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SYNTHESIS AND STRUCTURE OF CYCLOPENTADIENYL TIN(II) COMPOUNDS

The University of Oklahoma PH.D. 1983

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THE UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

SYNTHESIS AND STRUCTURE OF CYCLOPENTADIENYL TIN(II) COMPOUNDS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

THOMAS SHELDON DORY
Norman, Oklahoma
August 1983

SYNTHESIS AND STRUCTURE OF CYCLOPENTADIENYL TIN(II) COMPOUNDS

A DISSERTATION

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TO MY PARENTS

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"'The time has come,' the Walrus said,
'To talk of many things:
Of shoes—and ships—and sealing wax—
Of cabbages—and kings—
And why the sea is boiling hot—
And whether pigs have wings.'"

Lewis Carroll
Through the Looking Glass

ABSTRACT

The synthesis of novel organotin(II) compounds was carried out in an attempt to understand the physical and chemical properties in these very reactive systems. Compounds comprising two new classes of organotin(II) complexes were prepared. Two single crystal x-ray data sets were collected with one successfully solved.

The reaction of tin(II) chloride with thallium(I) cyclopentadiene salts, TlC_5H_4X, where X = Cl, Br, I produces a mixture of products instead of the desired $Sn(\eta^5-C_5H_4X)_2$. In the attempt to produce trimethyltin(IV) chlorocyclopentadiene from trimethyltin(IV) chloride and chlorocyclopentadienylthallium(I), the known compound N-trimethyltin(IV) succinimide was synthesized. Thallium(I) succinimide was produced in the synthesis of chlorocyclopentadienylthallium(I) and reacted with trimethyltin(IV) chloride in preference to chlorocyclopentadienylthallium(I).

A new class of divalent tin compounds, stannocenophanes, having the general formula $C_6H_4(CH_2C_5H_4)_2Sn$, were prepared from the *ortho-*, *meta-* and *para-*isomers of the disodium salts of phenylenemethylenedicyclopentadienide and tin(II) chloride. The boron trifluoride adduct of the *meta-*isomer was synthesized and characterized.

A second new class of divalent organotin compounds was produced by the reaction of cyclopentadienyltin(II) chloride with the ring-substituted thallium(I) salts TlC_5H_4R, where R = $C(O)CH_3$, $C(O)OCH_3$, $C(O)OCH_2CH_3$. The products are the first examples of ring-substituted stannocenes, $(\eta^5\text{-}C_5H_5)Sn\text{-}(\eta^5\text{-}C_5H_4R)$.

The boron trifluoride adduct of stannocene was prepared and its single crystal x-ray structure solved at 138 K. The complex is described by the formula $BF_4\cdot(\eta^5\text{-}C_5H_5)_3Sn_2\cdot C_4H_8O$. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.258, b = 13.252, c = 16.437Å. The solution was refined to a final R value of 0.0374. Individual $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF units are linked together in a three-dimensional lattice. The interactions include fluorine bridging between tetrafluoroborate and stannocene moieties and coordination by THF to the stannocenium cation. Each cyclopentadienyl ring lies along a tin-tin vector to give a three-dimensional network of bridging $\eta^5\text{-}C_5H_5$ groups.

The boron trifluoride adduct of stannocene was reacted with the molybdenum hydride, $HMo(CO)_3(\eta^5\text{-}C_5H_5)$. The compound was characterized by microanalytical analysis, melting point, NMR, ir, Mössbauer and mass spectroscopy. A crystal was grown from solutions of THF and acetone-ethanol, but the x-ray data could not be solved for the structure. The tin(IV) hydride, $HSn[Mo(CO)_3\text{-}\eta^5\text{-}C_5(CH_3)_5]_3$, was synthesized and characterized.

TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION

1.1 Historical Background...................... 1

1.2 Stannocene and Its Boron Trifluoride Adduct.................................. 7

1.3 Comments on Stannocenophanes.............. 11

1.4 Ring Substituted Cyclopentadienes and Reactions............................. 14

1.5 Reactions Involving Transition Metal Hydrides with Tin(II) Compounds........... 19

II. CRYSTAL AND MOLECULAR STRUCTURE OF THE BORON TRIFLUORIDE ADDUCT OF STANNOCENE

2.1 Introduction.............................. 30

2.2 Data Collection........................... 30

2.3 Structure Determination and Refinement..... 32

2.4 Description of the Structure.............. 33

2.5 Conclusions............................... 45

III. SYNTHESIS AND CHARACTERIZATION OF N-(TRIMETHYLSTANNYL)SUCCINIMIDE

3.1 Introduction.............................. 62

3.2 Synthesis of N-Trimethylstannylsuccinimide. 62

Chapter Page

3.3 Characterization of N-Trimethylstannylsuccinimide.......................... 66

3.4 Conclusions................................ 73

IV. SYNTHESIS AND CHARACTERIZATION OF STANNOCENES

4.1 Introduction................................ 78

4.2 Synthesis of α,α'-Dicyclopentadienylxylene.. 79

4.3 Synthesis of Disodium (Phenylenedimethylene) dicyclopentadienide......................... 80

4.4 Synthesis of Phenylenedimethylene Bis(η^5-Cyclopentadienyl)tin(II)............. 81

4.5 Synthesis of *meta*-Phenylenedimethylene Bis[η^5-cyclopentadienyltin(II)] Bis(η^5-cyclopentadienyl).................... 82

4.6 Synthesis of *meta*-Phenylenedimethylene Bis(η^5-cyclopentadienyl)tin(II) BF_3 Derivative................................ 82

4.7 Characterization of Phenylenedimethylene Bis(η^5-cyclopentadienyl)tin(II)............. 83

4.8 Characterization of *meta*-Phenylenedimethylene Bis[η^5-cyclopentadienyltin(II)] Bis(η^5-cyclopentadienyl).................... 100

4.9 Conclusions................................ 102

V. SYNTHESIS AND CHARACTERIZATION OF RING SUBSTITUTED STANNOCENES

5.1 Introduction................................ 108

5.2 Synthesis of Sodium Acetylcyclopentadienide. 111

Chapter Page

5.3 Synthesis of Sodium Methoxycarbonylcyclopentadienide.................... 112

5.4 Synthesis of Sodium Ethoxycarbonylcyclopentadienide.................... 112

5.5 Synthesis of Thallium Halocyclopentadienides. 113

5.6 Reactions Involving Triorganotin Chlorides... 115

5.7 Reaction of Tin(IV) Chloride and Thallium Bromocyclopentadienide........................ 117

5.8 Reactions Involving Tin(II) Chloride......... 118

5.9 Synthesis of Acetylstannocene................ 121

5.10 Synthesis of Methoxycarbonylstannocene....... 122

5.11 Synthesis of Ethoxycarbonylstannocene........ 124

5.12 Discussion.................................. 125

5.13 Conclusions................................. 135

VI. REACTIONS BETWEEN TIN(II) AND MOLYBDENUM COMPOUNDS

6.1 Introduction................................ 145

6.2 Synthesis of Pentamethylcyclopentadienyltricarbonylmolybdenym Hydride................ 146

6.3 Synthesis of Tris(pentamethylcyclopentadienyltricarbonylmolybdenum)tin(IV) Hydride.. 148

6.4 Reactions of the Boron Trifluoride Adduct of Stannocene with Cyclopentadienyltricarbonylmolybdenum Hydride.................. 150

6.5 Discussion.................................. 153

6.6 Conclusions................................. 157

Chapter Page

VII. APPENDIX

7.1 Physical Methods.......................... 160

7.1a Melting Points.............................. 160

7.1b Elemental Analyses........................ 160

7.1c Infrared Spectra............................ 160

7.1d Nuclear Magnetic Resonance Spectra.......... 160

7.1e Mass Spectra................................ 161

7.1f Mössbauer Spectra.......................... 161

7.1g Raman Spectra............................... 161

7.2 Solvents..................................... 161

LIST OF TABLES

Table Page

1.1 Comparison of Analytical Data for Possible Cyclopentadienyltin(II) Boron Fluorides............ 12

2.1 Crystal Data for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.............................. 47

2.2 Data Collection Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.......... 48

2.3 Final Position Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2\text{-}Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$............................ 49

2.4 Thermal Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.............................. 50

2.5 Intramolecular Distances for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2\text{-}Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$............................ 51

2.6 Intramolecular Angles in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.............................. 53

2.7 Deviations from Least-Square Planes in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.......... 54

2.8 Hydrogen Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.............................. 55

2.9 Least-Square Planes in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.............................. 56

2.10 Least-Sugare Planes through Tin Atoms and Center of Rings.................................. 57

Table Page

2.11 π-Sn(II)-Carbon Ring Distances...................... 58

3.1 Physical Properties of $(CH_3)_3Sn\overline{NC(CO)CH_2CH_2C}(CO)$.... 65

3.2 Infrared Spectrum of $(CH_3)_3Sn\overline{NC(CO)CH_2CH_2C}(CO)$...... 67

3.3 ^{13}C NMR Data for $(CH_3)_3SnR$ Compounds................ 72

3.4 Mass Spectrum of $(CH_3)_3Sn\overline{NC(CO)CH_2CH_2C}(CO)$.......... 75

4.1 Tin 119Mössbauer Data for Diorganotin Derivatives... 87

4.2 Infrared Bands for the Bis[(Phenylenedimethylene)-η^5-dicyclopentadienyl]tin(II) Isomers............... 89

4.3 Mass Spectral Data for the Bis[(Phenylenedimethylene)-η^5-dicyclopentadienyl]tin(II) Isomers.. 98

4.4 Mass Spectral Data for the *m*-Bis[(Phenylenedimethylene)-η^5-dicyclopentadienyl]tin(II) BF_3 Derivative................................... 99

4.5 Tin 119Mössbauer Data for π-Bonded Organotin(II) Compounds.. 101

5.1 Mass Spectrum of Acetylstannocene.................. 123

6.1 Mass Spectral Data for the BF_3Adduct of Stannocene + $HMo(CO)_3$-η^5-C_5H_5....................... 152

6.2 Possible Formulations of the Product of the BF_3 Adduct of Stannocene and $HMo(CO)_3$-η^5-C_5H_5........... 155

LIST OF FIGURES

Figure Page

2.1 The Asymmetric Unit of $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+.THF\}_n$ 34

2.2 The Unit Cell of $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ 35

2.3 Schematic View of Extended Coordination Around Tin Atoms in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ 38

2.4 Coordination Around Sn(1) in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2\text{-}Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ 40

2.5 Coordination Around Sn(2) in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2\text{-}Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ 42

3.1 Solid and Solution Infrared Spectra of $(CH_3)_3Sn\overline{NC(CO)CH_2CH_2C}(CO)$ 69

3.2 ^{119}Sn Mössbauer Spectrum of $(CH_3)_3Sn\text{-}\overline{NC(O)CH_2CH_2C}(CO)$ 74

4.1 ^{119}Sn Mössbauer Spectrum of *meta*-$C_6H_4(CH_2C_5H_4)_2Sn$

4.2 ^{119}Sn Mössbauer Spectrum of Air Oxidized *meta*-$C_6H_4(CH_2C_5H_4)_2Sn$ 84

4.3 Possible Structures of Monomeric Stannocenophane Isomers 95

4.4 Possible Structures of Polymeric Stannocenophane Isomers 96

Figure Page

5.1 ^{119}Sn Mössbauer Spectrum of $SnCl_2$ + $NaC_5H_4C(O)CH_3$..... 119

5.2 Calculated and Actual Isotopic Pattern for the $TlSnCl_2$ Ion.. 129

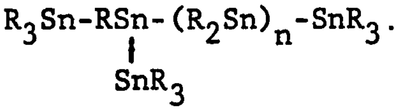
5.3 ^{119}Sn Mössbauer Spectrum of $SnCl_2$ + TlC_5H_4Br.......... 130

CHAPTER I

INTRODUCTION

1.1 HISTORICAL BACKGROUND

Tin is a group IV A element with an outer electronic configuration $5s^2 5p^2$. It can form compounds in both the 2+ and 4+ oxidation states. In the 2+ oxidation state, tin contains a filled 5s-orbital and empty 5p- as well as 5d-orbitals that can be used in bonding. On the basis of the outer electron configuration for tin, there are four possible ways to form a tin(II)-ligand bond. These include loss of two 5p-electrons to form the Sn^{2+} ion, use of the two 5p-electrons for covalent bond formation, by complex formation utilizing the empty 5p and 5d orbitals as acceptor orbitals and by overlap of the lone pair electrons with an empty orbital on an acceptor atom. Usually more than one of these possibilities are involved in the formation of organotin(II) compounds.

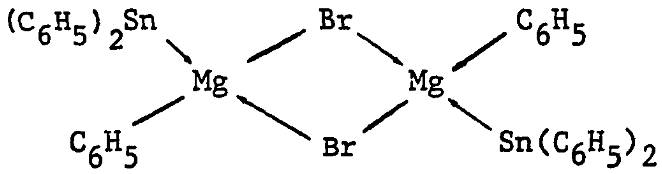
Thermodynamically, the most stable compounds of the group IV A elements are those where the metal is in the tetravalent state, except for lead. The synthesis of the first claimed diorganotin(II) compound, called diethyltin, was published in 1852.[1] This report was followed by other claimed diorganotin(II) compounds including "Ph_2Sn", "$cHex_2Sn$" and Ar_2Sn" (Ar = 4-tolyl, 1-naphthyl, 9-phenanthryl) which are reviewed in Reference 2. However, Neumann and co-workers demonstrated in the late 1960's that these compounds were in fact, a mixture of oligomeric, polymeric and ring compounds containing Sn-Sn chains such as R_3Sn-$(R_2Sn)_n$-SnR_3, $(R_2Sn)_n$ and  $R_3Sn\text{-}\underset{\displaystyle SnR_3}{\underset{|}{RSn}}\text{-}(R_2Sn)_n\text{-}SnR_3$.

These compounds were then classed as tin(IV) compounds.[3] Only four true organotin(II) compounds were known as late as 1970. They include dicyclopentadienyltin(II), [stannocene, $(\eta^5\text{-}C_5H_5)_2Sn$],[4] bis(methylcyclopentadienyl)-tin(II) [dimethylstannocene, $(\eta^5\text{-}C_5H_4CH_3)_2Sn$],[5] bis(2-phenyl-1,2-dicarba-closo-dodecarborane(12)-1-yl)tin(II)[6] and 1-stanna-2,3-dicarba-closo-dodecarborane(11).[7,8] The first mono-organotin(II) halides, cyclopentadienyltin(II) chloride and bromide, were reported in 1972.[9a] The crystal structure of $(\eta^5\text{-}C_5H_5)SnCl$, reported in 1975, showed this compound to contain asymmetric chlorine bridges linking the tin atoms.[9b]

In 1973, the first true dialkyltin(II) compound was reported.[10] Containing two bis(trimethylsilyl) methyl groups, $\{[(CH_3)_3Si]_2CH\}_2Sn$ was shown to be a monomer in solution,[11] but in the solid, the single crystal x-ray structure shows this compound to be a dimer.[12] In solution it can behave like a Lewis acid by forming a complex with pyridine,[13] a Lewis base with formation of $\{[(CH_3)_3Si]_2CH\}_2Sn\text{-}M(CO)_5$, M = Cr, Mo,[10,14] and will undergo insertion-addition reactions with CH_3I, Cl_2, HCl, $CH_2{=}C(CH_3)C(CH_3){=}CH_2$ and $Fe(CO)_9$.[13] The iso-electric stannylamine, $\{[(CH_3)_3Si]_2N\}_2Sn$ has been prepared and shown to be monomeric in solution.[15a,b] The x-ray crystal structure shows this to be monomeric in the solid phase as well.[15c]

Compounds of the type $B\text{-}SnR_2Cr(CO)_5$, where B = THF, R = CH_3, t-Bu, were reported in 1971 and claimed to be organotin(II) compounds.[16] The solution of the x-ray crystal structure for $(t\text{-}Bu)_2SnCr(CO)_5 \cdot C_5H_5N$[17] with Mössbauer and ESCA studies concluded that the tin is in the tetravalent state, rather than the divalent state.[18]

In another organotin compound, $(Ph_3SnMgBr)_2$, the tin was proposed to be in the divalent state with a possible structure of

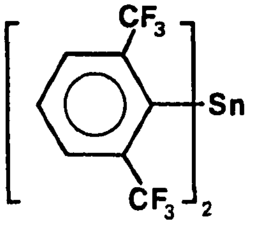


based on chemical reactivity.[19] Mössbauer data, however, suggested that the tin was in the tetravalent state and a cyclic compound having tin in the ring was suggested.[20]

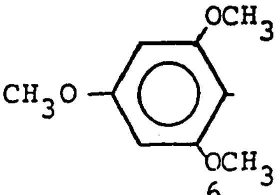
In the last 10 years, there has been a large increase in the number of monomeric tin(II) compounds reported. Bis(pentamethylcyclopentadienyl)tin(II), decamethylstannocene, has been synthesized[21] and its crystal structure solved showing it to be monomeric.[22] The crystal structure of stannocene has also been solved showing it to be monomeric.[23]

The pentamethylcyclopentadienyltin(II) cation appears to be relatively stable. Several compounds involving this cation are known. The crystal structure of pentamethylcyclopentadienyltin(II) tetrafluoroborate has been solved.[24] Each tin atom is associated with two fluorine atoms of the $[BF_4]^-$ anion. This cation shows an electrophilic character forming compounds with $[AlCl_4]^-$, $[CF_3SO_3]^-$, $[CCl_3CO_2]^-$, $[BF_4]^-$[25a] and $[C_5(COOCH_3)_5]^-$.[25b] The crystal structure of the 1:1 pyridine adduct of $[\eta^5\text{-}C_5(CH_3)_5]_2Sn^+$ $CF_3SO_3^-$ has been reported.[26] The tin is distorted from the center of the ring (pentahapto-bonding) to one side of the ring (dihapto-bonding). In another reaction, both pentamethylcyclopentadienyl rings were substituted by the acid $HC_5(COOCH_3)_5$ forming the tin compound $Sn[C_5(COOCH_3)_5]_2$.[25b]

The first stable divalent aryltin compound was reported using trifluoromethyl groups in the 2,6-position of a phenyl ring to stabilize the tin.[27] The compound was formulated as:



Similar compounds were soon reported for the R_2Sn system, where R = 2,6-di-t-butyl-4-methylphenoxy,[28]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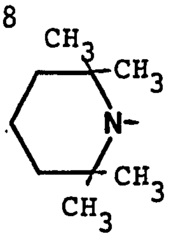

[29] ,

Several η^6-arene complexes with tin(II) have been reported, including $(\eta^6\text{-}C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$,[30] $(\eta^6\text{-}C_6H_6)Sn(AlCl_4)Cl$[31] and $(\eta^6\text{-}p(CH_3)_2C_6H_4)_2Sn\text{-}(AlCl_4)Cl$.[31] The crystal structures for these compounds show the tin centered over the ring bonding in a hexahapto-mode.In one other tin(II) compound, $Sn[S_2P(OC_6H_5)_2]_2$, coordination of the tin(II) lone pair to a phenyl ring has been suggested.[31b] The crystal structure shows a dimer held together by sulfur bridges. Intermolecular lone pair coordination to a phenyl ring was used to rationalize the stability of the dimeric solid with respect to air.

In this last decade, there has been a large increase in the synthesis and reported reactions of molecular tin(II) compounds. This is well illustrated by the number of review articles that have appeared recently, including structural tin(II) reviews,[32-34] and reviews on the synthesis and reactions of tin(II) compounds.[35,36]

The difficulty of assigning the oxidation state of tin(2+ or 4+) can be overcome using ^{119m}Sn Mössbauer or γ-resonance spectroscopy. Mössbauer spectroscopy is based on the recoiless resonant absorption of γ-rays.

The resonant energy of a nucleus is altered significantly, but by a very small amount, when the electron distribution, especially the s-electron density, changes as a result of changes in the chemical environment at the nucleus. In order to observe the resonant absorption, the energy of the γ-ray coming from the source, must exactly match the resonant energy of the absorber (sample). The exact match-up of energy is provided by the Doppler effect when the source is moved with respect to the absorber. Experimentally, the isomer shift (IS) is the displacement of the source from zero relative velocity, which is the mismatch between the sets of nuclear energy levels of the source and absorber.
The IS is also a measurement of the electron density at the nucleus which is related to the electron density in the valance shell of the tin atom.

The value of the quadrupole splitting (QS) is directly related to the electric field gradient (E.F.G.) at the tin nucleus. When the environment of the absorber tin nucleus is not spherical, the E.F.G. has a positive value and two peaks are usually observed in the Mössbauer spectrum. The distance between the peaks is called the quadrupole splitting. Causes of E.F.G. (and so QS) can be an imbalance in the polarity of tin-ligand σ-bonds along with distortions in the π-bonding. Changes in bond angle and orbital hybridization of the tin lone pair electrons can also give rise to a QS.

From the value of the IS, conclusions can be drawn about the valency of the tin in a tin compound. Comparison between the hybrid orbitals used for bonding in tin(II) and tin(IV) compounds, reveals a theoretical decrease in the s-electron density at the tin ongoing from +2 to +4 oxidation state. So IS values for tin(II) compounds will be greater than those for tin(IV) compounds. The standard scale now used is relative to SnO_2 which has been given the value of zero mm s^{-1}. On this scale, the IS value of β-Sn(2.56mm s^{-1}) is taken as the dividing line between the two valencies. The IS of tin(II) compounds being larger and the IS of tin(IV) compounds being smaller than that of β-Sn. The Mössbauer effect has been the subject of many reviews and books, several of which have been listed in References 37 to 42. It must be noted, however, that $\{[(CH_3)_3Si]_2CH\}_2Sn(II)$[10] with an IS of 2.12mm s^{-1} is below the IS value of β-Sn. So it is difficult to draw conclusions about the valency of the tin atom when its IS is near that of β-Sn.

1.2 STANNOCENE AND ITS BORON TRIFLUORIDE ADDUCT

The synthesis of stannocene was published[43] shortly after ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, was reported.[44] Wilkinson and co-workers, noting the similarity between the IR spectra of stannocene, plumbocene and ferrocene, suggested an angular sandwich structure for stannocene and plumbocene.[45] Stannocene is now a well characterized compound. Its IR,[46] UV,[45] NMR,[47] ^{119m}Sn Mössbauer,[47] He(I) photoelectric,[48] and mass[47] spectra have been reported. The x-ray crystal structure has been published proving the monomeric angular sandwich structure originally suggested.[23] Using self-consistant field X_α scattered wave (SCF X_α SW) calculations on stannocene, it was found that the highest occupied molecular orbitals (HOMO) are π-type and almost completely localized on the cyclopentaidenyl rings.[49]

It was not until 1970 that the first Lewis acid adduct, using boron trifluoride, was reported.[50] Based on Mössbauer, IR, NMR and mass spectra, it was concluded that this adduct involved a simple donation of the tin(II) lone pair electrons to the boron. Following this, other reports of stannocene-Lewis acid adducts appeared using a variety of Lewis acids (Equations 1.1 and 1.2).[51,52]

$$2(C_5H_5)_2Sn + Al_2X_6 \longrightarrow 2(C_5H_5)_2Sn\text{-}AlX_3 \qquad (1.1)$$

$$2(C_5H_5)_2Sn + Et_2O\cdot BX_3 \longrightarrow (C_5H_5)_2Sn\text{-}BX_3 + Et_2O \qquad (1.2)$$

$$X = F,\ Br$$

Reactions of stannocene with BI_3 yield a ligand-exchange product formulated as $I_2Sn\text{-}B(C_5H_5)_2I$.[53] With BCl_3-etherate a ligand exchange reaction also occurs resulting in $SnCl_2$ as the main product.[52] The product of decamethylstannocene and $AlCl_3$ was found to be $[\eta^5\text{-}C_5(CH_3)_5Sn]^+[AlCl_4]^-$.[54] It seems that at least some of the donor-acceptor reactions using stannocene are in fact, halide-cyclopentadienyl ligand exchange reactions. The products are salts rather than the anticipated adducts.

The preparation of the boron trifluoride adduct of stannocene was accompanied by the disappearance of the tin satellites from the ^1H NMR spectrum of stannocene.[47] In fact, in no report of which we are aware, are tin satellites observed in the NMR spectra of any of the claimed donor-acceptor products.[25,51,52,54] We interpret these negative results in terms of a dynamic phenomena involving the acceptor halide-induced exchange of cyclopentadienyl groups between donor and acceptor atom sites. The structure of the BF_3 adduct of stannocene seems to represent a frozen intermediate in the intermolecular exchange of cyclopentadienyl groups between two tin sites, rationalizing and depicting the rapid making and breaking of η^5-C_5H_5-Sn(II) bonds. The structure contains individual $[BF_4]^-$, $[\eta^5\text{-}C_5H_5Sn]^+$, $(\eta^5\text{-}C_5H_5)_2Sn$ and THF groups. The structure is discussed in detail in Chapter II.

The question of why the lone pair electrons are not the site of attack of the BF_3 forming the simple $(\eta^5\text{-}C_5H_5)_2\text{-}Sn\rightarrow BF_3$ adduct can now be answered. Recent theoretical calculations on stannocene using SCF X_α SW techniques give the two highest occupied molecular orbitals as π-type and almost completely localized on the cyclopentadienyl rings.[49] These are followed in order of decreasing energy by two MO's which account for the primary interaction with the tin 5s and 5p atomic orbitals. The orbital holding the lone pair is 2.0eV lower than the HOMO and is the fifth MO. This result disagrees with semi-empirical MO calculations which places the stannocene lone pair orbital as the HOMO.[22] But SCF X_α SW results are corroborated by He(I) ultraviolet spectral results[48] in which an ionization energy at 9.58eV was attributed to electron ejection from the stannocene lone pair orbital. Ionization from the HOMO was observed at 7.57eV.[49] Also, cyclic voltammetry does not oxidize stannocene to $[(\eta^5\text{-}C_5H_5)_2Sn]^{2+}$ as would be expected if the lone pair occupied the HOMO, but an irreversible oxidation wave was observed instead.[49]

As a final note on this subject, two items deserve to be mentioned. First, analytical data are often insensitive, even to gross changes in molecular composition (See Table 1.1 for the $F_3B\text{-}Sn(C_5H_5)_2$ example). Second, the reaction of decamethylstannocene with HBF_4 produces $[\eta^5\text{-}C_5(CH_3)_5Sn]^+[BF_4]^-$ in good yield. In the ^1H NMR, tin-proton coupling is observed with $^2J(^{119}Sn\text{-}^1H)$ = 2.0Hz and in the ^{13}C NMR, tin-carbon coupling is observed with $^1J(^{119}Sn\text{-}^{13}C)$ = 51.5Hz. In a tin(II) compound not involved with exchanging cyclopentadienyl rings, tin coupling can be observed.

1.3 COMMENTS ON STANNOCENOPHANES

Stannocene and its derivatives are angular sandwich compounds with the stereochemically-active lone pair electrons occupying the third site of the trigonal coordination of the tin atom. Substitution on the rings will alter their steric and electrical properties. This in turn, will alter the angles made by the tin to the two cyclopentadienyl rings, and hence the hybridization, spatial extension and basicity of the lone pair electrons. In Chapter V, I discuss the synthesis of several ring-substituted stannocenes made by using ring-substituted sodium salts and $(\eta^5\text{-}C_5H_5)SnCl$.

Another approach to alter the properties of the lone pair electrons is to design ligands containing two linked cyclopentadienyl anions in varying proximity and juxtaposition. Such systems can be based upon the disodium salts of (phenylenedimethylene)dicyclopentadienide isomers. The *meta*-isomer was used to bond two transition metal moieties together having the general formula $m\text{-}C_6H_4[CH_2C_5H_4M(CO)_3R]_2$ where M = Mo, R = H, CH_3, C_2H_5, I and M = W, R = CH_3, C_2H_5.[55] The bimetallic, metal-metal bonded derivative, $m\text{-}C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$ was also reported. These low melting point, soluble products, were formulated as monomers. The idea of making a ring-bridged stannocene, a stannocenophane, by synthesizing the ligand first, then adding the tin, look promising.

Table 1.1. Comparison of Analytical Data for Possible Cyclopentadienyltin(II) Boron Fluorides.

	Found(%)[a]	$(C_5H_5)_3Sn_2BF_4C_4H_8O$	$(C_5H_5)_2SnBF_3$	$(C_5H_5)_3Sn_2BF_4$	$C_5H_5SnBF_4$[b]
C	40.38	38.53	37.92	34.68	22.19
H	4.19	3.92	3.19	2.92	1.86
Sn	38.3	40.08	37.48	45.69	---
B	2.87	1.82	3.41	2.08	4.00
F	17.20	12.83	18.00	14.63	28.08
O	---	2.70			

[a] From ref. 50.

[b] From ref. 52.

The disodium salts of the (phenylenedimethylene)dicyclopentadienide isomers seemed to be well-suited for the synthesis of stannocenophanes. So we reacted tin(II) chloride with the *ortho-*, *meta-* and *para-*isomers of the disodium salt of (phenylenedimethylene)dicyclopentadienide. The resulting stannocenophanes, reported in Chapter IV, represent the first report of this new class of tin(II) compounds.

A change in the angles made by the tin to the two cyclopentadienyl rings will cause a change in the electric field gradient (E.F.G.) at the tin nucleus which effects QS values. The E.F.G. should increase with percentage p-character in the lone pair and s-character in the bonding orbitals. The minimum E.F.G. should occur when there are two linearly bonded ligands to tin with the lone pair in a spherically symmetrical 5s-atomic orbital. The tin atom in stannocene is roughly sp^2 hybridized and gives a QS of 0.86mm s^{-1}.[50] The more electron releasing η^5-methylcyclopentadienyl group in dimethylstannocene should cause the lone pair to be in an orbital with more p-character. Indeed, a slightly smaller QS value has been reported for this compound (0.78mm s^{-1}).[46] The electron releasing effect of the methyl groups should maximize in decamethylstannocene, with the lone pair in a more purely atomic 5p-orbital. However, the QS value for decamethylstannocene is within experimental error to that of stannocene.

The QS value for decamethylstannocene came from a weak spectrum of an impure material which could help explain the lack of change in the QS value from that of stannocene. The QS values for the three stannocenophane isomers, particularly the *ortho-*, are all larger than that of stannocene. This indicates narrow angles between the tin and two cyclopentadienyl rings. This was predicted from model studies of the isomers.

The BF_3 adduct of *meta*-stannocenophane was prepared from BF_3-etherate and *meta*-stannocenophane. The BF_3 adduct of stannocene was shown to contain $[BF_4]^-$, $[\eta^5\text{-}C_5H_5Sn]^+$, $(\eta^5\text{-}C_5H_5)_2Sn$ and THF moieties. In BF_3-stannocenophane, individual $[\eta^5\text{-}C_5H_5Sn]^+$ moieties are not possible because the rings are connected through a phenyl group. The structures of the two BF_3 adducts cannot be the same. In BF_3-stannocenophane there is no counter ion for a $[BF_4]^-$ ion so it is assumed that the $[BF_4]^-$ is not present. An x-ray crystal structure of BF_3-stannocenophane would be useful.

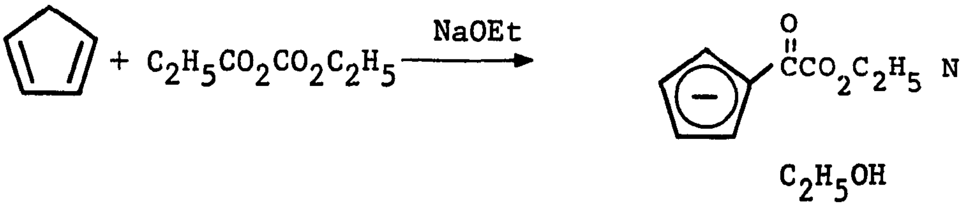
1.4 RING-SUBSTITUTED CYCLOPENTADIENES AND REACTIONS

Cyclopentadienyl-metal chemistry began with the discovery of ferrocene in 1951.[44] Shortly after this report Woodward, Rosenblum and Whiting reported that ferrocene would undergo Friedel-Crafts acylation.[56] The reaction of ferrocene with acetyl chloride in the presence of aluminum trichloride gave a mixture of acetylferrocene, 1,2-diacetylferrocene and 1,1-diacetylferrocene.[57] Ferrocene was also shown to undergo alkylation,[58] formylation,[59] mercuration,[60] and sulfonation.[61] Cyclopentadienyl ring-substituted chemistry had started. The synthesis of functionally substituted (η^5-cyclopentadienyl)-metal compounds was now known.

Because only a limited number of η^5-C_5H_5 metal compounds undergo ring substitution reactions like ferrocene, another synthetic method needed to be developed to expand this class of functionally substituted ring compounds. Almost all of the known (η^5-C_5H_5)ML_n compounds have been synthesized by reactions of C_5H_5Tl, C_5H_5Na, C_5H_5Li or C_5H_5MgX with an appropriate metal halide fragment, M = metal, L_n = ligands.

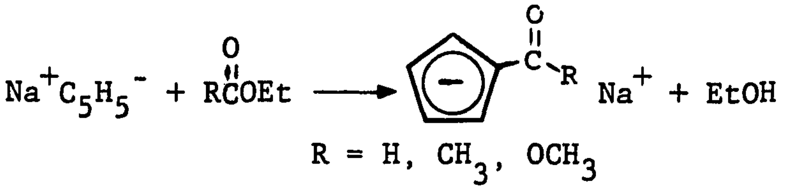
It would seem logical, then, that the reaction of substituted cyclopentadienide reagents with metal halides should lead to ring-substituted compounds of the type (η^5-C_5H_4R)ML_n, R = a reactive functional group. This type of reaction was known to work for the trivial case of methylcyclopentadienyl-metal compounds.

Sodium cyclopentadienides containing aldehyde, ketone or ester functional groups were first synthesized by Thiele in 1900.[59] He found that cyclopentadiene could be condensed with diethyl oxalate in the presence of sodium ethoxide to form sodium ethoxalylcyclopentadienide (Equation 1.3).



(1.3)

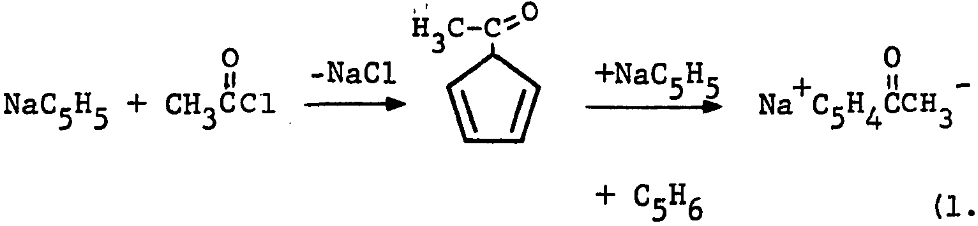
Sodium cyclopentadienide was shown to react with ethyl formate, methyl acetate and dimethyl carbonate producing sodium formyl-,[60] acetyl,[61] and carbomethoxycyclopentadienide[62] (Equation 1.4).



(1.4)

Potassium formalcyclopentadienide has been prepared from the reaction of potassium cyclopentadienide and ethyl formate.[63]

Sodium carbomethoxycyclopentadienide was also prepared from sodium cyclopentadienide and methylchloroketone followed by addition of another mole of sodium cyclopentadienide (Equation 1.5).[60]



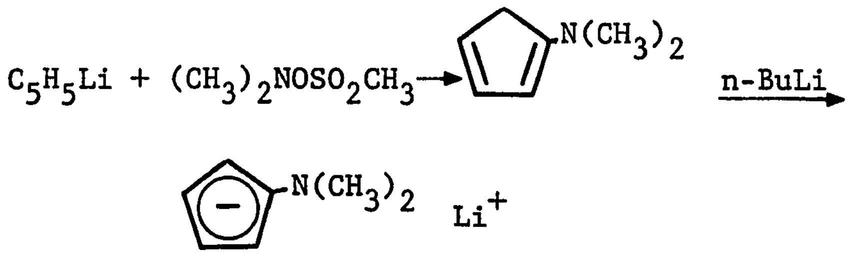
(1.5)

Sodium carbomethoxycyclopentadienide has been obtained by the reaction of sodium cyclopentadienide with methyl chloroformate with sodium metal present.[64] However, this method is not preferred because of the formation of sodium 1,2-dicarbomethoxycyclopentadienide.

Metal cyanocyclopentadienides can be prepared in two steps. The first involves the reaction of equal molar amounts of cyclopentadiene and cyanogen chloride forming dicyanocyclopentadiene dimer. When this is heated and so cracked with potassium carbonate, potassium cycanocyclopentadienide is formed.[65] When the dimer is cracked into the thallium(I) ion, thallium cycanocyclopentadienide is formed.[66]

Halo-substituted cyclopentadienide thallium salts have been recently prepared.[67,68] Thallium(I) cyclopentadienide was reacted with N-chlorosuccinimide, N-bromosuccinimide or iodine forming the halocyclopentadienes in situ, which on mixing with thallium(I) ethoxide forms thallium(I) chloro-, bromo- and iodocyclopentadienides, respectively.

Sodium nitrocyclopentadienide was first reported in 1900[59] from a reaction between cyclopentadiene and ethyl nitrate in the presence of sodium ethoxide. In 1980, lithium nitrocyclopentadiene was prepared from lithium cyclopentadienide and ethyl nitrate.[69] Lithium N,N-dimethylaminocyclopentadienide has been prepared via a two step synthesis (Equation 1.7).[70]

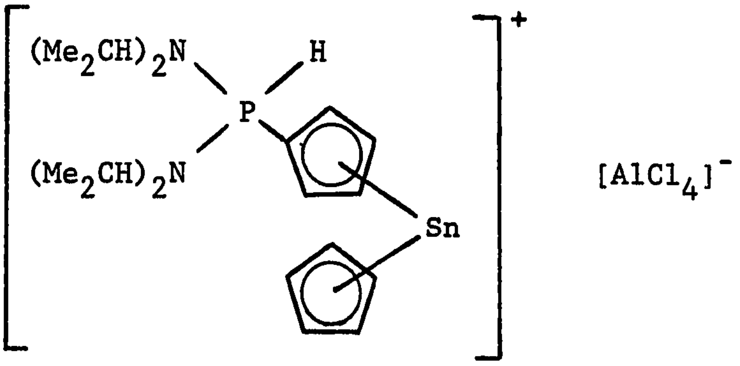


(1.7)

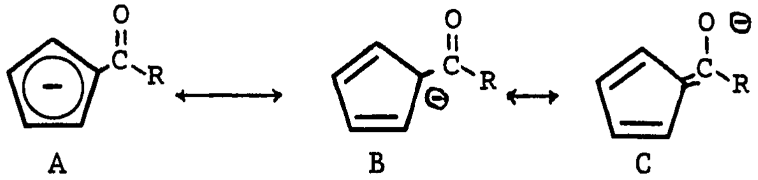
Lithium dimethylaminomethylcyclopentadienide has been reported through the reaction of 6-dimethylaminofulvene with lithium aluminum hydride.[71] Recently, lithium isopropenylcyclopentadienide and lithium vinylcyclopentadienide were prepared from 6,6-dimethylfulvene and 6-methylfulvene with lithium diisopropylamide, respectively.[72]

As can be seen from this short review of ring-substituted metal salts, many are known and a few for over eighty years. They have been used extensively to form π and σ bonded ring-substituted transition metal complexes. A good review covering the synthesis of these compounds along with multi-substituted cyclopentadiene rings is found in Reference 73.

However, to date no report of functionally substituted cyclopentadienyl ring metal salts with tin compounds has been published. We reported the synthesis of the first functionally substituted stannocenes.[74] Since that time, only one report of a monosubstituted stannocene has been published.[75] The reaction of stannocene with $[(i\text{-}Pr_2N)_2P]^+$ results in an oxidative addition reaction of a C-H bond in one cyclopentadienyl ring. The structure was formulated on the basis of NMR data.



Part of the difficulty in the synthesis of functionally substituted stannocenes, lies in the resonance structures possible for some of the substituted cyclopentadienide salts used in Chapter V (Equation 1.8).



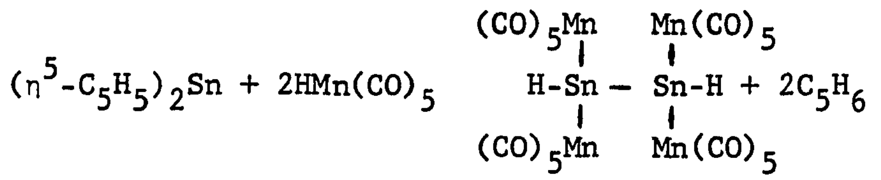
(1.8)

The existence of these resonance structures has been suggested since 1964[60] when sodium carbomethoxycyclopentadienide was first reported. Structure C seems to be most reactive in THF solutions when mixed with $SnCl_2$, Me_3SnCl or Ph_3SnCl.

1.5 REACTIONS INVOLVING TRANSITION METAL HYDRIDES WITH TIN(II) COMPOUNDS

Organotin(II) compounds are known to form a great number of transition-metal compounds. They can be classified on the basis of structure as terminal, for example, $Cr(CO)_5Sn[CH(SiMe_3)_2]_2$[14] and $(C_5H_5)_2SnCr(CO)_5$,[76] base-stabilized, $t\text{-}Bu_2Sn(py)Cr(CO)_5$,[17] or bridging, $[Fe(CO)_4]_2Sn[CH(SiMe_3)_2]_2$[14] and $[Ph_2SnFe(CO)_4]_2$.[77] In each of these reactions, the tin(II) was oxidized to tin(IV). These types of reactions are often called oxidative-addition reactions. Two well written recent reviews in this area of tin(II) chemistry are listed in Reference 36 and 78.

Stannocene has been reported to undergo oxidative-addition reactions with three transition metal hydrides. The first reaction with pentacarbonylmanganese hydride forms a ditin(IV) dihydride (Equation 1.9).[79]



$$(\eta^5\text{-}C_5H_5)_2Sn + 2HMn(CO)_5 \qquad \begin{array}{cc} (CO)_5Mn & Mn(CO)_5 \\ | & | \\ H\text{-}Sn\,- & Sn\text{-}H \\ | & | \\ (CO)_5Mn & Mn(CO)_5 \end{array} + 2C_5H_6 \qquad (1.9)$$

The single crystal x-ray structure shows a linear H-Sn-Sn-H chain in the molecule.[79] In the second reaction with cyclopentadienyltricarbonylmolybdenum hydride, a tin(IV) hydride forms, $HSn[Mo(CO)_3C_5H_5]_3$.[80] The product of the third reaction with cyclopentadienyltricarbonyltungsten hydride is the object of some dispute. The product was originally formulated as "$Sn[W(CO)_3C_5H_5]_2$". However, a more detailed look into this reaction indicates the correct formulation should be the tin(IV) hydride, $HSn[W(CO)_3\text{-}C_5H_5]_3$.[82,83]

In Chapter VI we report the synthesis of a fourth tin(IV) hydride made from $HMo(CO)_3C_5(CH_3)_5$ and stannocene, $HSn[Mo(CO)_3C_5(CH_3)_5]_3$. Chapter VI also discusses the reaction between the boron trifluoride adduct of stannocene and cyclopentadienyltricarbonylmolybdenum hydride. The reaction was performed at a time when stannocene was thought to form a single donor-acceptor adduct with BF_3. It was thought that by complexing the tin(II) lone pair electrons in stannocene, an oxidative-addition reaction would not occur, but rather a simple ligand exchange involving loss of the cyclopentadienyl rings with formation of F_3B-$Sn[Mo(CO)_3C_5H_5]_2$. However, it is now known that the BF_3 adduct of stannocene is not a simple donor-acceptor adduct, but has a more complex associated polymeric structure. The reaction of this adduct with the molybdenum hydride produces an understandably more complex product.

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CHAPTER II

CRYSTAL AND MOLECULAR STRUCTURE OF THE BORON TRIFLUORIDE ADDUCT OF STANNOCENE

2.1 INTRODUCTION

The reaction of stannocene with boron trifluoride etherate in THF results in the formation of a compound best formulated as $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$, rather than the original formulation of $(\eta^5\text{-}C_5H_5)_2Sn{:}\rightarrow BF_3$.[1] The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.258, b = 13.252, c = 16.437Å, V = 2016.6Å^3, z = 4 and ρ_{calcd} = 1.947.

Individual $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF units are linked together in a three-dimensional lattice by weak interactions. These interactions include a fluorine bridge between the tetrafluoroborate and stannocene moieties and coordination by the oxygen atom in THF to the stannocenium cation. Also, each cyclopentadienyl ring lies along a tin-tin vector, and normal to the vector, giving a network of bridging $\mu\text{-}\eta^5\text{-}C_5H_5$ groups.

2.2 DATA COLLECTION

Crystals of the title compound were obtained by recrystallization from THF-hexane under argon as colorless cubes. The crystals quickly decompose upon exposure to air. A suitable crystal was chosen from an argon-filled crystallizing dish cooled to 195 K by Dry Ice using a fine glass rod tipped with stopcock grease. The crystal was immediately transferred to an N_2 stream in the diffractometer.

The data were obtained at 135(2) K on a Enraf-Nonius CAD-4 counter diffractometer controlled by a PDP8/e computer and fitted with a low temperature device using MoK radiation (λ=0.70926Å). The space group was determined from the systematic absences (h00 h=2n+1, 0k0 k=2n+1, 001 1=2n+1).

The intensity of all reflections with $2\Theta<53^{o}$ was measured applying Θ-2Θ scan techniques. The maximum scan time for each reflection was 60s. The intensities were scaled according to their scan rate. Three orientation central reflections were centered after every 150 reflections. If an angular change greater than 0.12^{o} was found, a new orientation matrix was automatically determined from 16 reflections.

Out of 2080 independent reflections measured, 14 were considered unobserved $I<2\sigma(I)$. Crystal data and data collection parameters are summarized in Tables 2.1 and 2.2, respectively.

2.3 STRUCTURE DETERMINATION AND REFINEMENT

The positions of the tin atoms were determined from a three-dimensional Patterson map. All non-hydrogen atoms were located from difference Fourier maps. The identified peak positions were subtracted from the next difference Fourier map.

The least-square refinement was carried out using first isotropic and then anisotropic-thermal parameters for all atoms except hydrogens. All hydrogen atom positions were located and refined isotropically.

The final R factor ($R = \Sigma|K|F_o| - F_c||/\Sigma|F_o|$) is 0.0343 for 2066 reflections used in the least-square refinement. In the last cycle of least-square refinement there was no parameter shift greater than 5% of the corresponding standard deviation for non-hydrogen atoms. Scattering factors for B, C, O and F were taken from reference two. Scattering factors for Sn were taken from reference 3 and those for H were taken from reference 4.

Tables 2.3 and 2.4 contain the final positional and thermal parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$, respectively. Bond distances and angles are listed in Tables 2.5 and 2.6, respectively. Table 2.7 lists the least-square planes and deviations of the cyclopentadienyl rings. Figure 2.1 is a view of one independent unit of $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$. Figure 2.2 is a view of the unit cell. Table 2.8 lists the final positional parameters for all hydrogen atoms.

2.4 DESCRIPTION OF THE STRUCTURE

The BF_3 adduct of stannocene crystallizes into $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF moieties in a loosely associated, three-dimensional lattice. The structure is complex with many weak interactions.

The low melting point of 58-60°C and free solubility in several organic solvents argues for a charge delocalized structure and not an ionic one as written. Charge delocalization is achieved through several methods.

The oxygen atom of the THF molecule is within bonding distance of Sn(2) in the stannocenium ion with [d(Sn(2)-O(1)) = 2.845(10)Å]. This distance falls in the range of other Sn(II)-oxygen distances. In the structure of two nitrate salts, 2-aminobenzothiazolototin(II) nitrate[5] and $(C_6H_5)_3Sn(IV)Sn(II)NO_3$[6], thetin(II)-oxygen distances range from 2.50 - 2.92 and 2.38 - 2.84Å, respectively. In three carboxylate compounds, $KSn(O_2CH)_3$[7], $H_2SnEDTA$[8] and $Sn_2EDTA\cdot 2H_2O$[9], the carboxylate oxygen-tin(II) distances range from 2.14 - 3.08, 2.196 - 3.057 and 2.14 - 3.18Å, respectively. A more direct comparison can be made with the Sn(II)-THF oxygen atom bond distance in $[Sn_2(O_2C\text{-}C_6H_4NO_2)_4\cdot THF]_2$ of 2.430A.[10]

One of the fluorine atoms, F(1), of the tetrafluoroborate moiety is directed toward the Sn(1) atom at a distance of 2.862(6)Å. This fluorine atom is attached to

Figure 2.1. The Asymmetric Unit of $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.

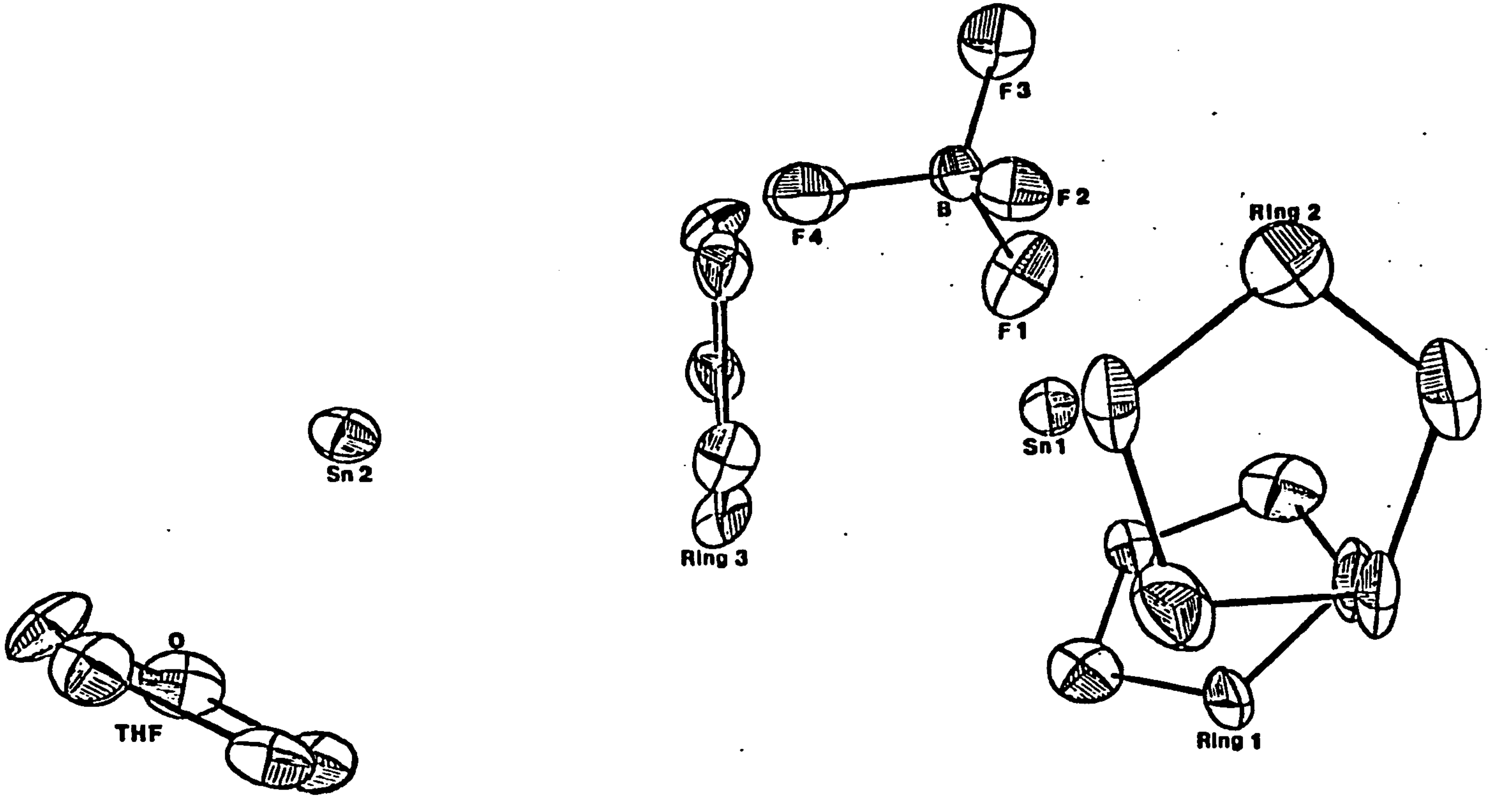
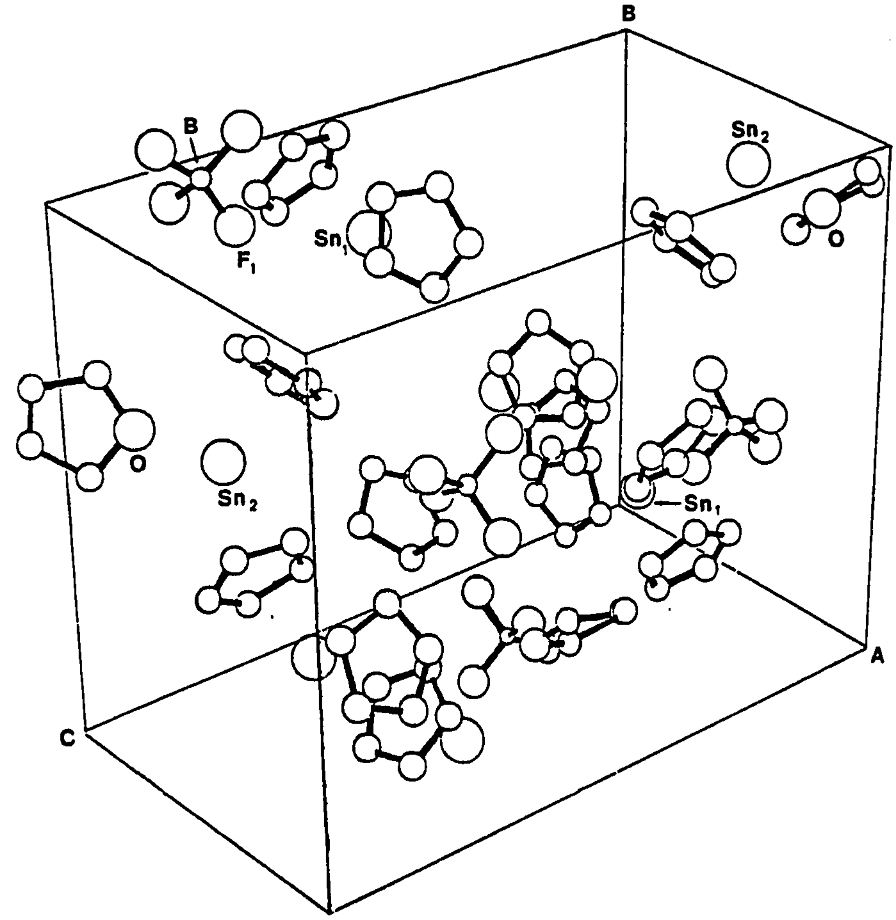


Figure 2.2 The Unit Cell of $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.



the boron atom through the longest of the four B-F bonds, [d(B(1)-F(1)) = 1.405(9)Å]. The other three distances are listed in Table 2.5 and range from 1.370 - 1.394Å. Long tin(II)-fluorine coordination is found in the structure of SnF_2 in the orthorhombic modification. Two short (2.15Å), one medium (2.45Å) and three long (2.80-3.00Å) Sn-F bonds are found in this polymeric structure.[11] Other known Sn-F distances are 2.391Å in SnFCl[12], 2.387Å in $(Sn_2O_2F_4)Sn_2$[13] and 2.587Å in $(SnF)_3 \cdot 3AsF_6$.[14]

Coordinated tetrafluoroborate anions have been suggested for $Ni(C_5H_5N)_4(BF_4)$[15] and $(CH_3)_3Sn(BF_4)$[16] based on infrared data. X-ray structural data, now available, confirms coordinated tetrafluoroborate anions in several copper and nickel compounds. A short fluorine bridge between the coordinated tetrafluoroborate anion and nickel is found in $[Ni(en)_2H_2O(BF_4)]^+[BF_4]^-$ at [d(Ni-F) = 2.21Å].[17] In the $Cu(en)_2(BF_4)_2$ copper forms an octahedral geometry with two long bonds to fluorine at d(Cu-F) = 2.56Å and an angle of Cu-F-B = 116.3°. In $Cu[P(C_6H_5)_3]_3BF_4$ the coordinated $[BF_4]^-$ anion forms a linear bridge of d(Cu-F) = 2.306Å (avg).[19] In two of these examples, $[Ni(en)_2H_2O(BF_4)]^+[BF_4]^-$ and $Cu[P(C_6H_5)_3]_3BF_4$, the B-F bond of the bridging fluorine is the longest (d(B-F) = 1.41Å[17] and 1.39Å[19], respectively) as it is in our compound.

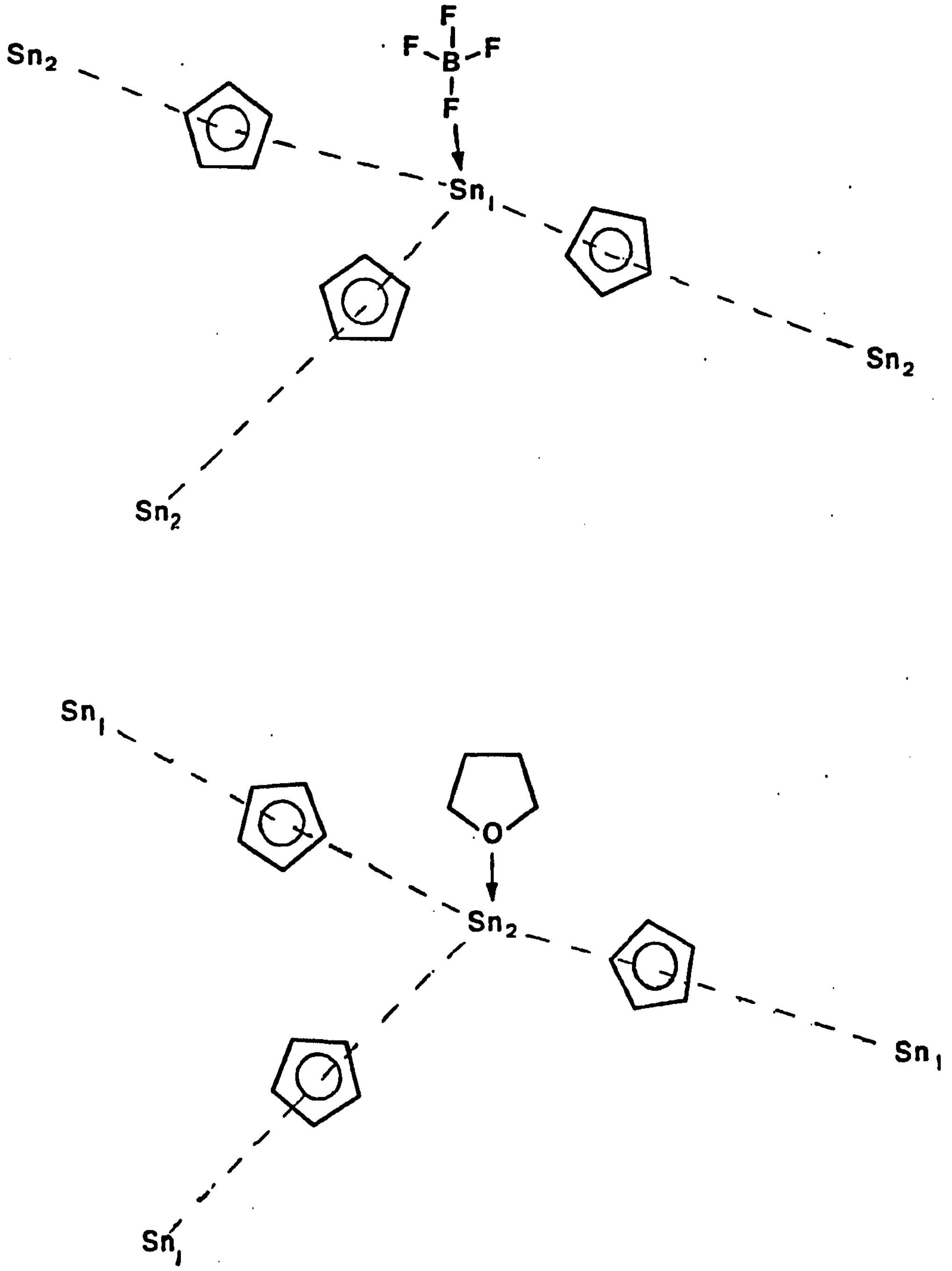
The η^5-cyclopentadienyl groups are located about the tin atoms in rather special positions. This is shown schematically in Figure 2.3. The cyclopentadienyl groups attached to Sn(2) in the stannocenium cation lies along the Sn(2)-Sn(1) vector. The center of this ring lies 2.362(2)Å from Sn(2) and 3.661(9)Å from Sn(1) and makes the angle <Sn(2)-cent(3)-Sn(1) = 173.5(4)°. The Sn(1)-carbon distances for this ring range from 3.729(8)Å to 3.950(9)Å (avg = 3.848Å). This is longer by more than one Ångstrom than any other η^5-cyclopentadienyl ring to a tin(II) atom in a stannocene derivative. This distance lies closer to η^6-phenyl ring to tin(II) distances listed in Table 2.11.

Long benzene and phenyl ring to π-tin(II) interactions are found in the polymeric solids η^6-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$[20], η^6-$C_6H_6SnCl(AlCl_4)$[21] and η^6-1,4-$(CH_3)_2C_6H_4SnCl(AlCl_4)$.[21] In all three examples the tin(II) atom is surrounded by chlorines and one benzene or phenyl ring symmetrically located to give local C_{6v} symmetry.

In the dimer $\{Sn[S_2P(OC_6H_5)_2]_2\}_2$ the center of one phenyl group lies almost perpendicular to the tin(II) lone pair vector of a second monomeric group at a distance of 3.655Å[22]. In this case, the π-Sn(II)-phenyl interaction contributes to the formation of a dimer and helps to rationalize the compound's chemical stability by shielding the tin(II) lone pair.

In the title compound a similar interaction is observed between Sn(1) and ring three. The center of the ring lies almost perpendicular to the Sn(1)-Sn(2) vector with an angle of 173.5(4)Å and at a distance [d(Sn(1)-cent(3) =

Figure 2.3. Schematic View of Extended Coordination Around Tin Atoms in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$



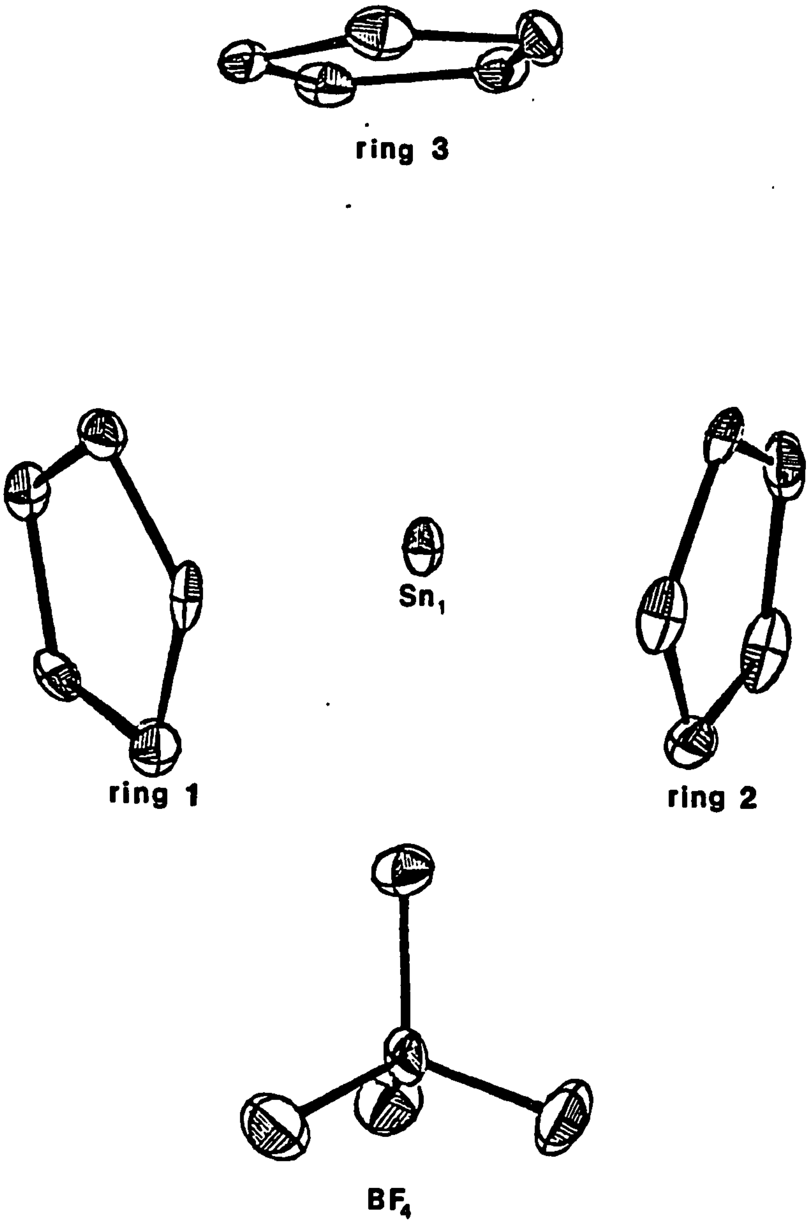
3.661(9)Å]. The significant position of ring three along the tin-tin vector argues for a weak interaction between Sn(1) and Sn(2). With the ring bridging the cation and anion, the charge of both the $[BF_4]^-$ and $[\eta^5-C_5H_5Sn]^+$ are delocalized and neutralized.

Such specially positioned $\mu-\eta^5-C_5H_5$ rings are found along each of the three tin-tin vectors. In this way, each tin atom is coordinated to three cyclopentadienyl rings. The coordination about Sn(1) is two short center of ring distances, [C(1)-C(5)] 2.518(8)Å and [C(6)-C(10)] 2.263(9)Å, and one long distance, [C(11)-C(15)] 3.661(9)Å. The coordination about Sn(2) is two long center of ring distances, [C(1)-C(5)] 2.806(8)Å and [C(6)-C(10)] 3.152(9)Å, and one short distance, [C(11)-C(15)] 2.362(2)Å.

The molecular unit is thus knit into a loose, three-dimensional lattice containing stannocene and stannocenium units associated by $\mu-\eta^5$-cyclopentadienyl bridges of unequal length along the tin-tin vectors. The result is a dissipation of the $[BF_4]^-$ and $[\eta^5-C_5H_5Sn]^+$ charges and a low melting material of ready solubility in polar organic solvents.

In this view, both Sn(1) and Sn(2) atoms can be said to be in $(\mu-\eta^5-C_5H_5)_3SnX$ (X=F, O) units. The stannocene Sn(1) atom resides in a site with two close η^5-cyclopentadienyl rings, one far η^5-cyclopentadienyl ring and a coordinated fluorine atom from an adjacent BF_4 molecule(See Figure 2.4). The stannocenium Sn(2) atom, on the other hand, resides in

Figure 2.4. Coordination Around Sn(1) in $\{[BF_4]^-(\mu-\eta^5-C_5H_5)_2Sn[\mu-\eta^5-C_5H_5Sn]^+\cdot THF\}_n$.

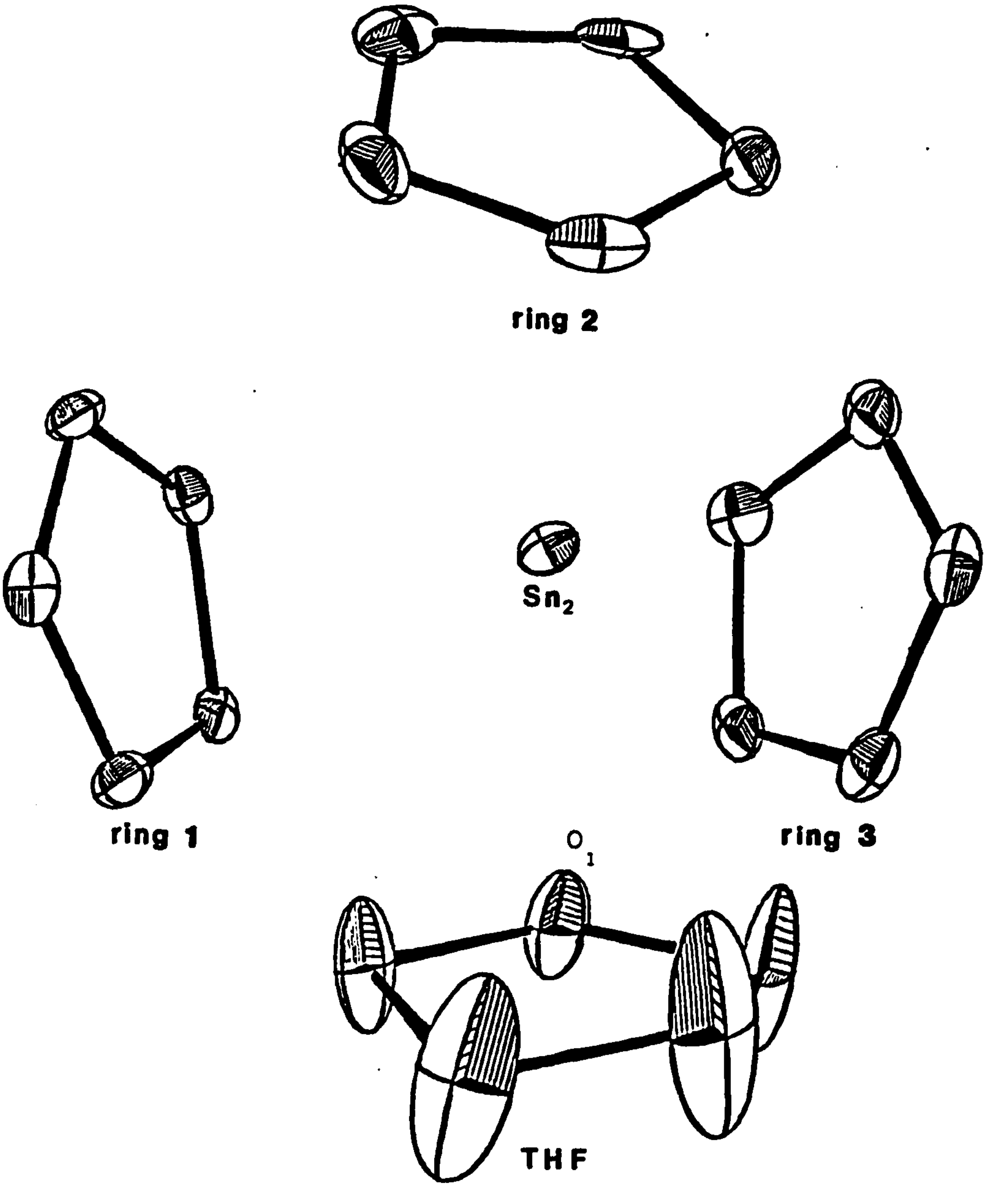


a site with one close η^5-cyclopentadienyl ring, two distant weaker linked η^5-cyclopentadienyl rings, and a coordinated oxygen atom from a neighboring THF molecule. The coordination about Sn(2) is shown in Figure 2.5. In each case, the coordination sphere of the tin atom in the $(\eta^5\text{-}C_5H_5)_3SnX$ units is completed by a lone pair of electrons which occupy an empty volume in the lattice. This gives a Ψ-5 coordination about each tin(II) atom.

Because the two non-equivalent tin atoms reside in a $(\eta^5\text{-}C_5H_5)_3SnX$ (X=F,O) unit, they give rise to only one doublet in a tin-119m Mössbauer resonance spectrum, despite the differences in relative ring distances. As noted earlier, the η^5-cyclopentadienyl ring (ring 3) in the stannocenium unit has the shortest tin-center of ring distance. This perhaps indicates the retention of some cationic character. In the pentamethylstannocenium cation the tin to center of ring distance is 2.158Å compared to the average tin to center of ring distance in decamethylstannocene of 2.394Å.[23]

Despite the great variations in the distances of the rings to the pair of tin atoms they lie between, all three rings are flat with the sums of the internal angles at 540.0°. The ring closest to Sn(2) in the stannocenium unit (ring 3) is most symmetrically held with only 0.072Å between the longest and shortest Sn(2) to ring carbon atom distances. The variation is 0.303Å for the ring next

Figure 2.5. Coordination Around Sn(2) in $\{[BF_4]^-(\mu-\eta^5-C_5H_5)_2Sn[\mu-\eta^5-C_5H_5Sn]^+\cdot THF\}_n$.



closest held (ring 2) and 0.340Å for the farthest of the rings (ring 1). These systematics are reversed in the stannocene system containing Sn(1). The farthest ring (ring 3) shows the least variation (0.221Å) and the closest ring (ring 1) shows the most (0.377Å) with ring 2 in between at 0.268Å.

The preparation of the title compound is accompanied by the disappearance of the tin satellites found in the proton NMR spectrum of stannocene.[1] Indeed, in no report of which I am aware are tin or lead satellites observed in the NMR spectrum of any of the claimed donor-acceptor products.[24-28] I interpret these negative results in terms of a dynamic phenomena involving the acceptor halide-induced exchange of cyclopentadienyl groups between donor and acceptor atom sites, or between the subvalent group IV atoms themselves. The structure of the title compound can then be said to represent one view of a frozen intermediate in the intermolecular exchange of cyclopentadienyl groups between two tin sites. This rapid making and breaking of η^5-C_5H_5-Sn bonds rationalizes the lack of tin satellites in the NMR. The reaction can be written as:

$$2n(\eta^5\text{-}C_5H_5)_2Sn + 2nBF_3 + nTHF \longrightarrow nC_5H_5BF_2 + \{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n \qquad (2.1)$$

which is a fluorine-cyclopentadienyl group transfer reaction and not a Lewis acid-base reaction involving the tin(II) lone pair electrons and a BF_3 molecule as first proposed.[1]

The question still remains why the lone pair of electrons is not the site of attack of the BF_3 producing the simple $(\eta^5\text{-}C_5H_5)_2Sn{:}\rightarrow BF_3$ adduct. Recent theoretical calculations give an answer. Using self-consistent field X_α scattered wave (SCF X_α SW) techniques give the order of the two highest occupied molecular orbitals (HOMO's) as π-type and almost completely localized on the cyclopentadienyl rings.[29] These are followed in order of decreasing energy by two MO's which account for the primary interaction of the C_5H_5 group with the tin 5s and 5p atomic orbitals. The orbital holding the lone pair is 2.0eV lower than the HOMO and is the fifth MO. These results are corroborated by He(I) ultraviolet spectral results (UV PES) as interpreted by the transition state method. The ionization energy at 9.58eV attributed to electron ejection from the stannocene lone pair orbital is approximately 2eV more stable than the HOMO observed at 7.57eV which is a ring localized π MO. This SCF X_α SW sequence of MO's explains why cyclic volammetric experiments on stannocene results in an irreversible oxidation wave rather than the expected process of:[29]

$$(\eta^5\text{-}C_5H_5)_2Sn \rightleftharpoons [(\eta^5\text{-}C_5H_5)_2Sn]^{2+} \qquad (2.2)$$

2.5 CONCLUSIONS

The material resulting from the reaction of stannocene in THF with boron trifluoride etherate originally formulated as $(\eta^5\text{-}C_5H_5)_2Sn: \rightarrow BF_3$, is $\{[BF_4]^-(\mu\text{-}\eta^5C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+ \cdot THF\}_n$. Individual $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF units are linked together into a three-dimensional lattice by weak interactions. These include fluorine bridging between the tetrafluoroborate and stannocene moieties and coordination by THF to the stannocenium cation. Also, each cyclopentadienyl ring lies along a tin-tin vector in a stereochemical-significant position to give a network of bridging $\eta^5\text{-}C_5H_5$ groups and complete charge delocalization to form a neutral complex.

The structure represents a view of a frozen intermediate in the intermolecular exchange of the cyclopentadienyl groups between two tin sites. The reaction between stannocene and boron trifluoride etherate is a fluorine-cyclopentadienyl group transfer and not a Lewis acid-base reaction involving the tin(II) lone-pair electrons and a BF_3 molecule.

Recent theoretical calculations using self-consistent field X_α scattered wave (SCF X_α SW) techniques tell us why the reaction is not a simple Lewis acid-base reaction. The two highest occupied molecular orbitals are π-type almost completely localized on the cyclopentadienyl rings. The orbital holding the lone pair is 2.0eV lower than the HOMO's and is the fifth MO.[29] This then explains the fluorine-cyclopentadienyl group transfer to form the title compound.

Table 2.1, Crystal Data for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn$
$[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$

Formula	$C_{19}H_{23}B_1F_4O_1Sn_2$
Fw	590.91
Crystal system	Orthorhombic
$\underline{a}$, Å	9.258
$\underline{b}$, Å	13.252
$\underline{c}$, Å	16.437
V, Å^3	2016
Space group	$P2_12_12_1$
Z	4
ρ_{calcd}, gm cm^{-3}	1.947
F(0,0,0)	1144

Table 2.2, Data Collection Parameters for $\{[BF_4]^- (\mu-\eta^5C_5H_5)_2Sn[\mu-\eta^5-C_5H_5Sn]^+\cdot THF\}_n$

diffractometer	Enraf-Nonius CAD-4
radiation	Mok$\bar{\alpha}$ (λ=0.71069Å)
temperature, K	135±2
scan technique	Θ-2Θ
2Θ limit, deg.	53
max. scan time, s	60
scan angle, deg.	1.0 + 0.2 tan Θ
aperture width, mm	3.25 + 0.86 tan Θ
aperture height, mm	6
aperture dist., mm	173
monitor reflection	3
orientation monitors	150 reflections[a]
no. of unique data[b]	2080
no. of observed data	2066
corrections	Lorentz-polarization anomalous dispersion

[a] New orientation matrix if angular change >0.12°.

[b] $I>2\sigma(I)$.

Table 2.3. Final Positional Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ $(\times 10^{-4})$[a]

Atom	x	y	z
Sn(1)	2606.5(6)	1438.1(3)	896.1(3)
Sn(2)	-2258.2(6)	-444.4(3)	1510.5(3)
C(1)	718(9)	149(6)	1434(6)
C(2)	442(10)	188(7)	581(6)
C(3)	-351(10)	1076(7)	4198(5)
C(4)	-569(10)	1588(7)	1147(6)
C(5)	64(9)	1023(7)	1775(5)
C(6)	4380(11)	106(7)	1320(6)
C(7)	4701(10)	2749(8)	504(6)
C(8)	5403(11)	1194(8)	420(6)
C(9)	5545(10)	1618(8)	1205(7)
C(10)	4928(10)	960(7)	1757(6)
C(11)	3364(10)	3938(7)	2115(6)
C(12)	3610(11)	3158(7)	2661(6)
C(13)	2291(11)	2756(5)	2893(5)
C(14)	1195(10)	3290(7)	2491(5)
C(15)	1876(10)	4038(7)	1998(5)
B(1)	2533(10)	-490(6)	3515(5)
F(1)	2533(6)	-1173(3)	4168(2)
F(2)	2661(6)	-1037(4)	2803(2)
F(3)	1237(6)	46(4)	3520(4)
F(4)	3648(6)	181(5)	3602(4)
O(1)	2122(7)	3328(4)	4902(3)
C(16)	1885(13)	3800(4)	5673(6)
C(17)	3763(24)	3209(12)	6269(9)
C(18)	3745(23)	2660(15)	5833(7)
C(19)	3212(18)	2588(10)	4988(7)

[a] Estimated standard deviations are in parentheses.

Table 2.4. Thermal Parameters for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$[a]

Atom	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	148(4)	155(2)	314(2)	6(2)	1(2)	48(2)
Sn(2)	253(4)	162(2)	219(2)	-8(2)	-12(2)	44(2)
C(1)	76(51)	209(42)	376(48)	14(30)	21(36)	96(39)
C(2)	219(58)	170(43)	341(48)	10(33)	12(36)	-12(36)
C(3)	183(56)	268(46)	172(40)	-58(33)	-74(32)	51(35)
C(4)	180(55)	130(43)	416(49)	15(32)	0(38)	-6(37)
C(5)	191(56)	256(44)	193(42)	-65(36)	19(32)	-12(36)
C(6)	208(57)	253(48)	388(55)	46(35)	57(37)	146(38)
C(7)	272(63)	359(58)	338(48)	144(43)	-82(38)	-141(45)
C(8)	206(64)	450(65)	452(61)	96(43)	99(42)	191(51)
C(9)	144(59)	261(56)	667(69)	45(37)	-77(46)	-113(49)
C(10)	167(60)	335(51)	375(55)	176(41)	-25(37)	-100(44)
C(11)	295(69)	293(47)	345(48)	-40(38)	62(40)	-156(40)
C(12)	203(62)	255(46)	457(56)	50(39)	-101(44)	-151(41)
C(13)	430(66)	191(34)	334(38)	16(42)	-17(46)	-59(30)
C(14)	245(60)	273(46)	281(42)	-38(36)	46(36)	-143(37)
C(15)	390(70)	300(44)	175(38)	-43(39)	-4(34)	-30(34)
B(1)	186(57)	350(43)	276(36)	-91(47)	-57(43)	-16(35)
F(1)	394(33)	369(23)	236(19)	-1(25)	-36(25)	38(17)
F(2)	504(37)	552(29)	273(22)	58(31)	-15(27)	-34(21)
F(3)	333(36)	643(45)	480(33)	224(28)	-47(29)	54(34)
F(4)	449(39)	513(37)	462(34)	-130(28)	36(28)	81(31)
O(1)	496(47)	363(31)	346(29)	222(32)	-88(29)	-51(24)
C(16)	423(75)	627(68)	388(50)	389(59)	-103(48)	-102(46)
C(17)	1504(199)	960(119)	544(68)	672(127)	-556(101)	-366(83)
C(18)	1755(180)	1642(172)	354(62)	1433(154)	-38(87)	182(84)
C(19)	1216(134)	649(80)	406(53)	725(86)	-139(64)	-119(54)

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[a] Estimated standard deviations in parentheses.

[b] x 10^{-4}.

Table 2.5. Intramolecular Distances (in Å) for $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ [a]

Sn(1)-Heteroatom Distances

Sn(1)-C(1)	2.599(8)
Sn(1)-C(2)	2.651(9)
Sn(1)-C(3)	2.888(9)
Sn(1)-C(4)	2.976(9)
Sn(1)-C(5)	2.816(8)
Sn(1)-C(6)	2.510(9)
Sn(1)-C(7)	2.560(9)
Sn(1)-C(8)	2.742(9)
Sn(1)-C(9)	2.778(9)
Sn(1)-C(10)	2.650(9)
Sn(1)-C(11)	3.935(10)
Sn(1)-C(12)	3.805(9)
Sn(1)-C(13)	3.729(9)
Sn(1)-C(14)	3.821(10)
Sn(1)-C(15)	3.950(6)
Sn(1)-F(1)	2.864(6)
Sn(1)-Sn(2)	5.427(1)

Sn(2)-Heteroatom Distances

Sn(2)-C(1)	2.868(8)
Sn(2)-C(2)	3.047(9)
Sn(2)-C(3)	3.224(9)
Sn(2)-C(4)	3.171(9)
Sn(2)-C(5)	2.932(8)
Sn(2)-C(6)	3.212(9)
Sn(2)-C(7)	3.401(9)
Sn(2)-C(8)	3.552(9)
Sn(2)-C(9)	3.444(9)
Sn(2)-C(10)	3.227(9)
Sn(2)-C(11)	2.612(8)
Sn(2)-C(12)	2.6.7(9)
Sn(2)-C(13)	2.579(9)
Sn(2)-C(14)	2.545(9)
Sn(2)-C(15)	2.571(9)
Sn(2)-O(1)	2.839(10)

C-C Distances in the Cyclopentadienyl Rings

C(1)-C(2)	1.427(13)
C(2)-C(3)	1.413(13)
C(3)-C(4)	1.389(12)
C(4)-C(5)	1.403(12)
C(5)-C(1)	1.422(12)
C(6)-C(7)	1.392(14)
C(7)-C(8)	1.387(15)
C(8)-C(9)	1.414(15)
C(9)-C(10)	1.381(14)
C(10)-C(6)	1.432(14)
C(11)-C(12)	1.388(14)
C(12)-C(13)	1.385(14)
C(13)-C(14)	1.402(13)
C(14)-C(15)	1.427(13)
C(15)-C(11)	1.398(13)

Table 2.5. continued

B-F Distances in Boron Tetrafluoride

B(1)-F(1)	1.405(9)
B(1)-F(2)	1.382(9)
B(1)-F(3)	1.394(11)
B(1)-F(4)	1.370(11)

Tetrahydrofuran Ring Distances

O(1)-C(16)	1.430(12)
C(16)-C(17)	1.494(21)
C(17)-C(18)	1.368(27)
C(18)-C(19)	1.477(18)
C(19)-O(1)	1.413(17)

[a] Estimated standard deviations in parentheses.

Table 2.6. Intramolecular Angles in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$[a]

Angles at the Ring Atoms[b]

C(1)-C(2)-C(3)	107.9(8)
C(1)-C(5)-C(4)	108.8(8)
C(2)-C(1)-C(5)	106.3(7)
C(2)-C(3)-C(4)	108.7(8)
C(3)-C(4)-C(5)	108.2(8)
C(6)-C(7)-C(8)	109.7(9)
C(6)-C(10)-C(9)	108.5(9)
C(7)-C(6)-C(10)	106.3(8)
C(7)-C(8)-C(9)	107.5(9)
C(8)-C(9)-C(10)	108.0(9)
C(11)-C(12)-C(13)	108.6(8)
C(11)-C(15)-C(14)	106.9(8)
C(12)-C(11)-C(15)	108.7(8)
C(12)-C(13)-C(14)	108.3(7)
C(13)-C(14)-C(15)	107.4(8)
O(1)-C(16)-C(17)	105.5(10)
O(1)-C(19)-C(18)	106.8(12)
C(16)-O(1)-C(19)	108.9(8)
C(16)-C(17)-C(18)	107.3(12)
C(17)-C(18)-C(19)	107.7(16)

Angles at Boron Tetrafluoride

F(1)-B(1)-F(2)	108.0(6)
F(1)-B(1)-F(3)	108.9(7)
F(1)-B(1)-F(4)	109.8(7)
F(2)-B(1)-F(3)	110.3(7)
F(2)-B(1)-F(4)	111.4(7)
F(3)-B(1)-F(4)	108.5(7)

Angles through Center of Rings

Sn(1)-cent(1)-Sn(2)	160.4(4)
Sn(1)-cent(2)-Sn(2)	164.3(4)
Sn(1)-cent(3)-Sn(2)	173.3(4)
cent(1)-Sn(1)-cent(2)	138.5(3)
cent(1)-Sn(1)-cent(3)	97.4(2)
cent(2)-Sn(1)-cent(3)	102.1(3)

[a] Estimated standard deviations in parentheses.

[b] In degrees.

Table 2.7. Deviations from Least-Square Planes in $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ (in Å)[a]

Plane	Atom	Deviation from the Plane[b]
1	C(1)	0.005(8)
	C(2)	-0.001(9)
	C(3)	-0.002(9)
	C(4)	0.005(9)
	C(5)	-0.006(9)
2	C(6)	0.003(9)
	C(7)	-0.004(9)
	C(8)	0.002(10)
	C(9)	-0.002(9)
	C(10)	-0.002(9)
3	C(11)	0.000(9)
	C(12)	-0.001(9)
	C(13)	0.001(7)
	C(14)	-0.001(9)
	C(15)	0.000(9)
4	O(1)	-0.010(6)
	C(16)	0.071(12)
	C(17)	-0.111(19)
	C(18)	0.105(20)
	C(19)	-0.055(15)

[a] Estimated standard deviations in parentheses.

[b] In Å units.

Table 2.8. Hydrogen Parameters for

$\{[BF_4]^-(\mu\text{-}\eta^5C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$ $(\times 10^{-4})$[a]

Atom	x	y	z
H(1)	1142(87)	-309(66)	1947(48)
H(2)	736(94)	-260(71)	241(50)
H(3)	-549(96)	1231(71)	-13(54)
H(4)	-1145(102)	2124(74)	1155(54)
H(5)	2(95)	1264(71)	2254(51)
H(6)	3886(89)	-396(70)	1563(49)
H(7)	4571(90)	-42(66)	-15(51)
H(8)	5831(96)	1552(69)	-131(51)
H(9)	5960(94)	2285(72)	1295(52)
H(10)	4652(85)	990(70)	2418(51)
H(11)	4189(92)	4339(67)	1883(50)
H(12)	4471(105)	2982(68)	2817(52)
H(13)	1972(89)	2249(63)	3315(47)
H(14)	75(114)	3301(66)	2548(56)
H(15)	1654(83)	4454(62)	1487(49)
H(16)	2350(89)	4617(60)	5700(43)
H(17)	1032(105)	3786(73)	5745(55)
H(18)	2813(101)	3318(63)	6788(51)
H(19)	2328(129)	2822(75)	6204(65)
H(20)	4761(61)	2393(66)	6026(49)
H(21)	3896(99)	1861(37)	5957(49)
H(22)	3763(105)	2528(71)	4601(55)
H(23)	2722(94)	1818(66)	4898(45)

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[a] Estimated standard deviations in parentheses.

Table 2.9. Least-Squares Planes in $\{[BF_4]^- (\mu-\eta^5-C_5H_5)_2Sn[\mu-\eta^5C_5H_5Sn]^+\cdot THF\}_n$ [a]

Equation: $m_1x + m_2y + m_3z + d = 0$; x,y,z are fractional coordinates.

Plane through atoms	m_1	m_2	m_3	d	Plane P	Dihedral angle between planes [P,P][a]	R.M.S. of atoms defining plane [P,P']
C(1), C(2), C(3), C(4), C(5)	7.9.23	6.6502	-2.1905	-0.3487	1		0.0045
C(6), C(7), C(8), C(9), C(10)	-8.1473	6.1129	-1.8574	3.7524	2	-59.6(2) [1,2]	0.0025
C(11), C(12), C(13), C(14), C(15)	0.4129	-8.5946	-12.4899	5.8882	3	-79.2(2) [1,3] -75.4(2) [2,3]	0.0006
O(1), C(16), C(17), C(18), C(19)	6.2548	9.4977	-2.8420	-3.1047	4	16.2(7) [1,4] -75.8(2) [2,4] -72.3(2) [3,4]	0.0794

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[a] Estimated standard deviations in parentheses.

Table 2.10. Least-Square Planes through Tin Atoms and Center of Rings

Equation $m_1x + m_2y + m_3z + d = 0$; x,y,z are fractional coordinates.

Plane through atoms	m_1	m_2	m_3	d	Plane P	Dihedral angle between planes [P,P][a]	R.M.S. of atoms defining plane [P,P']
Sn(1), Sn(2), cent(1), cent(2)	0.0145	-5.0383	-15.2027	2.0429	1		0.0334
Sn(1), Sn(2), cent(1), cent(3)	2.1495	6.2897	-13.9553	0.5467	2	52.8(2) [1,2]	
Sn(1), Sn(2), cent(2), cent(3)	4.3791	8.5569	-9.8530	-1.6261	3	71.9(2) [1,3] 22.3(3) [2,3]	0.1494
Sn(1), Sn(2), cent(1), cent(2),cent(3)	1.9443	6.5486	-13.8667	0.4386	4	53.6(2) [1,4] 1.7(31) [2,4] 22.5(3) [3,4]	0.4835

[a] Estimated standard deviations on parentheses.

Table 2.11. π-Sn(II)-Carbon Ring Distances

Compound	Range of d(Sn-C)[a]	Reference
$(\eta^5\text{-}C_5H_5)_2Sn$ e.d. [b]	2.706±0.024[c]	31
X-ray	2.56-2.85[d]	32
$\eta^5\text{-}C_5H_5SnCl$	2.45-2.75	33
$[\eta^5\text{-}(CH_3)_5C_5]_2Sn$	2.567-2.770[e]	23
$[\eta^5\text{-}(CH_3)_5C_5Sn]^+[BF_4]^-$	2.462±0.016	23
$\{[\eta^5\text{-}(CH_3)_5C_5]_2Sn(C_5H_5N)\}^+[CF_3SO_3]^-$	2.426-2.651	20
$\eta^6\text{-}C_6H_6Sn(AlCl_4)_2\cdot C_6H_6$	3.06±0.02	21
$\eta^6\text{-}C_6H_6SnCl(AlCl_4)$	3.05-3.39	34
$Sn[S_2P(OC_6H_5)_2]_2$ 2	3.457-4.317	22
$\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn$ $[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$		
Sn(1) to C(1)-C(5)	2.599(8)-2.976(4)	[f]
C(6)-C(10)	2.510(6)-2.778(9)	
C(11)-C(15)	3.729(8)-3.950(9)	
Sn(2) to C(1)-C(5)	2.868(8)-3.224(9)	
C(6)-C(10)	3.212(9)-3.552(9)	
C(11)-C(15)	2.545(9)-2.617(9)	

[a] In Ångstroms.

[b] Gas-phase electron diffraction.

[c] The angle between the ring planes is *ca.* 55°, so the angle between the pyramidal axes passing through the tin(II) is *ca.* 125°.

[d] There are two independent molecules in the unit cell.

[e] The angles between the pyramidal axes passing through the tin(II) atoms in the two independent molecules in the unit cell are 143.6° and 144.6°.

[f] This work.

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CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF N-TRIMETHYLSTANNYLSUCCINIMIDE

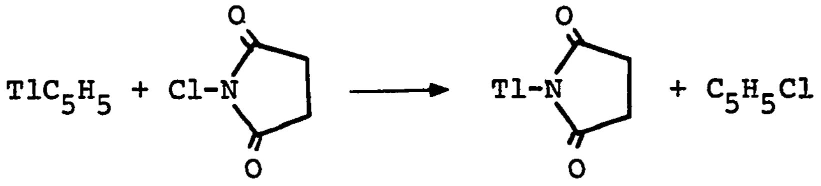
3.1 INTRODUCTION

The title compound was formed in the attempted synthesis of trimethylstannylchlorocyclopentadiene. Trimethylstannylsuccinimide was first prepared by the reaction of N-bromosuccinimide and *para*-tolytrimethyltin.[1] This product, like ours, is an air-stable white crystalline material that is only slightly soluble in common organic solvents. The melting point of our solid, 146-147°C, closely matches the literature value of 148°C.[1] In the ^1H NMR the methylene protons appear as a singlet at 2.65 ppm(lit. [1]2.70). The methyltin protons are observed as a singlet at 0.60 ppm(lit. [1]0.62) with $|^2J(^{119}Sn\text{-}C\text{-}^1H|=$ 59.7Hz (lit. [1]60Hz) when the spectrum is recorded in $CDCl_3$ at 80mHz.

3.2 SYNTHESIS OF N-TRIMETHYLSTANNYLSUCCINIMIDE

Thallium(I) succinimide was made using the method of Rausch for the synthesis of chlorocyclopentadienylthallium(I).[2] The ligand was isolated as an off-white solid, having a melting point of 140°C (lit. [2] 140-142°C).

Cyclopentadienylthallium (10.0g, 37.1mmole), N-chlorosuccinimide (4.95g, 37.1mmole) and diethylether (250mL) were placed in a 500mL three-necked, round-bottom flask equipped with an argon inlet stopcock, magnetic stirring bar and a glass frit filter stick connected to a Schlenk tube. The system was filled with argon and placed in an ice bath. The reactants were stirred for one hour. The resulting chlorocyclopentadiene was filtered into the Schlenk tube by inverting the round-bottom flask. To this solution, thallium(I) ethoxide (9.97g, 40.0mmole, 2.85mL) was added with stirring. A cream-colored solid formed almost immediately. The solution was stirred an additional 30 minutes and filtered under argon. The solid was washed with two portions of diethylether (20mL each). Drying under vacuum yielded a mixture of chlorocyclopentadienylthallium(I) and N-thallium(I) succinimide, 5.56g, according to:

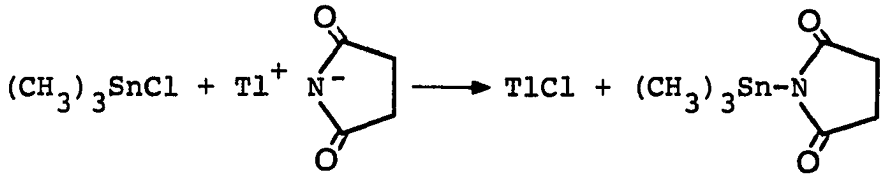


(3.1)

$$C_5H_5Cl + TlOCH_2CH_3 \longrightarrow TlC_5H_4Cl + HOCH_2CH_3 \qquad (3.2)$$

Proton NMR in DMSO-d_6 showed a singlet at 2.22ppm owing to N-thallium(I) succinimide and two triplets at 5.78 (lit. 5.76[2]) and 5.53 (lit. 5.52[2]) ppm owing to chlorocyclopentadienylthallium. The N-thallium(I) succinimide was not identified at this time, but was thought to be a minor impurity.

The cream-colored solid, 1.07g, was placed in an argon-filled 250mL three-necked, round-botton flask equipped with a gas inlet tube, fritted glass filter stick and magnetic stirring bar with dry, oxygen-free tetrahydrofuran (75mL). To the stirring solution at room temperature, a solution of trimethyltin(IV) chloride (0.70g, 3.5mmoles) in tetrahydrofuran (25mL) was added dropwise via syringe to precipitate immediately a white solid according to:



(3.3)

Stirring was continued for 30 minutes, then the mixture was filtered into an argon-filled Schlenk tube. The solvent was removed by vacuum leaving a light brown solid (0.83g). The solid was placed into a vacuum sublimator and heated to 30°C in an oil bath at 0.5 torr. A small amount of unreacted $(CH_3)_3SnCl$ sublimed. The cold finger was cleaned, and the temperature raised to 75°C at 0.5 torr. Clear crystalline $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$ (0.20g) was recovered (21.5% yield). A dark brown solid remained in the sublimator. Table 3.1 lists the physical properties of N-trimethylstannylsuccinimide.

Table 3.1. Physical Properties of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$

			literature[a]
melting point		146-147°C	148°C
%Sn	calcd.	45.32	
	found	44.92	
%C	calcd.	32.10	
	found	32.38	32.3
%H	calcd.	5.01	
	found	4.79	4.89
%N	calcd.	5.35	
	found		5.3

[a] reference 1.

3.3 CHARACTERIZATION OF N-TRIMETHYLSTANNYL SUCCINIMIDE

The infrared spectrum was taken of both the solid using a Nujol mull on cesium iodide plates and of a solution in chloroform using matched 0.1mm potassium bromide cells. The major bands in both spectra are listed in Table 3.2.

Both spectra show the two bands owing to the tin-carbon ν_{sym} and ν_{asym} stretches located at 540 and 510 cm^{-1} in the ir and at 549 and 517 cm^{-1} in the Raman spectra. The fact that both bands are observed indicates the non-planar nature of the $(CH_3)_3Sn$ system. A planar environment of the $(CH_3)_3Sn$ system would produce only the ν_{asym} in the ir and ν_{sym} in the Raman spectra. A non-planar environment of the $(CH_3)_3Sn$ system would produce both bands in the ir and Raman spectra.

The spectrum of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$ is similar to that observed for trimethyltin(IV) chloride in the solid phase. In the ir spectrum of $(CH_3)_3SnCl$, the ν_{asym} and ν_{sym} appear at 545 and 514 cm^{-1}, respectively.[3] The single crystal x-ray structure of $(CH_3)_3SnCl$ shows the nearly planar arrangement of the $(CH_3)_3Sn$ group.[4] The C-Sn-C angles of 117.2° compare well with 120° for an ideal planar arrangement of three methyl groups around a tin atom in this compound. A similar geometry of methyl groups about tin in N-trimethyltin succinimide is observed in the crystal structure where the average C-Sn-C angle was found to be 118.1°.[5] One oxygen atom

Table 3.2. Infrared Spectrum of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$

Solid[a]	Solution[a]
3342 ww	3400 w
3250 ww	3010 m
1862 w	2942 w
1765 w	1745 w
1733 m	1723 m
1640 s broad	1673 s
1345 s	1438 m sharp
1280 s sharp	1340 s
1213 s	1291 m sharp
1186 s	1200 s broad
1008 m sharp	1008 w sharp
980 w	990 w sharp
880 w	881 w
823 w	818 w
780 s	775 s broad
651 m	670 s
540 m sharp	540 m sharp
510 w	510 w
385 m sharp	332 m
328 m sharp	325 w

[a] s-strong; m-medium; w-weak; ww-very weak, cm^{-1}.

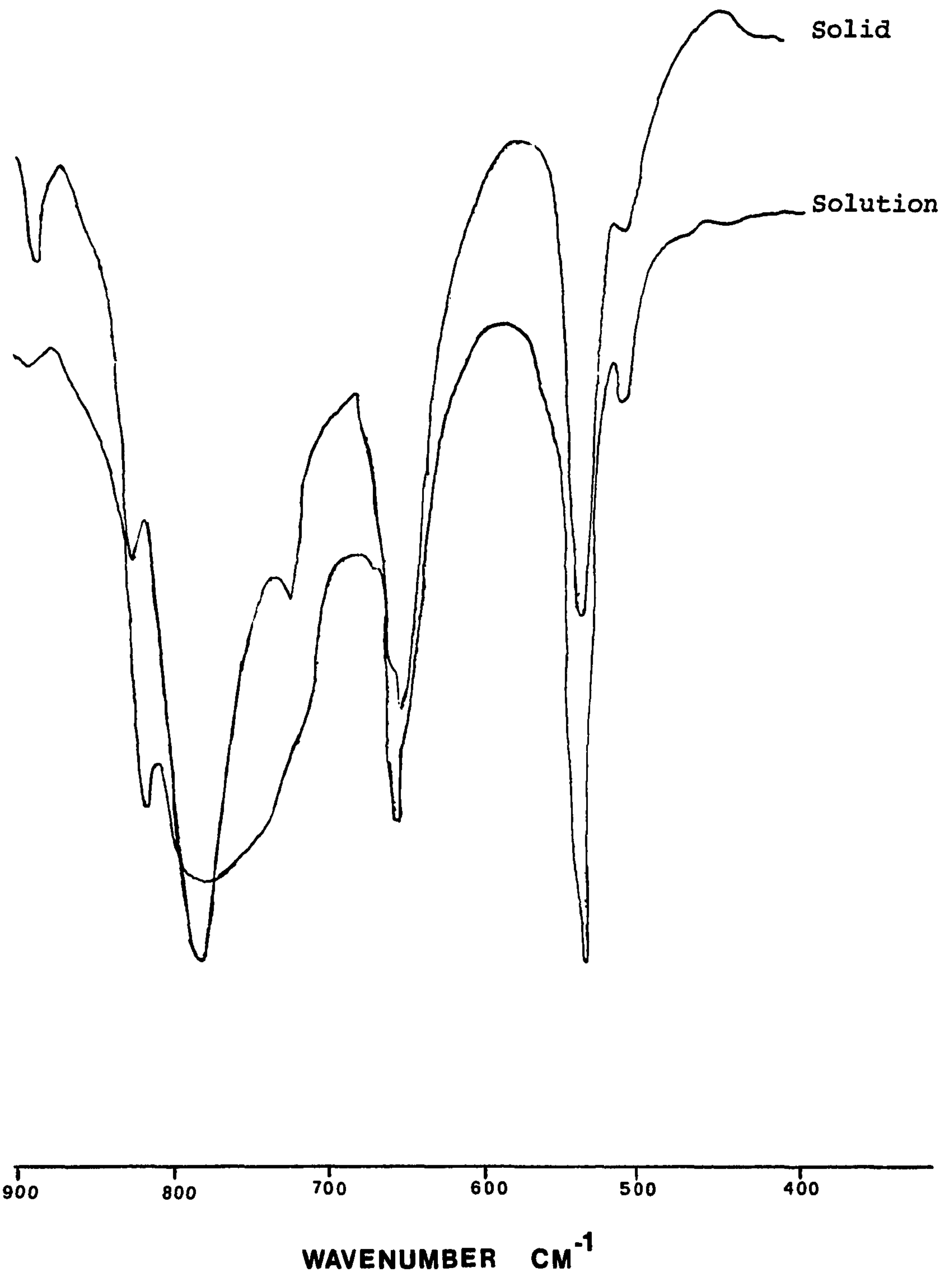
on each succinimide ring is coordinated to a tin atom in another molecule producing an infinite, one-dimensional, helical polymer.

Figure 3.1 shows the solid and solution ir spectra in the $(CH_3)_3Sn$ stretching region. In solution monomeric, tetrahedral $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$ molecules are expected based on nmr data. In the solution spectrum ν_{asym} and ν_{sym} are observed as expected. The solid spectrum also shows both bands in almost the same relative intensity as the solution spectrum even though the $(CH_3)_3Sn$ system is almost planar.

In the solid ir spectrum, the carbonyl band appears at 1640 cm^{-1}. The solution spectrum shows this band at 1673 cm^{-1}. The carbonyl band in the solid spectrum is quite broad and includes the 1673 cm^{-1} band seen in the solution spectrum. This suggests two different types of carbonyl groups in the solid. Coordination of one oxygen atom to tin would produce the observed effect. Carbonyl groups are generally weak donors toward tin. But amides are known to coordinate to Lewis acids through the oxygen atom of the carbonyl group.[6] The x-ray crystal structure shows one oxygen atom coordinated to a tin atom creating two different types of carbonyl groups in the solid.

The vibrational data are, therefore, confirmatory. The carbonyl region of the solid accurately predicts the two types of carbonyl groups as found in the x-ray structure. In the solution spectrum, the carbonyl region shows only

Figure 3.1. Solid and Solution Infrared Spectra of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C(O)}$



one band, one type of carbonyl, as suggested by nmr data. The tin-methyl stretching region is not as conclusive as the carbonyl region. What is observed in both solid and solution spectra are two bands with radically different intensities. Based on vibrational data, the solid and solution coordination about the tin and the molecular structure cannot be distinguished.

The ^{13}C NMR spectrum was recorded by Dr. Paul G. Schmidt on a home-made 300MHz instrument using Nicolet software at the Oklahoma Medical Research Foundation. The proton-decoupled, ^{13}C spectrum consists of a singlet at 185.93 ppm owing to the carbonyl carbons in the succinimide ring, a singlet at 31.20 ppm owing to the methylene carbons in the succinimide ring, and a singlet at -4.56 ppm owing to the methyltin carbon atoms. Carbon-tin coupling was observed with $|^{1}J(^{13}C-^{119}Sn)| = 394.96$Hz.

Table 3.3 lists the ^{13}C NMR chemical shifts of several compounds containing the trimethyltin group along with the $^{119}Sn-^{13}C$ spin-spin coupling constants for these compounds. The $|^{1}J(^{119}Sn-^{13}C_{Me})|$ constants have been shown to be a good test for the tin coordination number.[7] Coupling constants for tetraalkyltin compounds fall between 300 to 340Hz. In four-coordinated trialkyltin compounds $|^{1}J(^{119}Sn-^{13}C)|$ are in the range 330 to 390Hz. Five-coordinated trialkyltin(IV) compounds show a range of 450 to 480Hz. Four-coordinated dialkyltin (IV) compounds have tin-carbon couplings in the range of

370 to 480Hz, while the six-coordinated compounds have a range between 900 and 970Hz.

The crystal structure of $(CH_3)_3SnCl \cdot py$ has been found to be trigonal bipyramidal.[12] The three methyl groups lie in a plan. The compound is monomeric in the orthorhombic space group Pnma. The tin is five-coordinated in this structure. The $|^1J(^{119}Sn-^{13}C_{Me})|$ of 472Hz indicate that this compound is also five-coordinated in solution. In the crystal structure of $(CH_3)_3SnCl$ the tin is five-coordinated with chlorine atoms bridging two trimethyltin moieties. In solution, the compound is a monomer as evidenced by the small tin-carbon coupling constant of 386Hz.

N-trimethyltin succinimide shows a tin-methyl carbon coupling constant of 394.96Hz. Although this is near the upper observed limit for four-coordinated trialkyltin(IV) compounds, N-trimethyltin succinimide is clearly four-coordinated in solution. This rather high tin-carbon coupling, and the $Sn-C_{Me}$ ν_{sym} and ν_{asym} stretches in the solution ir may argue for some small amount of association in solution.

In the ^1H NMR of N-trimethyltin succinimide, the methyl protons were observed at 0.60 ppm $|^2J(^{119}Sn-C-^1H)| = 58.9Hz$ and the methylene succinimide protons at 2.65 ppm relative to tetramethylsilane in $CDCl_3$. The ring protons have been shifted downfield with respect

Table 3.3. ^{13}C NMR Data for $(CH_3)_3SnR$ Compounds

compound	$\delta C(CH_3)^{a}$	$\lvert {}^{1}J({}^{119}Sn-{}^{13}C)\rvert^{b}$	reference
$(CH_3)_3SnH$	-11.8	351.8	7
$(CH_3)_4Sn$	-9.6	337.8	7, 10
$(CH_3)_3SnC_5H_5$	-6.6	352.5	11
$(CH_3)_3SnCH_2CH_3$	-11.2	320.8	10
$(CH_3)_3SnCH_2CH_2CH_3$	-10.4	320.0	10
$(CH_3)_3SnCl$	0.0	386.0	8
$(CH_3)_3SnBr$	-0.1	372.0	8
$(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$	-4.56	394.96	this work
$(CH_3)_3SnN(CH_3)_2$	-8.7	381.2	9
$(CH_3)_3SnN(CH_2CH_3)_2$	-6.7	380.0	7, 9
$(CH_3)_3Sn\overline{NCH_2CH_2CH_2CH_2}$	-8.5	380.8	9
$(CH_3)_3Sn\cdot py$	2.1	472.0	7

[a] In ppm with respect to $(CH_3)_3Si$.

[b] In Hz.

to the protons in N-thallium(I) succinimide (2.22 ppm). The low ^{119}Sn-^{1}H coupling constant also indicates only four-coordination around the tin in solution.[13]

The ^{119}Sn Mössbauer spectrum of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$ consists of a doublet with an isomer shift of 1.31±0.03mm/sec and a quadrupole splitting of 3.14±0.06mm/sec. The spectrum is shown in Figure 3.2. The isomer shift is in the range assigned to tin(IV) compounds.[14] The rather large quadrupole splitting value when divided by the isomer shift yields a rho(ρ) value of 2.40. Rho values above 2.0 indicate a coordination number greater than four around the tin atom. This is confirmed by the x-ray crystal structure which shows a helical polymer bonded by a bridging oxygen atom in the succinimide ring.[5]

The mass spectrum also indicates an associated solid. The highest m/e value at 509, corresponds to a dimeric unit missing one methyl group. The base peak at 248 is caused by a monomer minus one methyl group. The rest of the spectrum shows progressive break-up of the succinimide ring and loss of methyl groups attached to tin. The spectrum is listed and interpreted in Table 3.4.

3.4 CONCLUSIONS

The compound N-trimethylstannyl succinimide was synthesized by the reaction of trimethyltin chloride with N-thallium(I) succinimide. This succinimide salt was produced in the preparation of chlorocyclopentadienyl-

Figure 3.2. ^{119}Sn Mössbauer Spectrum of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$

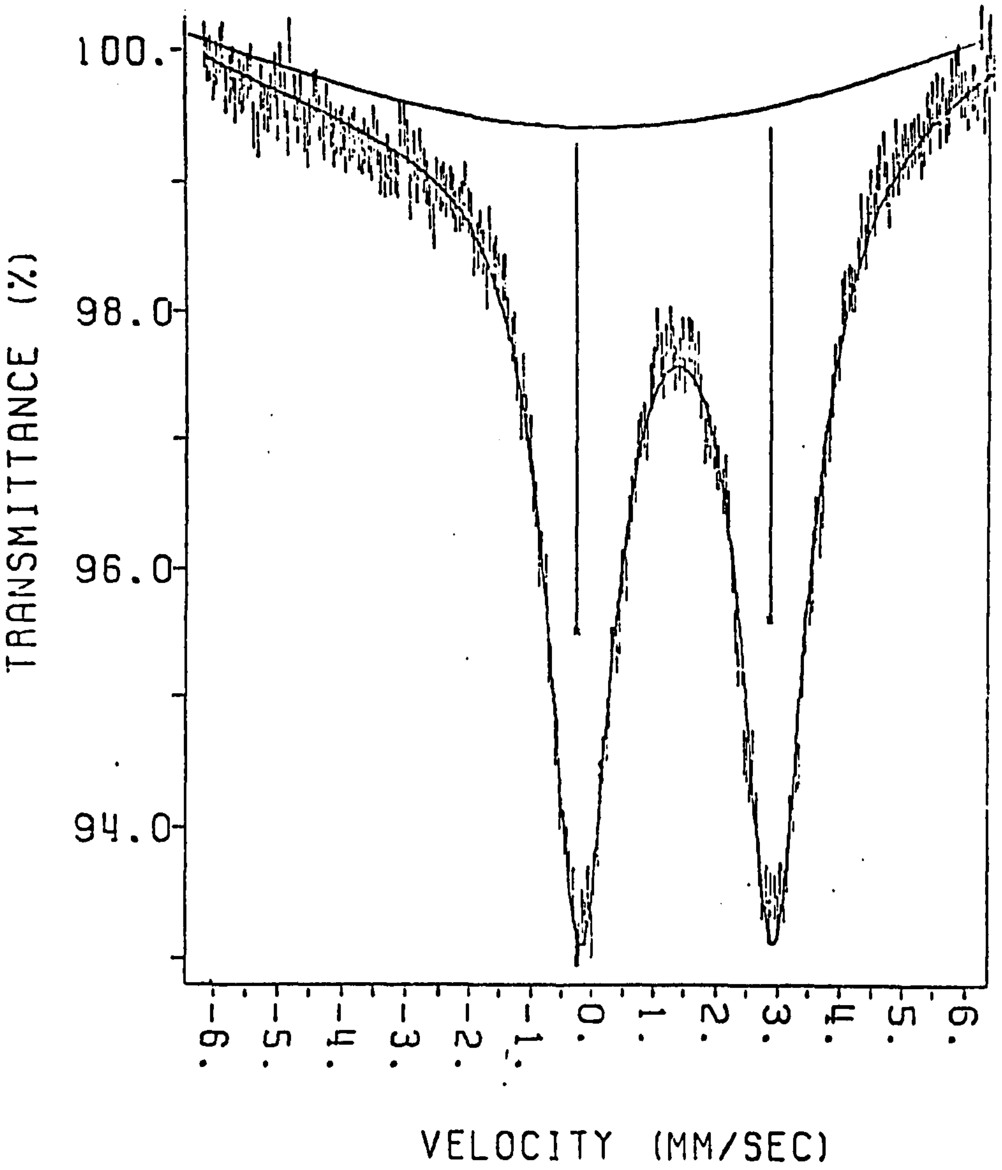


Table 3.4. Mass Spectrum of $(CH_3)_3Sn\overline{NC(O)CH_2CH_2C}(O)$

Peak Center[a]	Abundance	Assignment
509	2.0	$\{[(CH_3)_2SnNCH_2CH_2C(O)]_2\text{-}CH_3\}^{+\cdot}$
248	100.0	$[(CH_3)_2SnNC(O)CH_2CH_2C(O)]^+$
218	45.8	$[SnNC(O)CH_2CH_2C(O)]^+$
190	26.6	$[SnNC(O)CH_2CH_2]^+$
177	7.5	$[SnNC(O)CH_3]^+$
162	68.4	$[SnNC(O)]^+$
150	11.6	$[(CH_3)_2Sn]^{+\cdot}$
135	77.1	$[CH_3Sn]^{+\cdot}$
99	2.6	$[NC(O)CH_2CH_2C(O)]^+$
82	5.2	$[NC(O)CH_2CH_2C]^+$
70	38.9	$[NC(O)CH_2CH_2]^+$
56	26.3	$[NC(O)CH_2]^+$
55	30.7	$[NC(O)CH]^{+\cdot}$
42	12.8	$[NCO]^+$

---

[a] Atomic mass units based upon ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{120}Sn.

thallium(I). Following the synthesis of Rausch, two products were formed. The reaction of this mixture with trimethyltin(IV) chloride resulted in the isolation of only one (tin-containing) product, N-trimethylstannylsuccinimide. This compound was determined to be a monomer in solution using $|^1J(^{119}Sn-^{13}C)|$ and $|^2J(^{119}Sn-^1H)|$ coupling constants in the nmr spectra. In the solid phase, the compound was determined to have higher than four-coordination about the tin as shown by the Mössbauer rho value, ir ν_{sym} and ν_{asym} tin-carbon stretches in the ir and Raman and the mass spectrum. The ultimate proof of an associated solid was the single crystal x-ray structure.[5] The compound was found to be a helical, one-dimensional polymer formed by bridging oxygen atoms to a tin atom. The coordination number at tin was determined to be five.

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CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF STANNOCENES

4.1 INTRODUCTION

Stannocene and its derivatives are angular sandwich compounds with stereochemically, and presumed chemically active lone pair electrons present in the divalent state of tin. The lone-pair electrons occupy the third site of the trigonal coordination of the metal atom. Altering the steric and electrical properties of the cyclopentadienyl rings through substitution will alter the angles made by the tin to the two cyclopentadienyl rings. A change in bond angle will change hybridization, spatial extension and basicity of the lone-pair electrons. Attempts to synthesize ring-substituted stannocenes using methods that produce ring substituted ferrocenes have failed.

Another approach is to design ligands containing two linked cyclopentadienyl anions in varying proximity and juxtaposition. Several such ligands are known. They have been used to form bridged dimetallic compounds such as $[\eta^5\text{-}C_5H_4CR_1R_2CR_1R_2\text{-}\eta^5\text{-}C_5H_4]Fe_2(CO)_4$ where R_1 = H,

$R_2 = N(CH_3)_2$[1] and $R_1 = R_2 = CH_3$[2,3] and $(CH_3)_2Si[\eta^5-C_5H_4Fe(CO)_2]_2$.[4,5] Additional complexes of the silicon-bridged system which do not contain a metal-metal bond are $(CH_3)_2Si[\eta^5-C_5H_4M(CO)_3]_2$ where M = Mn, Re and $(CH_3)_2Si[\eta^5-C_5H_4Co(CO)_2]_2$.[6] Another ligand containing two linked-cyclopentadienyl anions is based upon the *meta*-isomer of α-α′-dicyclopentadienyl xylene.[4,7] Bridged bimetallic derivatives made from this ligand include *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$, *m*-$C_6H_4[CH_2C_5H_4M(CO)_3CH_3]_2$ and *m*-$C_6H_4[CH_2C_5H_4MC_2H_5]_2$, where M = Mo, W.[7]

I report here the synthesis of the *ortho*- and *para*-isomers of disodium (phenylenedimethylene)dicyclopentadienide and the use of only one metal atom, tin, to form ring bridged stannocenes, stannocenophanes. Model studies show that all three disodium (phenylenedimethylene)dicyclopentadienide isomers can bind a single tin(II) atom in a number of different angular positions in both monomer and polymer forms. The reaction of tin(II) chloride and π-cyclopentadienyltin(II) chloride with the *ortho*-, *meta*-, and *para*-isomers of the disodium salt of phenylenedimethylene dicyclopentadienide are described in this chapter.

4.2 SYNTHESIS OF α α′-DICYCLOPENTADIENYLXYLENE

α,α′-Dibromo *ortho*-, *meta*-, and *para*-xylenes were purchased from Aldrich Chemical Co. Freshly cracked cyclopentadiene (1.33g, 20.1mmol) in THF (10mL) was added to a suspension of sodium hydride (1.05g, 43.7mmol) in

THF (10mL) at 0°C over 15 minutes. The NaH was a 56% suspension in oil which was washed with three 10mL portions of THF before use. Stirring was continued until hydrogen production ceased, and the sodium cyclopentadienide product filtered under nitrogen to a pressure equalizing dropping funnel.

The sodium cyclopentadienide thus produced was added to the α,α'-dibromoxylene (2.64g, 10.0mmol) in THF (5mL) at 0°C under nitrogen. The mixture was stirred an additional 45 minutes and then filtered under nitrogen into a dropping funnel. The sodium bromide produced was washed twice with THF (5mL), and the washings added to the filtrate. The reaction is shown in Equation 4.1.

$$2NaC_5H_5 + C_5H_4(CH_2Br_2)_2 \rightarrow C_6H_4(CH_2C_5H_5)_2 + 2NaBr \qquad (4.1)$$

4.3 SYNTHESIS OF DISODIUM (PHENYLENEDIMETHYLENE) DICYCLOPENTADIENIDE

The light amber solution produced above was added dropwise to a THF (10mL) suspension of sodium hydride (3.37g, 140.mmol) under nitrogen at 0°C with stirring. The NaH had been previously washed twice with THF (10mL). After addition was completed, the mixture was allowed to warm to room temperature and stirred an additional 45 minutes until hydrogen evolution ceased. The clear, amber product mixture was filtered into a round-bottomed flask. This reaction is shown in Equation 4.2.

$$C_6H_4(CH_2C_5H_5)_2 + 2NaH \longrightarrow C_6H_4(CH_2C_5H_4Na)_2 + H_2 \quad (4.2)$$

Like other cyclopentadienide salts, this dianion is very air sensitive and solutions may vary from light amber to reddish brown depending on the care taken to exclude air in the preparation.

4.4 SYNTHESIS OF PHENYLENEDIMETHYLENE BIS (η^5-CYCLOPENTADIENYL)Tin(II)

To the THF solution of disodium (phenylenedimethylene) dicyclopentadienide produced above was added tin(II) chloride (1.89g, 10.0mmol) in THF (10mL) dropwise via syringe over *ca.* 20 minutes at room temperature with stirring. The solution turned from clear amber to a creamy white suspension which was allowed to stir for an additional 45 minutes and filtered under nitrogen to remove the sodium chloride formed according to Equation 4.3.

$$C_6H_4(CH_2C_5H_4Na)_2 + SnCl_2 \longrightarrow C_6H_4(CH_2C_5H_4)_2Sn + 2NaCl \quad (4.3)$$

The sodium chloride was washed twice with THF (10mL) and the washings combined with the filtrate. The clear yellow filtrate was evaporated under vacuum to give the product. For the *ortho*-isomer, using 2.26g, 8.56mmol of α-α'-dibromoxylene gave 1.43g of the product in 47.8% yield. For the *meta*-isomer, 2.64g, 10.0mmol gave 1.35g of product (38.5% yield) and for the *para*-isomer, 5.28g, 20.1mmol gave 3.28g of product for 46.5% yield. Microanalytical data calculated for $C_{18}H_{16}Sn$ is 61.58%C, 4.60%H, 33.81%Sn; for the *meta*-isomer, found 61.40%C, 5.55%H, 33.02%Sn.

4.5 SYNTHESIS OF *meta*-PHENYLENEDIMETHYLENE BIS η^5-CYCLOPENTADIENYLTIN(II) BIS(η^5-CYCLOPENTADIENYL)

To disodium (*meta*-phenylenedimethylene)dicyclopentadienide (5.0g, 18mmol) in THF (150mL) in an argon atmosphere was added a solution of η^5-cyclopentadienetin(II) chloride (7.8g, 35mmol) in THF (200mL) via syringe. A white solid formed shortly after the η^5-cyclopentadienetin(II) chloride was added. Stirring was continued for one hour. The solution was filtered and the solvent removed via vacuum leaving the product (6.3g, 75% yield) according to Equation 4.5.

$$m\text{-}C_6H_4(CH_2C_5H_4Na)_2 + 2\eta^5\text{-}C_5H_5SnCl \rightarrow m\text{-}C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2\text{-}Sn(\eta^5\text{-}C_5H_5)_2 + 2NaCl \qquad (4.5)$$

Microanalytical data calculated for $C_{28}H_{26}Sn_2$ was 39.57% Sn, found; 38.91% Sn.

4.6 SYNTHESIS OF *meta*-PHENYLENEDIMETHYLENE BIS (η^5-CYCLOPENTADIENYL)TIN(II) BF_3 DERIVATIVE

To *m*-phenylenedimethylene bis(η^5-cyclopentadienyl) tin(II) (5.0g, 1.4mmol) in THF (100mL) in an argon atmosphere was added freshly distilled boron trifluoride etherate (2.0g, 14mmol, 1.7mL) dropwise via syringe with stirring. Stirring was continued at room temperature for one hour subsequent to the end of addition. Approximately 80% of the solvent was removed by vacuum. Addition of ether (50mL) resulted in formation of the boron trifluoride adduct. Filtration and vacuum drying gave 5.1g, 85% yield. Microanalytical data calculated for $C_{18}H_{16}BF_3Sn$ was 28.34% Sn, found; 27.22% Sn.

4.7 CHARACTERIZATION OF PHENYLENEDIMETHYLENE BIS (η^5-CYCLOPENTADIENYL)TIN(II)

All products are air-sensitive, off-white powders soluble in THF, benzene, toluene and acetone. All products soften at *ca.* 230°C, but do not melt. Exposure to air causes darkening and conversion to the corresponding tin(IV) oxides:

$$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn + \tfrac{1}{2}O_2 \rightarrow C_6H_4(CH_2C_5H_4\text{-}\eta^1)_2SnO \qquad (4.6)$$

which were not isolated. Further reaction to air yields tin(IV) oxide. A similar oxidation has been proposed for stannocene.[8] This change from tin(II) stannocenophane to tin(IV) oxide can be followed using Mössbauer spectroscopy. Figure 4.1 shows the tin(II) stannocenophane *meta*-$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn$ with an isomer shift of 3.79 ± 0.02mm s^{-1}. Figure 4.2 illustrates the *meta*-isomer after exposure to air. The main resonance absorption at zero mm s^{-1} is caused by tin(IV) oxide. The other minor absorptions are a result of partially oxidized stanno-

Figure 4.1. ^{119}Sn Mössbauer Spectrum of *meta*-$C_6H_4(CH_2C_5H_4)_2Sn$

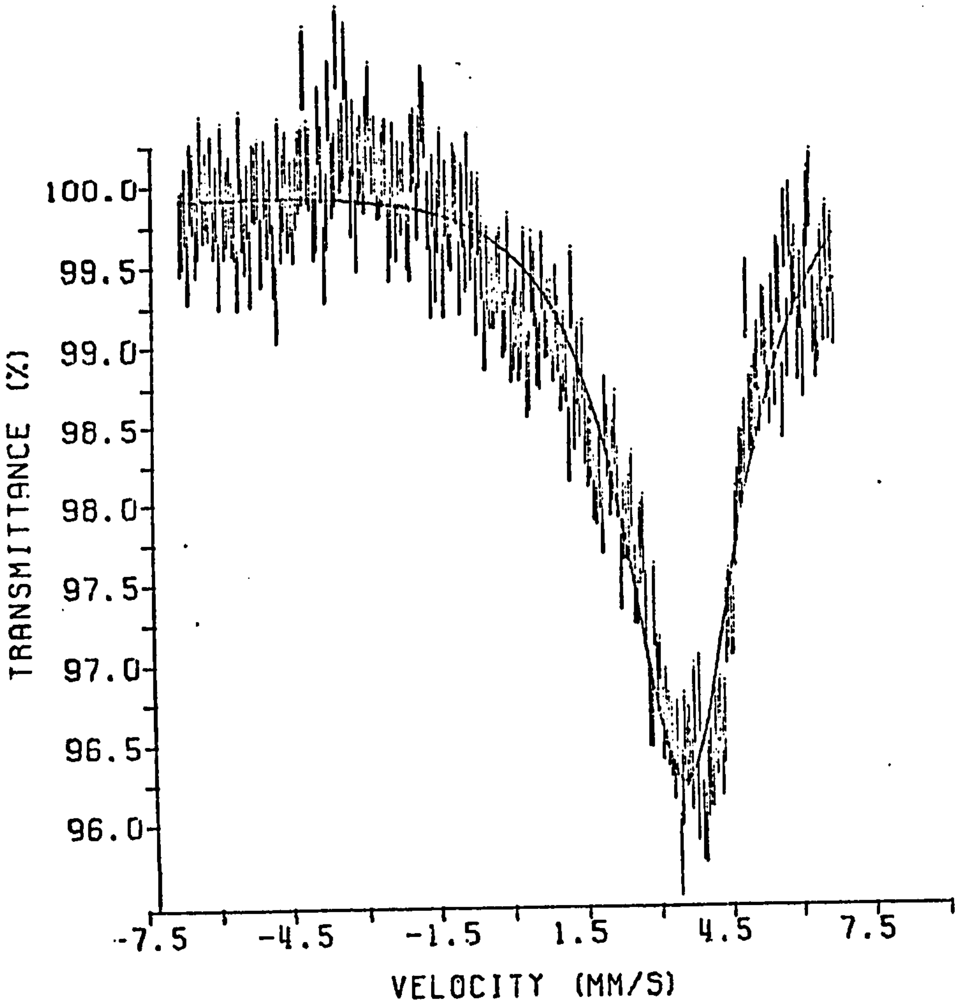
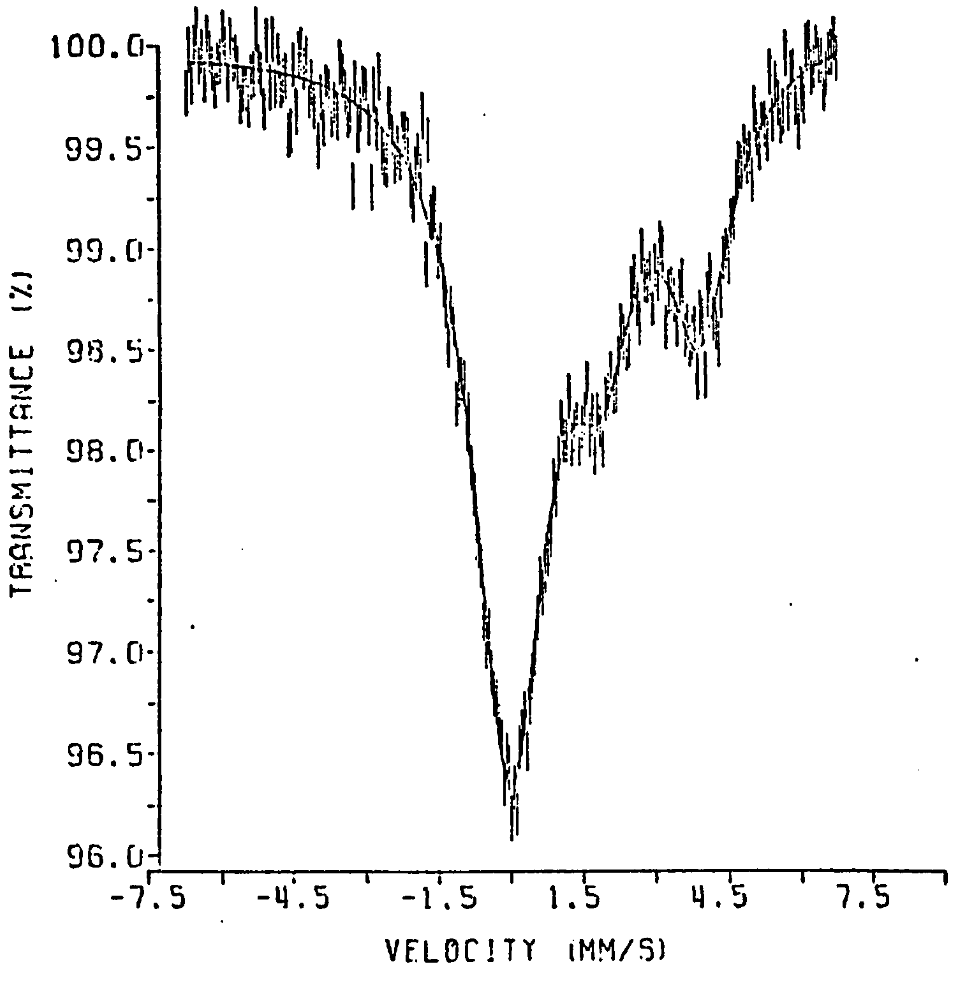


Figure 4.2. ^{119}Sn Mössbauer Spectrum of Air-Oxidized *meta*-$C_6H_4(CH_2C_5H_4)_2Sn$



cenophane.

The tin-119m Mössbauer data for all isomers are listed in Table 4.1 along with other diorganotin(II) derivatives for comparison. All stannocenophane isomers are compatible with divalent tin compounds[9,10] and resemble stannocene itself.[8] Angular distortion of the Ψ-trigonal coordination sphere of the tin atom would bring about a rehybridization of each of the three orbitals emanating from the tin atom to make its bonds. The sum of the s-electron density of the nucleus, $|\Psi_s(0)|^2$, should be unaffected and so the isomer shift (IS) will not change by much. Quadrapole splitting (QS) values are a measure of the electric field gradient at the tin nucleus. This gradient should increase with the percentage of p-character in the lone pair and s-character in the bonding orbital. The minimum QS value occurs when two linearly disposed ligands are bonded by atomic 5p-orbitals at tin and the lone pair is in a spherically symmertical, 5s-atomic orbital. In stannocene the tin atom is roughly sp^2-hybridized in the solid[11] and gas phases[12] which produces a QS of 0.86mm s^{-1}.[13]

The QS value for the *ortho*- and *para*-isomers are large. This implies a large electric field gradient at the tin nucleus caused by distortion of the Ψ-trigonal coordination sphere of the tin atom. Narrow angles between the cyclopentadienyl rings and tin atom as predicted from model studies of the isomers would cause the distortion observed in the large QS values. Model studies indicate the cyclo-

Table 4.1. Tin 119m Mössbauer Data for Diorganotin(II) Derivatives. [a]

Compound	I.S.	Q.S.	Ref.
ortho-$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn$	3.32±0.03	1.84±0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn$	3.79±0.03	0.93±0.06	[b]
para-$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn$	3.36±0.03	1.29±0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}\eta^5)_2Sn\text{-}BF_3$	3.79±0.03	0.93±0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}\eta^5\text{-}Sn\text{-}\eta^5\text{-}C_5H_5)_2$	3.23±0.03	2.08±0.06	[b]
$(\eta^5\text{-}C_5H_5)_2Sn$	3.74	0.86	8
$(\eta^5\text{-}CH_3C_5H_4)_2Sn$	3.83	0.78	15
$[\eta^5\text{-}(CH_3)_5C_5]_2Sn$	3.53±0.03	0.99±0.06	[b]
$[\eta^5\text{-}(CH_3)_5C_5Sn]^+[CF_3SO_3]^-$	3.81±0.03	0.00	[b]
$\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$ [c]	3.79	0.90	13,18
bis(phenylcarboranyl)tin(II)	2.95	1.90	19
$[2,6\text{-}(CF_3)_2C_6H_3]_2Sn$	3.37	1.93	20
$[2,4,6\text{-}(t\text{-}C_4H_9)_3C_6H_2]_2Sn$	3.28	1.90	20
$[\{[(CH_3)_3Si]_2CH\}Sn]_2$	2.16	0.00	21

[a] Recorded at 77K in mm s^{-1} *vs* a $Ca^{119m}SnO_3$ source held at ambient temperature.

[b] This work.

[c] A reformulation of the product of stannocene in THF with BF_3 etherate,[13] formerly thought to be $(\eta^5\text{-}C_5H_5)_2Sn\text{-}BF_3$.[18]

pentadienyl rings to tin angle in the *meta*-isomer should be closest to the average angle of 145.8°[11] found in stannocene. Similar values of QS are in support of this argument.

The infrared-spectral data for the phenylenedimethylene bis(η^5-cyclopentadienyl)tin(II) isomers and boron trifluoride derivative are listed in Table 4.2. Symmetry arguments can be used to rule out a σ-bonded diene-type cyclopentadienyl to tin(II) bonding.[14] Sigma-bonded cyclopentadienyl compounds have a lower symmetry than the symmetry π-bonded compounds. Accordingly, the infrared spectra will have a greater number of bonds when compared with π-bonded cyclopentadienyl compounds. Also, in the far infrared region metal-carbon stretching vibrations should appear. Bands owing to C=C bonds in the 1550 to 1650cm^{-1} region should be especially observable. These bonds are not observed for any of the isomers or the boron trifluoride derivative.

The observed infrared bonds compare favorably with those assigned to dicyclopentadienyltin(II) and bis (methylcyclopentadienyl)tin(II).[15] Using the idea of local symmetry and assuming the methyl group as a point mass, the symmetry of the methylcyclopentadienyl ring is C_{2v}. Twenty-four normal modes of vibration are expected and found. Using the same method of local symmetry, and assuming the methylene group as a point mass, the symmetry of the cyclopentadienyl rings in the phenyldimethylene bis(η^5-cyclopentadienyl)tin(II) isomers and boron

Table 4.2. Infrared Bands for the Bis[(Phenylenedimethylene)-η^5-dicyclopentadienyl]tin(II) Isomers and BF_3 Derivative.[a]

ortho-[b]	*meta*-[c]	*meta*-BF_3[d]	*para*-[b]
2908m	3005w	3175w	3048m
2850sh	2955m	2670w	2950sh
2255m	2920s	1600w	2922w
2140w	2855m	1260m	2000w
1880w	1950s	1152m	1908w
1750w	1800s	1088s	1735w
1483w	1605m	1072s	1612w
1445m	1430m	1038s	1512s
1430sh	1370m	968m	1430s
1253m	1260m	890m	1364m
1214m	1070m	842w	1258w
1182m	1005m	807m	1105m
1070w	905w	791m	1022m
942w	762s	670w	895m
790w	650m	266w	800s,br
760s	221w		675m
732m			580m,br
597s			385s
527m			340m
382s			268m
303s			
268w			

[a] In cm^{-1}. s=strong, m=medium, w=weak, sh=shoulder, br=broad.

[b] Cesium iodide pellet.

[c] Benzene solution in matching 0.5mm potassium bromide cells.

[d] Nujol mull on potassium bromide plates.

trifluoride derivative should also be C_{2v}. On this basis, many of the bands can be assigned. The phenylenedimethylene part of the molecule can be assigned C_{2v} local symmetry for the *ortho*- and *meta*-isomers or D_{2h} symmetry for the *para*-isomer. A comparison between the infrared spectra of *ortho*-, *meta*- and *para*-xylenes and the corresponding stannocenophane isomers shows many of the same bands.

For example, bands at 1612, 1512, 1430 and 1364 cm^{-1} in the spectrum of *para*-stannocenophane and at 1630, 1512, 1452 and 1378 cm^{-1} in the spectrum of *para*-xylene can be assigned to $C \overset{\cdots}{-} C$ phenyl ring stretches.[16] Also, located at 800 cm^{-1} for *para*-stannocenophane and at 792 cm^{-1} for *para*-xylene lies a bond assigned to the out of plane C-H bond.[16]

The asymmetric tin-cyclopentadienyl ring stretch has been assigned to a band at 260 cm^{-1} in the spectrum of stannocene, but is unassigned for the methylcyclopentadienyl analogue.[15] However, in the Raman spectrum of the methylcyclopentadienyl analogue a band at 237 cm^{-1} has been assigned this stretch.[15] The half-sandwich compound, $(\eta^{5}\text{-}C_5H_5)SnCl$, as a solid shows the asymmetric tin-ring stretch at 269 cm^{-1} in the infrared spectrum.[22] The adduct $(\eta^{5}\text{-}C_5H_5)SnAlCl_4$ has this stretch at 255 cm^{-1}.[22] The asymmetric tin-ring stretch of the *ortho*-, *meta*-, and *para*-isomers has been assigned to bands at 268, 221 and 268 cm^{-1}, respectively. The band at 266 cm^{-1} in the boron trifluoride adduct spectrum is assigned to the asymmetric tin-ring stretch.

The infrared spectrum of the boron trifluoride adduct of the *meta*-isomer contains additional bands at 1152 and 807 cm^{-1} not found in the spectrum of the *meta*-isomer. Bands at 1160 and 810 cm^{-1} have been assigned to $\nu_d(BF_3)$ and $\nu_s(BF_3)$, respectively in the spectrum of the boron trifluoride adduct of stannocene.[13] The same assignment has been made for bands at 1165 and 812 cm^{-1} found in the spectrum of dimethylsulfide boron trifluoride and at 1160 and 835 cm^{-1} in the spectrum of dimethylselenide boron trifluoride.[17] It has now been shown that the boron trifluoride adduct of stannocene, originally formulated as $(\eta^5\text{-}C_5H_5)_2Sn \rightarrow BF_3$,[13] is a loosely associated polymer containing $[BF_4]^-$ and $[\eta^5\text{-}C_5H_5Sn]^+$ moieties.[18] The boron trifluoride adduct of the *meta*-isomer with constrained cyclopentadienyl rings cannot contain individual $[\eta^5\text{-}C_5H_5Sn]^+$ units. This makes it difficult to imagine the $[BF_4]^-$ ion being present. A conclusion about these bands in the infrared is that they are due to vibrations other than simple B-F bends and stretches in a BF_3 moiety. However, they must surely be due, in part, to some kind of B-F bond vibration.

Thus, using the idea of "local" symmetry and assuming an angular π-bonded sandwich molecule, the vibrational spectra of the phenylenedimethylene bis(η^5-cyclopentadienyl) tin(II) isomers and boron trifluoride adduct can be adequately explained.

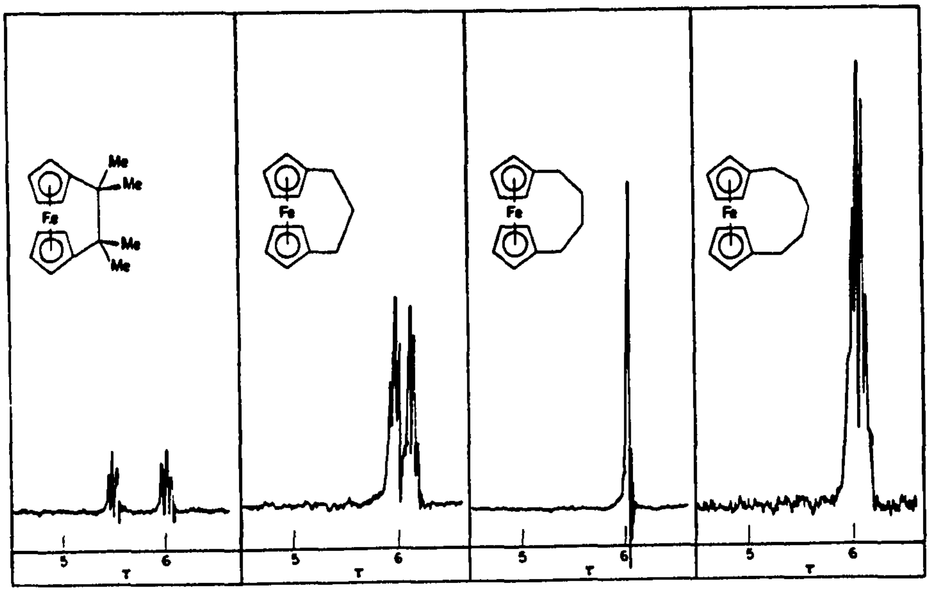
In the proton NMR, run in benzene-d_6, the phenyl nucleus gives rise to a multiplet centered at δ7.18, 7.16 and 7.20ppm for the *ortho-* and *meta-*isomers and *para-*isomers. The methylene protons give rise to a broad singlet at δ3.72ppm in each case. Broad singlets at δ5.92, 5.88 and 5.56ppm for the *ortho-*, *meta-* and *para-*isomers, respectively, are due to the cyclopentadienyl protons. The resonances arising from the methylene and cyclopentadienyl protons are roughly in the expected 4:8 area ratio, 4.0:8.00(*ortho*); 4.0:6.8(*meta*); 4.0:9.1(*para*), but satisfactory phenyl integration was not achieved.

The broad singlet observed in all cases for the cyclopentadienyl protons must represent an unresolved multiplet. Free rotation in the rings is not possible making the protons inequivalent. Indeed, for $(\eta^5\text{-}CH_3C_5H_5)_2Sn$, a partially resolved multiplet is observed within one stronger single line.[15] Others have reported only a single line for these protons.[23]

Proton NMR data is available for bridged bimetallic derivatives of disodium (m-phenylenedimethylene)dicyclopentadienide, *m*-$C_6H_4(CH_2C_5H_4Na)_2$. In all cases, the cyclopentadienyl protons appear as singlets. For example, *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$ has its cyclopentadienyl protons at 5.13 ppm and *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3I]_2$ shows its ring protons at 5.46 ppm.[7] Tungsten examples include the bimetallic compounds of *m*-$C_6H_4[CH_2C_5H_4W(CO)_3CH_3]_2$ and *m*-C_6H_4-

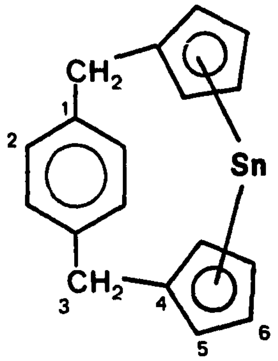
$[CH_2C_5H_4W(CO)_3C_2H_5]_2$ showing the cyclopentadienyl protons at 5.24 and 5.23 ppm, respectively.

For a series of [m]ferrocenophanes, m=2-5, the length of the methylene bridge connecting the two cyclopentadienyl rings can significantly alter the appearance of the ring protons. The figure taken from reference 24 demonstrates this.

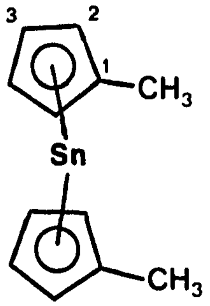


Cyclopentadienyl proton patterns in the PMR spectra (C_6D_6 solutions) of [m]ferrocenophanes.

The carbon-13 NMR of *para*-$C_6H_4(CH_2C_5H_4)_2Sn$ shows the expected signals. Phenyl carbons appear at 138.48(1) and 129.83(2) ppm, methylene carbon atoms appear at 32.88(3) ppm and cyclopentadienyl carbons are at 129.07(4), 128.67(5) and 127.72(6) ppm when recorded in benzene-d_6. Carbon atoms are numbered in parenthesis according to the figure.

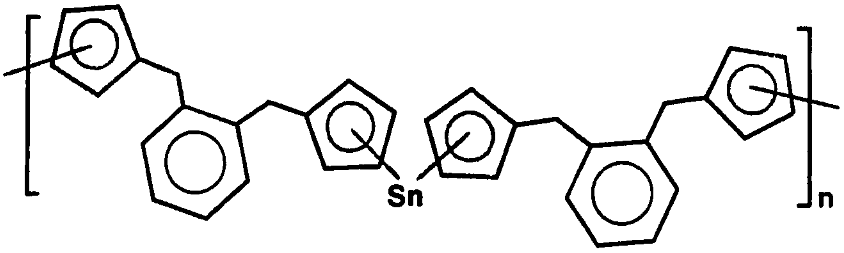


By comparison in the ^{13}C NMR spectrum of *meta*-xylene the phenyl carbons appear at 134.6(1) and 129.0(2) ppm with the methyl carbon atoms at 20.9(3)[25] ppm according to the above numbering scheme. In the ^{13}C NMR spectrum of bis(methylcyclopentadienyl)tin(II) the ring carbon atoms appear at 126.70(1), 113.80(2) and 111.20(3) ppm with the methyl carbon atoms at 16.76 ppm.[23] The figure indicates the numbering scheme of the atoms in parenthesis.

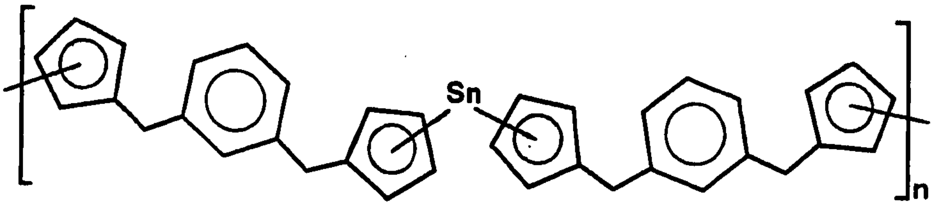


The mass spectra show parent molecular ions at m/e=352 for all isomers. This fact along with the absence of polytin fragments or of ions of mass greater than the parent m/e values can be used, along with the ready solubility of the stannocenophane isomers, to rule out the possible polymeric structures shown in Figure 4.3 in favor of the monomeric structures shown in Figure 4.4. The fragmentation patterns

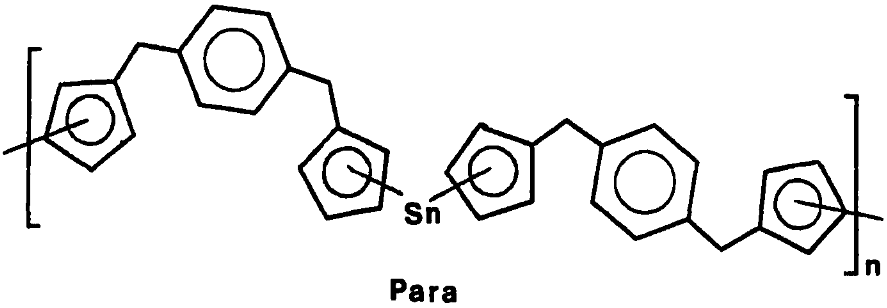
Figure 4.3. Possible Structures of Polymeric Stannocenophane Isomers.



Ortho

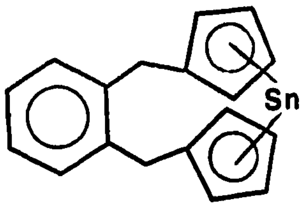


Meta

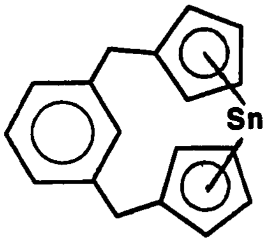


Para

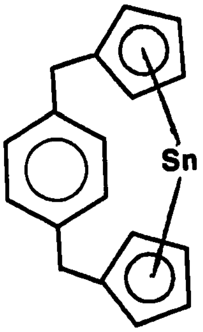
Figure 4.4. Possible Structures of Monomeric Stannocenophane Isomers.



Ortho



Meta



Para

are similar for all three isomers as shown in Table 4.3. Loss of one methylenecyclopentadienyl group to give the half-sandwich cation, $[C_6H_4CH_2C_5H_4Sn]^+$, at m/e=274 is observed for the *meta*- and *para*-isomers. Loss of η^5-C_5H_5Sn and stannocene to give $[CH_2C_6H_4CH_2C_5H_4]^+$ at m/e=168 and $[C_6H_4(CH_2)_2]^+$ at m/e=104, respectively, are observed in all three spectra along with the parent molecular ion of stannocene at m/e=248. The half-sandwich stannocenium ion is seen at m/e=185. This species has been isolated as its tetrafluoroborate salt.[26] The most abundant fragment in the spectra of the *ortho*- and *meta*-isomers is the ion at m/e=168 derived from the loss of $[\eta^5$-$C_5H_5Sn]^+$, while the $[C_5H_5]^+$ ion is the most abundant in the spectrum of the *para*-isomer. The most abundant tin-bearing ions for the *ortho*-, *meta*- and *para*-isomers are the $[Sn(C_4H_2)_2]^+$, $[SnC_5H_4]^+$ and Sn^+ at m/e=220, 185 and 120, respectively.

The mass spectrum of *m*-$C_6H_4(CH_2C_5H_4)_2Sn$-BF_3 shows as the parent ion the fragment $[C_6H_4(CH_2C_5H_4)_2Sn$-$BF_2]^+$ at m/e=401. This corresponds to the molecular ion-F fragment. Loss of a phenyl group is observed to give the ion $[F_2BSn(C_5H_4)_2CH_2CH]^+$ at m/e=336. The $[BF_2]^+$ fragment is observed at m/e=68. The most abundant ion is $[C_5H_6]^+$ at m/e=66. The most abundant tin-bearing ion is $[SnBF_3]^+$ at m/e=169. A fragment at m/e=155 is attributed to $[SnCl]^+$ which is an impurity from the unreacted starting material, tin(II) chloride. See Table 4.4.

Table 4.3. Mass Spectral Data for the Bis[(Phenylenedimethylene)-η^5-dicyclopentadienyl]tin(II) Isomers. [a]

	Abundance			
m/e	*ortho-*	*meta-*	*para-*	Assignment
352	0.8	3.2	10.0	$[C_6H_4(CH_2C_5H_4)_2Sn]^{+\cdot}$
274	-	1.4	2.2	$[C_6H_4CH_2C_5H_4Sn]^{+\cdot}$
248	0.9	1.5	10.9	$[Sn(C_5H_4)_2]^{+\cdot}$
234	25.8	4.4	30.7	$[C_5H_4SnC_4H_2]^{+\cdot}$
220	5.0	4.3	12.3	$[Sn(C_4H_4)_2]^{+\cdot}$
193	4.3	-	-	$[SnC_3H_3CH_2]^{+\cdot}$
185	1.5	18.6	53.3	$[SnC_5H_4]^{+\cdot}$
168	100	100	36.0	$[C_6H_4(CH_2)CH_2C_5H_4]^{+}$
120	-	11.8	66.7	$Sn^{+\cdot}$
66	24.5	90.5	60.1	$[C_5H_6]^{+\cdot}$
65	7.1	7.3	100	$[C_5H_5]^{+\cdot}$

[a] Mass numbers are based upon ^{120}Sn, ^{12}C and ^{1}H at 70 eV.

Table 4.4. Mass Spectral Data for the *m*-Bis[Phenylenedimethylene-η^5-dicyclopentadienyl]tin(II) BF_3 Derivative.[a]

m/e	Abundance	Assignment
401	6.9	$[C_6H_4(CH_2C_5H_4)_2Sn\text{-}BF_2]^+$
336	7.1	$[F_2BSn(C_5H_4)_2CH_2CH]^{+\cdot}$
235	4.3	$[C_5H_4SnC_4H_3]^+$
205	5.4	$[FSnC_5H_6]^+$
193	3.4	$[FSnC_4H_6]^+$
181	2.7	$[F_2BSnC]^+$
169	16.1	$[SnBF_2]^+$
155	30.0	$[SnCl]^+$
141	18.5	$[C_6H_4CH_2C_4H_3]^+$
115	11.8	$[C_6H_4CH_2CHC]^+$
111	28.1	$[C_7H_8F]^+$
97	52.7	$[C_6H_6F]^+$
91	61.4	$[C_6H_4CH_3]^+$
78	16.0	$[C_5H_4CH_2]^{+\cdot}$
71	54.5	$[C_4H_4F]^{+\cdot}$
68	8.7	$[BF_3]^+$
66	100.0	$[C_5H_6]^{+\cdot}$
65	52.2	$[C_5H_5]^{+\cdot}$

[a] Mass numbers are based upon ^{120}Sn, ^{19}F, ^{12}C, ^{11}B and ^{1}H at 70 eV.

4.8 CHARACTERIZATION OF *meta*-PHENYLENEDIMETHYLENE BIS [(η^5-CYCLOPENTADIENYL)TIN(II)] BIS(η^5-CYCLOPENTADIENE)

The tin-119m Mössbauer spectrum of m-$C_6H_4(CH_2C_5H_4$-η^5-Sn-η^5-$C_5H_5)_2$ is consistent with a tin(II) compound by having an isomer shift of 3.23 ± 0.03mm s^{-1}. However, the spectrum shows a rather large Q.S. value of 2.08 ± 0.06mm s^{-1}. Table 4.5 compares the isomer shift and quadrupole splitting of this compound with a number of other π-bonded tin(II) compounds. All have small Q.S. values except for three coordination complexes involving stannocene and tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane. The structures of these complexes are uncertain, but a high coordination number at the tin atom is implied. A highly coordinated tin atom in the title compound would occur if the lone pair electrons of the tin(II) atom were coordinated with the phenyl ring of another molecule. This type of coordination is not completely unknown. The x-ray crystal structure of bis(O,O′-diphenyl dithiophosphato) tin(II), $\{Sn[S_2P(OC_6H_5)_2]_2\}_2$, exists as a dimer held together in part by long η^6-C_6H_5 coordination between the tin(II) lone pair electrons and the phenyl ring of the second molecule in the dimer.[32]

In the proton NMR spectrum of m-$C_6H_4(CH_2C_5H_5$-η^5-Sn-η^5-$C_5H_5)_2$ the phenyl protons appear as a multiplet at δ7.25ppm with the methylene protons appearing as a broad singlet at δ3.70ppm. The two types of cyclopentadienyl rings can be distinguished with a multiplet due to the

Table 4.5. Tin 119m Mössbauer Data for π-Bonded Organotin(II) Conpounds.

Compound	I.S.	Q.S.	Reference
$m\text{-}C_6H_4(CH_2C_5H_4\text{-}\eta^5\text{-}Sn\text{-}\eta^5\text{-}C_5H_5)_2$	3.23±0.03	2.08±0.06	[a]
$(\eta^5\text{-}C_5H_5)_2Sn(tcne)$[b]	3.03	2.37	30
$(\eta^5\text{-}C_5H_5)_2Sn(tcne)_2$	3.12	2.26	30
$(\eta^5\text{-}C_5H_5)_2Sn(tcnq)$ [c]	3.84	1.30	30
$(\eta^5\text{-}C_5H_5)_2Sn$	3.74	0.86	8
$(\eta^5\text{-}CH_3C_5H_4)_2Sn$	3.83	0.78	15
$(\eta^5\text{-}(CH_3)_5C_5)_2Sn$	3.53	0.99	[a]
$\eta^5\text{-}C_5H_5SnCl$	3.71	1.04	27
$\eta^5\text{-}C_5H_5SnBr$	3.40	0.99	27
$\eta^5\text{-}C_5H_5SnI$	3.90	0.00	27
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}AlCl_3$	3.71	0.00	28
$(\eta^5\text{-}CH_3C_5H_4)_2Sn\text{-}AlCl_3$	3.71	0.00	28
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}AlBr_3$	3.83	0.00	28
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}BBr_3$	3.77	0.00	28
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}BF_3$ [d]	3.79	0.90	13
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}AlCl_4$	3.73	0.00	28
$(\eta^5\text{-}C_5H_5)_2Sn\text{-}AlBr_4$	3.75	0.00	28
$[\eta^5\text{-}(CH_3)_3SnC_5H_4]_2Sn$	3.58	0.89	29
$(\eta^5\text{-}C_6H_6)Sn(AlCl_4)_2C_6H_6$	3.93	0.00	31

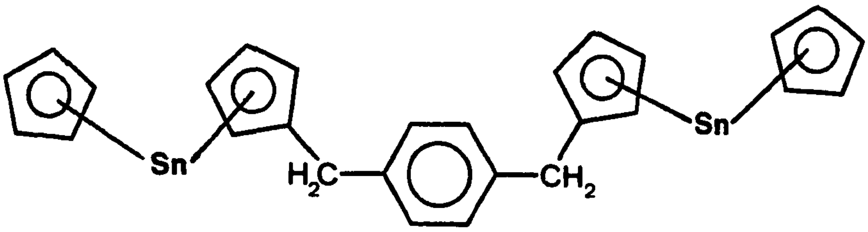
[a] This work.

[b] tcne = Tetracyanoethylene.

[c] tcnq = 7,7,8,8-Tetracyanoquinodimethane.

[d] A reformulation of this compound is $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn\text{-}[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\cdot THF\}_n$.[18]

C_5H_4 ring at δ5.75ppm and a singlet at δ5.90ppm due to the C_5H_5 ring. The spectrum was recorded in toluene-d_8 using tetramethylsilane as a zero reference. Satisfactory area integration of phenyl:methylene:C_5H_4:C_5H_5 (4:4:8:10) protons was achieved. The proposed structure is shown in the figure:



4.9 CONCLUSIONS

Three isomeric examples of a new class of stannocene derivatives in which the η^5-cyclopentadienyl rings are linked through methylene bridges to a phenyl system were prepared and characterized. The *ortho-*, *meta-*, and *para-*xylene derivatives were synthesized by the reaction of the disodium salt of (phenylenedimethylene) dicyclopentadienide with tin(II) chloride. The products are air-sensitive, off-white powders soluble in organic solvents, but show no definite melting points.

Tin 119m Mössbauer data corraborate the tin(II) oxidation state. Proton and carbon-13 NMR establish the presence of a phenyl ring, methylene bridge and cyclopentadienyl rings for all isomers. Analysis of the infrared spectra indicates penta-hapto bonding between the tin and cyclopentadienyl rings. Parent molecular ions at m/e=352 are the highest m/e value in the spectra. This, along with the absence of any polytin fragments, suggests these isomers are monomers as drawn in Figure 4.3, although polymeric structures can be drawn as shown in Figure 4.4.

The *meta*-stannocene isomer reacts with BF_3 etherate to form the BF_3 adduct. Mössbauer data establishes that the tin(II) oxidation state remains. Additional bands in the infrared can be assigned to complex vibrations due in part to B-F stretching and bending. In the mass spectrum, ions containing tin and fluorine are observed. This compound resembles the BF_3 adduct of stannocene. However, the stannocene adduct has been shown to be a loosely bound polymer containing $[BF_4]^-$ and $[\eta^5\text{-}C_5H_5Sn]^+$ ions.[18] Because the cyclopentadienyl rings are tied together in the BF_3 *meta*-stannocenophane adduct, this may represent a complex in which the tin(II) lone pair electrons are utilized in a donor-acceptor molecule involving boron trifluoride as originally proposed for the stannocene boron trifluoride adduct.

The action of η^5-cyclopentadienyltin(II) chloride on the disodium salt of *meta*-(phenylenedimethylene) dicyclopentadienide yields *meta*-phenylenedimethylene bis(η^5-cyclopentadienyl)tin(II) bis(η^5-cyclopentadiene).

The tin-119m Mössbauer spectrum confirms the tin(II) oxidation state. The rather large quadrupole splitting indicated a deviation from spherical symmetry by the tin

5s electrons. This implies a high coordination number at the tin atoms involving the lone pair electrons. This could be accomplished through coordination of the tin lone pair electrons with a phenyl ring in an adjacent molecule. The proton NMR indicates penta-hapto bonding between the tin atoms and cyclopentadienyl rings.

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CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF RING SUBSTITUTED STANNOCENES

5.1 INTRODUCTION

Stannocene, as noted in earlier chapters, is an angular sandwich compound with stereochemically-, and presumed chemically-active lone pair electrons present in the divalent state of tin. Altering the steric and electrical properties of the cyclopentadienyl rings through substitution will change the hybridization and angles made by the tin to the two cyclopentadienyl rings. A change in bond angle will change the spatial extension and reactivity of the lone pair electrons. Reaction conditions that produce ring-substituted ferrocenes from ferrocene produce oxidative addition reactions at the tin atom in stannocene.

Ferrocene, for example, will undergo Friedel-Crafts alkylation when reacted with an aluminum trichloride-alkyl chloride complex.[1,2] Stannocene, on the other hand, is known to form a donor-acceptor complex with aluminum trichloride.[3] Stannocene will react with methyl iodide at room temperature to form initially η^5-C_5H_5SnI which reacts further in a complex reaction to form $CH_3(\eta^1\text{-}C_5H_5)_2SnI$ in greater than 90% yield.

Other π-bonded cyclopentadienyl organometallic compounds have been found to exhibit the aromatic ring-substitution reactivity found in ferrocene. These include the sandwich compounds ruthenocene and osmocene,[5,6] the mixed (η^5-cyclopentadienyl)carbonylmetal compounds where the metal is manganese,[7,8] technetium or rhenium,[9-11] (η^5-cyclopentadienyl)dicarbonylnitrosylchromium,[12] (η^5-cyclopentadienyl)dicarbonylcobalt[13] and (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt,[14,15] all of which undergo Friedel-Crafts reactions. Stannocene, even though possessing π-bonded cyclopentadienyl rings,[16] does not undergo aromatic-type ring-substitution reactions.

Almost all of the above organometallic compounds have been synthesized from the reactions of C_5H_5Tl, C_5H_5Na, C_5H_5Li or C_5H_5MgX and the appropriate metal halide. It follows, then, that the reaction of substituted cyclopentadienide salts such as C_5H_4RTl, C_5H_4RLi or C_5H_4RNa with tin(II) chloride should produce the corresponding ring substituted stannocene. Indeed, bis(methylcyclopentadienyl)tin(II) has been synthesized by the reaction of $C_5H_4CH_3Na$ and $SnCl_2$ in THF.[17]

Monosubstituted sodium ethoxalylcyclopentadienyl was first synthesized in 1900 by the condensation of cyclopentadiene with diethyl oxalate and sodium ethoxide.[18] Reactions of sodium cyclopentadienide with ethyl formate, methyl acetate or dimethyl carbonate produce sodium formyl- acetyl- or carbomethorycyclopentadienide, respectively.[19-21]

Also, it has been reported that thallium cyclopentadienide reacts with N-chloro-, N-bromo- or N-iodosuccinimide to form intermediate halocyclopentadienes which react with thallium(I) ethoxide producing thallium chloro-, bromo- or iodocyclopentadienide, respectively.[22]

Using these known procedures, the synthesis of ring-substituted stannocenes was undertaken. A large number of reactions were performed. Among these, reactions involving R_3SnCl ($R = CH_3$, C_6H_5) with MC_5H_4R ($M = Na$, Tl; $R = Cl$, $C(O)CH_3$) were carried out to obtain an understanding of the reactivity of the ring-substituted salts. The results were surprising. The reaction of $(CH_3)_3SnCl$ or $(C_6H_5)_3SnCl$ with $NaC_5H_4C(O)CH_3$ produces only bis(trimethyltin) oxide, $[(CH_3)_3Sn]_2O$ and bis(triphenyltin) oxide, $[(C_6H_5)_3Sn]_2O$, respectively. As reported in Chapter III, trimethyltin chloride reacts with N-thallium succinimide in preference to thallium chlorocyclopentadienide to form N-trimethyltin(IV) succinimide. The addition of tin(II) chloride to MC_5H_4R (M = Tl, Na; R = Cl, Br, I, $C(O)CH_3$) yields at the major products SnO_2, TlCl or NaCl and unreacted $SnCl_2$. Tin(IV) chloride did not react when mixed with thallium bromocyclopentadienide. Unreacted $SnCl_4$ was the only compound recovered from the reaction mixture. Reactions involving cyclopentadienyltin(II) chloride and NaC_5H_4R (R = $C(O)CH_3$, $C(O)OCH_3$, $C(O)OCH_2CH_3$) did yield ring-substituted stannocenes with the general formula $(\eta^5\text{-}C_5H_5)Sn(\eta^5\text{-}C_5H_4R)$.[23] The synthesis and characterization of these compounds will be described in this chapter.

5.2 SYNTHESIS OF SODIUM ACETYLCYCLOPENTADIENIDE

This compound was prepared according to Rausch.[21,24]

Sodium cyclopentadienide was prepared in dry THF under a nitrogen atmosphere from sodium sand (4.68g, 0.20mol) and freshly cracked cyclopentadiene (20.0mL, 0.24mol) with hydrogen evolution. To the light-pink solution degassed ethyl acetate (19.5mL, 0.20mol) was added with stirring. The solution was slowly heated to reflux for two hours, cooled, then filtered under nitrogen. The off-white, air-sensitive solid was washed with dry ether and dried under vacuum producing 19.3g (90% yield, mp 165°C dec.). In the NMR in D_2O, the methyl protons are observed as a singlet at 2.30 (lit. 2.32[21]) ppm and the cyclopentadienide protons as multiplets at 6.20

(lit. 6.20[21]) and 6.65 (lit. 6.68[21]) ppm. The C-O stretching band in the IR is observed at 1538 cm^{-1} (CsI pellet). This salt, and all others described, is sufficiently air-stable to be weighed in the air if used immediately. It decomposes leaving black or brown stains on skin and clothes.

5.3 SYNTHESIS OF SODIUM METHOXYCARBONYLCYCLOPENTADIENIDE

This compound was prepared according to Rausch.[21,24]

Sodium cyclopentadienide (0.20 mol) was made as described above. To this THF solution, under nitrogen, was added degassed dimethyl carbonate (51.4mL, 0.60mol) with stirring at 25°C. The mixture was slowly heated to reflux for four hours, cooled on an ice bath, then filtered under nitrogen. The off-white, air-sensitive solid was washed with ether, then dried under vacuum, producing 20.9g (85% yield) of the title compound. The methyl protons appear as a singlet at 3.73 (lit. 3.74[21]) ppm with the ring protons appearing as multiplets at 6.60 (lit. 6.56[21]) and 6.10 (lit. 6.06[21]) ppm in the NMR spectrum (in D_2O). The carbonyl stretch in the IR was observed at 1618 cm^{-1} in a KBr pellet.

5.4 SYNTHESIS OF SODIUM ETHOXYCARBONYLCYCLOPENTADIENIDE

Sodium cyclopentadienide (0.44mol) was made as described above. To this THF solution, under nitrogen, was added degassed diethyl carbonate (131.7mL, 0.44mol). The mixture was slowly heated to reflux for four hours, then cooled to room temperature. The slurry was cooled further on an ice bath, filtered and dried under vacuum, producing 64.8g (92% yield) of sodium ethoxycarbonylcyclopentadienide according to Equation 5.1.

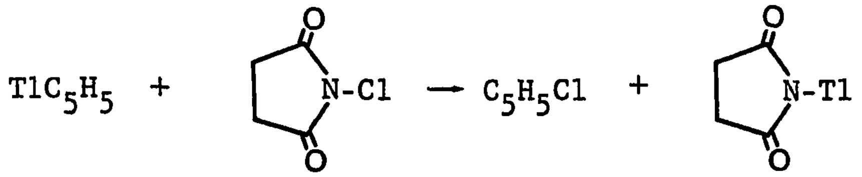
$$NaC_5H_5 + (CH_3CH_2O)_2CO \rightarrow Na^+[C_5H_4C(O)OCH_2CH_3]^- + CH_3CH_2OH \qquad (5.1)$$

In the NMR spectrum, the methyl protons produce a triplet at 1.13 ppm, the methylene protons a quartet at 3.54 ppm, and the ring protons are observed as multiplets at 5.92 and 6.42 ppm (in D_2O). In the IR spectrum $\nu_{c=o}$ appears at 1620 cm^{-1} and ν_{c-o} is at 1075 cm^{-1} in a KBr pellet.

5.5 SYNTHESIS OF THALLIUM HALOCYCLOPENTADIENIDES

These compounds were prepared according to Rausch.[22]

Thallium cyclopentadienide (50.0g, 0.19mol) and N-chlorosuccinimide (24.8g, 0.19mol) were mixed together in dry diethyl ether (200mL) under a nitrogen atmosphere for one hour on an ice bath. The solution was filtered, producing a clear ether solution of chlorocyclopentadiene according to Equation 5.2.



(5.2)

To this solution, thallium(I) ethoxide (23.7g, 6.72mL, 0.10mol) was slowly added with stirring. A flocculent cream-colored solid formed rapidly according to Equation 5.3.

$$C_5H_5Cl + TlOCH_2CH_3 \longrightarrow TlC_5H_4Cl + CH_3CH_2OH \qquad (5.3)$$

Stirring was continued for 30 minutes then the suspension filtered. The solid was washed with dry ether then dried under vacuum, producing 14.69g (72% yield). The NMR in DMSO-d_6 shows two multiplets at 5.50 (lit. 5.52[22])and 5.70 (lit. 5.76[22])ppm.

In a similar manner, thallium cyclopentadienide (50.0g, 0.19mol) and N-bromosuccinimide (33.8g, 0.19mol) were stirred together in dry diethyl ether (200mL) for one hour at 0°C. The resulting bromocyclopentadiene was filtered through a glass frit under nitrogen. To this solution, thallium(I) ethoxide (23.7g, 6.72mL, 0.10mol) was slowly added via syringe at 0°C. This resulted in the rapid formation of a cream-colored precipitate. The solid was collected by filtration on a glass frit and washed with diethyl ether. Drying in vacuum gave 32.75g (92% yield) of thallium bromocyclopentadienide as a cream-colored solid. The proton NMR in DMSO-d_6 shows two multiplets at 5.60 (lit. 5.61[22]) and 5.80 (lit. 5.83[22]) ppm.

A nitrogen purged, 1L round-bottomed flask was charged with thallium cyclopentadienide (50.0g, 0.19mol) and diethyl ether (200mL). The flask, equipped with a 500mL pressure-equalizing dropping funnel and gas-inlet tube, was placed in an ice bath. Into the dropping funnel was placed a solution of iodine (45.68g, 0.18mol) in diethyl ether (400mL). The iodine solution was added dropwise with stirring over 30 minutes and stirring continued an additional 30 minutes.[28]

The iodocyclopentadiene was filtered at 0°C under nitrogen through a glass frit. Thallium(I) ethoxide (47.4g, 13.44mL, 0.19mol) added dropwise via syringe, resulted in the immediate formation of a flocculent precipitate. The solid was separated by filtration, washed with diethyl ether and dried in a vacuum. The resulting thallium iodocyclopentadienide (63.86g, 85% yield) is a lemon-yellow, air-sensitive solid having multiplets at 5.70 (lit. 5.70[22]) and 5.85 (lit. 5.90[22]) ppm in the ^1H NMR spectrum (DMSO-d_6).

5.6 REACTIONS INVOLVING TRIORGANOTIN CHLORIDES

Trimethyltin chloride (7.66g, 38.4mol) was dissolved in dry THF (50mL) and degassed. This was added with stirring to a THF solution (50mL) containing sodium carbomethoxycyclopentadienide (5.0g, 38.4mmol) under a nitrogen atmosphere. The solution was stirred at 25°C for two hours. The resulting white solid was filtered then washed with cold diethyl ether. The white solid was identified as hexamethyldistannoxane, $[(CH_3)_3Sn]_2O$, by infrared and ^1H NMR spectroscopy (8.42g, 63.8% yield). In the ^1H NMR, a singlet at 0.10ppm was observed with Sn-H coupling. The infrared spectrum matched the spectrum of a known sample and agreed with the literature spectrum.[25] Microanalytical data calculated for $C_6H_{18}Sn_2O$ was 33.15% Sn; 32.89% Sn found.

Triphenyltin chloride (14.8g, 38.4mmol) was added with stirring to a THF solution (50mL) containing sodium carbomethoxycyclopentadienide (5.0g, 38.4mmol) under a nitrogen atmosphere. The solution was stirred for two hours, then filtered. The white solid was washed with cold diethyl ether and dried under vacuum. The solid was identified as hexaphenyl distannoxane, $[(C_6H_5)_3Sn]_2O$, by infrared and mass spectroscopy (21.72g, 79% yield). The infrared spectrum agreed with the spectrum of a known sample and published data.[26,27] In the mass spectrum, a molecular ion at m/e = 719 along with $[SnO]^+$(m/e=136), $[(C_6H_5)_3Sn]^+$(m/e=351)and $[Sn]^+$(m/e=120) were observed along with phenyl fragments at m/e = 77 and 52.

5.7 REACTION OF TIN(IV) CHLORIDE AND THALLIUM BROMOCYCLOPENTADIENIDE

A solution of thallium bromocyclopentadienide (1.00g, 2.87mmol) in THF (60mL) was placed under an argon atmosphere. To this, tin(IV) chloride (0.08mL, 0.718mmol) in THF (10mL) was added with stirring. A white precipitate formed immediately. The reaction mixture was stirred an additional 30 minutes, then filtered. The THF solution was placed under vacuum removing the solvent, leaving a light brown powder. The melting point is greater than 260°C; however, the solid darkens at 187°C with formation of a clear liquid at the top of the melting point capillary tube.

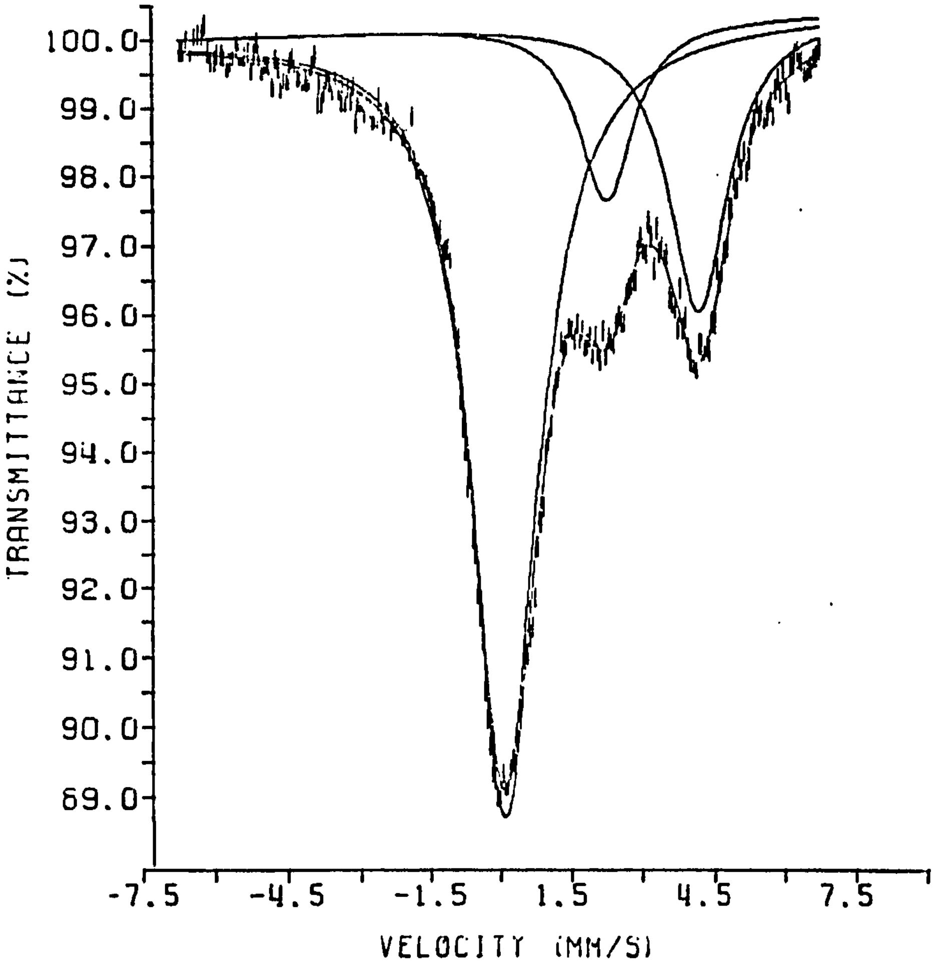
The proton NMR spectrum in $CDCl_3$ shows only multiplets at 1.79 and 3.60ppm owing to THF. The ^{119m}Sn Mössbauer spectrum consists of a broad singlet at IS = 0.35mm s^{-1}, Γ = 1.73mm s^{-1}. The mass spectrum contains fragments owing to $[SnCl_4]^+$ (m/e=260), $[SnCl_3]^+$ (m/e=225), $[SnCl_2]^+$ (m/e=190), $[SnCl]^+$ (m/e=155), Sn^+ (m/e=120), $[C_4H_8O]^+$ (m/e=72) and $[C_4H_7O]^+$ (m/e=71). A mass spectrum of the residue contains fragments owing to $[TlC_5H_4]^+$ (m/e=269), $[SnCl_4]^+$ (m/e=260), $[SnCl_3]^+$ (m/e=225), Tl^+ (m/e=203,205) $[SnCl_2]^+$ (m/e=190), $[SnCl]^+$ (m/e=155), $[Sn]^+$ (m/e=120) and $[Br]^+$ (m/e=79, 81).

5.8 REACTIONS INVOLVING TIN(II) CHLORIDE

Sodium acetylcyclopentadienide was made as described above. To a solution of this salt (15.0g, 0.12mol) in THF (300mL) was added, tin(II) chloride (10.9g, 0.06mol) in THF (150mL) under nitrogen with stirring. A white precipitate formed almost immediately. Stirring was continued for 2 hours, the solution filtered and the solvent removed by vacuum, leaving a red-brown solid (9.3g). The ^{119m}Sn Mössbauer spectrum shown in Figure 5.1 has three lines at IS (1) = 0.06(3), IS (2) = 2.18(3) and IS (3) = 4.20(3)mm s^{-1}. The proton NMR in C_6D_6 shows four multiplets at 6.8, 6.2, 5.9 and 5.5ppm. Two singlets at 2.0 and 1.8ppm were also observed. In the mass spectrum, ions were observed at m/e=190(18.1), 155(100.0), 152(18.2), 136 (10.8), 120(26.6), 72(12.1) and 71(14.7) owing to $[SnCl_2]^+$, $[SnCl]^+$, $[SnO_2]^+$, $[SnO]^+$, Sn^+, $[C_4H_8O]^+$ and $[C_4H_7O]^+$ respectively. The relative abundances are in parenthesis. The infrared spectrum shows bands at 2962(w), 2940(sh), 1690(sh), 1655(s), 1420(w), 1372(m), 1270(m), 1020(w), 1045(w), 540(s) and 280(m) in CsI.

Thallium chlorocyclopentadienide (1.5g, 4.9mmol) with THF (200mL) were placed in a 500mL round-bottomed flask and purged with nitrogen. A solution of tin(II) chloride (0.47g, 2.5mmol) in THF (50mL) was added dropwise with stirring at room temperature. Stirring was continued

Figure 5.1. ^{119}Sn Mössbauer Spectrum of $SnCl_2 + NaC_5H_4C(O)CH_3$



for one hour subsequent to completion of addition, then filtered under nitrogen through a glass frit. The volume of the solution was reduced by half under vacuum. Addition of degassed hexane casued the precipitation (0.38g) of a light-brown solid. The proton NMR in acetone-d_6 shows two small multiplets at 5.96 and 5.68ppm of approximately equal areas. The ^{119m}Sn Mössbauer spectrum consists of three lines at 0.04(3), 1.74(3) and 3.86(3)mm s^{-1}. Mass spectral data was collected at 70eV and 12eV. Both spectra contained masses at m/e values of 430(0.7), 395(10.5), 205(100.0), 190(13.8), 155(39.8), 136(0.8), 128(1.0), 120(10.9), 99(1.5) and 65(0.9) corresponding to $[TlSnCl_3]^+$, $[TlSnCl_2]^+$, Tl^+, $[SnCl_2]^+$, $[SnCl]^+$, $[SnO]^+$, $[C_{10}H_8]^+$, Sn^+, $[C_5H_4Cl]^+$ and $[C_5H_5]^+$, respectively. Relative abundances are in parenthesis. The solid did not melt to 260°C, but darkened and appeared to soften at this temperature.

Thallium bromocyclopentadienide (1.50g, 4.31mmol) in THF (150mL) were placed in a nitrogen filled round-bottomed flask. A solution of tin(II) chloride (0.41, 2.15mmol) in THF (30mL) was added dropwise with stirring at room temperature, forming a white precipitate. Stirring was continued for one hour subsequent to completion of addition, then filtered under nitrogen. When one-half of the solvent had been removed by vacuum, hexane was added causing the precipitation of a light-brown solid (0.56g).

The ^{119m}Sn Mössbauer spectrum of this powder consists of three lines at -0.03(3), 1.48(3) and 4.28(3)mm s^{-1}.

Thallium iodocyclopentadienide (2.0g, 5.1mmol) with THF (150mL) were placed in a round-bottomed flask purged with nitrogen. A solution of tin(II) chloride (0.48g, 2.5mmol) in THF (30mL) was added dropwise with stirring at room temperature, forming an off-white precipitate. After stirring for one hour, the solution was filtered and solvent removed via vacuum, leaving a light brown powder (0.38g). The ^{119m}Sn Mössbauer spectrum of this powder consists of one line at 0.23(3)mm s^{-1}.

5.9 SYNTHESIS OF ACETYLSTANNOCENE

η^5-Cyclopentadienyltin(II) chloride[29] (1.86g, 8.48mmol) in THF (50mL) was added dropwise to sodium acetylcyclopentadienide (1.72g, 8.50mmol) in THF (100mL) at 0°C under nitrogen. After one minute of addition, a white precipitate started to form. The solution was allowed to warm to room temperature, stirred one hour subsequent to addition, and filtered through a glass frit. Approximately one-half of the solvent was removed under vacuum, then dry, degassed hexane added precipitating the light-brown acetylstannocene (2.47g, 100% yield).

The ^{119m}Sn Mössbauer spectrum shows a doublet with an isomer shift of 2.98(3)mm s^{-1} and a quadrupole splitting of 2.21(6)mm s^{-1}. A trace amount of SnO_2 is also apparent in the spectrum with an isomer shift of -0.07(3)mm s^{-1}. The solid is infusible to 270°C. The infrared spectrum shows the carbonyl band at $1650cm^{-1}$ in a saturated THF solution. Microanalytical data calculated for $C_{12}H_{12}SnO$ was 40.80% Sn; found 41.57% Sn. The proton NMR in C_6D_6 has a singlet at 5.8ppm owing to the unsubstituted ring with two multiplets at 5.9 and 5.7ppm owing to the substituted ring. A singlet at 0.3ppm is due to the methyl protons. Satisfactory integration was achieved (5:4:3 for C_5H_5:C_5H_4:CH_3) Mass spectrum data is listed in Table 5.1. The molecular ion is observed at m/e=292.

5.10 SYNTHESIS OF METHOXYCARBONYLSTANNOCENE

η^5-Cyclopentadienyltin(II) chloride (3.0g, 13.7mmol) in THF (100mL) was added dropwise to sodium methoxycarbonylpentadienide (1.75g, 13.7mmol) in THF at 0°C under nitrogen. Shortly after addition started, a white precipitate began to form. The solution was allowed to warm to room temperature, stirred one hour subsequent to addition, and filtered through a glass frit. Approximately one-half of the solvent was removed under vacuum then hexane added, precipitating an off-white solid. Filtering and drying under vacuum produced methoxycarbonylstannocene (3.9g, 94.3% yield). The solid does not melt to 260°C. The infrared spectrum shows the $\nu_{c=o}$ at $1615cm^{-1}$ and the ν_{c-o} at $1340cm^{-1}$ in a KBr pellet. Microanalytical data

Table 5.1. Mass Spectrum of Acetylstannocene.

m/e [a]	Relative Abundance	Assignment
292	2.5	$[C_5H_5SnC_5H_4C(O)CH_3]^{+\cdot}$
227	0.3	$[SnC_5H_4C(O)CH_3]^{+\cdot}$
185	37.7	$[SnC_5H_5]^{+\cdot}$
120	16.4	$Sn^{+\cdot}$
108	5.7	$[C_5H_5C(O)CH_3]^{+\cdot}$
107	4.7	$[C_5H_4C(O)CH_3]^{+\cdot}$
105	4.8	$[C_5H_4C(O)CH]^{+\cdot}$
92	5.0	$[C_5H_4CO]^{+\cdot}$
77	8.6	$[C_5H_5C]^{+\cdot}$
76	1.5	$[C_5H_4C]^{+\cdot}$
66	100.0	$[C_5H_6]^{+\cdot}$
65	80.5	$[C_5H_5]^{+\cdot}$
64	2.8	$[C_5H_4]^{+\cdot}$

[a] Based on ^{1}H, ^{12}C, ^{16}O, ^{120}Sn.

calculated for $C_{12}H_{12}SnO_2$ was 38.67% Sn; found 40.57% Sn.

The ^{119m}Sn Mössbauer spectrum shows a doublet with an isomer shift of 2.84(3)mm s^{-1} and a quadrupole splitting of 2.21(6)mm s^{-1}. A trace amount of SnO_2 is also apparent in the spectrum having an isomer shift of -0.01(3)mm s^{-1}. The mass spectrum at 12eV does not show a molecular ion, but ions at m/e=277(27.1), 261(7.4), 206(11.6), 179(8.0), 167(76.4), 152(7.0), 136(13.1), 124(100.0), 109(7.5), 96(22.6), 82(12.1) and 72(4.3) correspond to $[C_5H_5SnC_5H_4CO]^+$, $[C_5H_5SnC_5H_4C]^+$, $[C_2H_3SnC(O)OCH_3]^+$, $[SnC(O)OCH_3]^+$, $[SnO_2CH_3]^+$, $[SnO_2]^+$, $[SnO]^+$, $[C_5H_5C(O)OCH_3]^+$, $[C_5H_5C(O)O]^+$, $[C_5H_5OCH_3]^+$, $[C_5H_5OH]^+$ and $[CH_3OC(O)CH]^+$, respectively. Numbers in parenthesis are the relative abundances. The proton NMR in benzene-d_6 has a singlet at 0.9ppm owing to the methyl protons, two multiplets at 5.7 and 5.9ppm owing to the substituted ring protons and a singlet at 5.8ppm owing to the unsubstituted ring. Satisfactory integration was achieved (5:4:3 for $C_5H_5:C_5H_4:CH_3$).

5.11 SYNTHESIS OF ETHOXYCARBONYLSTANNOCENE

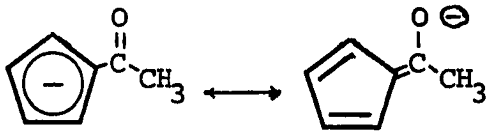
η^5-Cyclopentadienyltin(II) chloride (3.0g, 13.7mmol) in THF (100mL) was added dropwise to sodium ethoxycarbonylcyclopentadienide (2.2g, 13.7mmol) in THF at 0°C under nitrogen. The solution was stirred at 0°C for ten minutes, then allowed to warm to room temperature. A white precipitate formed during one hour of stirring at room temperature and was removed by filtration. The volume of the filtrate was reduced by one-half in a vacuum.

Dry, degassed hexane was added precipitating a light-brown powder. Filtering and drying under vacuum produced ethoxycarbonylstannocene (3.9g, 89% yield). The product did not melt to 260°C. The ^{119m}Sn Mössbauer spectrum shows a doublet with an isomer shift of 2.87(3)mm s^{-1} and a quadrupole splitting of 1.92(6)mm s^{-1}. The infrared spectrum shows the carbonyl band at 1658cm^{-1} in a saturated THF solution. In the ^{1}H NMR (C_6D_6) spectrum the methyl protons appear as a triplet at 1.68ppm, the methylene protons as a quartet at 4.15ppm, the unsubstituted ring as a singlet at 5.8ppm and the substituted ring protons appearing as multiplets at 5.6 and 6.0ppm. Satisfactory integration was achieved (5:4:2:3 for C_5H_5:C_5H_4:CH_2:CH_3).

5.12 DISCUSSION

Triorganotin(IV) chlorides react with sodium acetylcyclopentadienide forming triorganostannoxanes. This implies the negative charge in the sodium salt is not located predominately in the ring. A better description of the salt would locate the negative charge in the carbonyl function. This would help explain the attack of the tin preferentially at the oxygen and not at the ring as initially expected.

The extremely low wave number of the carbonyl band of the salt in the IR (1538cm^{-1}) lies closer to a C-O single bond stretch than to a C=O bond, supporting a predominate resonance structure with the negative charge on the oxygen rather than on the ring as shown below.



Tin(IV) chloride mixed with thallium bromocyclopentadienide in THF produces only the $SnCl_4 \cdot 2THF$ complex. There are no absorptions in the NMR except those owing to THF. The Mössbauer spectrum is consistent with $SnCl_4 \cdot 2THF$ having an isomer shift of 0.35mm s^{-1}. Also, in the mass spectrum, only $SnCl_4$ and THF fragments are observed. The complex did not melt, but at approximately 187°C, a clear liquid (THF?) was observed forming at the cooler top of the melting point capillary, suggesting the complex was dissociating at this temperature.

Oxygen donor complexes are known for tin(IV) chloride. The Mössbauer spectra have been recorded. They include $SnCl_4 \cdot 2THF$(IS=0.70mm s^{-1} [30]; also reported at IS=0.43mm s^{-1}, QS=1.14mm s^{-1} [31]), $SnCl_4 \cdot 2Et_2O$(IS=0.45mm s^{-1}, QS=1.10mm s^{-1} [21]), $SnCl_4 \cdot 2CH_3OH$(IS=0.43mm s^{-1}, QS=0.70mm s^{-1} [30]), $SnCl_4 \cdot 2EtOH$ (IS=0.33mm s^{-1}, QS=0.70mm s^{-1} [30]) and $SnCl_4 \cdot 2DMSO$(IS=0.40mm s^{-1} [30]).

In the reaction of tin(II) chloride with sodium acetylcyclopentadienide, the main product is tin(IV) oxide as observed in the Mössbauer spectrum with an isomer shift of 0.06mm s^{-1}. Also present are unreacted tin(II) chloride (IS=4.20mm s^{-1}) and a tin(IV) compound with an isomer shift of 2.18mm s^{-1}. The mass spectrum of the reaction product shows only $SnCl_2$, SnO_2 and THF molecules present. However, based on the Mössbauer IS of 2.18mm s^{-1}, NMR and IR spectra a tin complex with acetylcyclopentadienide must also be present. The synthesis of SnO_2 is not totally surprising when the resonance structure having the negative charge on the oxygen is considered. The other tin-containing product cannot be completely identified. Based on the NMR, IR and Mössbauer spectra, it is a tin(IV) compound containing ring-substituted cyclopentadienyl ligands. Ring protons are present at δ6.8, 6.2, 5.9 and 5.5ppm as multiplets. Also, in the IR spectrum, C-H stretches are observed at 2962 and 2940cm^{-1} with a C-O stretch at 1655cm^{-1}.

Tin(II) chloride was also reacted with TlC_5H_4X (X=Cl, Br, I) salts. Here, a mixture was isolated. The ^1H NMR shows two weak multiplets at δ5.96 and 5.68ppm after 300 scans in a Fourier-Transform experiment. These multiplets were first though to be caused by a ring-substituted stannocene. But when the Mössbauer and mass spectra data were considered, these lines were assigned to fulvalene, $C_{10}H_8$. The Mössbauer spectrum contains three lines. One small line at IS=0.04mm s^{-1} is consistent with SnO_2. Another at IS=3.86mm s^{-1} can be assigned to a tin(II) compound. The third line corresponds to a tin(IV) complex with an IS=1.74mm s^{-1} (See Figure 5.2.).

Using the mass spectrum to help identify these compounds, ions corresponding to $[C_5H_4]^+$, $[C_5H_5]^+$, $[C_5H_4Cl]^+$, Sn^+, $[C_{10}H_8]^+$, $[SnCl]^+$, $[SnCl_2]^+$, Tl^+ and $[TlCl]^+$ were observed at m/e=64(0.5), 65(0.9), 99(1.5), 120(10.9), 128(2.5), 155(39.8), 190(13.8), 205(100) and 240(2.3), respectively (relative abundances in parenthesis). Also, a set of peaks corresponding to the ion $[TlSnCl_3]^+$ and $[TlSnCl_2]^+$ were observed centered around m/e=430(0.7) and 395(10.5), respectively. The identification was made by calculating the relative abundances of all stable isotopes of Tl, Sn and Cl in all possible combinations, using a method suggested by Glockling.[32] The result of the calculation, along with the actual data, is shown in Figure 5.3. The match is very good. It is better than any combinations of Sn or Sn and Cl.

Inorganic tin(II) salts of the type $MSnCl_3$ where M = K, Rb, Cs and NH_4, are well defined. Vibrational,[33] microanalytical,[34] and Mössbauer[34] data have been collected.

Figure 5.2. ^{119}Sn Mössbauer Spectrum of $SnCl_2 + TlC_5H_4Br$

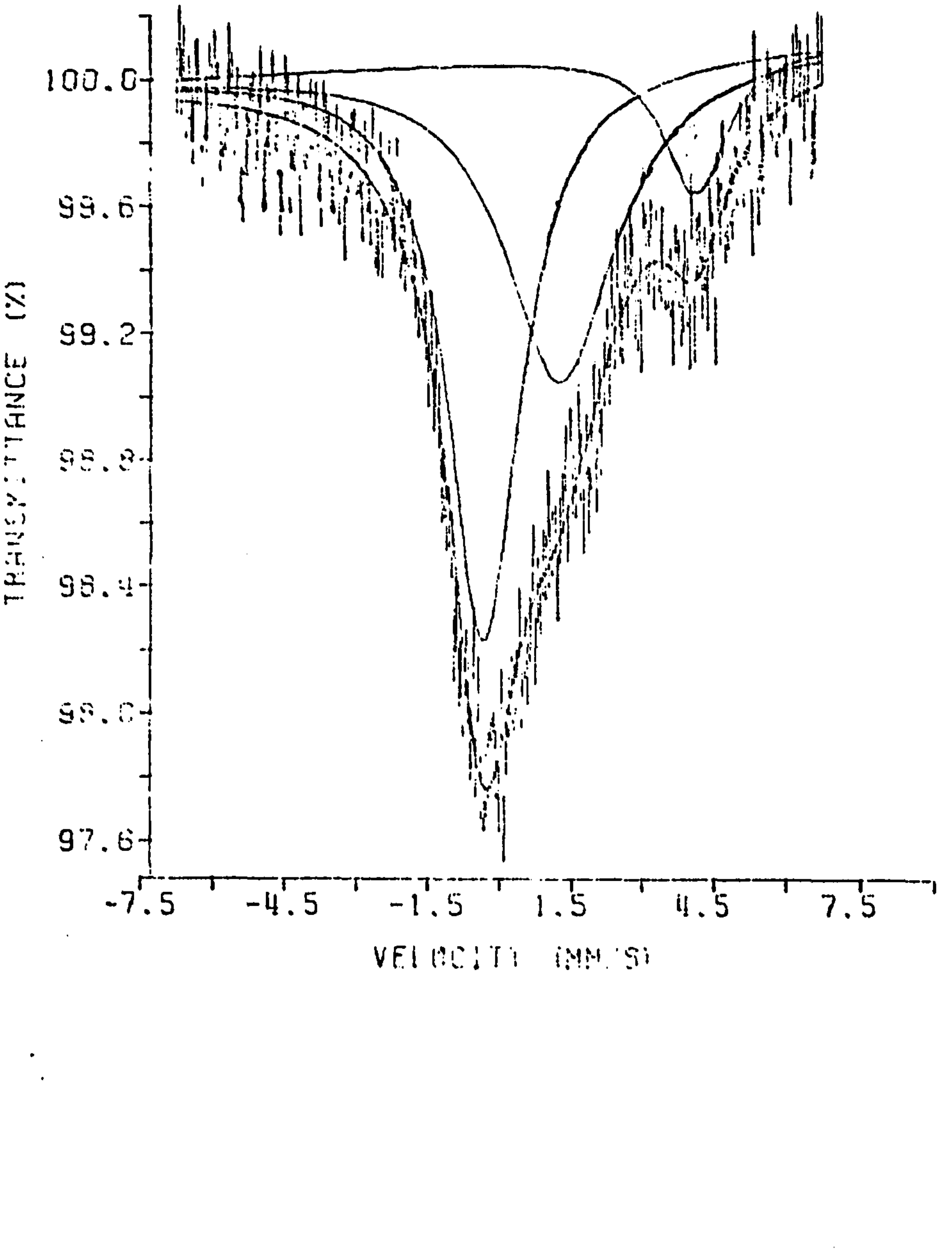
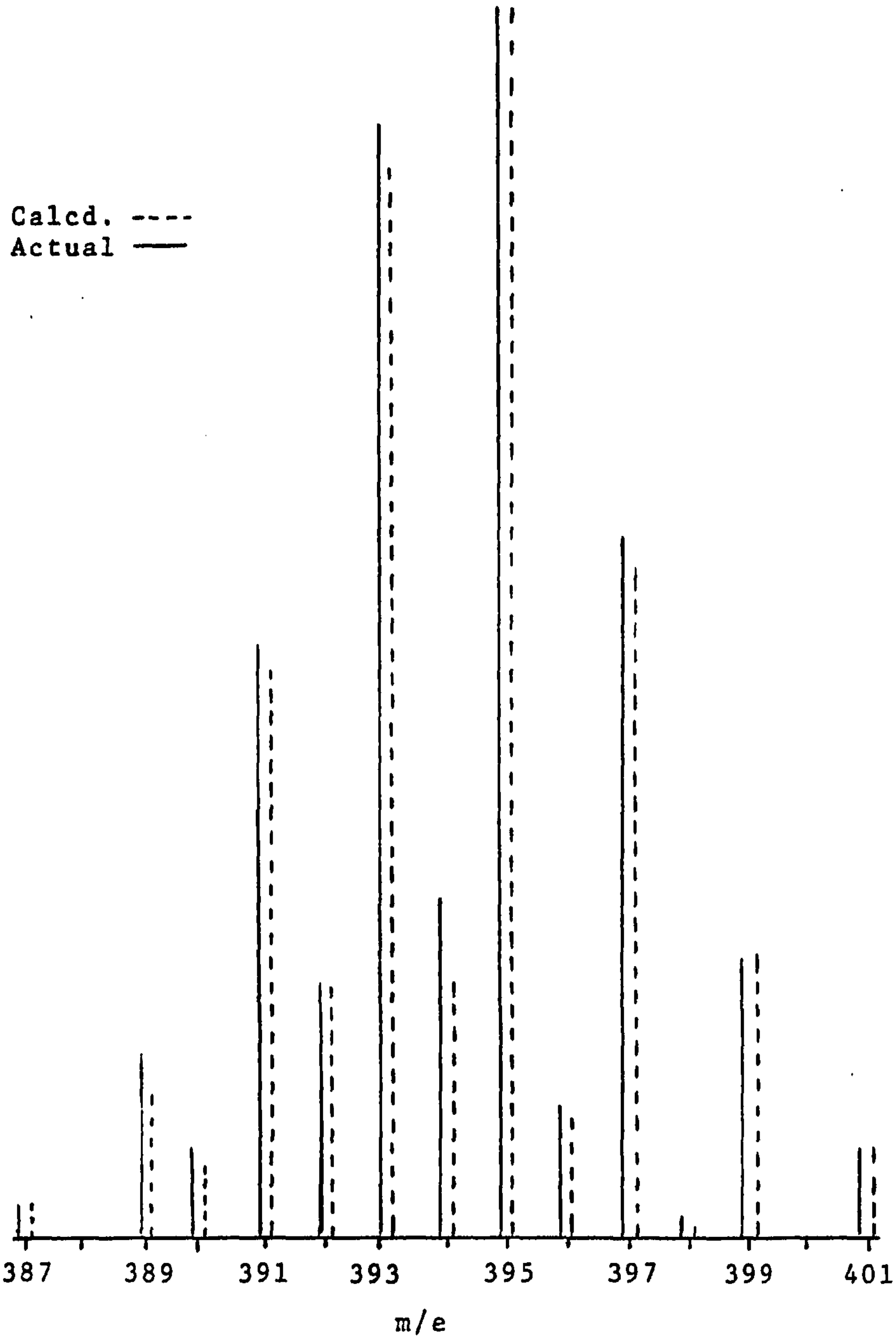
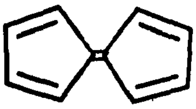


Figure 5.3. Calculated and Actual Isotopic Pattern for the $TlSnCl_2$ Ion.



The crystal structure of $CsSnCl_3$ has been determined.[35] The Mössbauer isomer shifts for these compounds range from 3.56mm s^{-1} for NH_4SnCl_3 to 3.76mm s^{-1} for $KSnCl_3$.[34] The compound $TlSnCl_3$ is less well-defined. The melting point of 258.0°C was determined from phase diagrams of molten $SnCl_2$-TlCl systems.[36] The compound is described as a thallium(I) chloride adduct of tin(II) chloride, $SnCl_2 \cdot TlCl$. This adduct would be consistent with the Mössbauer isomer shift of 3.86mm s^{-1} observed. The reported melting point of 258°C for $SnCl_2 \cdot TlCl$, agrees with the darkening and softening of the reaction product I observed at 260°C.

The mass spectrum shows an ion at m/e = 240 which has the correct isotopic pattern for $[TlCl]^+$. Also, an ion at m/e = 198 can be formulated as $[C_{10}H_8]^+$, fulvalene, which is a by-product of the reaction shown in Equation 5.4.

$SnCl_2 + 2TlC_5H_4Cl \rightarrow SnCl_2 \cdot TlCl + TlCl +$  (5.4)

Fulvalene can be made by flash vacuum pyrolysis of nickelocene followed by air oxidation,[37] by oxidatively coupling sodium cyclopentadienide using iodine to form dihydrofulvalene followed by deprotonation,[38] or by photolysis of diazocyclopentadiene in a fluorocarbon-ether matrix at 77K.[39] Fulvalene is described as a red or red-orange liquid that is air-stable, but quickly polymerizes at room temperature.[38] No NMR data has been reported. The two multiplets observed at δ5.96 and 5.68ppm in the ^1H NMR can be assigned to the protons of the fulvalene molecule. In the ^1H NMR of 9,10-dihydrofulvalene, the ring protons were assigned to a multiplet at δ6.5ppm in $CDCl_3$.[37] The red-brown color of the product from the $SnCl$-TlC_5H_4Cl reaction can be attributed to fulvalene.

The Mössbauer resonance at 1.74mm s^{-1} is due to a tin(IV) compound. Identification of this compound is not possible. There are no major unaccounted for tin-containing peaks in the mass spectrum of the reaction mixture. The ^1H NMR shows two very weak multiplets at 6.43ppm that are not caused by fulvalene. Based on the NMR spectrum, this represents only a small fraction of the reaction product.

The reaction of tin(II) chloride and thallium(I) bromocyclopentadienide produces several products. The ^{119m}Sn Mössbauer spectrum contains three lines. The first with an isomer shift of -0.03mm s^{-1} can be assigned to SnO_2. The weak line at 4.28mm s^{-1} can be attributed to unreacted $SnCl_2$. The position of the third line is somewhat uncertain as it is a shoulder of the SnO_2 line (Figure 5.3). The best fit using our curve-fitting program places this line at 1.48mm s^{-1} indicating a Sn(IV) compound. It is clear, however, that the hoped for product, 1,1′-dibromostannocene, $(\eta^5\text{-}C_5H_4Br)_2Sn$, is not present owing to the lack of any other Sn(II) resonances in the Mössbauer spectrum.

The reaction of tin(II) chloride with thallium(I) iodocyclopentadienide does not produce 1,1′-diiodostannocene as first expected. The light-brown solid isolated from the reaction contains only a tin(IV) adduct as shown by a Mössbauer isomer shift of 0.23mm s^{-1}. It is not unreasonable to suggest that the compound isolated was $SnCl_2I_2 \cdot 2THF$. The isomer shift of frozen solutions of $SnX_4 \cdot 2THF$, where X = Cl, Br, I, increases from 0.20mm s^{-1} when X = Cl to 0.22 for X = Br to 0.72mm s^{-1} for X = I.[40]

Cyclopentadienyltin(II) chloride reacts with $NaC_5H_4C(O)R$, where R = CH_3, OCH_3, OCH_2CH_3, to produce the expected acetyl-, methoxycarbonyl-, and ethoxycarbonylstannocenes. For acetylstannocene, the molecular ion is observed in the mass spectrum at m/e = 292. The ^{119m}Sn Mössbauer spectrum shows a tin(II) doublet spectrum with IS=2.98 and QS=2.21mm s^{-1}. The IS is somewhat lower than that reported for stannocene[41] (IS=3.73), but is still in the area associated with tin(II) compounds.[42] The lower isomer shift indicates a lowering of s-electron density about the tin nucleus. Partial coordination of the carbonyl oxygen to the tin atom would change the electron density at the tin atom. Many such examples of Sn(II)-O coordination are known in the literature.[43] The coordination number at tin varies from 3 in $Ca[Sn(O_2CCH_3)_3]_2$[44] to 4 in $Sn[OCH(C_6H_5)CH_2CH(C_6H_5)O]_2$[45] and $Sn(O_2CH)_2$[46] to 6 in β-$SnWO_4$[47] and to 8 in $Sn(H_2PO_4)_2$.[45] Tin(II)-oxygen distances vary from 2.14Å in $Ca[Sn(O_2CCH_3)_3]_2$[42] to 3.048Å (avg) in $Sn(H_2PO_4)_2$.[48] The high melting point (>270°C) and low carbonyl stretch in the IR spectrum ($1650cm^{-1}$) argue for Sn-O coordination. The carbonyl stretching band is at a shorter wavelength than in the ligand ($1538cm^{-1}$). This is expected if the negative charge on the anion part of the salt $[C_5H_4C(O)CH_3]^-$ is no longer localized on the C-O part of the molecule. Bonding of the ring to the tin brings this about.

Methoxycarbonylstannocene also has a high melting point (>260°C) and the rather low C-O stretching bands in the IR of $1615cm^{-1}$ for $\nu_{c=o}$ and $1340cm^{-1}$ for ν_{c-o}. But these bands do not differ significantly from the C-O stretching bands in the IR spectrum of the ligand ($\nu_{c=o}$ = $1618cm^{-1}$, ν_{c-o} = $1310cm^{-1}$).

All three ring-substituted stannocenes have large quadrupole splittings. The QS value is directly related to the electric field gradient (E.F.G.) at the tin nucleus. One major cause of an E.F.G. is an imbalance in the polarity of the tin-ligand bonds. This can be expected when one of the ligands contains polarizable groups such as carbonyls. Another cause of E.F.G. is bond angle between the tin and ligands. The E.F.G. should increase with the percentage of ρ-character in the tin lone pair electrons and δ-character in the bonding orbitals, from a minimum value for the case of two linearly bound ligands with the lone pair in a spherically symmetrical, 5s-atomic orbital.

5.13 CONCLUSIONS

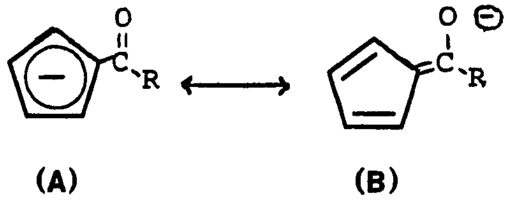
It was first hoped that the reactions of $SnCl_2$ with ring-substituted salts of the form MC_5H_4R, where M = Na, R = $C(O)CH_3$; M = Tl, R = Cl, Br, I, would produce ring-substituted stannocenes of the general formula $(\eta^5\text{-}C_5H_4R)_2Sn$. This did not occur. Instead, tin(II) chloride and sodium acetylcyclopentadienide produce mainly tin(IV) oxide, SnO_2, in an oxidation reaction. When $SnCl_2$ and TlC_5H_4Cl were reacted, the major product isolated was the inorganic tin(II) salt, $TlSnCl_3$. Mössbauer data, the mass spectrum and the melting point, all support the identification of this product. Fulvalene was also identified as a side product by its mass spectrum.

The reaction of $SnCl_2$ and TlC_5H_4X, X = Br, I, does not produce the corresponding $TlSnCl_2X_2$ type compounds.

A mixture of SnO_2 and an unidentified Sn(IV) compound were isolated in the case of bromocyclopentadienide. When TlC_5H_4I was reacted with $SnCl_2$, only a tin(IV) compound having an IS=0.23mm s^{-1} was isolated. Based on Mössbauer data for other halotin(IV) adducts with donor solvents, the product was formulated as $SnCl_2I_2 \cdot 2THF$.

Two trialkyltin(IV) chlorides were reacted with sodium acetylcyclopentadienide. The products found in these two reactions were not the expected trialkyltin(IV) cyclopentadienyls, $R_3Sn(\eta^1\text{-}C_5H_4C(O)CH_3)$. Hexamethyldistannoxane and hexaphenyldistannoxane were the only products isolated from the reaction of $NaC_5H_4C(O)CH_3$ with CH_3SnCl and $(C_6H_5)_3SnCl$, respectively. A combination of IR, NMR and mass spectrocopy was used to identify these compounds.

These reactions can be understood if one considers the resonance structures possible for these salts. As shown below, the negative charge can be placed on the oxygen atom of the salt. This then, would be the point of addition to the tin compounds.



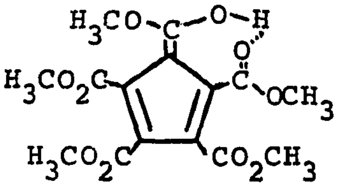
The low $\nu_{C=O}$ observed in the IR for this salt, indicates the C=O bonds strength is lower than that found in normal C=O bonds. This suggests Structure B.

The reaction of cyclopentadienyltin(II) chloride with sodium acetyl-, methoxycarbonyl- and ethoxycarbonylcyclopentadienide produces acetyl-, methoxycarbonyl- and ethoxycarbonylstannocene, respectively. These are the first reported ring-substituted stannocenes with the exception of the simple methyl- and pentamethylcyclopentadienes. In a very recent report, the reaction between decamethylstannocene and the acid $HC_5(COOCH_3)_5$ was reported of product $[C_5(CH_3)_5]Sn[C_5(COOCH_3)_5]$ and $[C_5(COOCH_3)_5]_2Sn$, depending on solvent and stochiometric ratios used.[50]

$$HC_5(COOCH_3)_5 + [\eta^5\text{-}C_5(CH_3)_5]_2Sn \rightarrow [\eta^5\text{-}C_5(CH_3)_5SnC_5(COOCH_3)_5] + HC_5(CH_3)_5 \qquad (5.5)$$

$$2HC_5(COOCH_3)_5 + [\eta^5\text{-}C_5(CH_3)_5]_2Sn \rightarrow [C_5(COOCH_3)_5]_2Sn + 2HC_5(CH_3)_5 \qquad (5.6)$$

The authors describe the former tin compound as an ionic salt. Very little information is provided on the latter compound. The crystal structure of the acid has been solved, showing the following structure:[51]



Because the acidic proton is attached to the oxygen, the structure of the tin compound probability involves a Sn-O bond rather than π-bonded rings, as would be observed in a ring-substituted stannocene.

For the case of acetylstannocene, the molecular ion was observed in the mass spectrum. All three stannocenes had isomer shifts in the tin(II) region of the Mössbauer spectrum. The proton NMR spectra of these three substituted stannocenes is consistent with the formulation of $(\eta^5\text{-}C_5H_5)Sn(\eta^5\text{-}C_5H_4R)$, R = $C(O)CH_3$, $C(O)OCH_3$, $C(O))CH_2CH_3$. The carbonyl bands in the IR spectra are higher in the stannocenes when compared to the free ligands. For example, $\nu_{c=o}$ in $NaC_5H_4C(O)CH_3$ is $1538cm^{-1}$ vs. the $\nu_{c=o}$ of $1650cm^{-1}$ found in acetylstannocene. The increase of over 100 wavenumbers indicates a strengthening of the C=O bond with more double bond character present in acetylstannocene. If the tin atom was bonded through the oxygen atom of the ligand, there would not be an increase in $\nu_{c=o}$ expected. The large QS values are owing to an asymmetric electric field gradient at the tin atom. Having two different ligands, C_5H_5 and C_5H_4R, attached to tin, will produce an assymetric electric field gradient, as will tin-oxygen coordination, if present. The structure for these ring-substituted stannocenes can be assumed to be similar to the parent stannocene[49] which is a bent sandwich molecule. But due to the high melting points (>260°C) of these compounds, an associated polymer with bonding through carbonyl oxygen to Sn(II) coordination must certainly be present.

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CHAPTER VI

REACTIONS BETWEEN TIN(II) AND MOLYBDENUM COMPOUNDS

6.1 INTRODUCTION

Stannocene is known to undergo substitution reactions involving loss of the cyclopentadienyl rings and formation of new tin(II) compounds when reacted with protonic acids according to Equation 6.1 [1]

$$Sn(\eta^5\text{-}C_5H_5)_2 + 2HR \rightarrow SnR_2 + 2C_5H_6 \qquad (6.1)$$

where $R = OR'$, CN Cl, OC_6H_5, SR', O_2CR', $ONCR'$; $R' = CH_3$, C_6H_{13}, C_7H_{15}, $CH_2C_6H_5$, C_6H_5, t-Bu.

When the acid is cyclopentadienyltricarbonylmolybdenum hydride an oxidative-addition reaction takes place, Equation 6.2, forming a tin(IV) hydride.[2]

$$Sn(\eta^5\text{-}C_5H_5)_2 + 3HMo(CO)_3\text{-}\eta^5\text{-}C_5H_5 \rightarrow HSn[Mo(CO)_3\text{-}\eta^5C_5H_5]_3 + 2C_5H_6 \qquad (6.2)$$

It was thought that if the lone-pair electrons in stannocene were restrained by coordination with the Lewis acid boron trifluoride, a simple substitution reaction would take place and not the oxidative-addition reaction.

The boron trifluoride adduct of stannocene was prepared then reacted with cyclopentadienyltricarbonylmolybdenum hydride. The product, isolated as orange hexagonal shaped needle-like crystals, was characterized by ^{1}H, ^{11}B, ^{19}F, ^{119}Sn NMR, IR, melting point, Mössbauer, mass spectroscopy and microanalytical analysis. Two single crystal x-ray diffraction data sets were collected. The data would not refine to a satisfactory solution.

The reaction between stannocene and $HMo(CO)_3C_5(CH_3)_5$-η^5 produced the expected tris(pentamethylcyclopentadienyltricarbonylmolybdenum)tin(IV) hydride, $HSn[Mo(CO)_3$-η^5-$C_5(CH_3)_5]_3$. This compound was characterized by ^{1}H NMR, IR, melting point, Mössbauer spectroscopy and microanalytical analysis.

The new compound pentamethylcyclopentadienyltricarbonylmolybdenum hydride was synthesized and characterized. It was made later, but first reported by M. R. DuBois.[3]

6.2 SYNTHESIS OF PENTAMETHYLCYCLOPENTADIENYLTRICARBONYLMOLYBDENUM HYDRIDE

All reactions were carried out in a pure nitrogen atmosphere.

A three-necked round-bottomed flask equipped with a reflux condenser, pressure equalizing dropping funnel and gas inlet tube was charged with pentamethylcyclopentadiene

(2.60mL, 19.4mmol) in THF (25mL) then placed in an ice bath. The dropping funnel was charged with n-butyllithium (5.35mL, 18.8mmol) in THF (25mL). With stirring the n-butyllithium solution was added dropwise. Butane gas was given off with the formation of lithium pentamethylcyclopentadienide.

The dropping funnel was charged with a molybdenum hexacarbonyl (5.0g, 18.9mmol) THF (50mL) slurry. The flask was warmed to room temperature and the slurry added. The flask was heated to reflux for eight hours resulting in a clear dark yellow solution. Heating was stopped when no more carbon monoxide was observed coming off. During the first hour of heating, unreacted molybdenum hexacarbonyl may sublime onto the condenser. This should be scraped back into the flask. If not, it may block the passage of carbon monoxide from the flask resulting in a pressure build-up and explosion. The dark yellow solution contains $LiMo(CO)_3$-η^5-$C_5(CH_3)_5$ produced according to Equation 6.3.

$$LiC_5(CH_3)_5 + Mo(CO)_6 \longrightarrow LiMo(CO)_3C_5(CH_3)_5\text{-}\eta^5 + 3CO \quad (6.3)$$

To this solution, degassed glacial acetic acid (3mL, 42mmol) was added with stirring. The solution was stirred for two hours during which time, the light yellow solid pentamethylcyclopentadienyltricarbonylmolybdenum hydride formed, Equation 6.4.

$$CH_3C(O)OH + LiMo(CO)_3C_5(CH_3)_5 \longrightarrow HMo(CO)_3C_5(CH_3) + CH_3C(O)OLi \qquad (6.4)$$

The solvent was removed by vacuum leaving a yellow-brown solid. Hexane was used to recrystallize yellow $HMo(CO)_3C_5(CH_3)_5$ (3.64g, 60.8% yield) from the crude product. The hydride can also be isolated by vacuum sublimation at 48°C and 0.4mmHg.

The melting point was found to be 92-94°C with some decomposition. The pentamethylcyclopentadienyl protons appear as a singlet at δ1.65ppm with the metal hydride proton appearing as a singlet at -5.05ppm in C_6D_6. The correct integration ratio of 15:1 was found. The IR spectrum in C_6H_6 showed bands at 2945(m), 2908(m), 2858(m), 2035(s), 2010(s), 1995(s), 1923(s), 1850(m), 1823(m), 1448(w), 1380(m), 1260(m, sharp), 1050(m), 800(m, sharp) cm^{-1}. The carbonyl bands appear between 2035 and 1823 cm^{-1}. Microanalytical data calculated for $HMo(CO)_3C_6(CH_3)_5$ was 49.37%C, 5.11%H; found 49.91%C, 5.23%H.

6.3 SYNTHESIS OF TRIS(PENTAMETHYLCYCLOPENTADIENYLTRICARBONYLMOLYBDENUM)TIN(IV) HYDRIDE

A three-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel, fritted glass filter stick and a gas inlet tube was charged with stannocene (5.0g, 20.1mmol) and hexane (100mL). The dropping funnel was charged with $HMo(CO)_3C_5(CH_3)_5$ (19.1g, 60.4mmol) in hexane (100mL). The molybdenum hydride was added with stirring. Within ten minutes, a red-brown solid formed. Stirring was continued for two hours then stopped. The solution stood an additional hour and filtered producing the title compound, $HSn[Mo(CO)_3C_5(CH_3)_5\text{-}\eta^5]_3$ (18.2g, 85% yield) according to Equation 6.5.

$$3HMo(CO)_3C_5(CH_3)\text{-}\eta^5 + Sn(\eta\text{-}C_5H_5)_2 \rightarrow HSn[Mo(CO)_3\text{-}C_5(CH_3)_5\text{-}\eta^5]_3 + 2C_5H_6 \qquad (6.5)$$

The red powder melts with decomposition at 275°C. In C_6D_6, the ^1H NMR resonance of the hydride proton is at δ6.18ppm with the methyl protons on the ring appearing at 1.77ppm. The integration ratio of 1:43 (1:45 calcd) was found. The IR spectrum in C_6H_6 showed bands at 2982(w), 2920(w), 2880(m), 2820(w), 2030(w), 1963(m), 1935(s), 1900(s), 1880(sh), 1452(m), 1382(w), 1355(w), 1200(m), 1109(s), 855(w), 750(w), 655(w) and 272(w) cm^{-1}. The ^{119m}Sn Mössbauer spectrum contains a well resolved doublet at I.S. = 1.86(3)mm s^{-1} and Q.S. = 1.56(6)mm s^{-1}. Microanalytical data calculated for $HSn[Mo(CO)_3\text{-}\eta^5\text{-}C_5(CH_3)_5]_3$ was 45.24%C, 4.49%H; found 41.59%C, 4.52%H.

6.4 REACTIONS OF THE BORON TRIFLUORIDE ADDUCT OF STANNOCENE WITH CYCLOPENTADIENYLTRICARBONYLMOLYBDENUM HYDRIDE

The boron trifluoride adduct of stannocene[4] and cyclopentadienyltricarbonylmolybdenum hydride[5] were freshly prepared according to literature methods. The molybdenum hydride was sublimed (0.1Torr, 50°C) just before use. The boron trifluoride adduct of stannocene was recrystallized from THF/hexane. The reaction was carried out in a nitrogen-filled dry box using standard Schlenkware. A Schlenk tube was charged with the tin adduct (2.0g, 6.3mmol) and hexane (250mL). To this solution the molybdenum hydride (3.11g, 12.6mmol) in THF (75mL) was added slowly with stirring. Stirring was continued for two hours resulting in a small amount of a light gray-brown solid. The solution was filtered with the filtrate saved. Standing overnight produced orange hexagonal needle-like crystals. The crystals were removed, washed with hexane and dried, producing 3.86g with a melting point of 215-217°C. The ^1H NMR in C_6D_6 showed a singlet at δ4.95ppm owing to cyclopentadienyl protons. The IR spectrum (CsI pellet) showed bands at 3120(w), 2950(sh), 2925(m), 2010(sh), 1995(s), 1980(s), 1913(s), 1896(sh), 1425(m), 1355(w), 1262(w), 1062(w), 1010(w), 836(m), 816(m, sharp), 582(m), 558(s, sharp), 508(m), 455(m), 392(m), 295(m), 282(s, sharp) and 258(w) cm^{-1}. The

^{119m}Sn Mössbauer spectrum contains a doublet at IS = 1.87(3) mm s^{-1} and QS = 1.55(6)mm s^{-1}. Microanalytical data found was 35.08%C, 2.47%H, 16.96%Sn, 21,64%Mo, 1009 molecular weight.

The ^{11}B NMR ($C_6D_6/BF_3 \cdot Et_2D$) spectrum showed three broad lines at δ192.51, 51.14 and -164.21ppm. The ^{19}F NMR (C_6D_6/CF_3COOCH) spectrum contains a singlet at -79.35ppm showing a fluorine-tin coupling of $^{1}J(^{19}F-^{119}Sn)$ = 2610Hz. The ^{119}Sn NMR (C_6D_6/Me_4Sn) spectrum contains one doublet centered at 662.5ppm with $^{1}J(^{119}Sn-^{19}F)$ = 2608Hz. Using standard flotation techniques the density was found to be 2.035g/cm^3 for these orange crystals.

X-ray data were collected twice on two different crystals. One set of crystals were grown from a THF/ hexane solution. The second set of crystals were formed in an acetone/ethanol solution. Both sets produced the same cell parameters. However, in both cases, the data would not refine regardless of the space group tried.

Mass spectral data were collected at 12eV using a single crystal. The parent ion (m/e = 629) corresponds to $\{FSn[Mo(CO)_3C_5H_5]\}^+$. Loss of the six carbon monoxide ligands was observed along with the break-up of a single $[Mo(CO)_3C_5H_5]^+$ ion. The ion at m/e = 72 was assigned to THF$^+$ while the ion at m/e = 66 was assigned to $[F_2BOH]^+$. The spectrum is listed in Table 6.1.

Table 6.1. Mass Spectral Data for the BF_3 Adduct of Stannocene + $HMo(CO)_3$-η^5-C_5H_5

m/e	Relative Abundance	Assignment[a]
629	2.9	$\{FSn[Mo(CO)_3C_5H_5]_2\}^+$
490	4.0	$\{[Mo(CO)_3C_5H_5]_2\}^+$
462	20.6	$[Mo_2(CO)_5(C_5H_5)_2]^+$
434	100.0	$\{[Mo(CO)_2C_5H_5]_2\}^+$
406	55.1	$[Mo_2(CO)_3(C_5H_5)_2]^+$
378	62.6	$\{[Mo(CO)C_5H_5]_2\}^+$
350	6.3	$[Mo_2(CO)(C_5H_5)_2]^+$
322	78.9	$\{[MoC_5H_5]_2\}^+$
247	46.9	$[Mo(CO)_3C_5H_5]^+$
219	61.4	$[Mo(CO)_2C_5H_5]^+$
191	26.3	$[Mo(CO)C_5H_5]^+$
163	23.1	$[MoC_5H_5]^+$
72	9.4	$[C_4H_8O]^+$
66	5.4	$[F_2BOH]^+$

[a] Based on ^{1}H, ^{11}B, ^{12}C, ^{16}O, ^{19}F, ^{98}Mo, ^{120}Sn.

6.5 DISCUSSION

The synthesis of pentamethylcyclopentadienyltricarbonylmolybdenum hydride follows the synthesis of cyclopentadienyltricarbonylmolybdenum hydride.[5] There is a slight shift in the resonance of the hydride proton in the NMR from δ-5.40 to -5.05ppm for $HMo(CO)_3C_5H_5$ and $HMo(CO)_3C_5(CH_3)_5$, respectively. The metal carbonyl bands appear at 2035, 1995, 1923 (C_6H_6 solution) vs. 2030, 1949 cm^{-1} (CS_2 solution) for $HMo(CO)_3C_5(CH_3)_5$ and $HMo(CO)_3C_5H_5$, respectively. There is not much difference in the properties of the two compounds. It was noted, however, that the pentamethylcyclopentadienyl derivative is less air sensitive than the cyclopentadienyl derivative, but both still decompose when exposed to air.

The synthesis of $HSn[Mo(CO)_3C_5(CH_3)_5]_3$ followed the literature preparation of $HSn[Mo(CO)_3C_5H_5]_3$.[2] There is a large increase in melting point on going from $HSn[Mo(CO)_3C_5H_5]_3$ (mp = 175d°C)[2] to $HSn[Mo(CO)_3C_5(CH_3)_5]_3$ (mp = 275d°C). There is a shift in the metal hydride proton resonance from δ5.58ppm to 6.18ppm for $HSn[Mo(CO)_3C_5H_5]_3$ and $HSn[Mo(CO)_3C_5(CH_3)_5]_3$, respectively. This is a shift towards a less shielded proton in the pentamethyl compound. There is not a significant change in the metal carbonyl stretching frequencies of 2030 (2026), 1963(1985), 1935(1929) and 1900(1907) cm^{-1}; $HSn[Mo(CO)_3C_5H_5]_3$ in parenthesis.

The reaction of the boron trifluoride adduct of stannocene with $HMo(CO)_3C_5H_5$ is somewhat complicated. One reason for this was that the completion of the single crystal x-ray structure of $(\eta^5\text{-}C_5H_5)_2Sn{\rightarrow}BF_3$ produced a remarkably different structure than what was originally proposed, $(\eta^5\text{-}C_5H_5)_2Sn{\rightarrow}BF_3$.[4] A more correct formulation can be written as $[BF_4]^-[\eta^5\text{-}C_5H_5Sn]^+(\eta^5\text{-}C_5H_5)_2Sn{\cdot}THF$. The structure contains one tin coordinated to the oxygen in THF and the other tin to a fluorine in BF_4^-. This structure is discussed in detail in Chapter II of this dissertation. With the correct adduct structure known, a rethinking of the expected reaction product with $HMo(CO)_3C_5H_5$ was necessary.

The analytical data collected on these orange crystals at first seemed somewhat conflicting. Microanalytical data found for %C, %H, %Sn, %Mo and molecular weight does not fit any reasonable formulation. The possible and not so possible formulas and data are listed in Table 6.2. The compound has a high but sharp melting point of 215-217°C. The Mössbauer parameters of IS = 1.87, Q.S. = 1.55 mm s^{-1} are consistant with a tin(IV) compound having a very asymmetric electric field gradient. The asymmetric electric field gradient can be caused by a tin-fluorine bond. Further support of a tin-fluorine bond is the observation of $^1J(^{19}F\text{-}^{119}Sn)$ coupling of

Table 6.2. Possible Formulations of the Product of the BF_3 Adduct of Stannocene and $HMo(CO)_3(\eta^5-C_5H_5)$

	Found	$THF\cdot SnMp_3BF_4$ [a]	$THF\cdot Sn(F)Mp_2BF_2$	$THF\cdot Sn(F)Mp_2BF_3$	$THF\cdot Sn(F)Mp_2BF_4$
%C	34.87	33.19	32.08	31.29	30.53
%H	2.48	2.29	2.43	2.37	2.31
%Sn	16.96	11.72	15.85	15.46	15.09
%Mo	21.64	28.42	25.63	24.99	24.40
mole. wt. [b]	1009	1013	749	768	787

[a] $Mp = Mo(CO)_3(\eta^5-C_5H_5)$

[b] Determined by V.P.O.

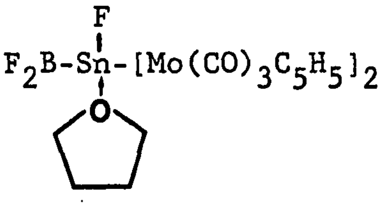
2610Hz in the ^{19}F NMR. The ^{1}H NMR spectrum shows a singlet at δ4.95ppm which is consistant with a π-molybdenum bonded cyclopentadienyl ring. Several of these systems are known. A few examples include $HSn[Mo(CO)_3C_5H_5]_3$ at 4.83ppm[2], $HMo(CO)_3C_5H_5$ at 5.4ppm[5], $ClSn[Mo(CO)_3C_5H_5]_3$ at 4.95ppm[2] and $[Mo(CO)_3C_5H_5]_2$ at 4.73ppm. The absence of the molybdenum hydride proton resonance (-5.05ppm) in the product indicates a reaction took place.

Also observed in the ^{1}H NMR, were two multiplets at 3.60 and 1.86ppm owing to THF. The integration ratio of THF:C_5H_5 was found to be 13:19 (16:20 calcd for THF:$2C_5H_5$) which approximates one THF molecule for every two cyclopentadienyl molecules. The crystals were placed in a vacuum oven (0.4mmHg, 75°C) for eight hours with no change in the integration ratio between THF and cyclopentadienyl protons.

The IR carbonyl stretching bands are consistent with terminally bonded metal carbonyl ligands. The crystals are freely soluble in benzene, acetone, toluene and THF. The density measured using standard flotation techniques was found to be $2.04 g/cm^3$.

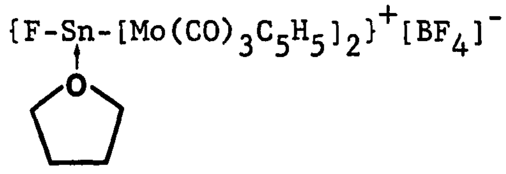
The ^{119}Sn NMR spectrum contains one doublet at 662.5ppm with $^{1}J(^{119}Sn-^{19}F) = 2608Hz$. The ^{19}F NMR spectrum contains a singlet at -79.35ppm with $^{1}J(^{19}F-^{119}Sn) = 2610Hz$. This is good agreement between the coupling constants in the spectra. This is a large coupling but not completely unknown. The $^1J(^{19}F-^{119}Sn)$ of 2298Hz has been reported for $(C_6H_5CH_2(CH_3)_2 \cdot C)_3SnF$.[8] Tin(IV) fluoride adducts with pyridine-N-oxides also have coupling constants near 2000Hz in the ^{19}F NMR.[9] The ^{19}F NMR also shows three small peaks at approximately -34, -38 and -41ppm. The peaks at -34 and -41 are rather broad.

Based on this collection of data, a reaction product can be written starting from $[BF_4]^-[\eta^5-C_5H_5Sn]^+(\eta^5-C_5H_5)_2Sn \cdot THF$. The product can be formulated as a tin(IV)-fluorine compound having two $Mo(CO)_3C_5H_5$ ligands and one THF ligand. Two possible structures are:



$F_2B-Sn(F)(THF)-[Mo(CO)_3C_5H_5]_2$

(A)



$\{F-Sn(THF)-[Mo(CO)_3C_5H_5]_2\}^+[BF_4]^-$

(B)

In both A and B, the cyclopentadienyl rings have been replaced by $Mo(CO)_3C_5H_5$ groups in the BF_3 adduct of stannocene while the tin-oxygen coordination with THF remains.

6.6 CONCLUSIONS

Pentamethylcyclopentadienyltricarbonylmolybdenum hydride was synthesized. It was later reported in the literature.[3] The reaction of this ligand with stannocene produces the expected tin(IV) hydride, $HSn[Mo(CO)_3C_5(CH_3)_5]_3$. The reaction between the boron trifluoride adduct of stannocene and cyclopentadienyltricarbonylmolybdenum hydride does not produce the tin(II) compound, $F_3B \leftarrow Sn[Mo(CO)_3C_5H_5]_2$. By solving the single crystal x-ray structure of the stannocene boron trifluoride, it was realized that the compound is not a simple adduct. This helped to rationalize the product from the reaction of these two compounds as a tin(IV) fluoride.

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APPENDIX

EXPERIMENTAL

7.1 PHYSICAL METHODS

a. Melting Points.

Melting points were measured on a Thomas-Hoover capillary melting point apparatus using sealed capillary tubes and are uncorrected.

b. Elemental Analyses.

Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. Percent tin was done in this laboratory using standard gravimetric techniques.

c. Infrared Spectra.

Infrared spectra were recorded on a Beckman 4250 spectrometer in the 4000 to 200cm^{-1} range using 0.1mm matched KBr cells, KBr pellets of CsI plates.

d. Nuclear Magnetic Resonance Spectra.

Nuclear magnetic resonance spectra were recorded on a Varian T60 instrument for proton resonance and on an IBM N-80 FT spectrometer for proton and carbon spectra. Tetramethylsilane was used as an internal standard for all spectra. Boron, fluorine and tin spectra were recorded at the Colorado State University Regional NMR Center at Fort Collins, Colorado.

e. Mass Spectra.

Mass spectra were recorded on a Hewlett-Packard 5985B GS/MS system. All spectra were recorded at 70eV except where noted.

f. Mössbauer Spectra.

Mössbauer spectra were recorded on a Ranger Engineering constant acceleration spectometer. The spectrometer was equiped with a NaI scintillation counter using $Ca^{119}SnO_3$ as both source and standard reference material for zero velocity. The spectra were recorded at 77 K. The velocity calibration was based on natural iron at 298 K. The data were fitted to Lorentzian curves by standard, nonlinear, least-squares techniques.

g. Raman Spectra.

Raman spectra were recorded on a Spex Ramalog 5 laser spectrometer using sealed capillary tubes to hold the samples.

7.2 SOLVENTS

Solvents used were of reagent grade. All solvents were dried and freed from oxygen by refluxing under nitrogen with benzophenone and sodium or potassium metal just prior to use or stored under nitrogen.