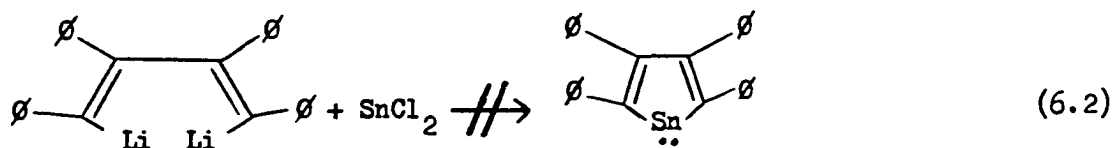
00 241 DICYCLOPENTADIENYLTIN DICHLORIDE

Q.S. =  $1.88 \pm 0.02$ , vs. lit<sup>(190)</sup> I.S. =  $1.51 \pm 0.06$ , Q.S. =  $1.83 \pm 0.12$  mm/s).



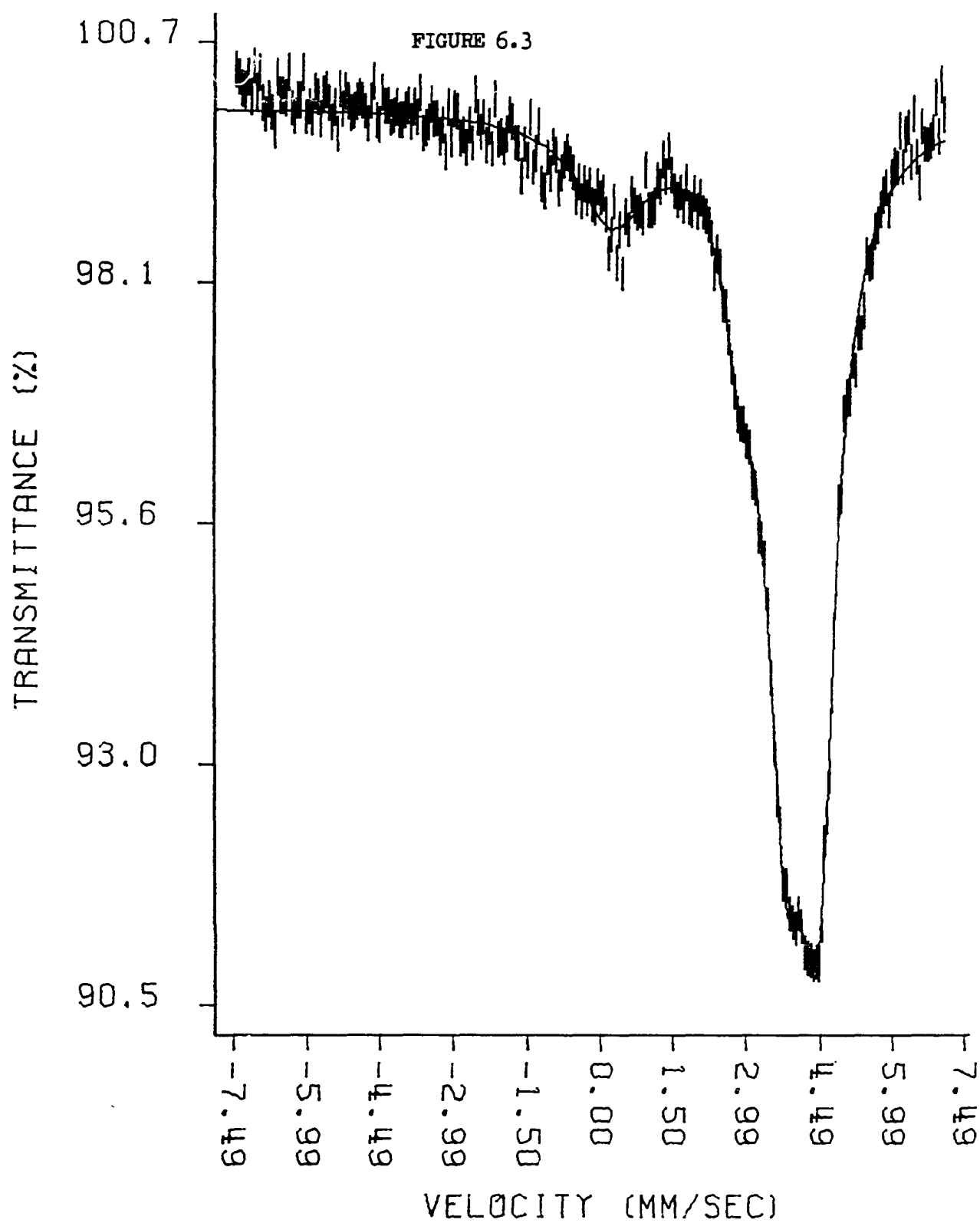
Freshly prepared dicyclopentadienyltin dichloride was then reacted with a tetrahydrofuran solution of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene. The dark red solution of dilithium reagent lightened to a yellow-brown color when added to the dicyclopentadienyltin dichloride. It was impossible, however, to isolate a pure tin-containing solid from this reaction. A brown colored oil results when the solvent is removed in vacuo. This oil is soluble in toluene and benzene but completely insoluble in hexane. The addition of small amounts of hexane to a toluene solution caused an oily material to separate from solution. This oil became solid upon drying in a vacuum for four hours, but contained more than one tin site according to the four resonances obtained from the Mössbauer spectrum.

## 6.2 REACTION OF TIN(II) CHLORIDE WITH 1,4-DILITHIO-1,2,3,4-TETRAPHENYLBUTADIENE



Another unsuccessful reaction was that between 1,4-dilithio-1,2,3,4-tetraphenylbutadiene and tin(II) chloride which was attempted





PRODUCT FROM LTPBD WITH TIN(II) CHLORIDE AND THEN BORON TRIFLUOR



## CHAPTER VII

### EXPERIMENTAL

#### 7.1 PHYSICAL METHODS

##### 7.1a MELTING POINTS

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

##### 7.1b ELEMENTAL ANALYSES

Elemental analyses were carried out by Galbraith Laboratory, Inc., Knoxville, Tennessee. Tin was determined gravimetrically as the oxide<sup>(59)</sup>. Halogens, with the exception of fluorine, were determined by potentiometric titration with silver(I) nitrate.

##### 7.1c MASS SPECTRA

Mass spectra were recorded on a Hewlett-Packard 5985B GC/MS System at 70 eV.

##### 7.1d NUCLEAR MAGNETIC RESONANCE SPECTRA

Nuclear magnetic resonance spectra were recorded on Varian A-60 and XL-100 instruments. Tetramethylsilane was used as an external standard.

##### 7.1e INFRARED SPECTRA

Infrared spectra were recorded in the 4,000 to 200  $\text{cm}^{-1}$  range on Beckman 4250 or IR-12 spectrometers. The far infrared spectra were recorded in the 400 to 33  $\text{cm}^{-1}$  range on a Beckman IR-11 spectrometer.

7.1f MÖSSBAUER SPECTRA

Mössbauer spectra were recorded on a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter using  $\text{Ca}^{119\text{m}}\text{SnO}_3$  (New England Nuclear Corp.) as both source and standard reference material for zero velocity. Velocity calibration was based on both  $\beta$ -tin and natural iron. Data were fitted to Lorentzian curves by standard, non-linear, least squares techniques. The Ranger Engineering variable temperature liquid nitrogen dewar and controller used in this study are regulated by a variable bridge, silicon-controlled-rectifier circuit and are accurate to  $\pm 1^\circ\text{K}$ .

7.2 PREPARATION OF 1,4-DILITHIO-1,2,3,4-TETRAPHENYLBUTADIENE<sup>(20)</sup>

To a solution of diphenylacetylene (10.69g, 0.06 moles) in anhydrous diethyl ether (30 mL) was added lithium wire (0.7 g, 0.1 moles) and the solution stirred at room temperature under a nitrogen atmosphere for four hours. After a ten minute induction period, an intense red color developed, and a yellow solid began to precipitate. This induction time increased significantly with decreasing diphenylacetylene concentration, and was about 30 minutes for a 0.3 to 0.4 molar solution. At concentrations below 0.3 molar, it was found that any moisture in the system greatly retarded the rate of reaction. If freshly dried equipment is not used the surface moisture increases the induction period from ca. 30 minutes to as much as 12 hours. The reaction is initially mildly exothermic, and if the concentration of diphenylacetylene is doubled, cooling with a rapid flow of nitrogen gas becomes necessary.

This procedure is favored over previous methods<sup>(14,18)</sup>

because the precautions necessary to omit water are much less stringent.

### 7.3 PREPARATION OF 1,1,2,3,4,5-HEXAPHENYLSTANNOLE (15,16,18,122,195)

Diphenyltin dichloride (10.32 g, 0.03 moles) was placed in a three-necked flask equipped with a pressure-equalizing funnel, condenser, and gas inlet tube. The diphenyltin dichloride was then dissolved in freshly distilled tetrahydrofuran (200 mL). A solution of the dilithium reagent was then added to the addition funnel via a hypodermic syringe. This technique allowed the excess lithium to remain in the flask. The red solution and yellow precipitate were then added dropwise to the colorless diphenyltin dichloride solution. An additional 100 mL of diethyl ether was used to transfer the dilithio compound to the organotin solution, which was cooled in an ice bath during the addition. The reaction was mildly exothermic. The resulting green-yellow solution was stirred under nitrogen at reflux for two hours. The ether layers were then removed in vacuo. Dichloromethane (250 mL) was added to the residue, and the resulting suspension was filtered. After concentration to about 75 mL, absolute ethanol (100 mL) was added. The yellow title compound precipitated upon cooling with Dry Ice. Recrystallization from dichloromethane/ethanol (1:1) resulted in a yellow solid (m.p. 172-73°C), in a yield of 65%. The compound was identified by comparison of infrared and Mössbauer data with an authentic sample: I.S.  $1.39 \pm 0.02$ ,  $\Gamma = 1.96 \pm 0.06$  mm/s.

An additional tin-containing material was isolated from this reaction. A white powder (m.p. 108-110°C) was isolated in 20% yield during an attempt at increasing the yield of hexaphenylstannole. The Mössbauer spectrum contained a doublet with I.S. of  $1.31 \pm 0.02$  and

and Q.S. of  $2.77 \pm 0.04$ ,  $\Gamma = 1.20 \pm 0.03$  mm/s.

The infrared spectrum contained prominent bands at 3060(w), 3040(w), 3020(w), 1600(w), 1575(w), 1432(m), 1075(m), 1023(m), 1000(m), 730(s), 695(s), and 440(s)  $\text{cm}^{-1}$ . The 1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyldiphenyltin chloride structure is consistent with this data. (Calcd. for  $\text{C}_{40}\text{H}_{31}\text{ClSn}$ : C, 72.18; H, 4.66; Cl, 5.26; Sn, 17.89%; Found: C, 69.87; H, 4.51; Cl, 4.92; Sn, 17.05%).

#### 7.4 PREPARATION OF 1,1-DIBROMO-2,3,4,5-TETRAPHENYLSTANNOLE<sup>(122)</sup>

A solution of hexaphenylstannole (23.5 g, 37.3  $\mu\text{moles}$ ) in carbon tetrachloride (200 mL) was cooled in a Dry Ice-acetone bath to  $-30$  to  $-40^\circ\text{C}$  under a nitrogen atmosphere, and bromine (12.0 g, 75.0  $\mu\text{moles}$ ) in carbon tetrachloride (200 mL) added dropwise. The original yellow-green color lightened with the addition of bromine. The rate of decolorization decreased after half of the bromine had been added, and the remainder of the reaction was carried out at  $-20$  to  $-30^\circ\text{C}$  for a period of two hours. The solution passed from yellow-green to white to light brown to reddish-orange. The cloudy solution became clear when it was allowed to warm to room temperature. The solvent was then stripped under vacuum to leave a yellow colored oil. This was dissolved in methylene chloride and ethanol to give white crystals (21.8 g, 34.3  $\mu\text{moles}$ , m.p.  $167-168^\circ\text{C}$  with decomposition). The yield was 92% based on hexaphenylstannole.

The Mössbauer spectrum contained a doublet with I.S. of  $1.48 \pm 0.02$  and Q.S. of  $2.88 \pm 0.04$ ,  $\Gamma = 1.70 \pm 0.01$  mm/s.

The Mössbauer spectrum and melting point were consistent with this formulation<sup>(122)</sup>.

## 7.5 PREPARATION OF 1,1-DIIODO-2,3,4,5-TETRAPHENYLSTANNOLE

Hexaphenylstannole (5.9 g, 9.3 mmoles) was dissolved in carbon tetrachloride (50 mL) and stirred under nitrogen for 15 minutes while being cooled to 0°C in an ice bath. To this was added an iodine solution (4.8 g, 18.75 mmoles) in carbon tetrachloride (150 mL). The original yellow solution lightened with the addition of iodine. The solution passed from yellow to orange to pink to red to purple. The solution was stirred under nitrogen at room temperature for two hours after the addition of iodine was complete.

The solvent was removed in vacuo, and the remaining red-brown oil was dissolved in methylene chloride and filtered. Precipitation resulted with the addition of absolute ethanol and cooling in Dry Ice. After recrystallization from methylene chloride/ethanol a white solid was obtained (m.p. 167-168°C, 5.02 g, 74% yield). The mother liquor from the solid was concentrated and found to contain iodobenzene, identified by comparison of its infrared spectrum with that of an authentic sample.

The infrared spectrum contained prominent bands at 3050(w,b), 1600(w), 1574(w), 1490(w), 1442(m), 762(m), 731(s), 695(s), 565(m), 548(s), 513(m), 444(m), 345(w), 184(m), and 80(w) cm<sup>-1</sup>.

The Mössbauer spectrum was a doublet with I.S. of  $1.61 \pm 0.02$  and Q.S. of  $2.32 \pm 0.04$ ,  $\Gamma = 1.03 \pm 0.04$  mm/s.

(Calculated for C<sub>28</sub>H<sub>20</sub>SnI<sub>2</sub>: C, 46.10; H, 2.74; Sn, 16.32; I, 34.84%; Found: C, 45.77; H, 2.82; I, 36.62; Sn, 15.79%).

## 7.6 PREPARATION OF 1,1-DIACETATO-2,3,4,5-TETRAPHENYLSTANNOLE

To a solution of diiodostannole (3.00 g, 4.1 mmoles) in tetrahydrofuran (100 mL) was added silver(I) acetate (1.4 g, 8.4 mmoles) in tetrahydrofuran (250 mL). The mixture was stirred under nitrogen at reflux for two hours and then at room temperature for 10 hours. The solution changed from yellow to white, but remained cloudy. During the reaction the flask was wrapped with aluminum foil to prevent decomposition of the silver acetate by light.

The tetrahydrofuran was then removed in vacuo and toluene (100 mL) added. The resulting suspension was filtered and a clear yellow-orange solution obtained along with a light yellow solid (did not melt up to 400°C) which was assumed to be silver(I) iodide. The solution was concentrated to 25 mL and hexane (25 mL) was added. Precipitation occurred when the solution was cooled in Dry Ice. A white, air stable solid was obtained (m.p. 182-183°C) in 64% yield, based upon diiodostannole.

The infrared spectrum contained prominent bands at 3057(w), 1635(m), 1618(s), 1596(m), 1567(s), 1442(m), 1323(s), 1066(m), 933(m), 760(m), 728(s), 692(s), 615(s), 490(w), 295(m), and 279(w)  $\text{cm}^{-1}$ .

The Mössbauer spectrum was a doublet with I.S. of  $1.09 \pm 0.02$ , and Q.S. of  $2.87 \pm 0.04$ ,  $\Gamma = 1.36 \pm 0.05$  mm/s.

The n.m.r. spectrum in  $\text{CDCl}_3$  contained a single resonance at 2.18 ppm, relative to TMS, in addition to the phenyl group multiplet. The proton integration ratio was found to be  $1:3.5 = \text{CH}_3:\text{C}_6\text{H}_5$  vs. the calculated ratio of 1:3.3.

(Calculated for  $\text{C}_{32}\text{H}_{26}\text{O}_4\text{Sn}$ : C, 64.76; H, 4.38; O, 10.79; Sn, 20.07%;



Found: C, 63.69; H, 4.26; Sn, 18.98%).

#### 7.7 PREPARATION OF 1,1-DIAZIDO-2,3,4,5-TETRAPHENYLSTANNOLE

Lithium azide was prepared by a modification of the procedure of Huisgen and Ugi<sup>(196)</sup>. Lithium chloride (0.35 g, 8.4 mmoles) was dissolved in dry methanol (10 mL) and refluxed for 5 hours with sodium azide (0.6 g, 8.3 mmoles) under nitrogen. The solution was allowed to cool and then filtered.

The above solution was then added slowly to a solution of diiodostannole (3.00 g, 4.1 mmoles) in methylene chloride (50 mL). The solution was stirred at room temperature under nitrogen for one hour after the addition of the lithium azide solution was completed. The solvent was then removed in vacuo, toluene (50 mL) added, and the solution filtered. The addition of hexane caused a white solid to precipitate (m.p. 153-154°C, 1.33 g) in 58% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 2090(s), 1600(w), 1570(w), 1445(m), 1320(w), 1275(w), 1072(s), 1030(m), 937(w), 767(m), 731(s), 690(s), 472(s), 400(w), and 270(s)  $\text{cm}^{-1}$ .

The Mössbauer spectrum was a doublet with I.S. of  $1.18 \pm 0.01$  and Q.S. of  $2.44 \pm 0.02$ ,  $\Gamma = 1.53 \pm 0.03$  mm/s.

(Calculated for  $\text{C}_{28}\text{H}_{20}\text{N}_6\text{Sn}$ : C, 60.11; H, 3.58; N, 15.03; Sn, 21.29%; Found: C, 58.98; H, 3.92; Sn, 20.64%).

#### 7.8 PREPARATION OF 1,1-DICYANATO-2,3,4,5-TETRAPHENYLSTANNOLE

Silver(I) cyanate was prepared by a modification of the procedure of Hassner and Heathcock<sup>(197)</sup>. Silver(I) nitrate (20.0 g,

0.12 moles) in distilled water (600 mL). The solution was then stirred at room temperature for one hour. The solution was then filtered and washed with water, methanol and ether. The product was dried for 12 hours under vacuum and stored in the dark until needed.

Diiodostannole (5.0 g, 6.86 mmoles) in 100 mL of mixed absolute ethanol and benzene (3:2) was refluxed with silver(I) cyanate (2.06 g, 13.72 mmoles) under nitrogen for one hour, and then stirred at room temperature for one hour to produce a clear solution and a white precipitate. The solvent was removed in vacuo, benzene added, and a white solid collected upon filtration. The title compound precipitated from solution with the addition of hexane and cooling in Dry Ice. A white solid (m.p. 163-165°C, 1.61 g) was obtained in 42% yield (based upon diiodostannole).

The infrared spectrum contained prominent bands at 3060(w), 2210(s), 1596(s), 1573(m), 1445(m), 1350(m), 1150(m), 1070(s), 1025(m), 995(w), 940(w), 785(w), 760(w), 728(s), 693(s), 610(w), 385(m), and 265(w)  $\text{cm}^{-1}$ .

The Mössbauer spectrum contained a doublet with I.S.  $1.05 \pm 0.01$  and Q.S.  $2.47 \pm 0.02$ ,  $\Gamma = 1.16 \pm 0.02$  mm/s.

(Calculated for  $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2\text{Sn}$ : C, 64.40; H, 3.58; N, 5.01; O, 5.72, Sn, 21.29%: Found; C, 65.21; H, 2.96; N, 4.87; Sn, 20.86%).

#### 7.9 PREPARATION OF 1-FLUORO-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE

Diiodostannole (3.9 g, 5.3 mmoles) was dissolved in tetrahydrofuran (50 mL). Potassium fluoride (0.62 g, 10.7 mmoles) in absolute ethanol (10 mL) was added dropwise under a nitrogen atmosphere at room temperature. The mixture was heated to reflux for 10 hours

with continuous stirring. A milky white solution resulted which when filtered gave a clear, light yellow solution and a white solid. The solution was evaporated to dryness under vacuum. The resulting white oil was dissolved in tetrahydrofuran (15 mL) and then hexane (15 mL) was added. Precipitation occurred when the solution was cooled in Dry Ice. The white, title compound (m.p. 182-184°C, 1.41 g) was obtained in 43% yield (based on diiodostannole).

The infrared spectrum showed prominent bands at 3058(w), 1595(m), 1575(w), 1440(w), 1178(m), 1150(w), 1066(m), 1035(m), 1000(w), 930(m), 913(s), 786(m), 762(s), 735(s,b), 696(s), 611(s), 570(s), 550(s), 520(m), 449(s), 350(m), 315(m), and 275(w)  $\text{cm}^{-1}$ .

The Mössbauer spectrum contained a doublet with I.S. of  $1.22 \pm 0.02$  and Q.S.  $2.74 \pm 0.03$ ,  $\Gamma = 1.08 \pm 0.02$  mm/s. (Calculated for  $\text{C}_{28}\text{H}_{20}\text{FISn}$ : C, 54.11; H, 3.22; F, 3.10; I, 20.45; Sn, 19.16%; Found: C, 53.90; H, 3.58; I, 19.64; Sn, 18.32%).

#### 7.10 PREPARATION OF 1,1-BIS(DIPHENYLPHOSPHINO)-2,3,4,5-TETRAPHENYL-STANNOLE

Into a three-necked, 100 mL flask was placed 50 mL of freshly distilled diethyl ether. The solution was placed under a nitrogen atmosphere and cooled to -78°C in a Dry Ice/acetone bath. Diphenylphosphine (1.09 mL, 1.17 g, 6.30 mmoles) was added and the solution stirred for 15 minutes. *n*-Butyllithium (1.91 mL of 3.3M solution in hexane, 6.30 mmoles) was added dropwise via syringe. The solution was then stirred for one hour while warming to room temperature. The colorless solution turned cloudy yellow with the addition of the *n*-butyllithium. The solution was then cooled again to -78°C and

dibromostannole (2.00 g, 3.15 mmoles) added via a solid addition tube. The mixture was then stirred at  $-78^{\circ}\text{C}$  for one hour and allowed to warm to room temperature for three hours. Upon addition of the dibromostannole the solution passed from a yellow to gold to an orange color. The solution became yellow colored again as it was allowed to warm to room temperature, at which time a precipitate could be seen at the bottom of the flask.

The ether was removed under vacuum, and toluene (50 mL) was added. The solid was filtered under nitrogen and found to contain lithium by a flame test. The clear yellow colored filtrate was then concentrated to 30 mL and hexane (20 mL) was added to obtain a yellow, air-sensitive, solid (m.p.  $165\text{--}167^{\circ}\text{C}$ , 1.52 g) in 57% yield (based upon dibromostannole).

The infrared spectrum contained bands at 3070(w), 3060(w), 1585(w), 1437(m), 1310(w), 1180(s), 1110(s), 1090(s), 1070(m), 1028(m), 998(m), 737(s), 715(s), 692(s), 552(m), 485(s), and  $354(\text{m},\text{b})\text{ cm}^{-1}$ .

The Mössbauer spectrum contained a narrow doublet with I.S.  $1.51 \pm 0.01$  and Q.S.  $0.83 \pm 0.03$ ,  $4.20 \pm 0.08\text{ mm/s}$ .

(Calculated for  $\text{C}_{52}\text{H}_{40}\text{P}_2\text{Sn}$ : C, 73.85; H, 4.73; P, 7.34; Sn, 14.08%; Found: C, 72.49; H, 4.81; Sn, 13.62%).

#### 7.11 PREPARATION OF 1,1-BIS(DIMETHYLAMINO)-2,3,4,5-TETRAPHENYL-STANNOLE

Dimethylamino lithium was prepared by a modification of the procedure used by Foley and Zeldin<sup>(137)</sup>. A 100 mL three-necked flask was cooled to  $-78^{\circ}\text{C}$  in a Dry Ice/acetone bath. Freshly distilled

diethyl ether (25 mL) was added and stirred under nitrogen for 15 minutes. To this was added dimethylamine (0.45 mL, 6.86 mmoles) followed by *n*-butyllithium (1.94 mL of 3.53M in hexane, 6.86 mmoles). The mixture was stirred at  $-78^{\circ}\text{C}$  for 30 minutes. A white precipitate was formed when the *n*-butyllithium was added. Diiodostannole (2.5 g, 3.43 mmoles) was then added at  $-78^{\circ}\text{C}$  via a solid addition tube. The milky white solution turned yellow upon the addition of diiodostannole and was stirred while warming to room temperature for eight hours. The ether was then removed under vacuum, toluene (25 mL) added, and the resulting solution filtered under nitrogen. The white solid that was filtered was found to contain lithium by a flame test. Precipitation was achieved by the addition of hexane (20 mL). A yellow colored, air-sensitive, solid was obtained (m.p.  $158-169^{\circ}\text{C}$ , 1.33 g) in 69% yield (based upon diiodostannole).

The Mössbauer spectrum contained a narrow doublet with I.S.  $1.25 \pm 0.02$  and Q.S.  $0.72 \pm 0.08$ ,  $\Gamma = 1.66 \pm 0.13$  mm/s.

The infrared spectrum contained prominent bands at 3060(w), 3030(w), 1587(w), 1556(w), 1430(w), 1260(w), 1170(s), 1130(m), 1070(m), 1020(w), 950(m), 760(m), 725(s), 690(s) and 530(s)  $\text{cm}^{-1}$ .

The n.m.r. spectrum in  $\text{CDCl}_3$  contained a single resonance at 2.38 ppm (relative to TMS) in addition to the phenyl group multiplet. The proton integration ratio was found to be  $1:1.5 = \text{CH}_3:\text{C}_6\text{H}_5$  vs. the calculated ratio of 1:1.67.

(Calculated for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{Sn}$ : C, 68.21; H, 5.68; N, 4.97; Sn 21.14%: Found: C, 66.92; H, 4.97; Sn, 20.94%).

7.12 ATTEMPTED PREPARATION OF 1,1-DICHLORO-2,3,4,5-TETRAPHENYL-STANNOLE

Hexaphenylstannole (2.0 g, 3.18 mmoles) was dissolved in carbon tetrachloride (200 mL) and the system flushed with nitrogen and cooled to  $-38^{\circ}\text{C}$  in a Dry Ice/acetone bath. Chlorine gas was condensed on a Dry Ice cold finger and a small amount was allowed to drip into the solution. The yellow solution darkened with the addition of chlorine. The reaction was then stirred for two hours while warming to room temperature.

The solvent was then removed in vacuo. Methylene chloride was added to the residue and the solution was then filtered. Precipitation was induced by the addition of absolute ethanol. A white solid was obtained (m.p.  $163-164^{\circ}\text{C}$ , 1.30 g) in 96% yield (based on hexaphenylstannole). This material, however, contained no tin. Its melting point, elemental analysis and infrared spectrum agree with the formulation of 1,4-dichloro-1,2,3,4-tetraphenylbutadiene<sup>(34)</sup>.

(Calculated for  $\text{C}_{28}\text{H}_{20}\text{Cl}_2$ : C, 78.87; H, 4.69; Cl, 16.44%; Found: C, 77.71; H, 4.95; Cl, 17.67%).

Another white solid was isolated from this reaction (m.p.  $39-41^{\circ}\text{C}$ ) This solid contained tin and gave a doublet Mössbauer spectrum with I.S.  $1.32 \pm 0.02$  and Q.S.  $2.79 \pm 0.03$ ,  $f = 1.15 \pm 0.05$  mm/s. From its melting point and Mössbauer spectrum this compound was identified as diphenyltin dichloride<sup>(84)</sup>.

7.13 REACTION OF HEXAPHENYLSTANNOLE AND ACETIC ACID

Hexaphenylstannole (4.0 g, 6.4 mmoles) was dissolved in

glacial acetic acid (50 mL). Acetic anhydride (5 mL) was added and the solution refluxed for 12 hours under argon. The cloudy, intense yellow solution lightened and became clear when reflux was achieved. After 12 hours of refluxing the solution was a clear, deep red color that lightened and threw down a white precipitate when cooled. The solvent was removed in vacuo, methylene chloride added, and the resulting solution filtered. White needles were collected (m.p. 176–178°C, 1.40 g) after the addition of absolute ethanol (59% yield based on hexaphenylstannole). This material, however, contained no tin. The melting point, elemental analysis and infrared spectrum agree with the formulation of tetraphenylfuran.

(Calculated for  $C_{28}H_{20}O$ : C, 90.32; H, 5.38; O, 4.30%; Found: C, 90.78; H, 6.43%).

No pure tin-containing material was isolated from this reaction.

#### 7.14 DIIODOSTANNOLE ADDUCT WITH PYRIDINE

1,1-Diiodo-2,3,4,5-tetraphenylstannole (3.5 g, 4.8 mmol) was dissolved in pyridine (30 mL), and the resulting golden-brown solution was then refluxed for one hour. The solution gradually darkened as the reaction proceeded. The pyridine was then removed under vacuum to give a red-brown oil. This oil was then dissolved in benzene and hexane. A tan solid precipitated (m.p. 158–160°C, 2.47 g) in 58% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 1592(m), 1575(s), 1480(w), 1440(m), 1430(m), 1218(s), 1140(m),

1070(s), 1010(s,b), 996(s), 913(s), 805(s), 722(s), 690(s), 534(m), 440(s) and 310(s)  $\text{cm}^{-1}$ .

The Mössbauer spectrum contained a doublet with I.S.  $1.19 \pm 0.01$  and Q.S.  $2.55 \pm 0.01$ ,  $f' = 1.15 \pm 0.02$  mm/s.

(Calculated for  $\text{C}_{38}\text{H}_{30}\text{SnI}_2\text{N}_2$ : C, 51.41; H, 3.38; Sn, 13.42; I, 28.64; N, 3.16%; Found: C, 51.08; H, 3.52; Sn, 12.96; I, 29.13%).

#### 7.15 DIIDOSTANNOLE ADDUCT WITH 2,2'-BIPYRIDINE

Diiodostannole (1.0 g, 1.4 mmoles) was dissolved in benzene (15 mL). A solution of 2,2'-bipyridine (0.21 g, 1.4 mmoles) in anhydrous diethyl ether (10 mL) was added dropwise with no apparent evolution of heat. The mixture was stirred at room temperature under a nitrogen atmosphere for 30 minutes. The solvent was removed under vacuum, and the resulting material was then dissolved in benzene (20 mL). When the solution was cooled to  $0^\circ\text{C}$  a white solid [m.p.  $163\text{--}164^\circ\text{C(d)}$ , 0.69 g] was obtained in 56% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 1590(w), 1565(w), 1440(w), 1378(s), 1285(m), 1150(m), 1065(m), 1020(m), 990(w), 905(w), 780(m), 755(m), 723(s), 690(s), 534(m), and 435(w)  $\text{cm}^{-1}$ .

The Mössbauer spectrum was a doublet with I.S.  $1.21 \pm 0.01$  and Q.S.  $2.49 \pm 0.02$ ,  $f' = 1.15 \pm 0.04$  mm/s.

(Calculated for  $\text{C}_{38}\text{H}_{28}\text{SnI}_2\text{N}_2$ : C, 51.53; H, 3.16; Sn, 13.45; I, 28.70; N, 3.16%; Found: C, 51.85; H, 3.37; Sn, 13.30; I, 28.46%).



7.16 DIIODOSTANNOLE ADDUCT WITH 1,10-PHENANTHROLINE

Diiodostannole (1.0 g, 1.4 mmoles) was dissolved in benzene (20 mL). To this was added 1,10-phenanthroline·H<sub>2</sub>O (0.25 g, 1.4 mmoles) dissolved in anhydrous diethyl ether (15 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for 30 minutes. The solvent was removed in vacuo, benzene (30 mL) added, and the resulting solution was then filtered. A white solid precipitated when the solution was cooled to 0°C [m.p. 169–171°C(d), 1.01 g] in 79% yield (based on diiodostannole).

The Mössbauer spectrum contained a doublet with I.S.  $1.14 \pm 0.01$  and Q.S.  $2.61 \pm 0.02$ ,  $\Gamma = 1.29 \pm 0.04$  mm/s.

The infrared spectrum contained prominent bands at 3047(w), 1595(m), 1570(w), 1445(w), 1431(w), 1258(w), 1065(m), 1020(m), 990(w), 780(w), 720(s), 688(s), and 555(w) cm<sup>-1</sup>.

(Calculated for C<sub>40</sub>H<sub>28</sub>SnI<sub>2</sub>N<sub>2</sub>: C, 52.81; H, 3.08; Sn, 13.09; I, 27.94; N, 3.08%; Found: C, 53.06; H, 3.62; Sn, 12.42; I, 28.37%).

7.17 DIIODOSTANNOLE ADDUCT WITH 2,2',2''-TERPYRIDINE

Diiodostannole (1.0 g, 1.4 mmoles) was dissolved in benzene (15 mL). A solution of 2,2',2''-terpyridine (0.16 g, 0.69 mmoles) in benzene (5 mL) was prepared and the two solutions were mixed with no apparent evolution of heat. The mixture was then refluxed under nitrogen for 30 minutes. The solvent was then removed in vacuo, methylene chloride added, and the resulting solution was filtered. Dry methyl alcohol was then added and the solution cooled in an ice bath. A white solid [m.p. 167–169°C(d), 0.76 g] was isolated in 32%

yield.

The infrared spectrum contained bands at 3070(w), 1595(m), 1570(w), 1478(w), 1440(w), 1428(w), 1210(m), 1065(m), 1020(m), 910(w), 785(s), 755(m), 721(s), 690(s), and 558(w)  $\text{cm}^{-1}$ .

The Mössbauer spectrum contained a doublet with I.S.  $1.49 \pm 0.02$  and Q.S.  $2.49 \pm 0.03$ ,  $f \approx 1.21 \pm 0.06$  mm/s.

(Calculated for  $\text{C}_{71}\text{H}_{51}\text{Sn}_2\text{N}_3\text{I}_4$ : C, 50.38; H, 3.06; Sn, 14.07; N, 2.48; I, 30.04%; Found: C, 51.37; H, 3.39; Sn, 13.96; I, 28.83%).

#### 7.18 REACTION OF 1,4-DILITHIO-1,2,3,4-TETRAPHENYLBUTADIENE WITH PHENYLTIN TRICHLORIDE

Diphenylacetylene (5.35 g, 0.03 moles) was stirred for four hours in anhydrous diethyl ether (30 mL) under nitrogen with lithium (0.35 g, 0.05 moles) wire. A red solution formed after 10 minutes and a yellow solid precipitated. The slurry was added rapidly to a solution of phenyltin trichloride (4.52 g, 0.015 moles) in tetrahydrofuran (200 mL). An additional 100 mL of anhydrous diethyl ether was used to transfer the dilithio reagent. The mixture was stirred under nitrogen for two hours at room temperature. The ether layers were then removed in vacuo to leave a green oil. The oil was then dissolved in methylene chloride (200 mL) and the resulting suspension filtered. After concentration to 25 mL, absolute ethanol (50 mL) was added, and precipitation achieved by cooling the green solution to  $-78^\circ\text{C}$  in Dry Ice.

The white solid product (m.p.  $156-158^\circ\text{C}$ ) was identified as 1,2,3,4-tetraphenyl-cis, cis-1,3-butadienylphenyltin dichloride. The

Mössbauer spectrum of this compound contained a doublet with I.S.

$1.15 \pm 0.02$  and Q.S.  $1.70 \pm 0.04$ ,  $\Gamma = 1.24 \pm 0.04$  mm/s.

The infrared spectrum contains prominent bands at 3065(w), 3050(w), 1595(w), 1432(m), 1060(m), 1020(m), 997(m), 915(m), 885(m), 764(w), 729(s), 695(s), 365(s), and 345(m)  $\text{cm}^{-1}$ .

The n.m.r. spectrum in  $\text{CDCl}_3$  contained a singlet resonance at 5.2 ppm (relative to TMS) in addition to the phenyl group proton multiplet.

(Calculated for  $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{Sn}$ : C, 65.49; H, 4.17; Cl, 11.24; Sn, 19.10%; Found: C, 64.57; H, 3.52; Cl, 12.49; Sn, 18.64%).

#### 7.19 FLUOROIODOSTANNOLE ADDUCT WITH 2,2',2''-TERPYRIDINE

1-Fluoro-1-iodostannole (1.00 g, 1.61 mmoles) was dissolved in freshly distilled benzene (10 mL). A solution of 2,2',2''-terpyridine (0.40 g, 1.72 mmoles) in benzene (2 mL) was prepared and the two solutions were mixed together with no apparent evolution of heat. The mixture was then refluxed under nitrogen for one hour. The milky solution cleared and turned a light yellow color upon refluxing. The solution was allowed to cool to room temperature and the benzene removed in vacuo. The resulting light yellow solid was then dissolved in methylene chloride (15 mL) and the solution filtered to give a clear, yellow solution. Hexane (10 mL) was then added and the solution cooled in Dry Ice. A white solid [m.p.  $179\text{--}182^\circ\text{C(d)}$ ] was isolated in 39% yield (based on fluoriodostannole).

The infrared spectrum contained bands at 3050(w), 3025(w), 1590(w), 1568(w), 1540(w), 1485(w), 1445(w), 1430(m), 1140(m), 1108(s), 1072(m), 1022(s), 998(s), 872(s), 805(s), 781(s), 768(m), 737(s),

695(s), 653(s), 617(s), 568(s), 545(s), 520(s), and 443(s)  $\text{cm}^{-1}$ .

The Mössbauer spectrum contained a doublet with I.S.

$1.20 \pm 0.05$  and Q.S.  $2.94 \pm 0.08$ ,  $f' = 1.65 \pm 0.06$  mm/s.

(Calculated for  $\text{C}_{71}\text{H}_{51}\text{Sn}_2\text{F}_2\text{I}_2\text{N}_3$ : C, 57.76; H, 3.46; Sn, 16.14; F, 2.58; I, 17.22; N, 2.85%; Found: C, 55.97; H, 3.52; Sn, 15.98; I, 18.04%).

## 7.20 PREPARATION OF LITHIUM-1,1-DICYCLOPENTADIENYL-1-iodo-2,3,4,5-TETRAPHENYLSTANNOLE

Freshly cracked cyclopentadiene monomer (1.30 mL, 15.75 mmoles) in tetrahydrofuran (30 mL) was cooled in a Dry Ice/acetone bath and treated with n-butyllithium (2.76 mL, 3.53M in hexane, 9.76 mmoles) dropwise at  $-60$  to  $-70^\circ\text{C}$ . The resulting clear solution was then allowed to warm to room temperature with stirring under a nitrogen atmosphere.

To the solution of lithium cyclopentadiene was added diiodo-tetraphenylstannole (3.44 g, 4.72 mmoles) at room temperature to give a light brown colored solution which was stirred under nitrogen for four hours. The tetrahydrofuran-hexane solvent was removed in vacuo, and the light brown colored solid was treated with toluene (30 mL), and the lithium iodide removed by filtration under nitrogen. The solution was concentrated to 10 mL under vacuum and hexane (10 mL) added.

A light brown colored solid was obtained by cooling to Dry Ice temperature (0.69 g, 0.94 mmoles, 20% yield). The solid began to melt at  $153^\circ\text{C}$  and decomposed at  $156^\circ\text{C}$ .

The infrared spectrum showed bands at 3060(w), 1595(m),

1575(m), 1485(m), 1442(s), 1075(m), 1025(s), 914(m), 883(s), 785(s), 753(s), 726(s), 695(s), 581(s), 552(s), 332(m), 328(s), and 255(m)  $\text{cm}^{-1}$ .

The Mössbauer spectrum was a doublet with I.S.  $1.49 \pm 0.03$  and Q.S.  $0.96 \pm 0.05$ ,  $f = 1.05 \pm 0.04$  mm/s.

The proton n.m.r. spectrum at room temperature contained two resonances attributed to the tin-cyclopentadienyl system in addition to the phenyl group multiplet. The resonances were located at 5.79 and 5.46 ppm (relative to TMS) in  $\text{CDCl}_3$ .

(Calculated for  $\text{C}_{38}\text{H}_{30}\text{SnILi}$ : C, 61.71; H, 4.06; Sn, 16.10; I, 17.19; Li, 0.95%; Found: C, 62.93; H, 4.32; Sn, 15.62; I, 16.43%).

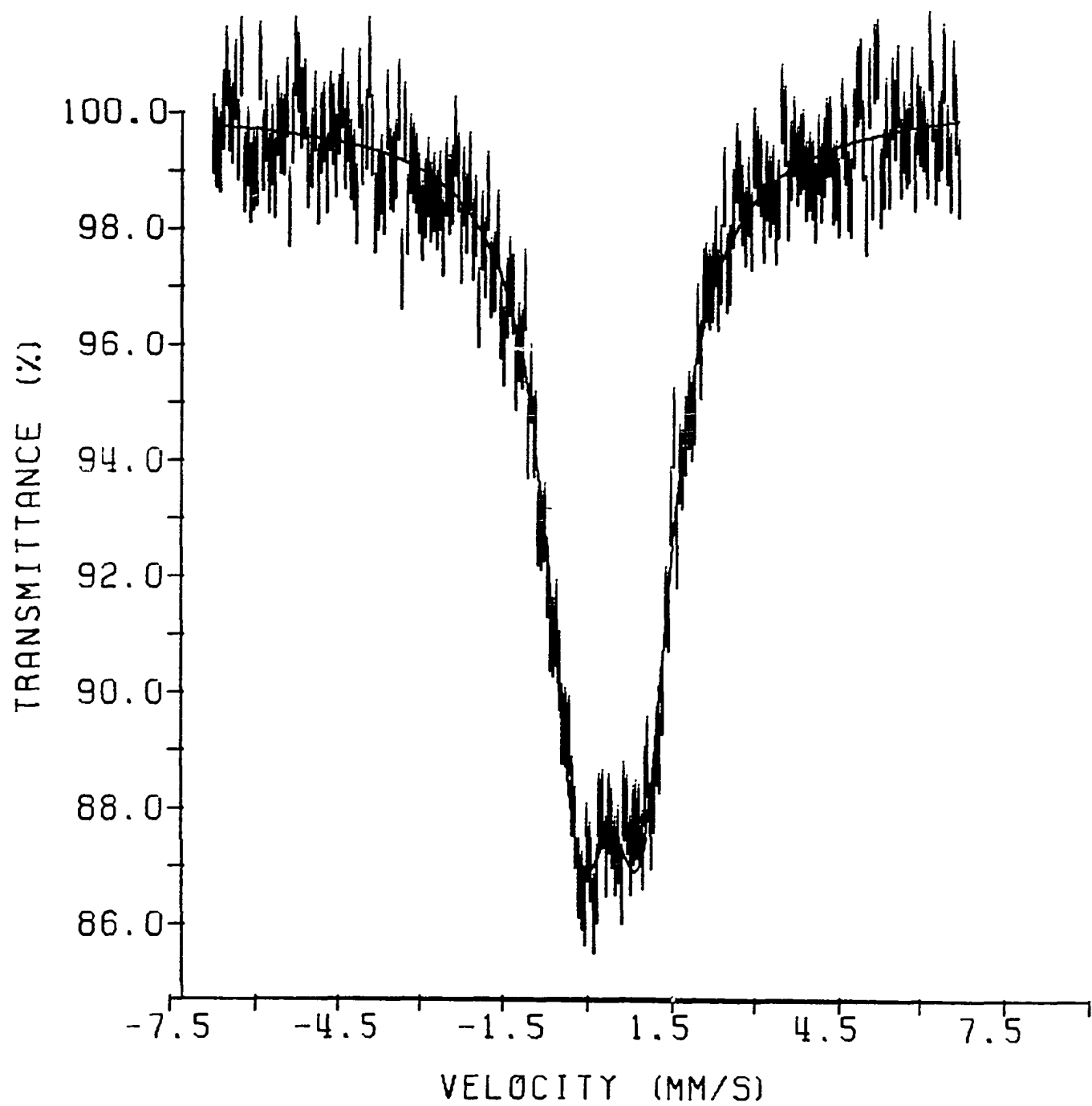
## APPENDIX

### DIGLYME ADDUCT OF TIN(IV) CHLORIDE

An excellent method for the removal of water and oxygen from aromatic solvents is distillation from potassium metal. The usual procedure is to add potassium metal and benzophenone to the solvent flask and reflux under dry nitrogen or argon until the purple color of the ketal, indicative of the absence of water, persists<sup>(198,199)</sup>. One slight problem that is encountered is the insolubility of the ketal in some aromatic solvents. This problem can be solved by the addition of small amounts of diglyme (2-methoxyethyl ether) to the solvent flask.

During the synthesis of tetrakis(cyclopentadienyl)tin(IV) and dicyclopentadienyltin dichloride, tin(IV) chloride solutions, in benzene or toluene, are added to lithium cyclopentadiene and tetrakis-(cyclopentadienyl)tin(IV) respectively<sup>(172)</sup>. It was noted that addition, under nitrogen, of tin(IV) chloride to freshly distilled benzene or toluene resulted in the formation of a green-black colored oil. The formation of an oil by this sequence was completely unknown to this research group. The oil was filtered (by gravity) under nitrogen and dried in vacuo for two hours. Upon drying the material changed from a green-black colored oil to a light grey colored solid, which became an oil again when exposed to the atmosphere.

FIGURE A.1



00 208 STANNIC CHLORIDE PLUS BENZENE

The amount of solid isolated was quite small (1.3 g obtained from 11.2 g  $\text{SnCl}_4$ ), but the results were reproducible (m.p. 120–123°C(d)).

The infrared spectra (Nujol and Halocarbon mulls and CsI plates) contained prominent bands at 2955(s), 1445(s), 1279(s), 1246(m), 1193(s), 1119(m), 1008(m), 923(s), 904(s), 826(m), 786(m), 322(w), and a very broad band at  $1020\text{ cm}^{-1}$ .

The Mössbauer spectrum (Figure A.1) contains a doublet with I.S.  $0.49 \pm 0.01$  and Q.S.  $1.10 \pm 0.02\text{ mm/s}$ , thus indicating that very electronegative elements are bonded to tin, and that the tin atom has a coordination number greater than four ( $\rho = \text{QS/IS} = 2.25$ ,  $\Gamma = 1.05 \pm 0.03\text{ mm/s}$ ).

The mass spectrum (Figure A.2) is identical with that of  $\text{SnCl}_4$ , with no peaks higher than  $M/e = 263$  (Calculated  $M/e = 259$  for  $^{119}\text{Sn}$ ).

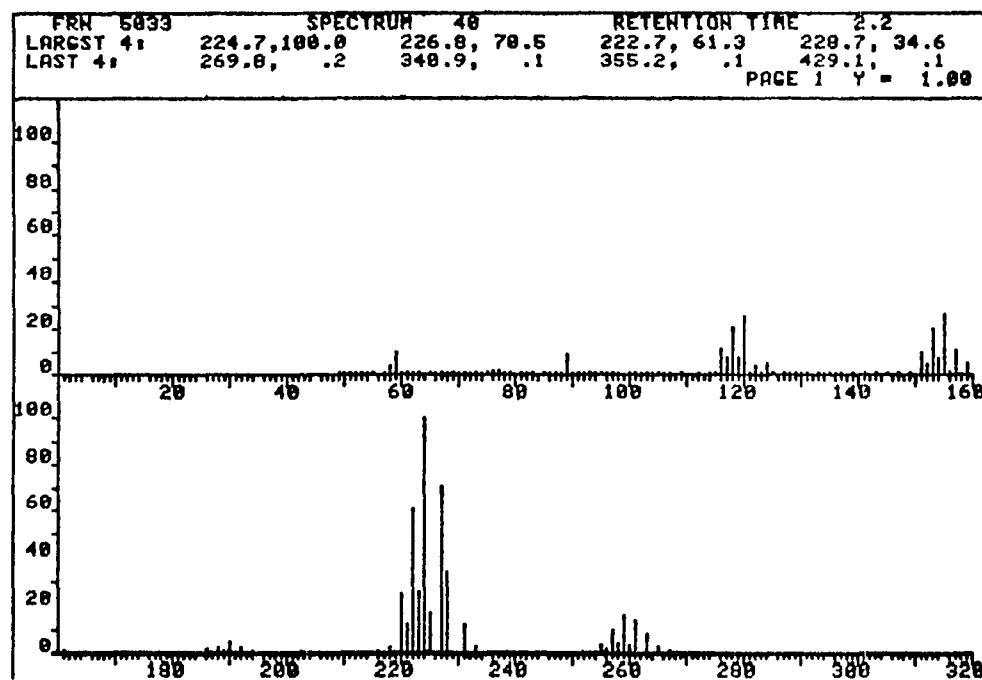
The analytical data for the compound are: Found: C, 14.45; H, 2.75; O, 15.48; Sn, 32.38; Cl, 35.34%. These data correspond to an empirical formula of  $\text{SnCl}_4 \cdot \text{C}_4\text{H}_{10}\text{O}_4$  (Calculated: C, 12.60; H, 2.62; O, 16.80; Sn, 31.23; Cl, 36.75%). This is the formula of a 1:1 complex between tin(IV) chloride and diglyme. All of the data given previously are also consistent with this formulation.

A diglyme adduct of tin(IV) chloride was reported in the late 1960's by Gol'dshtein<sup>(200,201)</sup>, but while the authors reported the dipole moments, heats of formation, and dielectric titration curves, no spectroscopic data or physical properties were given. This, to our knowledge, is the first time that this adduct has been isolated and characterized.



FIGURE A.2

MASS SPECTRUM OF THE DIGLYME ADDUCT OF TIN(IV) CHLORIDE



As a result of this work, the use of diglyme for ketal solubilization must be accompanied by the use of a distillation column of suitable length in order to avoid small amounts of diglyme from distilling with the solvent.

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