# CYCLOPENTADIENYL AND RELATED DERIVATIVES OF GERMANIUM AND TIN

by

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B.Sc., Queens University of Belfast, N. I., 1976

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Chemistry

We accept this dissertation as conforming
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## ABSTRACT

The preparation and spectroscopic properties of six poly-cyclopentadienyl and -methylcyclopentadienyl derivatives of germane and stannane are described. The temperature dependence of $^1$H and $^{13}$C NMR data are discussed, leading to conclusions regarding the nature of metallotropic migrations in both ring systems. Metallotropic shifts within the methylcyclopentadienyl derivatives result in the interconversion of different isomers, the relative concentrations of which depend on both the size of the metal atom and steric requirements of the substituents.

The NMR properties of a number of polyindenyl derivatives of germane and stannane are examined over a wide range of temperatures. The relative concentrations of isomers present in solutions of these compounds are consistent with zero free energy differences between the ground states of the isomers for any particular compound. Interconversion between these isomers occurs as a result of facile migration of the metal substituent across each indenyl ring. The solid state structure of one isomer of tetra(1-indenyl)stannane, the *meso*-form, has been determined by X-ray crystallography; some commentary on the significance of this structure which belongs to the symmetry point group $S_4$ is given.

Three analogues of cyclopentadiene, bearing the same asymmetric tin substituent have been prepared and their spectral properties are discussed. The nature of the rearrangement process in these compounds is identified through the examination of diastereotopic effects among substituents on the chiral tin center. Migration in each case involves retention of configuration at the metal center and possesses characteristics similar to a Woodward-Hoffmann [1,5] shift.

The synthesis of bis(methylcyclopentadienyl)germanium(II) is described and its physical and chemical properties discussed. Synthesis and spectroscopic properties of nine germylene derivatives of enolisable diketones are described. Two platinum(0) derivatives having either bis(acetylacetonato)-tin(II) or -germanium(II) ligands in which the groupIVA metal (metalloid) functions as a two electron donor have been isolated and their spectroscopic properties are described. The solid state structure of the tin complex has been determined by X-ray crystallography and some important features are discussed.

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| | |
|---|---|
| acacH | acetylacetone |
| $Bu^{\underline{t}}$ | *tertiary*butyl |
| Et | ethyl |
| IR | infrared |
| *i*-Pr | *iso*propyl |
| Me | methyl |
| MS | mass spectrum |
| NMR | nuclear magnetic resonance |
| Ph | phenyl |
| ppm | parts per million |
| R | alkyl or aryl |
| THF | tetrahydrofuran |
| TMP | trimethylphosphite |
| TMS | tetramethylsilane |

# ACKNOWLEDGEMENTS

I would like to thank Dr. S. R. Stobart for his advice and support throughout the past several years.

I would also like to thank the University of Victoria and the Research Corporation (Cottrell Foundation) for financial support.

To Helen.

# PREFACE

The work described in this thesis deals with the synthesis and properties of a variety of compounds of germanium and tin. Chapter One outlines the scope of the thesis and provides background information to work contained in the subsequent chapters.

In Chapter Two the non-rigid properties associated with metallocyclopentadienes and metallomethylcyclopentadienes is examined through the use of variable temperature $^{1}$H and $^{13}$C NMR spectroscopy. Related migrations in polyindenyl derivatives of germanium and tin are reported in Chapter Three. Chapter Four lists information derived about the rearrangement processes in pentamethylcyclopentadiene, methylcyclopentadiene and indene ring systems bearing a chiral tin substituent.

Chapter Five describes both the physical and chemical properties of a number of new derivatives of bivalent germanium and tin.

# CHAPTER ONE

# INTRODUCTION

## A. GENERAL

The unique position of carbon among the ninety natural elements is primarily the result of its ability to form stable long-chain and cyclic compounds having adjacent carbon atoms connected by single, double or triple bonds. The valence state of carbon in such compounds is invariably four, a situation paralleled by the lower group IVA elements in the majority of their known compounds. In the latter the coordination number is also often four, the central atom assuming a geometry which closely approximates to tetrahedral, but the tendency towards adoping higher coordination numbers increases with increasing atomic number.[1,2,3] This is thought[2,3] to be facilitated in part by utilization of vacant outer *nd* orbitals, and leads to coordination numbers of five and six through both inter- and intra-molecular coordination. Eight coordinate species have been characterized[2,3] for both tin and lead.

The multiple bonds observed in carbon chemistry which result from overlap between singly occupied *2p* orbitals on adjacent carbon atoms are not a feature of the chemistry of the other group IVA elements. Recently, however, a variety of intermediates containing silicon-carbon double bonds have been postulated;[4] and a thermally stable example $(Me_3Si)_2Si = C(CMe_3)(OSiMe_3)$, has now been isolated.[5,6]

Multiple-bond character of a different type, arising from overlap between vacant *3d* orbitals on silicon and filled "non-bonding" orbitals on adjacent atoms, (Figure 1.1) has been proposed [7,8] to explain the stronger silicon-halogen bonds compared to corresponding carbon-halogen bonds, and the structural planarity and lower basicity of silylamines compared to carbon analogues. This effect is greatest for silicon and much less apparent in the chemistry of germanium, tin, and lead.

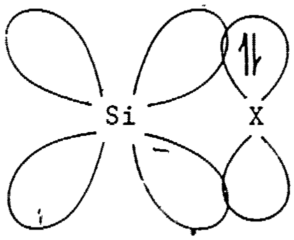
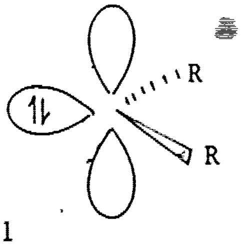


FIGURE 1.1. Proposed $d\pi - p\pi$ overlap in some silicon compounds.

The group IVA elements have an outer valence shell ground-state electronic configuration of $ns^2np_x^1np_y^1$, where $n$ changes from 2 for carbon to 6 for lead. The bivalent state requires only two electrons to form the two bonds in, for example, $MA_2$, while for the quadrivalent state one electron must be promoted from the $ns$ orbital to the $np_z$ orbital to give the outer electron configuration $ns^1np_x^1np_y^1np_z^1$ : this allows for the formation of four equivalent $sp^3$ hybrid bonds in, for example, $MA_4$. The relative stabilities of these two oxidation states are thus controlled by (i) size of promotion energy, and (ii) bond strengths, *i.e.* formation of four bonds in $MA_4$ as compared to only two in $MA_2$. Decrease in the (group IVA)-(other element) bond strength as the group is descended allows a balance to be struck whereby the energy required for electron promotion is comparable to that achieved by additional bond formation and is the basis of the so-called "inert pair effect".[9]

Compounds having carbon in the bivalent state (carbenes) were first proposed[10] as intermediates about the end of the nineteenth century. These highly reactive species are used extensively as *in situ* reagents in organic chemistry, typically undergoing a variety of insertion reactions and additions to olefins giving cyclopropanes. Carbenes can have either a singlet (1) or triplet (2 and 3) spin state. Results from experimental observation and thereoretical calculations indicate that most carbenes have a non-linear triplet ground state (*i.e.* 2), however dihalogenocarbenes and carbenes with oxygen, nitrogen or sulfur attached to the bivalent carbon may have singlet ground states (*i.e.* 1).



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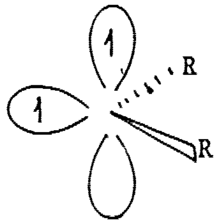

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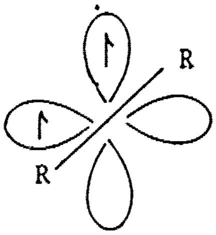

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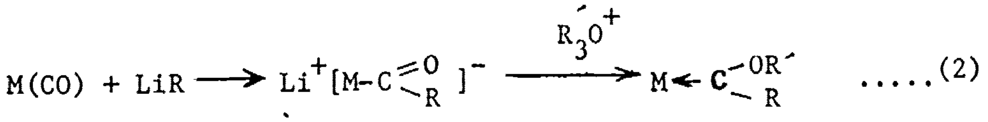
Carbenes are most often prepared from the corresponding diazoalkane (equation (1)); however there are a variety

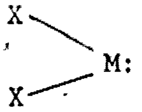
$$R^1R^2C = N_2 \longrightarrow :CR^1R^2 + N_2 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

of other useful methods and these have been discussed in detail elsewhere.[10] Transition metal complexes have been used to stabilize a variety of carbenes, the carbene functioning as a two electron donor (Lewis base) towards the metal. These compounds have been prepared by several different methods[11], one of the most convenient[12] involving addition of an organolithium reagent to a coordinated carbon monoxide molecule followed by alkylation (equation (2)).



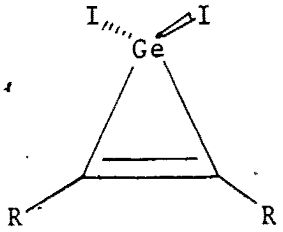
$$M(CO) + LiR \longrightarrow Li^+[M{-}C\genfrac{}{}{0pt}{}{\lesssim O}{\searrow R}]^- \xrightarrow{R_3O^+} M \leftarrow C\genfrac{}{}{0pt}{}{\nearrow OR'}{\searrow R} \quad \ldots\ldots(2)$$

In contrast with the special character of carbenes, there are numerous examples[13] of stable inorganic derivatives of bivalent germanium (germylenes), tin (stannylenes), and lead (plumbylenes). While these compounds do not contain metal-metal bonds, they frequently have structures based on bridged polymeric arrays in the solid state. The gas phase structures of two examples, $SiF_2$[14] and $SnCl_2$,[15] have been determined and both have the bent structure 4, consistent with stereochemical activity of



4

the non-bonding electron pair. These compounds are significantly less reactive than the corresponding carbene derivatives although they undergo similar reactions: for example germanium(II) and tin(II) dihalides readily insert into carbon-halogen bonds.[16] Interestingly, the reaction of $GeI_2$ with certain acetylenes had been reported[17] to give the three membered ring (5). It has subsequently been shown[18] that the product is in fact the six membered ring (6) containing two germanium atoms.



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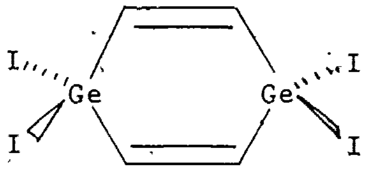

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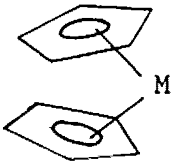
Germanium(II) and tin(II) dichlorides are easily converted to the tetrachlorides by reaction with $Cl_2$,[9] (equations (3) and (4)), however in the case of lead[9] forcing conditions are necessary, the tetrachloride reverting explosively to the dichloride at temperatures above *ca.* 20°C (equation (5) ), reflecting the greater thermodynamic stability of the lower oxidation state for lead.

$$\text{"}GeCl_2\text{"} + Cl_2 \xrightarrow[\text{(at 25}^\circ\text{C)}]{\text{rapid}} GeCl_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$SnCl_2 + Cl_2 \xrightarrow[\text{(at 25}^\circ\text{C)}]{\text{slow}} SnCl_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$PbCl_4 \xrightarrow{20^\circ C} PbCl_2 + Cl_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

The first authentic organometallic derivatives to be prepared in which the metal (metalloid) is in the bivalent state were the cyclopentadienyl derivatives, $M(C_5H_5)_2$, M = Ge,[19] Sn,[20] and Pb,[20] although oligomeric quadrivalent organometallics had been incorrectly identified as such previously.[21] Structures in which the metal (metalloid) is bonded to two $\eta^5$-$C_5H_5$-rings, as shown in 7, have been established.[22,23] A summary of the properties of compounds like 7 is given in Section B together with a review of the chemistry of other derivatives in which the group IVA element is in the bivalent state.



M = Ge, Sn, and Pb.

7

By contrast with 7, cyclopentadienyl derivatives in which the metal is in the +4 oxidation state involve bonding to the saturated carbon atom of the $C_5$-ring, as shown in 8.

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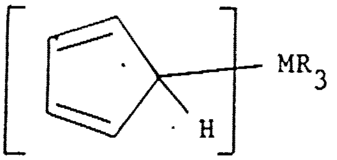
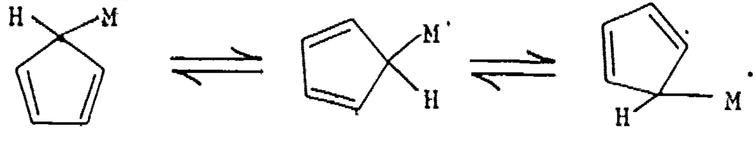


M = Ge, Sn, and Pb.

These molecules exhibit non-rigid characteristics associated with the migration of the metal atom around the five carbon atoms of the $C_5$-ring[24] (equation (6)).



....(6)

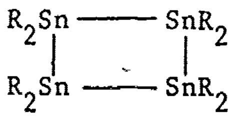
This leads to exchange between the magnetic environments of the five ring protons (and ring carbons), and brings about observable effects in the $^1H$ and $^{13}C$ NMR spectra of many representatives. The non-rigid character of metallocyclopentadienyls and related cyclopolyenyl systems is reviewed in Section C.

Experimental techniques required by the characteristic properties of group IVA-element compounds, together with associated spectroscopic and synthetic methods, are discussed in Section D.

## B. STRUCTURE AND REACTIVITY OF ORGANOMETALLIC[*] AND ORGANIC DERIVATIVES OF BIVALENT GERMANIUM, TIN, AND LEAD.

### B.1. Synthesis.

Attempts to synthesize organoderivatives of bivalent tin date back to the middle of the nineteenth century,[21] when reactions of organolithium or organomagnesium halides with tin(II) halides yielded high-melting, relatively insoluble, tin containing products. It was later shown[25,26] that these materials were in fact mixtures of compounds containing either rings, *eg.* 9 and 10, or straight or branched chains, *eg.* 11, of tin atoms, thus involving the metal in a formally quadrivalent state.



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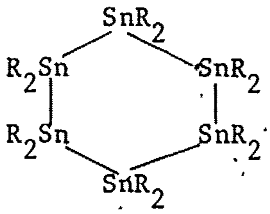

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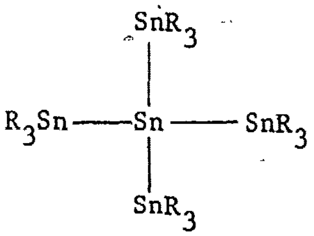

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[*] Group IVA compounds may be categorized as follows:

1. Organogroup IVA compounds; compounds which contain at least one group IVA element - carbon bond.
2. Organic compounds; compounds which contain one or more organic groups, but have no group IVA - carbon bond.
3. Inorganic compounds; compounds which do not belong to classes (1) and (2).

Cyclopentadienyl-[19,20] and bis(trimethylsilyl)methyl-[27,28] lithium do however react with bivalent germanium, tin, and lead halides to give the corresponding bivalent group IVA compound, equations (7) and (8) respectively.

$SnCl_2 + 2Li(C_5H_5) \longrightarrow Sn(\eta^5\text{-}C_5H_5)_2 + 2LiCl$ ............(7)

$PbCl_2 + 2LiCH(SiMe_3)_2 \longrightarrow Pb[CH(SiMe_3)_2]_2$ ..............(8)

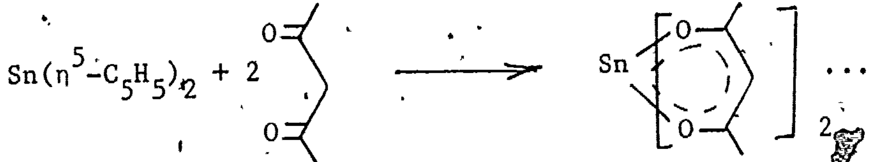
Similar reactions using the lithium or sodium salts of acetylacetone[29,30] (equation (9) ) or hexamethyldisilazane[31] ($HN(SiMe_3)_2$), (equation (10) ), also afford bivalent group IVA derivatives.

$CsGeCl_3 + 2Na(acac) \longrightarrow Ge(acac)_2$ .......................(9)

$SnCl_2 + 2Li[N(SiMe_3)_2]_2 \longrightarrow Sn[N(SiMe_3)_2]_2$ ...............(10)

The tin cyclopentadienyls, $Sn(\eta^5\text{-}C_5H_5)_2$ and $Sn(\eta^5\text{-}C_5H_4CH_3)_2$, have been shown [32,33,34] to be useful precursors to a variety of previously unknown, or otherwise difficult to prepare derivatives of bivalent tin, *eg.* equations (11) and (12).

$Sn(\eta^5\text{-}C_5H_5)_2 + 2HCN \longrightarrow Sn(CN)_2$..................(11)

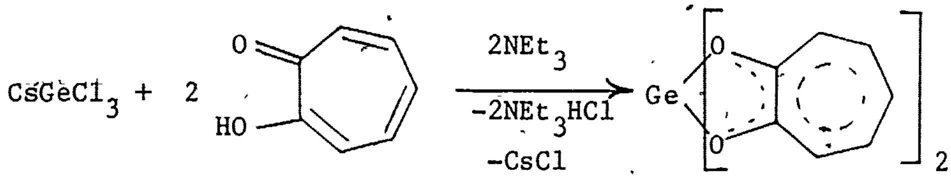


.........(12)

The reaction of tin(II) halides with compounds having an acidic hydrogen, in the presence of triethylamine gives the corresponding tin(II) derivative (equation (13) ),[35,36]

$SnCl_2 + 2MeOH + 2NEt_3 \longrightarrow Sn(OMe)_2 + 2NEt_3HCl$.............(13)

while related reactions for germanium(II) halides have recently been reported,[30] equation (14).



...(14)

Alternative methods for the synthesis of these types of compound are generally limited in scope, and have been reviewed elsewhere.[37]

A number of compounds have been reported in which the bivalent group IVA metal (metalloid) functions as a neutral two-electron donor towards the transition metal center.[38,39] Where the bivalent group IVA derivative is stable, the transition metal compound is easily formed by displacement reactions similar to those shown in equations (15)[38] and (16)[39].

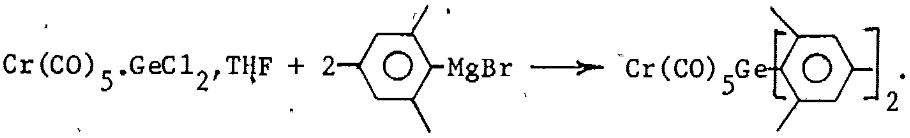
$$M(CO)_5.THF + Sn(\eta^5\text{-}C_5H_5)_2 \longrightarrow M(CO)_5Sn(\eta^5\text{-}C_5H_5)_2 \ldots\ldots (15)$$

(M = Cr, Mo, and W)

$$M(CO)_6 + Sn[CH(SiMe_3)_2]_2 \xrightarrow{h\nu} M(CO)_5Sn[CH(SiMe_3)_2]_2 \ldots (16)$$

(M = Cr and Mo)

Some transition metal derivatives, for which the free bivalent metal compound is unstable, have been prepared by "indirect methods". Thus reaction of a coordinated germanium dihalide with two equivalents of an alkylmagnesium halide gives the organogermanium(II) transition metal complex[40] as shown in equation (17).



....(17)

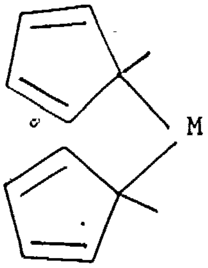
Similarly the reduction of quadrivalent tin in suitably substituted dialkyltin dihalides by $Cr(CO)_5^{2-}$, gives the base stabilized compounds[41] $R_2Sn(THF)Cr(CO)_5$ (equation (18)).

$$Cr(CO)_5^{2-} + SnR_2Cl_2 \xrightarrow{THF} Cr(CO)_5SnR_2(THF) \ldots\ldots\ldots\ldots(18)$$

(R = Me, $Bu^t$)

## B.2. Structure

The true organo-tin(II) and -lead(II) derivatives, bis($\eta^5$-cyclopentadienyl)-tin(II) and -lead(II), were first reported[20] by Fischer and Grubert in 1956. Wilkinson *et al.* subsequently reported[42] the synthesis of the methylcyclopentadienyl analogues, while the germanium compounds Ge($\eta^5$-$C_5H_5$)$_2$[19] and Ge($\eta^5$-$C_5H_4CH_3$)$_2$[43] have been isolated more recently. Although it was initially suggested[20] that the tin and lead cyclopentadienyls have the *sigma*-bonded structure shown in 12, comparison of their IR spectra with that of ferrocene led Piper and Wilkinson to propose[24] that these compounds had the angular sandwich structure shown in 13.



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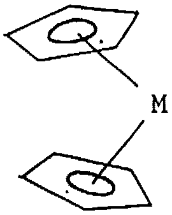


13

Electron diffraction studies of $Sn(\eta^5-C_5H_5)_2$ and $Pb(\eta^5-C_5H_5)_2$ have shown[22] that these molecules assume structure 13 in the gas phase. The solid state structure of $Sn(\eta^5-C_5H_5)_2$ has recently[23] been reported to be monomeric, having discrete units with the angular sandwich structure 13, however the solid state structure of the lead compound has been shown by X-ray crystallography[44] to be polymeric. In this compound each pair of lead atoms is bridged by a cyclopentadienyl ring, the plane of which is at right angles to the lead-lead axis; coordination of each metal atom is completed by a terminal $\eta^5-C_5H_5$-ring, as shown in Figure 1.2.

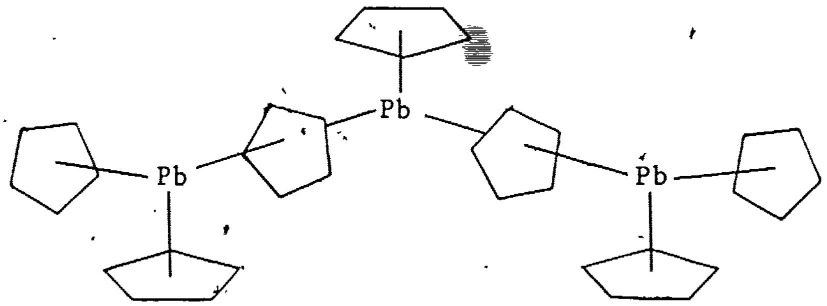
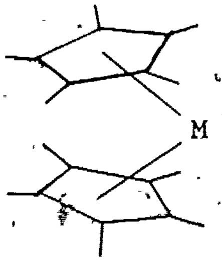


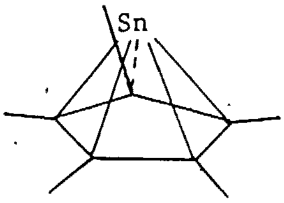
FIGURE 1.2. The solid state structure of bis($\eta^5$-cyclopentadienyl)lead(II)

The crystal structures of the pentamethylcyclopentadienyls, $M[\eta^5-C_5(CH_3)_5]_2$, M = Sn[45] and Pb,[23] consist of discrete monomeric units having the angular sandwich structure depicted in 14.

14



The related compound, $Sn[\eta^5-C_5(CH_3)_5]^+BF_4^-$, formed by the reaction of $Sn[\eta^5-C_5(CH_3)_5]_2$ with $HBF_4$, has a crystal structure[46] having pentagonal pyramidal $Sn[\eta^5-C_5(CH_3)_5]$ units 15, in which all five tin-carbon distances are approximately equal (average 2.46 Å). The tin atom of these units is further associated with two fluorine atoms of the $BF_4^-$ counterion.



15

The crystal structure of $Sn(\eta^5-C_5H_5)Cl$[47] consists of $Sn(\eta^5-C_5H_5)Cl$ units in which the cyclopentadienyl is asymmetrically bound to tin, with Sn-C bond distances ranging from 2.45 to 2.74 Å. The tin atoms of alternate units are bridged by chlorine atoms of adjacent $Sn(\eta^5-C_5H_5)Cl$ groups, as shown in Figure 1.3.

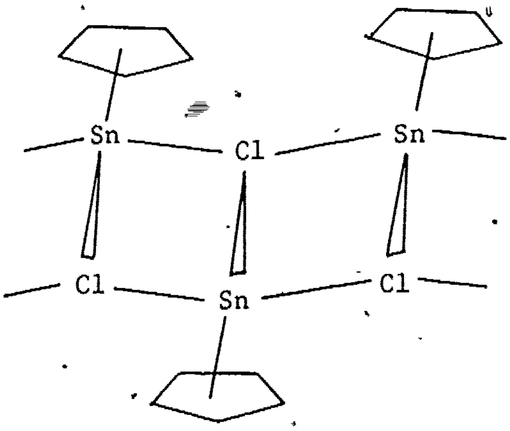
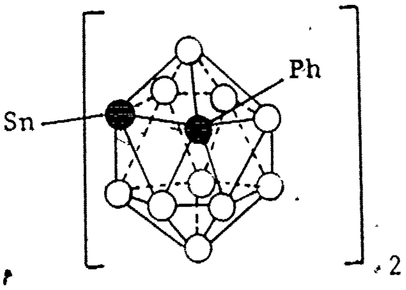


FIGURE 1.3. The crystal structure of (pentahaptocyclopentadienyl)tin chloride.

Apart from the cyclopentadienyl derivatives, there are rather few examples of stable compounds which have a bivalent germanium, tin, or lead atom bonded directly to carbon. The first, and somewhat exotic examples of such compounds were bis[2-phenyl-1,2-dicarba-*closo*-dodecarboran(12)-1-yl]tin(II) 16[48] and 1-germa-, 1-stanna-, and 1-plumba-2,3-dicarba-*closo*-dodecaborane(II),[49,50] 17 .



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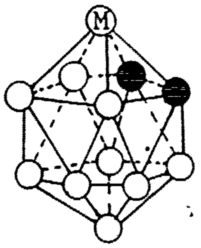


17

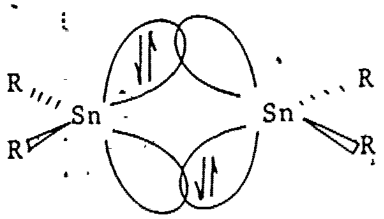
M = Ge,Sn, and Pb

● = C

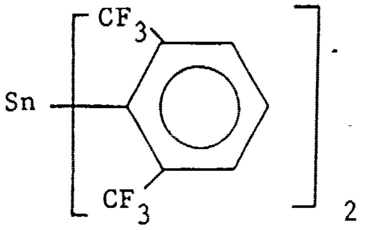
○ = B

Lappert *et al.* have reported[27,28] the first stable alkyl derivatives of bivalent germanium, tin, and lead, $M[CH(SiMe_3)_2]_2$, M = Ge,Sn, and Pb. Although the germanium and tin compounds have been shown[28] to be monomeric in the liquid and vapour phases, the crystal structure[51] of $Sn[(CH(SiMe_3)_2]_2$ consists of dimeric units, which have been suggested to result from interaction between the orbital containing the non-bonding electron pair on each tin atom, and the vacant orbital on the adjacent tin atom, as shown in 18.

18



The first stable aryl stannylene (19) was prepared recently,[52] its stability towards polymerization being attributed to the presence of the trifluoromethyl substituents in the 2- and 6- positions.



19

Amma and co-workers have reported[53,54] the novel compounds $[(\eta^6\text{-}C_6H_6)M(AlCl_4)_2\cdot(C_6H_6)]$, M = Sn, Pb. The crystal structure of the lead derivative[54] consists of a polymeric array, in which each lead atom is bound to a terminal, symmetric, $\eta^6$-benzene ring. The lead atom is further associated with six chlorine atoms, two from each of the three $AlCl_4$ units, with two of these $AlCl_4$ units forming bridges between adjacent lead atoms, as shown in Figure 1.4.

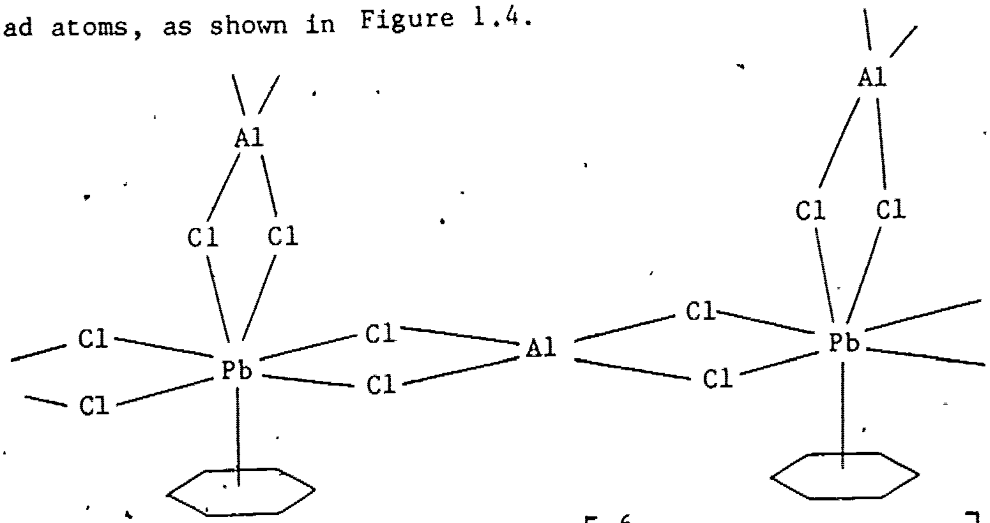


FIGURE 1.4. The crystal structure of $[(\eta^6\text{-}C_6H_6)Pb(AlCl_4)_2\cdot C_6H_6]$.

Several other $\eta^6$-arene complexes of bivalent tin and lead were subsequently reported,[55] and the crystal structures of $(\eta^6\text{-}C_6H_6)SnCl(AlCl_4)$ and $\mu\text{-}(\eta^6\text{-}p\text{-}(CH_3)_2C_6H_4)SnCl(AlCl_4)$ have been determined.[55] Asymmetry in the $\eta^6$-$C_6$-ring, observed for both these compounds was attributed to crystal packing forces.

The crystal structures of the transition metal derivatives of $M[CH(SiMe_3)_2]_2$, $Cr(CO)_5M[CH(SiMe_3)_2]_2$, M = Ge[56] and Sn,[57] have been determined (Figure 1.5). Significantly the atoms C(1), C(2), M and Cr all lie in approximately the same plane, a result which has been interpreted in terms of back donation from the transition metal to the stannylene (or germylene) ligand.

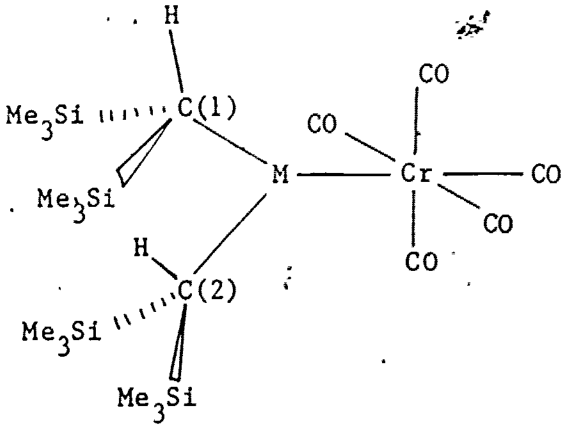


FIGURE 1.5. The crystal structure of $Cr(CO)_5M[CH(SiMe_3)_2]_2$, M = Ge and Sn.

The crystal structure of the pyridine adduct $Cr(CO)_5Sn(Bu^{\underline{t}})_2$-(pyridine), (Figure 1.6), has also been determined[58] and shows the Sn atom to be out of the C(1), C(2), Cr plane, consistent with a decrease in back donation from Cr to Sn upon incorporation of the pyridine molecule.

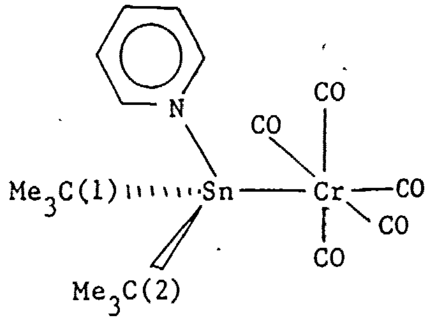
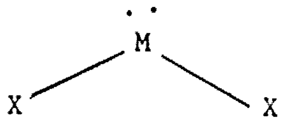


FIGURE 1.6. The crystal structure of $Cr(CO)_5Sn(Bu^{\underline{t}})_2$(pyridine).

A variety of germanium(II)-, tin(II)-, and lead(II)-halides ( and *pseudo*-halides) have been structurally characterized.[59] These compounds are generally polymeric, having halogen atoms (*pseudo*-halogen groups) bridging adjacent metal centers. Such structures are complex and have been reviewed in detail elsewhere.[59] By contrast, the gas phase structures of $SiF_2$[14] and $SnCl_2$[15] are monomeric, having the "bent" geometry shown in 20.



20

Bivalent tin and lead derivatives of simple oxy-acids have been subjected to extensive structural characterization.[59] These compounds are again polymeric and often have bridging oxygen atoms between adjacent metal centers. The structure of one compound of this type $Sn(IV)Ph_3Sn(II)NO_3$,[60] is of interest, since it contains both bivalent and quadrivalent tin connected by a tin-tin bond. The crystal structure is polymeric, with bridging $NO_3$ groups between adjacent bivalent tin atoms (Figure 1.7).

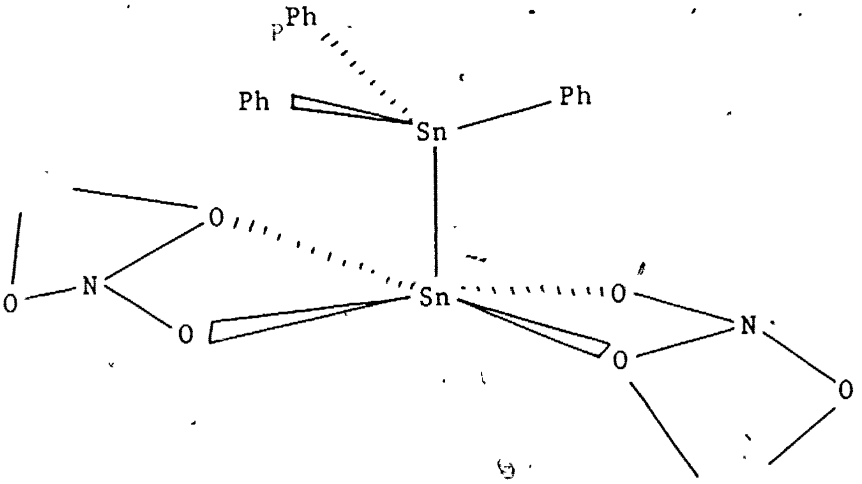
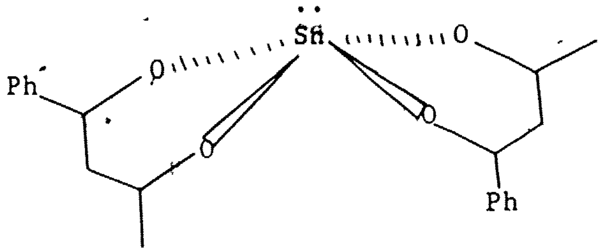
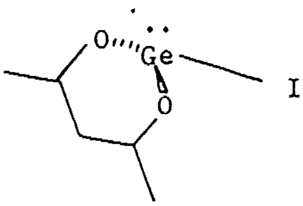


FIGURE 1.7. The crystal structure of $Sn(IV)Ph_3Sn(II)NO_3$.

The 1,3-diketonato-derivatives of germanium(II) and tin(II), which are monomeric in the vapour, liquid and solid phases, have been reported.[29,30,34] The crystal structure of the tin compound,[61] di(benzoylacetonato)tin(II), consists of the discrete monomeric units shown in 21, in which each metal atom is four (*pseudo*-five) coordinate. The chelating effect of the two ketoenolate groups, apparently results in a tin center which is coordinatively saturated, and thus prohibits intermolecular association. The crystal structure of a related germanium compound, (acetylacetonato)germanium(II) iodide has also been determined,[62] and consists of the units shown in 22, in which each germanium atom is three (*pseudo*-four) coordinate.

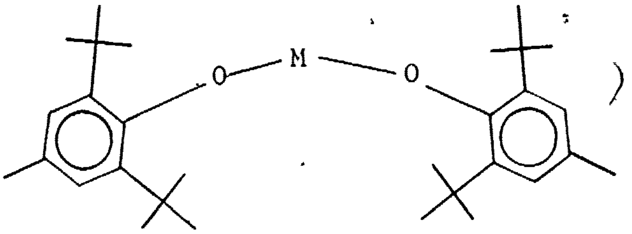


21



22

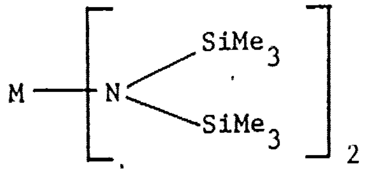
The structures of the di-*tert*-butylphenoxides, 23, M(OC$_6$H$_2$Me-4-Bu$^t_2$-2,6)$_2$, M = Ge or Sn, have recently been determined[63] by X-ray crystallography. These are the first examples of compounds to have been structurally characterized in the solid state for which the bivalent group IVA element has the low coordination number of two (*pseudo* three). The structures shown in 21 to 23 clearly demonstrated the strong stereochemical effect of the non-bonding electron pair in each case.



23

Possibly the most interesting nitrogen derivatives of the bivalent group IVA elements are bis[bis(trimethylsilyl)]amido-germanium(II),-tin(II) and-lead(II). (24).[31] While these compounds are monomeric in the vapour and liquid phases, the solid state structure of the tin compound has been suggested[31] to be dimeric, paralleling exactly the situation found[51] for the *iso*electronic tin alkyl, Sn[CH(SiMe$_3$)$_2$]$_2$.

24

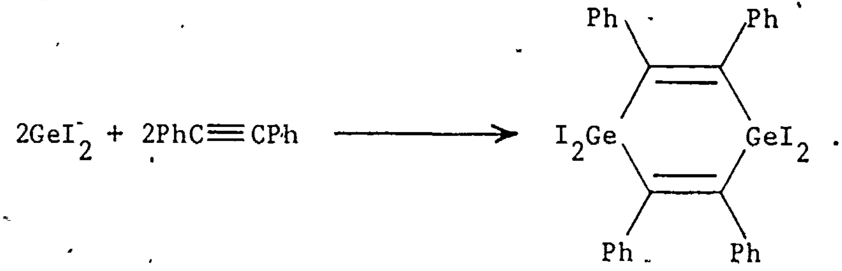


## B.3. Reactivity

The reactions of inorganic tin(II) compounds with organic halides, to give the corresponding tin(IV) compounds, have been known since 1851 [2,21] (equation (19)).

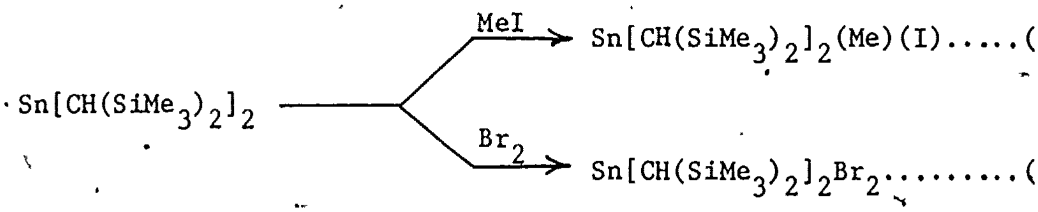
$$SnI_2 + MeI \longrightarrow MeSnI_3 \ldots\ldots\ldots\ldots\ldots (19)$$

This type of reaction has been used extensively in industry for the preparation of monoorganotin(IV) trihalides, which are important constituents of P.V.C. stabilizers. Similar reactions involving unsaturated organic compounds have also been reported,[18] (equation (20)).



.......(20)

The reaction of $Sn[CH(SiMe_3)_2]_2$ with alkyl halides or halogens [39] also gives the corresponding tin(IV) product, equations (21) and (22).



$$Sn[CH(SiMe_3)_2]_2 \xrightarrow{MeI} Sn[CH(SiMe_3)_2]_2(Me)(I) \ldots\ldots (21)$$

$$Sn[CH(SiMe_3)_2]_2 \xrightarrow{Br_2} Sn[CH(SiMe_3)_2]_2Br_2 \ldots\ldots\ldots (22)$$

Tin(II) halides readily insert into transition metal-metal bonds [64,65] to give the corresponding tin(IV) derivative, *eg* equation (23).

$$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2 + SnCl_2 \longrightarrow Sn[Fe(\eta^5\text{-}C_5H_5)(CO)_2]Cl_2 \quad ...(23)$$

These types of reactions are often complicated by the further reaction of the tin(IV) compound initially formed; thus $Sn[Co(CO)_4]_4$ was isolated [38] as one of the products from the reaction of $Sn(\eta^5\text{-}C_5H_4CH_3)_2$ with $Co_2(CO)_8$ (equation (24)).

$$Sn(\eta^5\text{-}C_5H_4CH_3)_2 + Co_2(CO)_8 \longrightarrow Sn[Co(CO)_4]_4 + ... \quad ....(24)$$

Similarly, the reaction of $Sn(\eta^5\text{-}C_5H_4CH_3)_2$ with $W(\eta^5\text{-}C_5H_5)(CO)_3(H)$, which had been reported [32] to give the bivalent tin compound $Sn[W(\eta^5\text{-}C_5H_5)(CO)_3]_2$, has recently been shown[66] to give the tin(IV) compound $Sn(H)[W(\eta^5\text{-}C_5H_5)(CO)_3]_3$ (equation (25)).

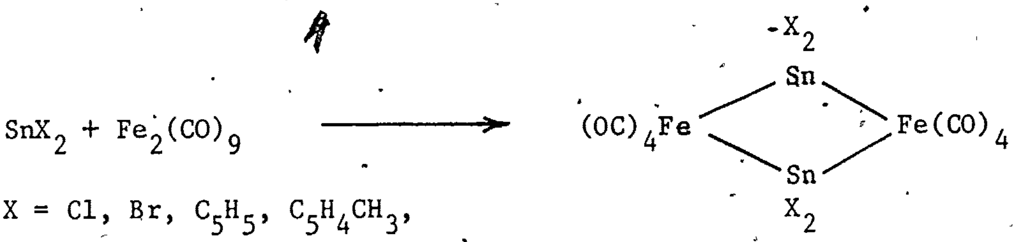
$$Sn(\eta^5\text{-}C_5H_4CH_3)_2 + 3W(\eta^5\text{-}C_5H_5)(CO)_3(H) \longrightarrow Sn(H)[W(\eta^5\text{-}C_5H_5)(CO)_3]_3 \quad ..(25)$$

Insertion into a metal-hydrogen and metal-carbon bonds have also been reported, [39] thus $Sn[CH(SiMe_3)_2]_2$ inserts into either a Mo-H or a Mo-C bond according to equation (26).

$$Mo(\eta^5\text{-}C_5H_5)(CO)_3\text{-}R \xrightarrow{Sn[CH(SiMe_3)_2]_2} Sn[CH(SiMe_3)_2]_2[Mo(\eta^5\text{-}C_5H_5)(CO)_3]R$$

$R = H, CH_3$ ...........(26)

Several tin(II) compounds have been shown[67] to react with diiron enneacarbonyl to give four-membered $Fe_2Sn_2$ ring compounds, in which the tin is in a formally quadrivalent state (equation(27)).



..(27)

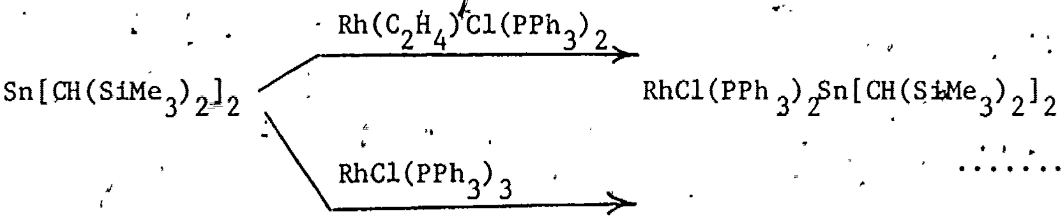
X = Cl, Br, $C_5H_5$, $C_5H_4CH_3$,
and 1,3-diketonato.

The bivalent group IVA element in these derivatives of germanium, tin, and lead can also function as a two electron donor to suitable acceptor sites, thus $Sn(\eta^5-C_5H_5)_2$ forms complexes with the Lewis acids $BF_3$[68] and $AlCl_3$[69] (equation (28)).

$$Sn(\eta^5-C_5H_5)_2 + MX_3 \longrightarrow (\eta^5-C_5H_5)_2Sn \rightarrow MX_3 \qquad \ldots\ldots\ldots\ldots(28)$$

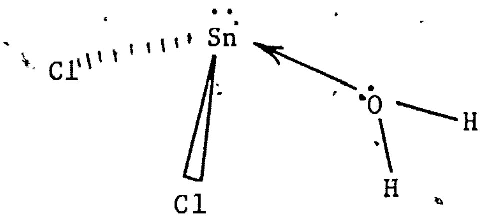
$MX_3 = BF_3, AlCl_3$.

Interestingly $Sn[CH(SiMe_3)_2]_2$ does not react with $BF_3.Et_2O$,[39] however with $AlCl_3$, below $-30^\circ C$, it forms a white solid, which decomposes at more elevated temperatures, the only isolable product being $Sn[CH(SiMe_3)_2]_2Cl_2$. More straightforwardly $Sn[CH(SiMe_3)_2]_2$ functions as a two electron donor to the metal carbonyls, $M(CO)_5$, M = Cr and Mo,[39] and also displaces ethylene from $Rh(C_2H_4)Cl(PPh_3)_2$ and $PPh_3$ from $RhCl(PPh_3)_3$ (equation (29)).



........(29)

For most derivatives of bivalent germanium, tin and lead, the metal (metalloid) can function as a Lewis acid, accepting an electron pair into an unoccupied $nsnp_xnd_y$ type molecular orbital. Thus in the crystal structure of $SnCl_2.2H_2O$,[70] the oxygen of one of the water molecules can be viewed as donating two electrons to tin, as shown in 25. Germanium(II) and tin(II) halides readily accept a further halide ion to form the complex ions $GeX_3^-$ [71] and $SnX_3^-$ [72] (equation (30)).



25

$$[GeCl_2]^* + CsCl \longrightarrow Cs^+ \, GeCl_3^- \ldots\ldots\ldots\ldots\ldots\ldots(30)$$

Both bis($\eta^5$-cyclopentadienyl)tin(II)[73] and bis (acetylacetonato)tin(II)[28] undergo redistribution reactions with tin(II) halides (equation (31)),

$$Sn(\eta^5\text{-}C_5H_5)_2 + SnCl_2 \longrightarrow 2Sn(\eta^5\text{-}C_5H_5)Cl \ldots\ldots\ldots\ldots(31)$$

---

$^*GeCl_2$ is prepared *in situ* from the reduction of $GeCl_4$ in acidic media.

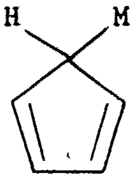
while similar exchange reactions have also been observed with tin(IV) halides,[74] (equation (32)).

$$\mathrm{Sn}(\eta^5\text{-}\mathrm{C_5H_5})_2 + \mathrm{SnMe_2Cl_2} \longrightarrow \mathrm{SnMe_2}(\eta^1\text{-}\mathrm{C_5H_5})\mathrm{Cl} + \mathrm{Sn}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl} \quad ..(32)$$

## C. SIGMATROPIC MIGRATIONS IN METALLO-CARBOCYCLIC SYSTEMS.

### C.1. Introduction.

The discovery of the phenomenon of stereochemical non-rigidity added a new dimension to the concept of molecular structure. The establishment of variable temperature NMR spectroscopy as a routine method further facilitated the rapid development of the study of stereochemically non-rigid molecules where the rate of rearrangement is of the order of $10^{-1}$ - $10^{+9}$ $s^{-1}$.[75] This has led in particular to the identification of migrations of *sigma*-bonded metal atoms between some, or all, of the carbon atoms in certain cyclopolyenyl systems. Sigmatropic shifts of this type have been thoroughly documented[24] for the cyclopentadienyl-ring system, shown in 26 while more recently migrations in other ring systems *i.e.* $C_3$, 27, $C_7$, 28, and $C_9$, 29, have also been observed. This section reviews this topic, discussing first the theoretical aspects (C.2), secondly the methods used to characterize these processes (C.3), and finally summarizing the experimental results available (C.4).



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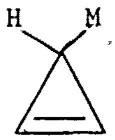

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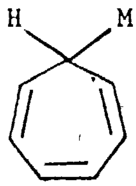

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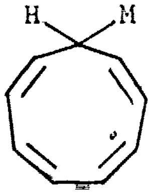
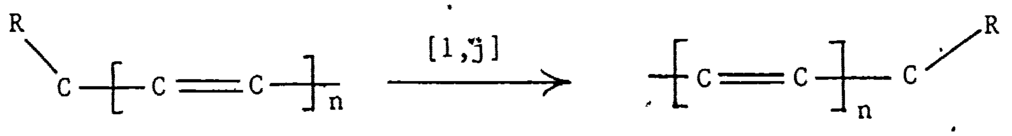


29

## C.2. Theoretical Considerations.

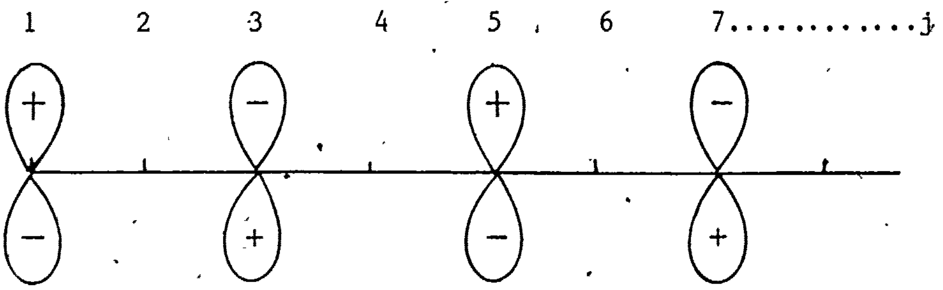
Several types of sigmatropic shifts have been distinguished by Woodward and Hoffmann.[76] For the purposes of this discussion, however, only rearrangements of order [1,j] will be considered, corresponding to the migration of a *sigma*-bonded atom or group (R) from one end to the other of a polyenylic chain as shown in equation (33).



...(33)

(j = 2n + 1)

Woodward and Hoffmann have defined[76] a sigmatropic change of order [i,j] as the migration of a *sigma* bond, flanked by one or more π-electron systems, to a new position whose termini are i-1 and j-1 atoms removed from the original bonded loci, in an uncatalyzed intramolecular reaction. Then provided the migrating group R remains bonded to both ends of the unsaturated system throughout (concerted reaction), orbital symmetry constraints would be derived from the form of the highest occupied molecular orbital (HOMO) of the hydrocarbon radical corresponding to the polyenylic chain. The HOMO for this system is the non-bonding allylic orbital which possesses the following symmetry.



A group R, when bound to the chain by a symmetric orbital (*eg.* an *s* orbital for R = H), can migrate from one end of the chain to the other in two distinct ways; consider the case of a 1,5 migration for the following pentadienyl:

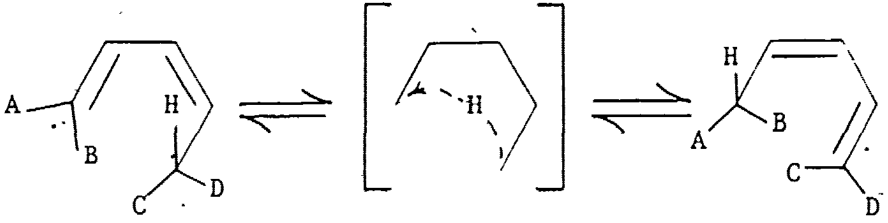


FIGURE 1.8(a). Suprafacial migration of a hydrogen atom.

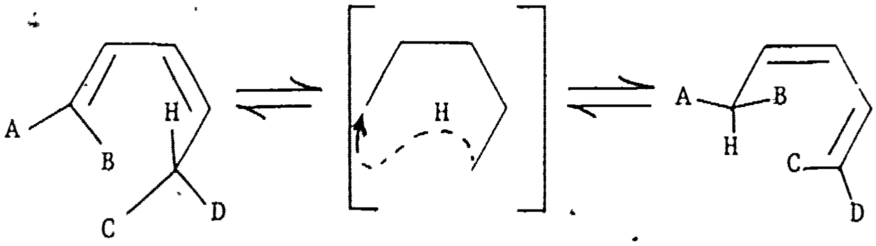


FIGURE 1.8(b). Antarafacial migration of a hydrogen atom.

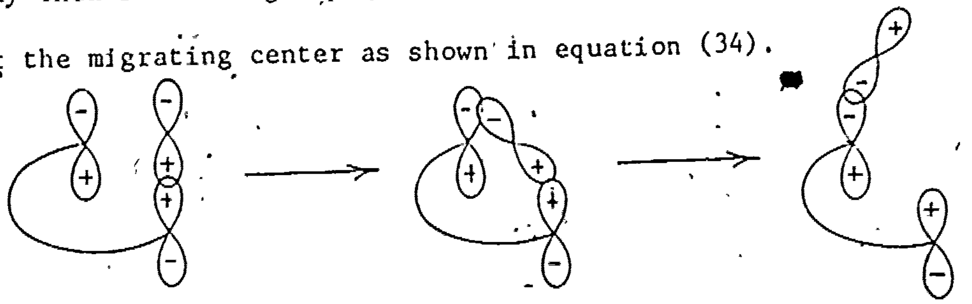
for a suprafacial process (Figure 1.8 (a)) the transferred hydrogen atom is associated at all times with the same face of the π system; for the antarafacial process (Figure 1.8(b)), the migrating atom passes from the top face of one carbon terminus to the bottom face of the other. The selection rules for such a sigmatropic reaction of order [1,j] are given in Table 1.1(a).

TABLE 1.1(a).

Selection rules for an allowed sigmatropic shift of order [1,j] of a hydrogen atom.

| [1,j] | Δ (thermal) |
|---|---|
| [1,3] | antara |
| [1,5] | supra |
| [1,7] | antara |
| [1,9] | supra |

Where R is a group other than a hydrogen atom (*eg* methyl), the orbital by which R is bound to the polyenyl system may be antisymmetric (*eg.* possess some *p* character). Alternate processes may then be envisaged proceeding with inversion of configuration at the migrating center as shown in equation (34).



..(34)

The selection rules are then precisely reversed if inversion takes place at the migrating center (Table 1.1(b)).

TABLE 1.1(b).

General selection rules for thermally allowed sigmatropic shifts.

| [1,j] | Suprafacial | Antarafacial |
|---|---|---|
| [1,3] | inversion | retention |
| [1,5] | retention | inversion |
| [1,7] | inversion | retention |
| [1,9] | retention | inversion |

Thus a [1,3]shift may be either antarafacial with retention, or suprafacial with inversion (Figure 1.9(a)), while a [1,5] shift will be suprafacial with retention, or antarafacial with inversion (Figure 1.9(b)).

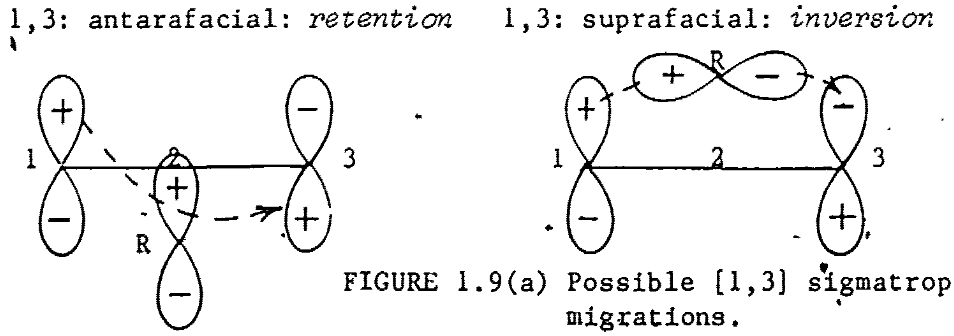


FIGURE 1.9(a) Possible [1,3] sigmatropic migrations.

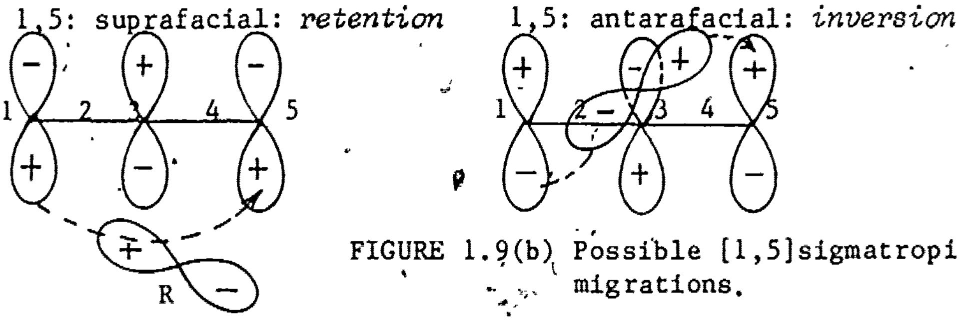


FIGURE 1.9(b) Possible [1,5]sigmatropic migrations.

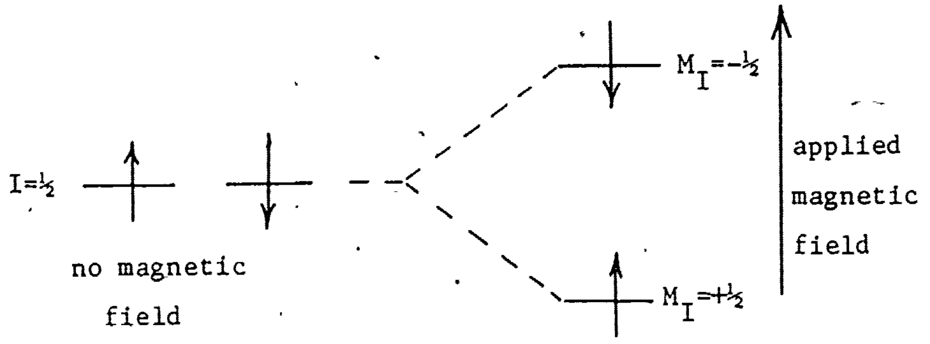
These rules, although originally conceived for straight chain polyenyls, are equally applicable to the corresponding cyclopolyenyl systems. It should be noted however, that rearrangements going by an antarafacial process have been ruled out for small ring-systems.[76] It follows that for a ring-system having n = 1 (*i.e.* $C_3H_3R$), the only Woodward-Hoffmann allowed shift will be a 1,3 suprafacial shift, involving an inversion of configuration at the metal center, while for n = 2 ($C_5H_5R$), two rearrangements are allowed, a 1,3 shift with inversion of configuration, or a 1,5 shift with retention of configuration. The relevance of these considerations to metallotropic rearrangements in metallocyclopentadienes has been suggested elsewhere.[77,78,79]

## C.3. The NMR Technique as Applied to Stereochemically non-rigid Molecules.

### C.3.(i). Theory

Electron spin resonance and nuclear magnetic resonance spectroscopy owe their existance to the fact that electrons and certain nuclei possess magnetic moments because they have both electrostatic charge and spin angular momentum. In the presence of a magnetic field, these magnetic moments become aligned either with or opposed to the applied magnetic field. Hence for a nucleus of spin quantum number $I = \frac{1}{2}$, there are two states;

$M_I = +\frac{1}{2}$ and $-\frac{1}{2}$



During the NMR experiment, nuclei aligned with the magnetic field (the ground state, $M_I = +\frac{1}{2}$), absorb energy and become aligned against the magnetic field (the excited state, $M_I = -\frac{1}{2}$). The energy difference, ΔE, between the ground and excited states is generally small, so that the uncertainty principle dictates that any measure of ΔE must require a significantly long time, *ie* $> 10^{-6}$s.[75] If a nucleus were to change its chemical or geometric environment during the time required to complete this measurement a large uncertainty in the latter would result. This has the effect of giving a series of energies rather than a single defined band.

If the nucleus changes its place between two magnetically different sites, *ie* which have different resonance positions, at a sufficiently rapid rate, a new band will start to appear at the median of the two former bands. This is consistent with the rate of rearrangement becoming comparable to the frequency separation between the two resonance positions, before and after the change in position. The "time required for measurement" is directly related to what is commonly referred to as the "time scale" of the experiment.[75] A list of the time scales for some common techniques are given in Table 1.2.

TABLE 1.2:

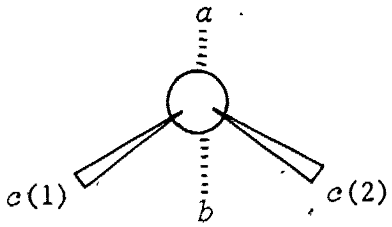
Approximate time scales for some different experimental techniques.

| | Approximate Time Scale(s) |
|---|---|
| electron diffraction | $10^{-20}$ |
| X-ray diffraction | $10^{-18}$ |
| ultraviolet | $10^{-15}$ |
| visible | $10^{-14}$ |
| IR, Raman | $10^{-13}$ |
| electron spin resonance | $10^{-4} - 10^{-8}$ |
| nuclear magnetic resonance | $10^{+1} - 10^{-9}$ |
| Mössbauer (iron) | $10^{-7}$ |
| Molecular beam | $10^{-6}$ |
| Experimental separation of isomers | $> 10^{2}$ |

The fact that the lifetime of so many stereochemically non-rigid molecules is comparable with the time scale of the NMR experiment has made NMR an invaluable tool, without which these processes would have remained unobserved, or at best observed only with difficulty.

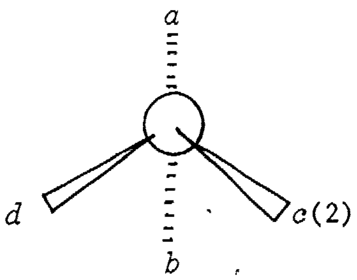
## C.3.(ii). The use of diastereotopic groups in determining the mechanism of rearrangement in metallocyclopentadienes.

<u>Definitions</u>. (<u>a</u>) Nuclei which experience equal magnetic shielding have identical chemical shifts and are termed *isochronous* or *homotopic*. (<u>b</u>) Two atoms (or groups of atoms) are *magnetically equivalent* if they are isochronous and if they are equally coupled to all other NMR active nuclei in the molecule. (<u>c</u>) Generally, for any tetrahedral molecule of the type $M_{abc_2}$ <u>30</u> where <u>a</u> and <u>b</u> are different nondissymmetric groupings, the two *c* nuclei will be *enantiomeric*, however they are also magnetically equivalent and isochronous.

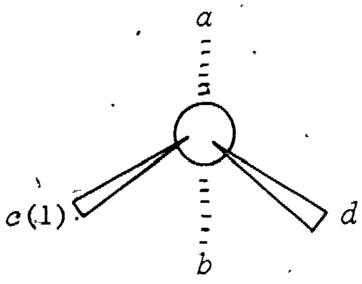


<u>30</u>

The environments of *c*(1) and *c*(2) are mirror images of each other, such that replacing either of them by another different nucleus or group *d* would give rise to the enantiomorphs <u>30</u>(a) and <u>30</u>(b).

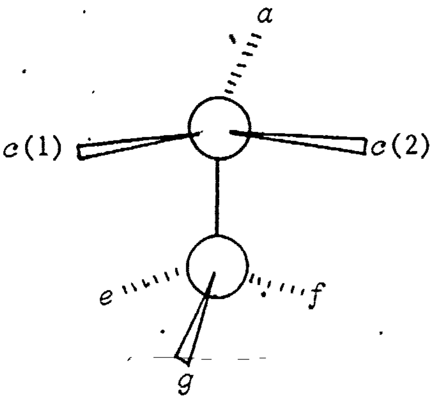


<u>30</u>(a)



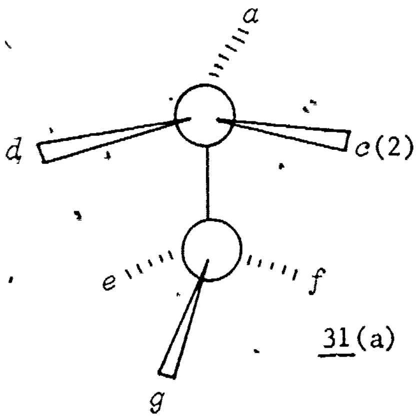
<u>30</u>(b)

(d) For 30, where either $a$ or $b$ are dissymetric, *ie* 31, the two nuclei $c(1)$ and $c(2)$ experience magnetically inequivalent environments and are *diastereomeric*.

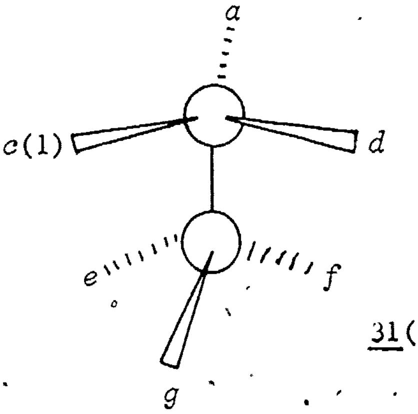


31

Replacing either $c(1)$ or $c(2)$ by another nucleus, $d$, then results in the diastereoisomers 31(a) and 31(b).



31(a)

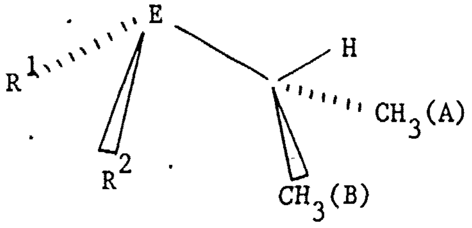


31(b)

A group like $M_{ac_2}$ is often referred to as a *diastereotopic group*.

## Application

One of the simplest examples of a molecule incorporating a diastereotopic group is shown in 32



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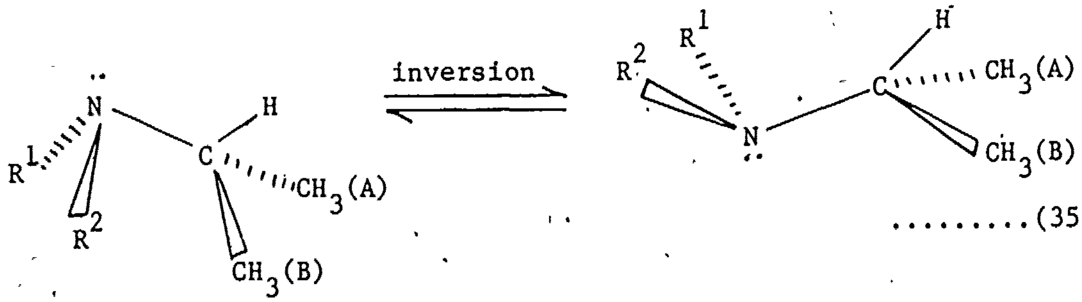
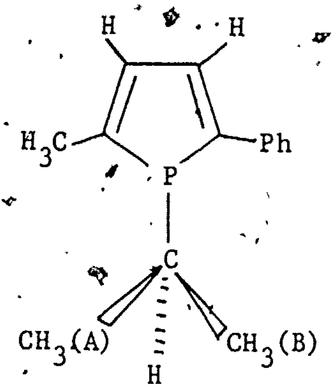
As defined above, the methyl groups (A) and (B) are magnetically inequivalent, in principle giving separate signals in the $^{13}$C NMR spectrum and a complex $^{1}$H NMR spectrum arising from an $a_3b_3x$ spin system, as opposed to the $a_6x$ system occurring when (A) and (B) are magnetically equivalent (*i.e.* $R^1 = R^2$).[80]

When E is a nitrogen atom, inversion at N (equation (35)) is rapid and causes exchange between the magnetic environments of (A) and (B).[80] Hence the two methyl groups are no longer distinguishable by NMR spectroscopy, and only one $C^{methyl}$ signal is observed in the $^{13}$C NMR spectrum. The corresponding resonance in the $^{1}$H NMR is a doublet *via* coupling to the methine proton.



.........(35)

Mislow *et al.*[81] have observed temperature dependent phenomena for a related phosphine derivative, 33. Thus spectra



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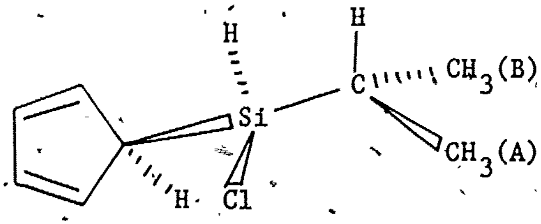
consistent with the static structure are observed at 0°C, showing the methyl groups (A) and (B) to be magnetically inequivalent. Inversion at the phosphorus center exchanges the magnetic environments of (A) and (B) at a rate such that, at temperatures above +60°C, they are indistinguishable on the NMR time scale.

A similar method has recently been used[79] to determine if migration in metallocyclopentadienes occurs with retention or inversion of configuration at the metal center. Thus for compound 34 the slow-limit $^{13}C$ NMR spectrum, observed at -30°C,



34

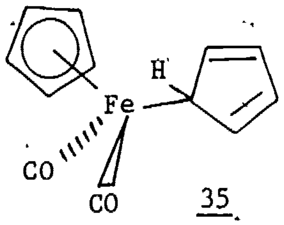
has two signals for the diastereomeric methyl groups (A) and (B). At higher temperatures, where the fluxional process is sufficiently rapid to bring about averaging of resonances for the cyclopentadienyl ring carbons, no broadening or change in chemical shift of the two methyl resonances was observed, showing the rearrangement takes place with retention of configuration at the silicon center.

## C.4. Experimental Observations of Sigmatropic Shifts in Metallomonohaptocyclopolyene Systems.

Several comprehensive reviews of the fluxional processes taking place in monohaptocyclopolyenylmetal systems have appeared.[24,82,83] This section sets out to summarize important, more recent developments, but some of the earlier material has also been included for completeness.

### C.4.(i). Metallocyclopentadienes

Metallocyclopentadienes, in which the metal is bonded *via* a *sigma*-bond to the saturated carbon atom of the $C_5$-ring, have been known since 1956, in which year compounds 35 and 36 were



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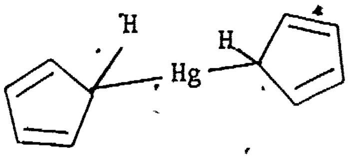
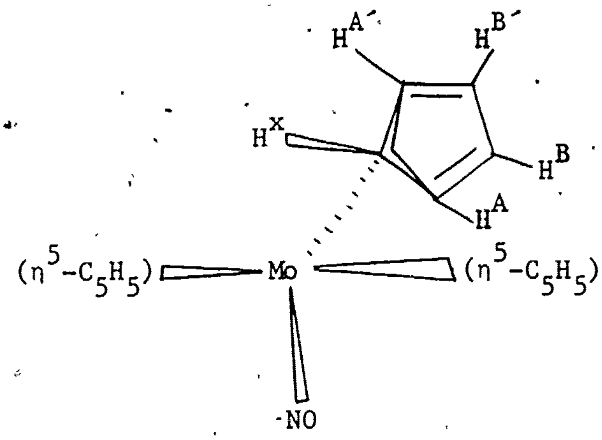


36

isolated by Piper and Wilkinson.[84] These species were found to exhibit surprisingly simple room-temperature $^1$H NMR spectra, singlet resonances being observed for both $\eta^1$-$C_5H_5$- and $\eta^5$-$C_5H_5$-ring nuclei. These observations were attributed to a fast metal-carbon rearrangement around the $\eta^1$-cyclopentadienyl ring, an interpretation which has subsequently been fully corroborated.[85] In a detailed re-investigation of the iron complex <u>35</u>, Cotton and coworkers,[85] using X-ray crystallography, demonstrated the existence of the two different types of cyclopentadienyl ring. As part of the same study, the $^1$H NMR spectrum of <u>35</u> was also shown to be temperature dependent, and at *ca* -80°C, a spectrum consistent with the static structure was obtained.

Determination of the rearrangement pathway was also attempted by analysis of the differential collapse of the <u>aa´bb´</u> multiplet in the slow-limit $^1$H NMR spectrum. Assignment of the portion of the <u>aa´bb´</u> multiplet which collapses first to $H^{A,A'}$ based on the magnitude of the coupling constants $\left|{}^3J(H^X\text{-}H^A)\right|$ and $\left|{}^4J(H^X\text{-}H^B)\right|$, and later[86] by comparison of chemical shifts with those of the monohaptoindenyl analogue $Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_9H_7)(CO)_2$, led to the conclusion that a 1,2 shift predominates.

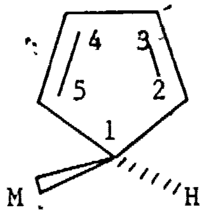
Further evidence for the assignment of the <u>aa´bb´</u> part of the spectrum has been arrived at for several other derivatives. Thus for $Mo(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NO)$,[87] the slow-limit $^1$H NMR spectrum is consistent with "freezing out" of the rotational configuration shown in 37 in which the two sides of the $\eta^1$-$C_5$-ring are magnetically inequivalent. It was assumed that the magnitude



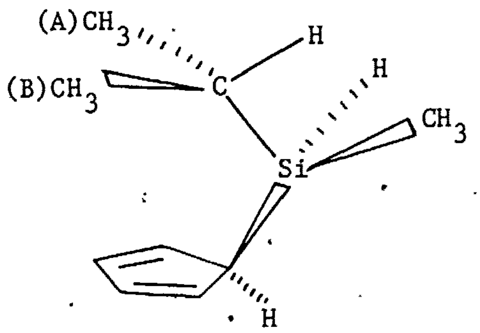
37

of this effect would be greatest for the A,A´ protons, an assignment which again supports a 1,2 shift. In two similar experiments an asymmetric metal center is σ-bonded to the $C_5$-ring. The anticipated larger diastereotopic splittings in the $^{13}C$ NMR spectrum of the $C^2$ and $C^5$ carbon resonances, relative to those for $C^3$ and $C^4$, again led to the conclusion that a 1,2 shift takes place in $Mo(\eta^5$-$C_5H_5)(\eta^1$-$C_5H_5)(NO)(S_2CNBu^n_2)$ [88] and $Si(H)(Bu^n)(\eta^1$-$C_5H_5)Cl$.[89]

For compounds of type $M(X)(Y)(Z)(\eta^1$-$C_5H_5)$, along with diastereotopic shifts among the $C_5$-ring nuclei, anisochromicity may be present within an appropriately substituted migratory group, M(X)(Y)(Z). The first such report[79] concerned



Si(H)(Me)(*i*-Pr)($\eta^1$-$C_5H_5$) where the slow-limit $^{13}C$ NMR spectrum is consistent with structure 38 showing diastereotopic effects



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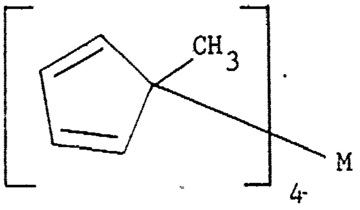
both within the ring and for the two methyls (A) and (B) of the *iso*propyl group. As the temperature was raised, collapse of the ring carbon resonances in the $^{13}C$ NMR spectrum was observed, but no broadening of resonances attributable to $C^A$ and $C^B$ was apparent, showing the magnetic environments of the two methyl groups remain unchanged throughout the rearrangement process. Thus the *iso*propyl group can be used to probe the stereochemical behaviour of the silyl substituent, since the above results are only consistent with retention of configuration at the silicon center, throughout the fluxional process.

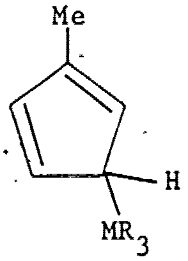
### C.4.(ii). Metallomethylcyclopentadienes.

Non-degenerate rearrangements in ring-substituted metallocyclopentadienes have only recently become well understood. In the earliest report of the synthesis of such species, Fritz and Kreiter [90] incorrectly interpreted the $^1H$ NMR spectrum for tetrakis($\eta^1$-methylcyclopentadienyl)stannane in terms of structure 39 in which the tin atom is surrounded by four $C_5$-rings each bonded exclusively by the carbon bearing the methyl group in a 'static' (stereochemically rigid) arrangement.



39

Davison and Rakita [91,92] subsequently pointed out that the observed data are also consistent with the rapid movement of the tin center around each of the methylcyclopentadienyl rings. It has further been shown that the $^1$H NMR spectrum of $SnMe_3(\eta^1-C_5H_4CH_3)$ is significantly broadened at -60°C, and that both $SiMe_3(\eta^1-C_5H_4CH_3)$ and $GeMe_3(\eta^1-C_5H_4CH_3)$ exhibit complex slow-limit spectra at *ca* 0 and -60°C respectively, which show characteristic spectral variations with increasing temperature. This evidence identifies a series of rearrangements which lead to interconversion between the three isomers 40, 41, and 42.



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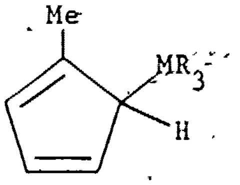

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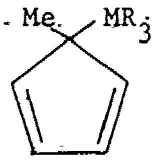
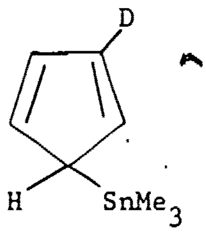


42

This type of rearrangement has been termed "*quasi*-fluxional"[93,94] implying a close relationship with the behaviour of the corresponding unsubstituted cyclopentadienyl derivatives; the difference from the latter is that interconversion occurs between chemically distinguishable isomers possessing different ground state energies. Hence, in a predictably more complicated way, the fast-limit NMR spectra of such compounds will result from the averaging of magnetic environments at fast rates of reversible isomerization.

Detailed investigation of rearrangements occurring in such molecules has been greatly assisted by the use of $^{13}C$ NMR spectroscopy. For $GeMe_3(\eta^1-C_5H_4CH_3)$,[95] it has been possible to completely assign the slow-limit $^{13}C$ NMR spectrum, using off-resonance selective proton decoupling, in terms of isomer types <u>40</u> and <u>41</u> in an *ca.* 2:1 ratio. More recently analysis of the slow-limit spectra of $MR_3(\eta^1-C_5H_4CH_3)$, $MR_3$ = $SiH_3$, $GeH_3$, and $GeMe_3$, has led to the proposal[94] that only isomers <u>40</u> and <u>41</u> occur in significant concentrations in solution. For $SnMe_3(\eta^1-C_5H_4CH_3)$ a rough estimate of the relative concentrations of <u>40</u> and <u>41</u> ([<u>40</u>] : [<u>41</u>]) at room temperature was also made, based on the frequency separation between the $^{13}C$ resonances for each of the two pairs of ring carbon atoms in the fast-limit spectrum. On the basis of this evidence, it was concluded that the ratio [<u>40</u>] : [<u>41</u>] was sensitive to both the size of the metal atom, and the steric demands of substituents on the metal.

A somewhat similar experiment on a system having a deuterium atom label, as opposed to a methyl group attached to the $C_5$-ring, has recently been reported.[96] For $SnMe_3(\eta^1-C_5H_4D)$, isotopic perturbation of the strictly fluxional rearrangement in $SnMe_3(\eta^1-C_5H_5)$ was observed, the fast-limit spectrum being consistent with an equilibrium between the three isomers 43, 44, and 45.



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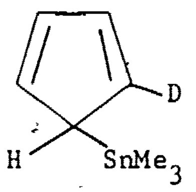

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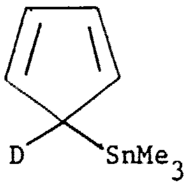

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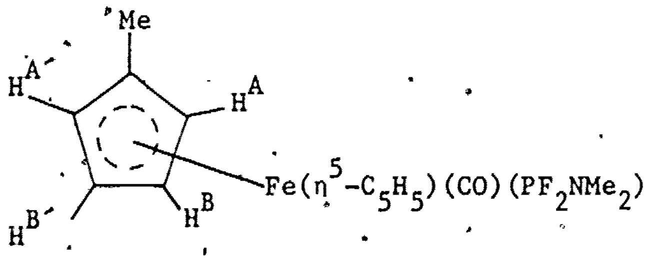
Recently, Fabian and Labinger[97] have shown that in $Fe(\eta^5-C_5H_5)(\eta^1-C_5H_4CH_3)(CO)(PF_2NMe_2)$, the metal atom moves around the methylcyclopentadienyl ring with retention of configuration at the metal center, applying arguments similar to those used for $Si(H)(CH_3)(i\text{- }Pr)(\eta^1-C_5H_5)$. It was also possible to show that in the fast-limit $^1H$ NMR spectrum, signals for the ring protons, $H^A$ and $H^B$ are diastereotopically shifted, see 46,

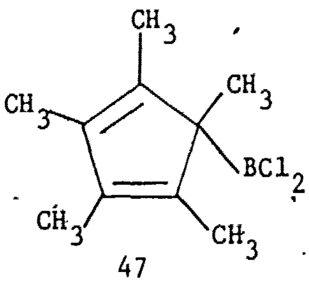
46



indicating that the fluxional process must involve either (i) suprafacial migration with retention of configuration at the metal center, or (ii) antarafacial migration with inversion of configuration. Since migration occurs with retention of configuration at the metal center, the rearrangement was therefore concluded to be suprafacial.

### C.4.(iii). Metallopentamethylcyclopentadienes.

There have been only a few reports of metallotropic shifts in monohaptopentamethylcyclopentadienyl derivatives. Pentamethylcyclopentadienyltrimethyl-germane and -stannane[92] both show similar non-rigid characteristics which correspond to those observed for the unsubstituted cyclopentadienyl analogues. Interestingly, it has been claimed that $Hg[\eta^1\text{-}C_5(CH_3)_5]_2$[98] is a 'static' molecule, in striking contrast to the several known monohaptocyclopentadienylmercury derivatives,[84,99] which are fluxional with very low activation energies for rearrangement ( *ca.* 20kJmol$^{-1}$).



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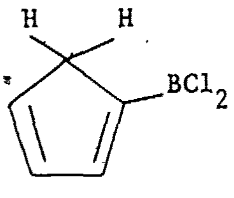

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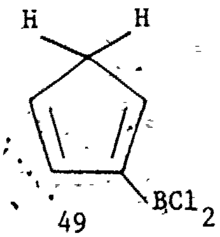
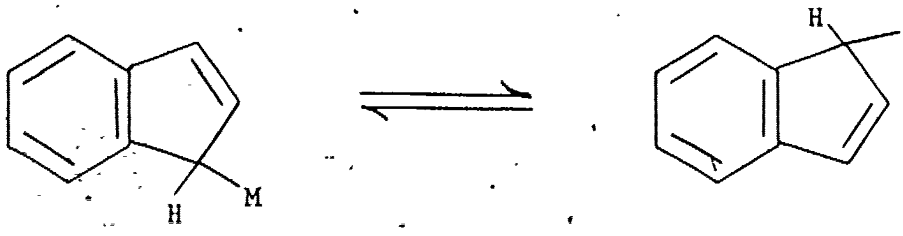


49

The first reported example [100] of a compound having boron bonded *via* a σ-bond to the allylic carbon of a $C_5$-ring is the pentamethylcyclopentadienyl $B[\eta^1-C_5(CH_3)_5]Cl_2$, shown in 47. The preferred vinyl isomers, 48 and 49 found exclusively for all previously known cyclopentadienylboranes is said[101] to be precluded here owing to the high activation energy of a 1,2 methyl shift, relative to a 1,2 hydrogen shift.

### C.4.(iv). Metallo(1-indenes).

During efforts to establish the nature of the fluxional process taking place in monohaptocyclopentadienyls, a number of derivatives of the related indene ring-system were prepared. It was hoped that a comparison of the $^1H$ NMR spectra of indenyl derivatives with those of cyclopentadienyl analogues would allow an unequivocal assignment of the slow-limit spectrum for the cyclopentadienyl, facilitating distinction between 1,2 and 1,3 shifts. Further should a 1,3 shift be the predominant rearrangement pathway for metallocyclopentadienyls, the rearrangement in the indenyl analogue (50(a)→50(b), equation(36)) might

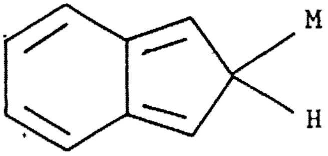


....(36)

50(a)

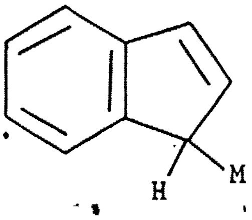
50(b)

be expected to proceed at a similar rate, while a 1,2 shift would result in intermediacy of the high energy *iso*-indenyl (51), significantly slowing the rate of rearrangement in 50.

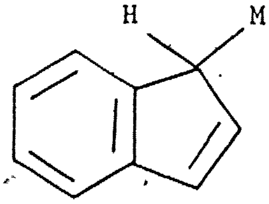


51

Cotton and co-worker[102] prepared $Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_9H_7)(CO)_2$ and found it to be non-fluxional, a result interpreted as supporting a 1,2 pathway in $Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2$. Bis($\eta^1$-indenyl)mercury, $Hg(\eta^1\text{-}C_9H_7)_2$, has been shown to be a fluxional molecule, but the rate of rearrangement is significantly slower than that for $Hg(\eta^1\text{-}C_5H_5)_2$. The NMR data are consistent with an overall 1,3 shift of the metal allowing for interconversion between 52 (a) and 52 (b).



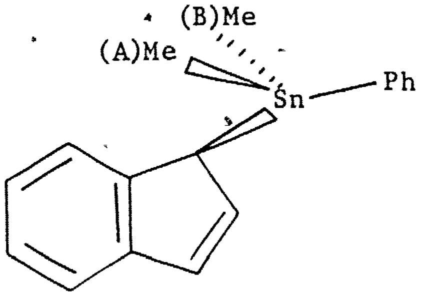
52(a)



52(b)

Davison and Rakita have shown[103] that similar rearrangements occur in some tin indenyls. Some mechanistic information was also obtained from examination of the DNMR spectrum of

$SnMe_2Ph(\eta^1-C_9H_7)$, 53. For the latter, the diastereotopic methyl groups (A) and (B) give rise to separate resonances in the slow-limit (-30°C) $^1H$ NMR spectrum, while fast metallotropic rearrangement results in averaging of the two methyl resonances, which, provided only suprafacial shifts are considered, is consistent with retention of configuration at the metal center during the rearrangement.



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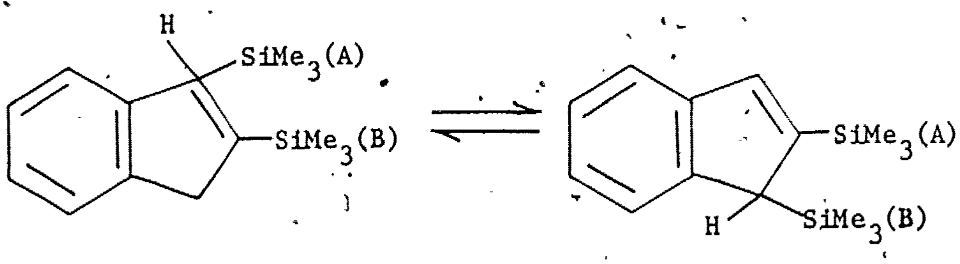
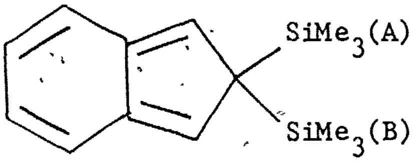
A detailed study[104] of the DNMR spectrum of the di-metallo-indene, 1,2bis(trimethylsilyl)indene, has provided some evidence for the pathway of the rearrangement. At elevated temperatures site-exchange between the two $SiMe_3$ groups occurs, such that only one coalesced $SiMe_3$ resonance is observed in the fast-limit $^1H$ NMR spectrum, equation (37).



.......(37)

These observations are consistent with the intermediacy of the *iso*-indene, 54, but do not rule out the possibility of a pair

54



of simultaneous, concerted 1,2 shifts, as shown in 55.

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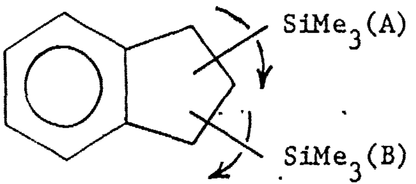
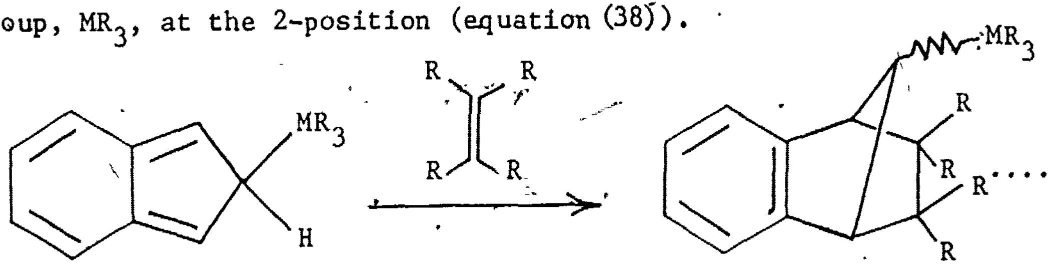


The possible intermediate (the *iso*-indene 51) has also been identified[105,106] by trapping experiments using the Diels-Alder reaction with dienophiles, to give adducts having the migratory group, $MR_3$, at the 2-position (equation (38)).



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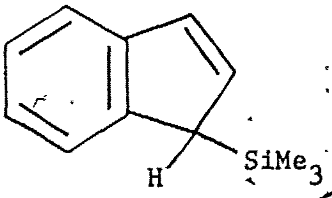

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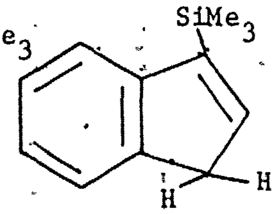

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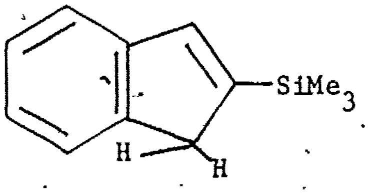

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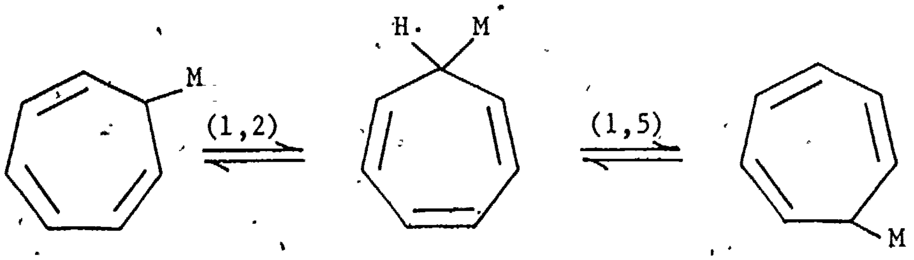
Thermolysis of trimethylsilyl($\eta^1$-indene), 56[106,107] results in an equilibrium mixture of starting material (56) along with two other products (57 and 58) each of which is the result of a prototropic shift(s). The presence of isomer 57 may be interpreted as further evidence for a rearrangement *via* the *iso*-indene 51.

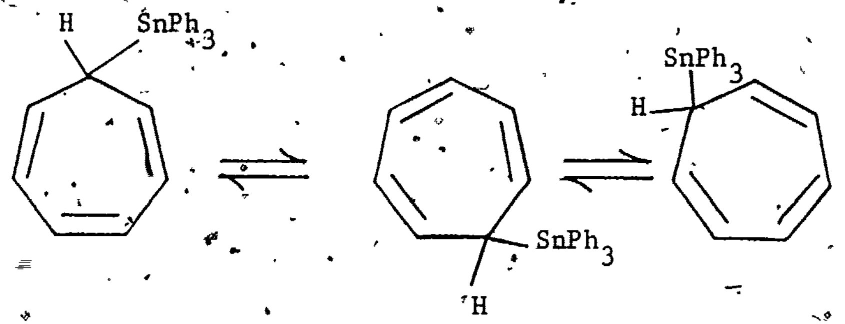
### C.4.(v). Metallocycloheptatrienes.

The observed pathway for migration in metallocyclopentadienes provides no evidence to distinguish between a 1,2, "least motion", shift and a 1,5 pathway topologically identical with a Woodward-Hoffmann symmetry-controlled [1,5] thermal rearrangement. In a $C_7$-ring system, 1,2 and 1,5 migrations will be differentiable, resulting in either a "least motion" shift or a "molecular broad jump" respectively, *i.e.*,



Thus the $C_7$-ring system provides a suitable model from which the rearrangement pathway established experimentally will distinguish between the two alternatives.

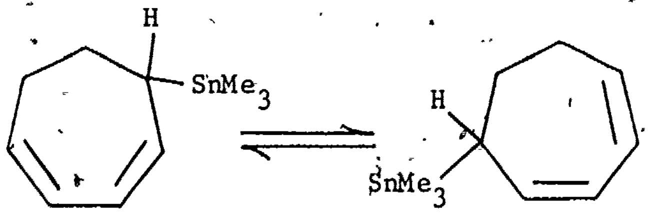
The first such molecule to be prepared was $SnPh_3(\eta^1-C_7H_7)$,[108] which exhibited a DNMR spectrum consistent with a 1,5 shift (equivalent to a 1,4 shift), of the $Ph_3Sn$-substituent about the $C_7$-ring (equation (39)). These observations have been reinvestigated by Mann and co-workers[109] who have essentially confirmed the earlier conclusions.



......(39)

More recently, the first transition metal *sigma*-bonded cycloheptatriene, $Re(\eta^1-C_7H_7)(CO)_5$ has been reported.[110] Interestingly, the molecule is alleged on the basis of Forsen-Hoffmann spin saturation experiments to undergo a least motions 1,2 (or 1,7) shift, not related to a Woodward-Hoffmann symmetry-allowed [1,5] shift.

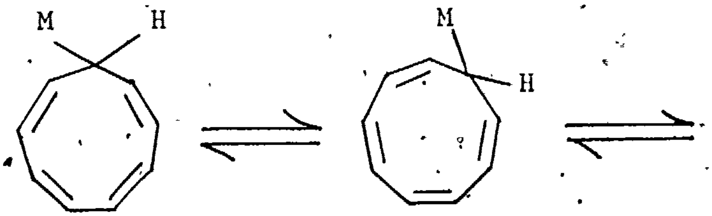
The related cycloheptadiene system has also been investigated.[111] Thus $SnMe_3(\eta^1-C_7H_9)$ has been shown to be a fluxional molecule, in which the tin moiety migrates *via* a 1,5 shift, at a rate similar to that observed for $SnPh_3(\eta^1-C_7H_7)$ (equation (40)).



.......(40)

### C.4.(vi). Metallocyclononatetraenes.

Metallotropism in metallo($\eta^1$-$C_9H_9$) systems have recently been reported.[112,113] A detailed investigation of the silyl, germyl and stannyl systems was completed in these laboratories by Dr. A. Bonny.[113] The rate of rearrangement appears to be comparable to that observed for the corresponding cyclopentadienyl derivatives, and significantly faster than those for related cycloheptatrienyl derivatives. This led to the conclusion that a 1,2 (or 1,9) "least motion" shift as opposed to the higher energy 1,5 (or 1,4) "molecular broad jump" was the lowest-energy pathway for rearrangement, (equation (41)).



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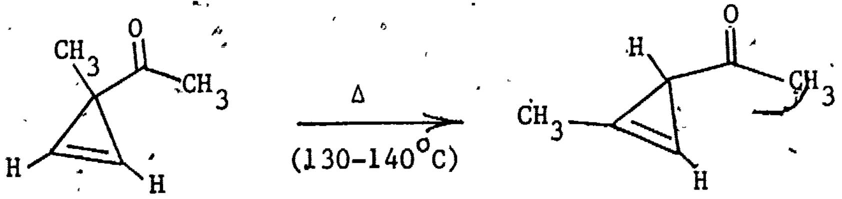
### C.4.(vii). Metallocyclopropenes.

Only a few reports of sigmatropic shifts in cyclopropenes have appeared. The first such observation[114] involved the thermal isomerization of 59 → 60 (equation (42)), presumably



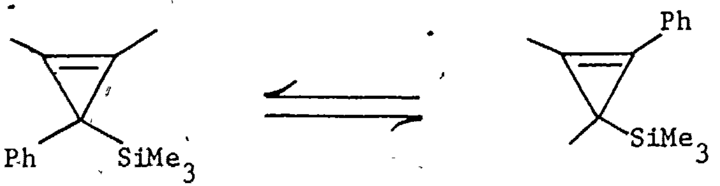
59

60

....(42)

*via* a 1,2 (or 1,3) sigmatropic shift; however the reaction is irreversible and no mechanistic information was obtained.

Recently, an equilibrium between 61 and 62 has been observed[115] (equation (43)). The derived activation energy, $E_a = 134 kJmol^{-1}$, is significantly higher than that for $SiMe_3(\eta^1-C_5H_5)$, $E_a = 54 kJmol^{-1}$, implying that the rearrangement between 61 and 62 takes place with inversion of configuration at the silicon center. The rearrangement was shown to be intramolecular, but no direct evidence was obtained to identify the stereochemistry of the reaction.



61 62 ......(43)

## D. GENERAL EXPERIMENTAL

### D.1. Spectroscopic Methods for Characterization Based on the Nuclear Properties of Isotopes of the Group IVA Elements.

### D.1.(i). Nuclear Magnetic Resonance.

Silicon, tin, and lead each have at least one isotope with the nuclear spin I = ½ (Table 1.3), in a sufficiently high concentration to bring about observable effects in the $^1$H and $^{13}$C NMR spectra of many of their compounds. Thus spin-coupling, between the NMR nuclei under investigation and the group IVA NMR-active isotope, resultsin spectra containing satellite lines which are symmetrically disposed about each central absorption. The technique of heteronuclear magnetic double resonance uses this magnetic relationship to determine indirectly the chemical shift for the particular NMR-active isotope.

TABLE 1.3

Percentage natural abundance [116] of NMR active isotopes of the group IVA elements having I = ½.

| Element | Isotope | % Natural Abundance |
|---|---|---|
| C | 13 | 1.11 |
| Si | 29 | 4.70 |
| Sn | 115 | 0.35 |
| | 117 | 7.61 |
| | 119 | 8.58 |
| Pb | 207 | 22.60 |

TABLE 1.4.

Representative examples of (a) $^{29}$Si and (b) $^{119}$Sn chemical shifts.

(a) $^{29}$Si[c]

| Compound | Chemical Shift δ[a,b] |
|---|---|
| $SiMe_4$ | 0.0 |
| $SiMe_3Cl$ | 30.2 |
| $SiMe_3(OMe)$ | 17.2 |
| $SiPh_4$ | -15.2 |
| $SiCl_4$ | -19.9 |

---

[a] Values of $^{29}$Si chemical shifts in ppm relative to tetramethylsilane, positive values to higher frequencies.

[b] Measurement at room-temperature on neat or $d_6$-benzene solutions of samples.

[c] Values obtained from references 117 and 118.

(b) $^{119}$Sn

| Compound | Chemical Shift δ[a,b] | Solvent |
|---|---|---|
| $SnMe_4$ | 0[c] | neat |
| $SnMe_3Cl$ | 171 | $CDCl_3$ |
| $SnMe_3(OMe)$ | 121 | $C_6H_6$ |
| $SnPh_4$ | -137 | $CHCl_2,CH_2Cl$(110°C) |
| $SnMe_3(\eta^1-C_5H_5)$ | 26.0 | $CCl_4$ |
| $Sn(\eta^1-C_5H_5)_4$ | -24.4 | $CCl_4$ |
| $Sn(\eta^5-C_5H_4CH_3)_2$ | -2171.1 | $CDCl_3$ |

---

[a] Values of $^{119}$Sn chemical shifts in ppm relative to tetramethyltin, positive values to higher frequency.

[b] Measurement at room-temperature unless otherwise stated.

[c] Values obtained from reference 119.

In the specific case of tin, where this technique has been used extensively,[2] the $^{119}Sn$ satellite line in the $^{1}H$ NMR spectrum of the compound is observed, while the sample is irradiated with an r.f. field which sweeps through the $^{119}Sn$ resonant frequency. The frequency at which the satellite line in the proton spectrum is most perturbed gives the $^{119}Sn$ chemical shift.

The advent of the Fourier transform NMR technique as a commonly available analytical tool has facilitated convenient observation of $^{29}Si$, $^{119}Sn$ and $^{207}Pb$ chemical shifts. Values of $^{29}Si$ and $^{119}Sn$ chemical shifts for some typical silicon and tin compounds are given in Tables 1.4(a) and 1.4(b) respectively.

### 1.1.(ii). Mass Spectrometry.[120]

The polyisotopic nature of all of the group IVA elements (Table 1.5), givesrise to characteristic fragmentation families in the mass spectra of their volatile compounds. Spectra of related volatile derivatives of the group IVA elements have many features in common, observed differences being attributable to a decrease in ionization potentials (Table 1.6), or a decrease in the bond strengths of bonds[9] between the group IVA elements and other elements, on descending the group.

The spectra are dominated by even-electron ions, the relative concentration of odd-electron ions being characteristically small. Radical elimination from odd-electron ions is common

## TABLE 1.5.

Percentage natural abundance of isotopes of the group IVA elements.[116]

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Isotope | 12 | 13 | | | | | | | | |
| | % Natural Abundance | 98.89 | 1.11 | | | | | | | | |
| Si | Isotope | 28 | 29 | 30 | | | | | | | |
| | % Natural Abundance | 92.21 | 4.70 | 3.09 | | | | | | | |
| Ge | Isotope | 70 | 72 | 73 | 74 | 76 | | | | | |
| | % Natural Abundance | 20.53 | 27.43 | 7.76 | 36.54 | 7.76 | | | | | |
| Sn | Isotope | 112 | 114 | 115 | 116 | 117 | 118 | 119 | 120 | 122 | 124 |
| | % Natural Abundance | 0.96 | 0.66 | 0.35 | 14.30 | 7.61 | 24.03 | 8.58 | 32.85 | 4.92 | 5.94 |
| Pb | Isotope | 204 | 206 | 207 | 208 | | | | | | |
| | % Natural Abundance | 1.48 | 23.6 | 22.6 | 52.3 | | | | | | |

## TABLE 1.6.

Ionization Potentials for the group IVA elements.[9]

| Element | Ionization Potentials (eV) | | | |
|---|---|---|---|---|
| | 1st | 2nd | 3rd | 4th |
| C | 11.264 | 24.376 | 47.864 | 64.476 |
| Si | 8.149 | 16.34 | 33.46 | 45.13 |
| Ge | 7.809 | 15.86 | 34.07 | 45.5 |
| Sn | 7.332 | 14.63 | 30.6 | 39.6 |
| Pb | 7.415 | 15.03 | 32.0 | 42.3 |

## TABLE 1.7

Typical values of the isomer shift and quadrupole splitting for some tin-containing compounds.[121]

| Compound | Isomer Shift[a,b,c] $\delta$ | Quadrupole Splitting[a,c] $\Delta$ |
|---|---|---|
| $SnMe_4$ | +1.29 | 0.0 |
| $SnMe_3CF_3$ | +1.31 | 1.38 |
| $SnMe_3Ph$ | +1.16 | 0.0 |
| $SnPh_4$ | +1.21 | 0.0 |
| $SnMe_3Cl$ | +1.43 | 3.41 |
| $Sn(\eta^1-C_5H_5)_4$ | +1.56 | 0.0 |
| $Sn(\eta^5-C_5H_5)_2$ | +3.76 | 0.0 |
| $SnCl_2$ | +4.07 | 0.0 |

---

[a] Values given in $mm.s^{-1}$.

[b] Relative to 0 for $SnO_2$.

[c] All spectra were recorded at -78°C.

and usually the dominant mode for decomposition of the molecular ion (equation(44)), with the radical lost commonly being that

$$MR_4^{+\cdot} \longrightarrow MR_3^{+} + R^{\cdot} \text{.......................} (44)$$

most weakly bound to the metal in the neutral molecule. The most familiar mode for decomposition of even-electron ions having alkyl substituents is alkene elimination (equation(45)),

$$MEt_3^{+} \xrightarrow{-C_2H_4} MEt_2H^{+} \xrightarrow{-C_2H_4} MEtH_2^{+} \xrightarrow{-C_2H_4} MH_3^{+} \text{ .....} (45)$$

while elimination of neutral species becomes increasingly common among the heavier group IVA elements (equation(46)).

$$MPh_3^{+} \longrightarrow MPh^{+} + Ph\text{-}Ph \text{.........................} (46)$$

M = Sn, Pb.

### D.1.(iii). Mössbauer Spectroscopy[121,122]

Mössbauer Spectroscopy, or γ-ray resonance spectroscopy, uses a source of γ-rays to excite a nucleus from its ground-state to the first nuclear excited-state. The radiation source for $^{119}Sn$ Mössbauer spectroscopy is the $^{119m}Sn$ isotope which has a half life of 250 days, emmitting a γ-ray of energy 23.8KeV. When the nuclear environment of the tin atoms in the source and absorber are different, absorption can occur only when the energy of the source is modulated. This is done through making use of the Doppler effect by moving the source relative to the absorber. The velocity at which maximum absorption occurs is called the isomer shift, δ (also known as the chemical shift, or chemical isomer shift) and is given by

$$\delta = K.\,\frac{\Delta R}{R}\left(\left|\Psi s\ (o)\right|^2_a - \left|\Psi s\ (o)\right|^2_s\right)$$

where K is a constant, ΔR/R is the fractional change in the nuclear charge radius of excitation and $|\Psi s\ (o)|^2_a$ and $|\Psi s\ (o)|^2_s$ are the total *s*-electron densities at the nuclei of the absorber and source respectively.

The first excitation state of $^{119}$Sn has a nuclear spin I = 3/2, such that deviations of the nuclear charge distribution from spherical symmetry can lead to a splitting of the energy levels, the quadrupole splitting, Δ.

The value of the isomer shift δ, is a measure of the *s*-electron density at the nucleus, and is therefore sensitive to changes in the oxidation state of the metal. Several workers[121] have proposed the isomer shift for α-tin as a dividing line between quadrivalent and bivalent tin, while others have used the value obtained for β-tin. Figure 1.10 shows the scale for this parameter relative to $SnO_2$ = 0, and some typical values for the isomer shift δ and for quadrupole splitting Δ, are given in Table 1.7.

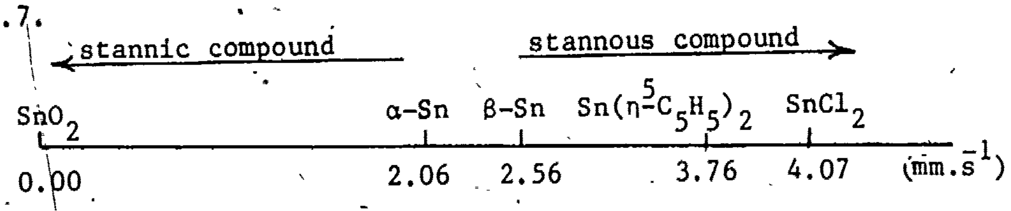


FIGURE 1.10. The $^{119}$Sn Mössbauer isomer shift scale.

## D.2. General Experimental Procedures and Instrumentation.

Due to air (oxygen) and water sensitivity, preparation of the majority of the compounds described in this thesis required the use of Schlenk-type apparatus in conjunction with a double manifold-type nitrogen atmosphere/vacuum system. Glassware was oven-dried at 110°C with flasks and Schlenk tubes being evacuated and purged with dinitrogen gas several times before use. All solvents were manipulated using syringes which were previously flushed with dinitrogen.

Pentane, hexane, toluene, diethyl ether and tetrahydrofuran were dried over potassium/benzophenone, presence of the characteristic blue color of the benzophenone ketyl radical indicating the solvent was sufficiently dry to be used immediately after distillation under an atmosphere of dinitrogen.

The instrumentation which was used is listed in Table 1.8, and commercially available starting materials are listed in Table 1.9; references for preparation of readily available starting compounds are also provided. Microanalysis was performed in this Department or by Canadian Microanalytical Service Ltd. (Vancouver, B.C.).

TABLE 1.8.

Instrumentation

| Technique | Spectrometer |
|---|---|
| Infrared | Perkin-Elmer 283 |
| $^{1}H$ NMR | Perkin- Elmer R12A and R12B(60MHz) |
| | Perkin-Elmer R32 (90MHz) |
| $^{13}C$ NMR | Nicolet TT-14 (15.1MHz) |
| $^{19}F$ NMR | Perkin-Elmer R32 (84.6MHz) |
| Mass Spectra | Hitachi Perkin-Elmer RMU-17 |
| | Finnigan 3300 |

### TABLE 1.9.

### Starting Materials

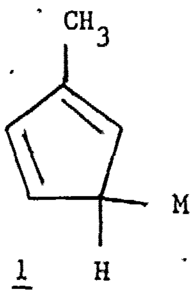
| Compound | Supplier (Reference) |
|---|---|
| $SnCl_4$ | Aldrich |
| $GeCl_4$ | Alfa |
| $GeI_2$ | 123 |
| $GeCl_2$. dioxan | 124 |
| $CsGeCl_3$ | 125 |
| $SnBu^n Cl_3$ | M & T Chemicals Inc. |
| $SnPhCl_3$ | Alfa |
| $SnPh_2Cl_2$ | M & T Chemicals Inc. |
| $SnPh_3Cl$ | M & T Chemicals Inc. |
| "cyclopentadiene dimer" | Aldrich |
| "methylcyclopentadiene dimer" | Aldrich |
| indene | Eastman |
| pentamethylcyclopentadiene | Aldrich |
| acetylacetone | Aldrich |
| benzoylacetone | Aldrich |
| dibenzoylmethane | Aldrich |
| tropolone | Aldrich |
| thujaplicine | Aldrich |
| 8-hydroxyquinoline | Fisher |
| dipivalcylmethane | Aldrich |
| boron trifluoride etherate | Eastman |

# CHAPTER TWO

## INTRAMOLECULAR REARRANGEMENT BEHAVIOUR OF TETRAKIS(CYCLOPENTADIENYL) AND TETRAKIS(METHYLCYCLOPENTADIENYL) DERIVATIVES OF GERMANIUM(IV) AND TIN(IV).[126]

### A. INTRODUCTION

From its origins, based on a suggestion by Piper and Wilkinson in 1956,[84] the concept of fluxional character of $\eta^1$- cyclopentadienyl metal derivatives has received continuing attention. Recent results [79, 89] obtained in these laboratories have established conclusively the nature and mechanism of the dynamic process giving rise to stereochemical non-rigidity in this class of compounds. By contrast, the non-rigid properties of related ring-substituted cyclopentadienyl derivatives have, until recently,[94] not received close scrutiny. In such molecules, any corresponding rearrangement must necessarily involve facile interconversion between isomers of the type 1, 2, and 3, (see also Chapter One).



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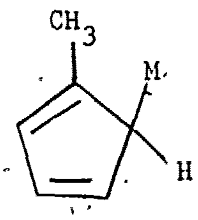

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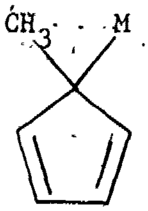

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Davison and Rakita, concluded[91,92] that the temperature dependent $^1H$ NMR spectra of $MMe_3(\eta^1-C_5H_4CH_3)$, M = Si, Ge, and Sn, are consistent with interconversion of these three isomers and that the rearrangement rates are similar to those found for the cyclopentadienyl analogues. The -30°C $^{13}C$ NMR spectrum of $GeMe_3(\eta^1-C_5H_4CH_3)$ has been assigned[95] to existence of a mixture of isomer types 1 and 2, following a comparison with $^{13}C$ NMR data for cyclopentadiene and methylcyclopentadiene. Stobart and Holmes-Smith[94] reached similar conclusions for $MR_3(\eta^1-C_5H_4CH_3)$, $MR_3$ = $SiH_3$, $GeH_3$, $GeMe_3$ and $SnMe_3$, and also estimated the relative concentrations of the two isomers (Table 2.1). It was assumed that isomer 1 was the configuration having lowest free energy on the basis of steric considerations.

TABLE 2.1.

Estimated concentrations of isomers 1 and 2 in $MR_3(\eta^1-C_5H_4CH_3)$-type systems.[94]

| Compound | [1] : [2] |
|---|---|
| $SiH_3(\eta^1-C_5H_4CH_3)$ | 1.2 : 1[a] |
| $GeH_3(\eta^1-C_5H_4CH_3)$ | 1 : 1[a] |
| $GeMe_3(\eta^1-C_5H_4CH_3)$ | 3.2 : 1[a]; *ca.* 2 : 1[b,c] |
| $SnMe_3(\eta^1-C_5H_4CH_3)$ | *ca.* 1 : 1[b,d] |

---

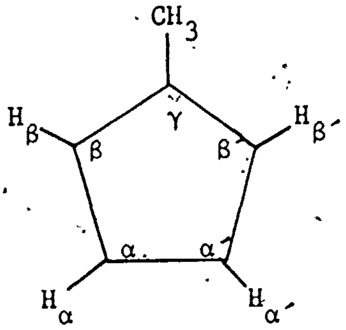
[a] Obtained from slow-limiting $^{13}C$ NMR data at -30°C.

[b] Obtained from fast-limiting $^{13}C$ NMR data.

[c] At +95°C.

[d] At +30°C.

As part of the same study, the separation of the two resonances due to $C^{\alpha,\alpha'}$ and $C^{\beta,\beta'}$ (see 4) in the fast-limiting $^{13}C$ NMR of these compounds was shown to be a function of the relative isomer concentrations. Thus for $SnMe_3(\eta^1-C_5H_4CH_3)$, where the



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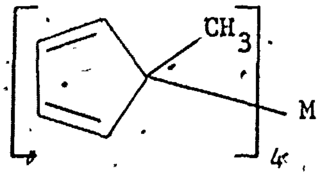
concentration of isomers 1 and 2 are similar, there is only a small separation between the two resonances (*ca.* 5.8 ppm), while for $GeMe_3(\eta^1-C_5H_4CH_3)$, the isomer ratio [1] : [2] = 2 : 1, results in a decrease in the olefinic character of $C^{\alpha,\alpha'}$, and leads to a larger separation between $C^{\alpha,\alpha'}$ and $C^{\beta,\beta'}$ of 12.2 ppm.

In 1965, Fritz and Kreiter reported[90] the synthesis of $Sn(\eta^1-C_5H_4CH_3)_4$, concluding from $^1H$ NMR data that this compound had the static structure 5; however Davison and Rakita subsequently pointed



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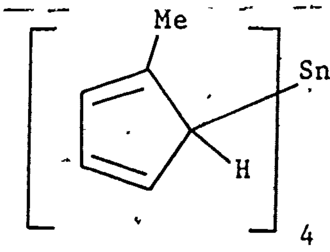
out [91] that the observed spectrum is precisely that expected for a dynamic $\eta^1$-$C_5H_4CH_3$ system, noting that cooling to -80°C led to significant broadening of resonances in the $^1H$ NMR spectrum. Campbell and Green [127] confirmed the non-rigid character of $Sn(\eta^1-C_5H_4CH_3)_4$ from an observation of the temperature dependence of both ($^1H$ - $^1H$) and ($^{117, 119}Sn$ - $^1H$) coupling constants, and further concluded that it exists almost entirely as one isomer form, ie either 6 or 7.



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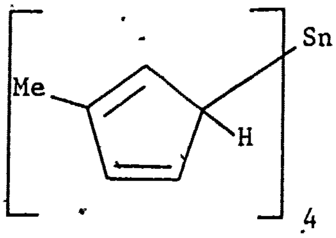

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A more thorough investigation of this situation has been completed as part of the present work and in this chapter the effect of total substitution of germanium and tin by both monohaptocyclopentadienyl and monohaptomethylcyclopentadienyl rings is discussed, giving compounds of the type $MR_4$, $R = \eta^1-C_5H_5$ or $\eta^1-C_5H_4CH_3$. For $R = \eta^1-C_5H_4CH_3$, the interchange between isomers with metal-ring bonding, as shown in 1, 2, and 3 is investigated, and changes effected by replacement of Sn by Ge in $M(\eta^1-C_5H_4CH_3)_4$ are examined.

## B. RESULTS AND DISCUSSION

Tetrakis($\eta^1$-cyclopentadienyl)germane (2.1), tetrakis($\eta^1$-cyclopentadienyl)stannane(2.2), chlorotris($\eta^1$-cyclopentadienyl)germane (2.3), and chlorotris($\eta^1$-cyclopentadienyl)stannane (2.4), were prepared in high yield (*ca.*75%) as light yellow (M = Ge), or bright yellow (M = Sn) solids, from the reaction of potassium cyclopentadienide with $MCl_4$ (M = Ge, or Sn). Exactly analogous reactions using potassium methylcyclopentadienide gave tetrakis-($\eta^1$-methylcyclopentadienyl)germane (2.5), and tetrakis($\eta^1$-methylcyclopentadienyl)stannane (2.6), again in high yield, as viscous yellow oils. Compounds 2.5 and 2.6 are air-sensitive and the germanium compound is thermally unstable: over a period of several days at room-temperature it forms a hard non-melting glass, insoluble in common organic solvents. Physical and analytical data for compounds 2.1 - 2.6 are given in Table 2.2.

### B.1. Mass Spectral Data.

Mass spectral data for compounds 2.1 - 2.6 are given in Table 2.3 and provide definitive characterization for each of the six compounds. While the molecular ion for the three germanium compounds is clearly discernible, those for the tin derivatives were not observed, reflecting a decrease in the metal-carbon bond strength. Subsequent fragmentation is dominated by the formation of even electron ions, *via* radical elimination,

TABLE 2.2.

Physical and analytical data for compounds 2.1 - 2.6.

| Compound | Colour | M.P. (°C) | Analysis |  |  |  | % yield |
|---|---|---|---|---|---|---|---|
|  |  |  | Theoretical |  | Actual |  |  |
|  |  |  | %C | %H | %C | %H |  |
| $Ge(\eta^1-C_5H_5)_4$ (2.1) | light yellow | 116° (dec) | 72.16 | 6.01 | 71.90 | 5.83 | 86% |
| $Sn(\eta^1-C_5H_5)_4$ (2.2) | yellow | 73-74° | 63.37 | 5.32 | 63.19 | 5.51 | 76% |
| $Ge(\eta^1-C_5H_5)_3Cl$ (2.3) | light yellow | 145° (dec) | 59.39 | 4.99 | 59.09 | 4.99 | 91% |
| $Sn(\eta^1-C_5H_5)_3Cl$ (2.4) | yellow | 165° (dec) | 51.55 | 4.30 | 51.31 | 4.13 | 79% |
| $Ge(\eta^1-C_5H_4CH_3)_4$ (2.5) | amber | oil | 74.09 | 7.26 | 73.71 | 6.98 | 74% |
| $Sn(\eta^1-C_5H_4CH_3)_4$ (2.6) | orange | oil | 66.24 | 6.48 | 66.51 | 6.57 | 82% |

TABLE 2.3.

Mass spectral data[a] for (a) $MR_4$[b,c] and (b) $MR_3Cl$[b,d].

(a)

| ion family | ion abundance[e] | | | |
|---|---|---|---|---|
| | $Ge(\eta^1\text{-}C_5H_5)_4$ | $Sn(\eta^1\text{-}C_5H_5)_4$ | $Ge(\eta^1C_5H_4CH_3)_4$ | $Sn(\eta^1C_5H_4CH_3)_4$ |
| $MR_4^{+\cdot}$ | 0.5 | n.o.[f] | 1.1 | n.o.[f] |
| $MR_3^+$ | 6.9 | 4.8 | 1.2 | 7.1 |
| $MR_2^{+\cdot}$ | 1.9 | 0.7 | 0.2 | 1.4 |
| $MR^+$ | 77.0 | 74.6 | 97.5 | 66.8 |
| $MC_3H_n^+$ | 8.0 | 3.0 | n.o.[f] | n.o.[f] |
| $MC_2H_n^+$ | 3.4 | 2.1 | n.o.[f] | n.o.[f] |
| $M^{+\cdot}$ | 1.0 | 14.7 | n.o.[f] | 13.2 |

(b)

| ion family | $Ge(\eta^1\text{-}C_5H_5)_3Cl$ | $Sn(\eta^1\text{-}C_5H_5)_3Cl$ |
|---|---|---|
| $MR_3Cl^{+\cdot}$ | 4.8 | n.o.[f] |
| $MR_3^+$ | 2.3 | 16.2 |
| $MR_2Cl^+$ | 11.1 | n.o.[f] |
| $MR_2^{+\cdot}$ | 9.9 | 7.8 |
| $MRCl^{+\cdot}$ | n.o.[f] | 1,6 |
| $MR^+$ | 48.8 | 49.8 |
| $MC_2H_n^+$ | 3.2 | n.o.[f] |
| $MCl^+$ | 19.3 | 20.9 |
| $M^{+\cdot}$ | 4.6 | 3.6 |

---

[a] 70eV ionizing voltage.

[b] M=Ge, or Sn.

[c] R=$\eta^1\text{-}C_5H_5$ or $\eta^1\text{-}C_5H_4CH_3$.

[d] R=$\eta^1\text{-}C_5H_5$.

[e] % metal containing ions, summed within each family resulting from isotope distribution and hydrogen loss.

[f] Not observed.

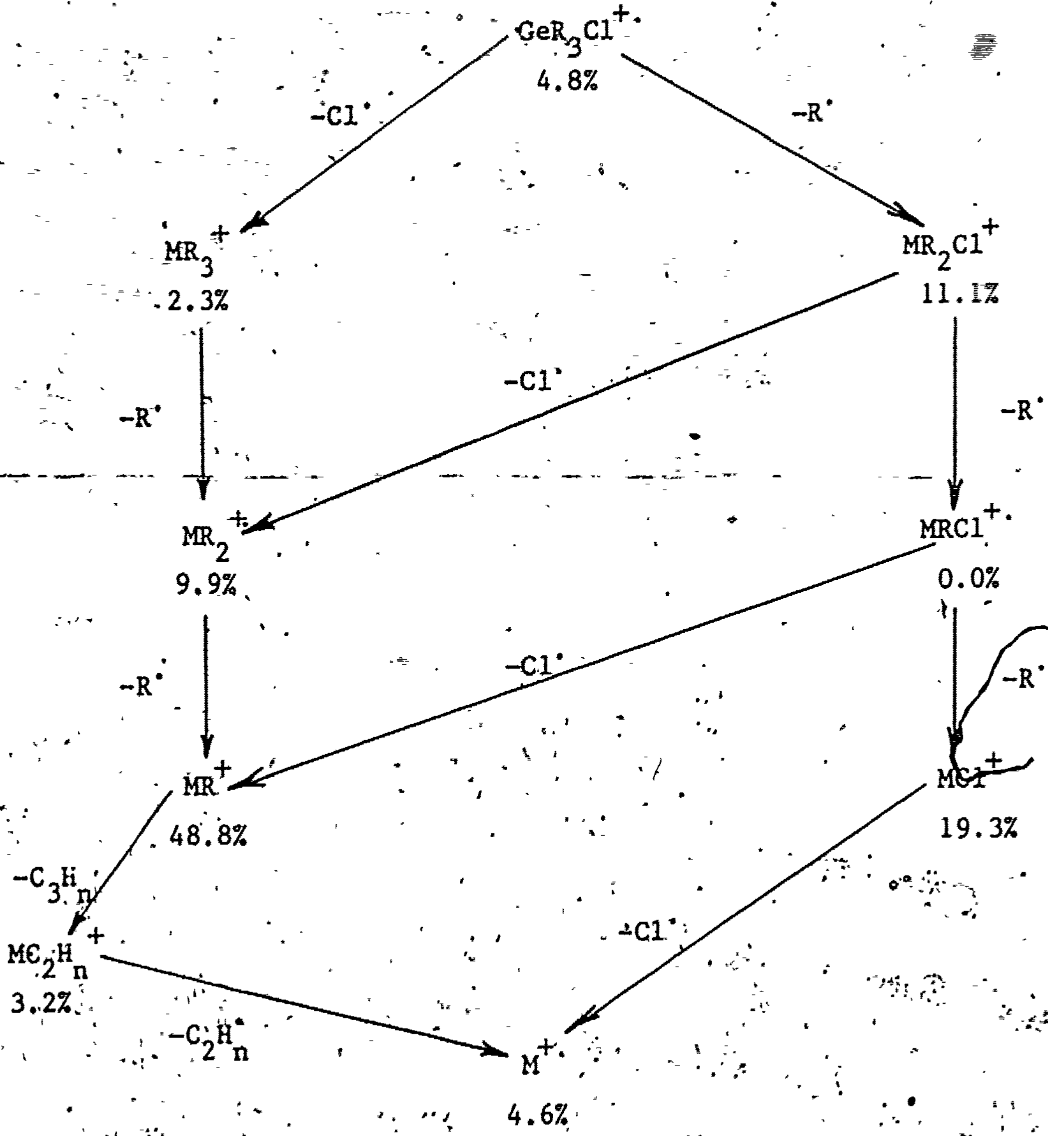

FIGURE 2.1. Fragmentation pathways for $Ge(\eta^1-C_5H_5)_3Cl$.

giving principally $MR^+$, a result similar to that observed for many other group IVA organometallics.[1,120] The ion $MR^+$ decomposes either by loss of the $C_5$-ring or by carbon-carbon bond cleavage within the ring, giving $MC_3H_n^+$ and $MC_2H_n^+$ fragments (Figure 2.1). These fragments have a relatively low abundance, consistent with the recent conclusion[128] that while $\eta^5$-cyclopentadienyls characteristically fragment *via* carbon-carbon bond fission, the main pathway for decomposition of $\eta^1$-cyclopentadienyl analogues is by breaking of the metal-carbon linkage.

TABLE 2.4.

$^{119}$Sn Mössbauer data[a] for compounds 2.2 and 2.4.

| Compound | Isomer Shift δ | Quadrupole Splitting Δ |
|---|---|---|
| $Sn(\eta^1-C_5H_5)_4$ | 1.56 | 0 |
| $Sn(\eta^1-C_5H_5)_3Cl$ | 1.56 | 1.45 |

[a] Measured at 77K by using a Harwell constant-acceleration spectrometer. Isomer shift in $mm.s^{-1}$ relative to 0 for $SnO_2$ and quadrupole splitting in $mm.s^{-1}$.

### B.2. Mössbauer Spectral Data.

The Mössbauer data obtained for compounds 2.2 and 2.4 are given in Table 2.4. The isomer shifts determined for both compounds are identical within experimental error, $\delta = 1.56 mm.s^{-1}$, and in the region expected for quadrivalent tin, being similar to isomer shifts obtained for other tetraorganotin(IV) compounds, but significantly lower than the value reported [131] for $Sn(\eta^5\text{-}C_5H_5)_2$, (Table 2.5).

TABLE 2.5.

Isomer shift values for some $SnR_4$ - type compounds.

| Compound | Isomer Shift δ (mm.s$^{-1}$) | Reference |
|---|---|---|
| $SnMe_4$ | 1.29 | 129 |
| $Sn(C_6H_{11})_4$ | 1.52 | 130 |
| $SnPh_4$ | 1.21 | 130 |
| $Sn(\eta^1\text{-}C_5H_5)_4$ | 1.56 | this work |
| $Sn(\eta^5\text{-}C_5H_5)_2$ | 3.76 | 131 |

The spectrum for compound 2.4 consists of a doublet with quadrupole splitting Q.S. = 1.45 mm.s$^{-1}$, consistent with non-spherical symmetry about the tin center. The value obtained is substantially smaller than those for some related triorganotin halides, as indicated in Table 2.6.

TABLE 2.6

Quadrupole splitting values for some $SnR_3Cl$ - type compounds.

| Compound | Quadrupole Splitting (mm.s$^{-1}$) | Reference |
|---|---|---|
| $SnMe_3Cl$ | 3.41 | 132 |
| $SnPh_3Cl$ | 2.5 | 130 |
| $Sn\ Bu^n_3Cl$ | 3.40 | 133 |
| $Sn(p\text{-}ClC_6H_4)_3Cl$ | 2.49 | 130 |
| $Sn(\eta^1\text{-}C_5H_5)_3Cl$ | 1.45 | this work |

TABLE 2.7.

Infrared spectra[a], 2800-3200 cm$^{-1}$ region for compounds 2.1-2.4[b].

| Ge($\eta^1$-$C_5H_5$)$_4$ | Sn($\eta^1$-$C_5H_5$)$_4$ | Ge($\eta^1$-$C_5H_5$)$_3$Cl | Sn($\eta^1$-$C_5H_5$)$_3$Cl |
|---|---|---|---|
| 3100 (w) | 3100 (vw) | 3095 (vw) | 3101 (w) |
| 3081 (w) | 3060 (w) | 3070 (w) | 3093 (w) |
| 3042 (mw) | 3040 (vw) | 3048 (vw) | 3073 (w) |
| 2904 (w) | 2950 (w) | 2954 (vw) | 2959 (w) |
| 2842 (vw) | 2920 (mw) | 2910 (w) | 2915 (vw) |
|  | 2850 (w) | 2845 (w) |  |

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[a] Values given in cm$^{-1}$.

[b] As KBr pellets.

## B.3. Vibrational Spectral Data.

The infrared spectra of compounds <u>2.1</u> - <u>2.4</u> each have at least five absorptions between 2800 and 3200 $cm^{-1}$ (Table 2.7), due to ring ν(CH). Using group theoretical considerations it is possible to predict[134] that for a $\eta^5$-$C_5H_5$-ring (local $D_{5h}$ symmetry), there should be two IR - active fundamentals due to the ring ν(CH), (2800 - 3200 $cm^{-1}$ range). In contrast a $\eta^1$-$C_5H_5$-ring ($C_s$ symmetry), should give rise to five stretching modes, one aliphatic - type (2800 - 3200 $cm^{-1}$) and four olefinic C-H stretches (3000 - 3200 $cm^{-1}$). Hence the presence of three or more bands in this region is positive evidence for monohapto-cyclopentadienyl bonding, and the observed spectra clearly point to the existence of such an arrangement in each of the four compounds.

## B.4. NMR Data.

### B.4.(i). Monohaptocyclopentadienyl Derivatives.

The $^1H$ NMR spectra of $Sn(\eta^1\text{-}C_5H_5)_4$ (<u>2.2</u>) and $Sn(\eta^1\text{-}C_5H_5)_3Cl$, (<u>2.4</u>) are superficially very similar (Table 2.8), each consisting of a single sharp line with symmetrically disposed satellite lines due to coupling between $^1H$ and $^{117,\,119}Sn(I = \frac{1}{2})$. The single line indicates magnetic equivalence between the five ring protons of each of the $C_5H_5$-rings, with the coupling constants, $^2J(^{117}Sn-^1H)$ and $^2J(^{119}Sn-^1H)$, being significantly different for the

## TABLE 2.8.

$^{1}$H NMR data[a,b] for compounds 2.1 - 2.4.

| Compound | Temperature °C | $\delta(H^{A,A'})$ | $\delta(H^{B,B'})$ | $\delta(H^{x})$ | $^{2}J(^{117}Sn-'H)^{f}$ | $^{2}J(^{119}Sn-'H)^{f}$ |
|---|---|---|---|---|---|---|
| $Ge(\eta^{1}-C_{5}H_{5})_{4}$, 2.1. | -65 ° | 6.63 | 6.28 | 3.26 | | |
| | 27 ° | | 6.31[c] | | | |
| $Ge(\eta^{1}-C_{5}H_{5})_{3}Cl$, 2.3. | -60 ° | 6.62 | 6.29 | 3.24 | | |
| | 27 ° | | 5.83 | | | |
| $Sn(\eta^{1}-C_{5}H_{5})_{4}$, 2.2. | 27 ° | | 5.92[c,d] | | 25.4 | 26.6 |
| $Sn(\eta^{1}-C_{5}H_{5})_{3}Cl$, 2.4. | 27 ° | | 5.81[c,e] | | 29.9 | 31.1 |

---

[a] Chemical shifts in ppm measured positive downfield from $SiMe_{4}$ in 5% $CDCl_{3}$ solution.

[b] Measured at 60.0 and 90.0 MHz.

[c] Exchange-broadened averaged chemical shift.

[d] See also reference 90. $\delta(^{13}C)$ = 114.5ppm, $^{1}J(Sn-C)$ = 17.7Hz ($^{117}Sn$, $^{119}Sn$ components not resolved) at 27°C.

[e] In $C_{6}D_{6}$ solution

[f] Values given in Hz.

two compounds, increasing upon introduction of the electron withdrawing Cl substituent.

The variable temperature $^1H$ NMR spectra of $Ge(\eta^1-C_5H_5)_4$ (2.1) and $Ge(\eta^1-C_5H_5)_3Cl$ (2.3), are also similar (Table 2.8). The $^1H$ NMR spectrum of compound 2.1 at -60°C, Figure 2.2(a), is assigned to an incompletely resolved aa´bb´x pattern, consistent with the presence of four magnetically equivalent $\eta^1-C_5H_5-$ rings attached to germanium. On raising the temperature above -60°C the spectrum broadens, the upfield portion of the aa´bb´ pattern collapsing more rapidly than the low-field part. At 0°C, Figure 2.2(d), the spectrum consists of a single broad absorption which shows a continuing decrease in half-height line-width with increasing temperature, eventually giving (above 100°C) a single sharp line similar to the room-temperature $^1H$ NMR spectrum of the two tin compounds.

The spectral broadening of the $^1H$ NMR spectra of the germanium compounds at temperatures above -60°C, is the result of a migration of the germanium center around the $\eta^1$-cyclopentadienyl rings ("ring whizzing"),[20] ultimately bringing about equivalence of the five ring protons of each of the $C_5-$ rings on the NMR timescale when this process becomes sufficiently fast. The unsymmetrical collapse of the aa´bb´ pattern for the four olefinic protons eliminates any pathway in which site exchange occurs either randomly, or *via* any configuration in which all sites become equivalent (*eg.* dissociative). Further

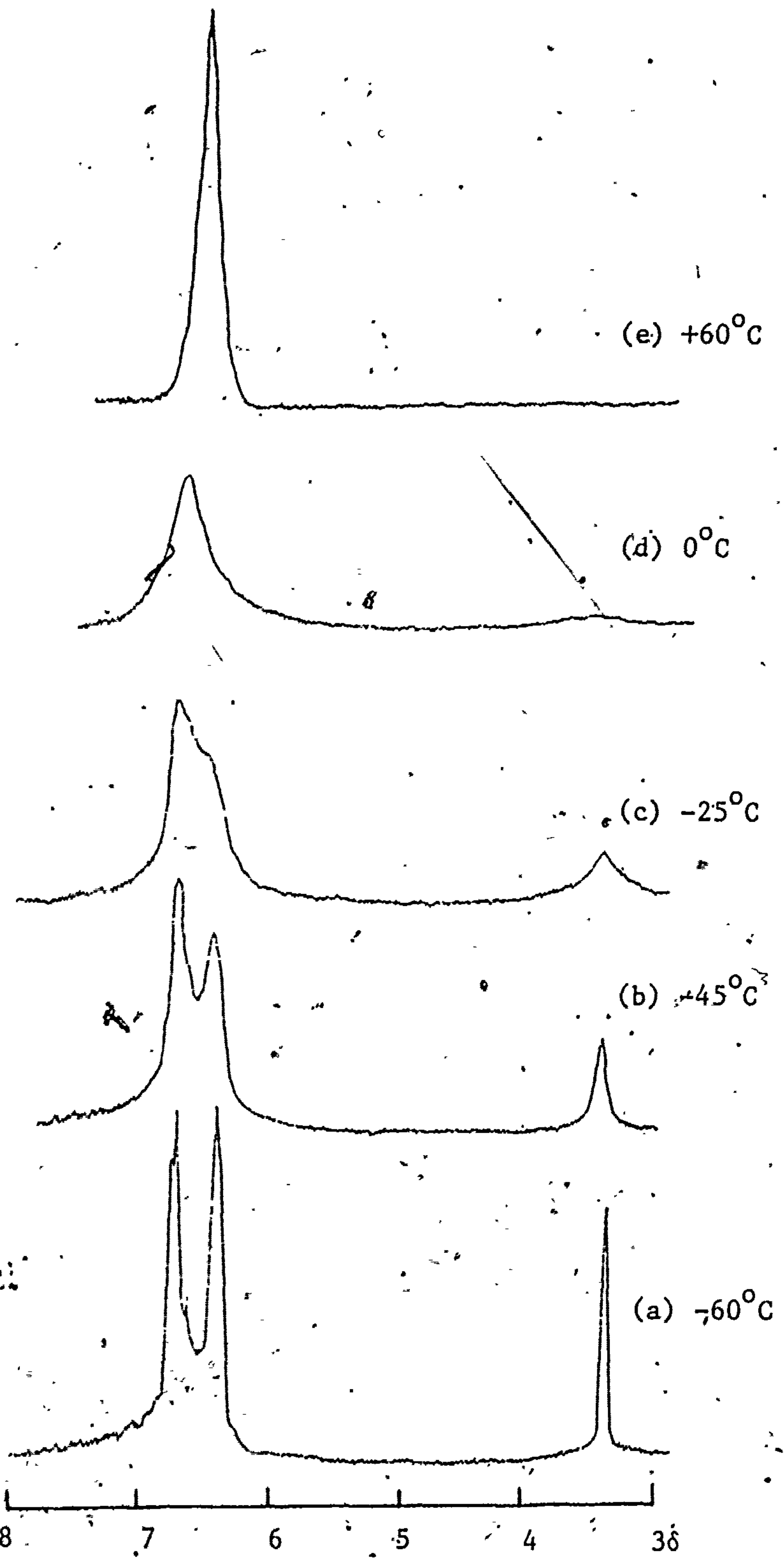
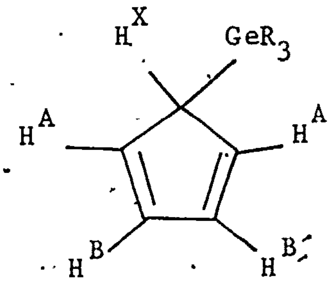


FIGURE 2.2. Variable temperature 90MHz $^1$H NMR spectrum of $Ge(\eta^1-C_5H_5)_4$, 2.1.

an assignment of the 1,2 pathway for the migration is also possible, if the upfield portion of the <u>aa'bb'</u> multiplet is assigned to the $H^{AA'}$, see <u>8</u>. Such conclusions have previously



<u>8</u>

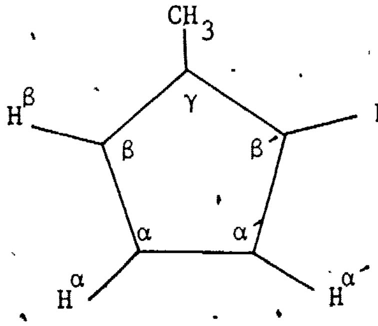
been reached for $GeMe_3(\eta^1-C_5H_5)$,[135,136] following a complete analysis of the variable temperature $^1H$ NMR spectrum, and for $Si(H)(Bu^{\underline{n}})(\eta^1-C_5H_5)Cl$,[89] chirality at the silicon center leading to the expected larger diastereotopic splitting between between signals for $H^A$ and $H^{A'}$, than for $H^B$ and $H^{B'}$, in the -60°C $^1H$ NMR spectrum.

The $^1H$ NMR spectra of the tin cyclopentadienyls[91] also indicate that fast metallotropic rearrangement is taking place, however the rearrangement rates are significantly faster than those observed for the germanium analogues. A similar conclusion has been reached for $SnMe_3(\eta^1-C_5H_5)$,[136] for which at very low temperature (-150°C) a spectrum consistent with a static $\eta^1-C_5H_5$ configuration was observed. Further, the solid state structure of $Sn(\eta^1-C_5H_5)_4$ (<u>2.2</u>) has been shown[137] by X-ray crystallography to contain four equivalent $\eta^1-C_5H_5$- rings.

Presence of $^{117,\,119}Sn$ satellite lines in the fast-limit spectra of the tin compounds provides conclusive evidence for identification of the rearrangement process as non-dissociative (*i.e.* intramolecular).

### 4.B.(ii). Monohaptomethylcyclopentadienyl Derivatives

At room-temperature, the $^1H$ NMR spectrum of $Sn(\eta^1-C_5H_4CH_3)_4$ (2.6) (Figure 2.3), consists of three absorptions at δ2.05, 4.95, and 5.97 in an intensity ratio of 3 : 2 : 2, assigned to $H^{CH_3}$, $H^{\alpha,\alpha'}$ and $H^{\beta,\beta'}$ respectively, see 4, while the $^{13}C$ NMR spectrum (Figure 2.4), has four signals at 15.4, 96.5, 123.6 and 139.5 ppm for $C^{CH_3}$, $C^{\alpha,\alpha'}$, $C^{\beta,\beta'}$ and $C^{\gamma}$ respectively.



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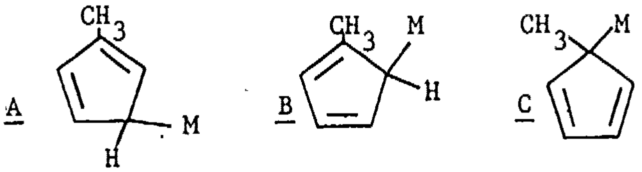
The deceptively simple appearance of both these spectra arises from an intramolecular rearrangement which must involve facile isomerization between the three possible configurations, A, B, and C. Work in these laboratories[94] has established



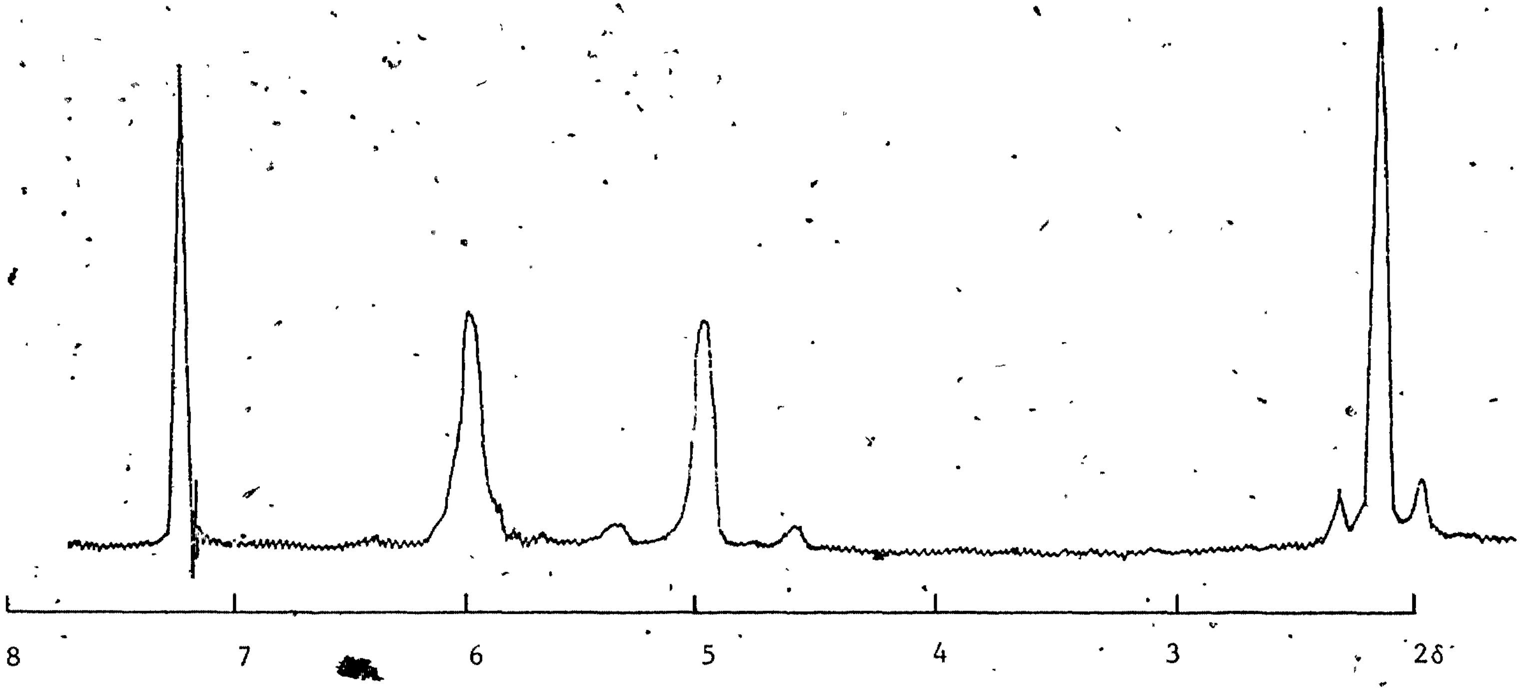


FIGURE 2.3. Room-temperature 90MHz $^1$H NMR spectrum of $Sn(\eta^1\text{-}C_5H_4CH_3)_4$.

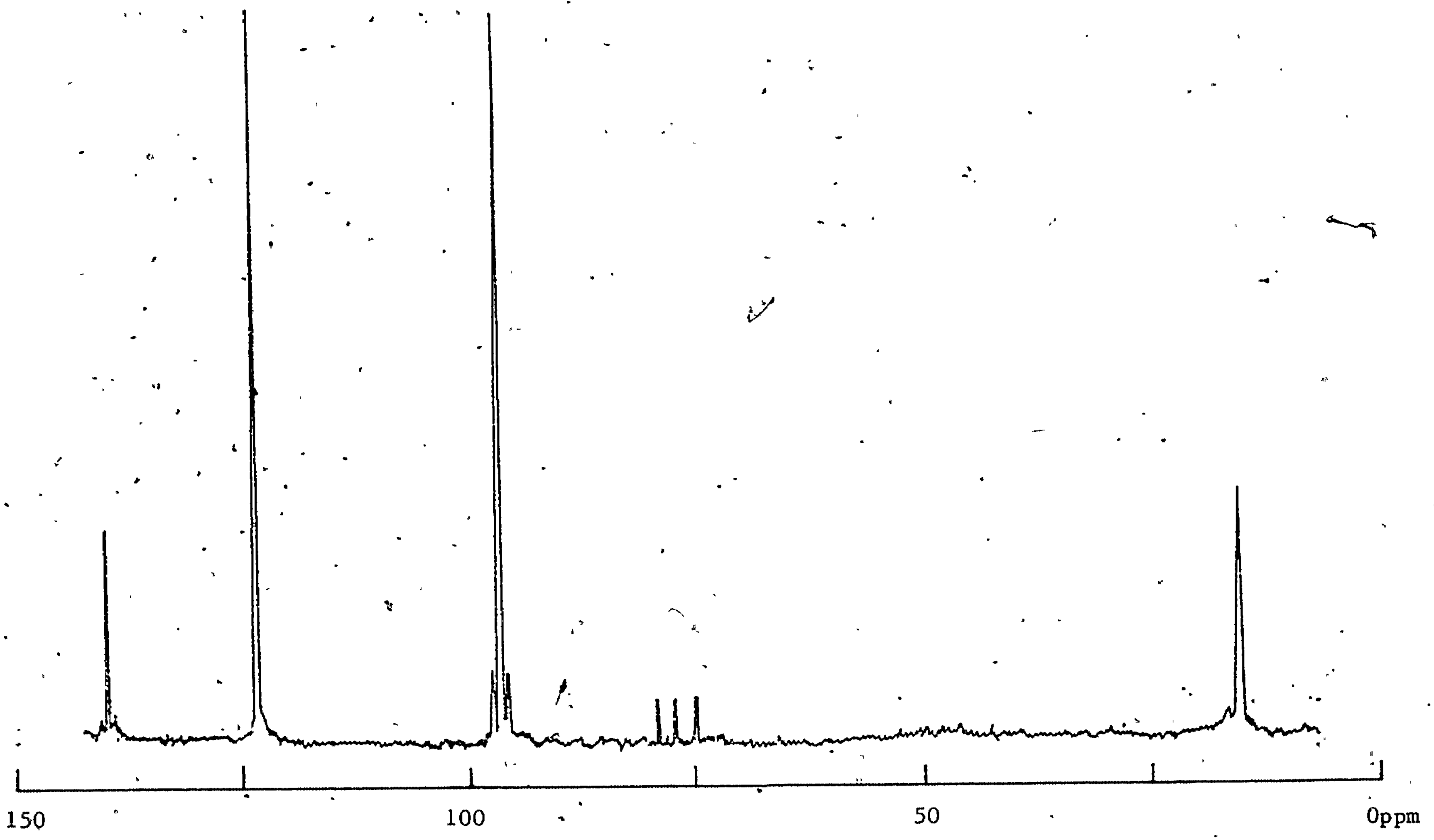


FIGURE 2.4. Room-temperature $^{13}C$ NMR spectrum of $Sn(\eta^1-C_5H_4CH_3)_4$.

that rearrangement in these types of ring system* results in fast-limiting $^{13}$C NMR spectra, having three resonances with frequencies $\nu_1$, $\nu_2$ and $\nu_3$ for the five ring carbons (equations (1)-(3)), in which $\nu_\alpha$, $\nu_{\alpha'}$, $\nu_\beta$, $\nu_{\beta'}$, and $\nu_\gamma$ are the resonant frequencies at the slow-limit for isomer A and a is its equilibrium molar fraction at T K; $\nu_{\alpha_1}$, $\nu_{\alpha_1'}$, $\nu_{\beta_1}$, $\nu_{\beta_1'}$ and $\nu_{\gamma_1}$ are the corresponding frequencies for, and b the molar fraction of, isomer B.

$$\nu_1 = \tfrac{1}{2}[a(\nu_\alpha + \nu_{\alpha'}) + b(\nu_{\alpha_1} + \nu_{\alpha_1'})] \ldots\ldots\ldots\ldots (1)$$

$$\nu_2 = \tfrac{1}{2}[a(\nu_\beta + \nu_{\beta'}) + b(\nu_{\beta_1} + \nu_{\beta_1'})] \ldots\ldots\ldots\ldots (2)$$

$$\nu_3 = a\nu_\gamma + b\nu_{\gamma_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

It was also shown [94] that for $GeMe_3(\eta^1\text{-}C_5H_4CH_3)$, where $(\nu_2 - \nu_1) =$ 12.2 ppm, the ratio of concentrations of isomers A and B is approximately 2:1, while for $SnMe_3(\eta^1\text{-}C_5H_4CH_3)$, the separation $(\nu_2 - \nu_1) = 5.8$ ppm indicates that the two isomers are present in approximately equal concentrations. Thus for $Sn(\eta^1\text{-}C_5H_4CH_3)_4$ where the separation between $\nu_1$ (96.5 ppm) and $\nu_2$ (125.6 ppm) is large, *ie* 29.1 ppm, isomer A must be present in a significantly higher concentration then isomer B. Significantly, Campbell and Green have also concluded [127] that $Sn(\eta^1\text{-}C_5H_4CH_3)_4$ exists almost exclusively as one isomer, based on the temperature dependence of ($^{117,119}$Sn - $^1$H) coupling constants.

The most distinctive feature of the room-temperature

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* The relative concentration of isomer C was assumed to be negligible. [94,95,127]

## TABLE 2.9.

NMR data[a] for tetrakis($\eta^1$-methylcyclopentadienyl) - germane and - stannane, compounds 2.5 and 2.6 respectively.

| Compound | Temperature (°C) | $^1H$[b] | | | |
|---|---|---|---|---|---|
| | | $\delta(H^{\beta,\beta'})$ | $\delta(H^{\alpha'})$ | $\delta(H^{\alpha})$ | $\delta(H^{CH_3})$ |
| $Ge(\eta^1-C_5H_4CH_3)_4$, 2.5 | -50°[c] | 6.25, 5.90 | 6.40 | 3.12 | 2.08 |
| | 27°[e] | 6.10 | 4.75 | | 2.06 |
| $Sn(\eta^1-C_5H_4CH_3)_4$[d], 2.6 | 27° | 5.97 | 4.95 | | 2.05 |

| Compound | Temperature (°C) | $^{13}C$ | | | | |
|---|---|---|---|---|---|---|
| | | $\delta(C^{\gamma})$ | $\delta(C^{\beta,\beta'})$ | $\delta(C^{\alpha'})$ | $\delta(C^{\alpha})$ | $\delta(C^{CH_3})$ |
| $Ge(\eta^1-C_5H_4CH_3)_4$, 2.5 | -50°[e] | 141.2 | 134.0, 128.0 | 134.0 | 49.0 | 15.5 |
| | 27°[e] | 141.0 | 131.2 | n.o. | | 15.3 |
| $Sn(\eta^1-C_5H_4CH_3)_4$, 2.6 | 27°[f] | 139.5 | 123.6 | 96.5 | | 15.4 |

---

[a] Chemical shifts, ppm, measured positive downfield from $SiMe_4$ in 10%($^1H$) or 50% ($^{13}C$) $CDCl_3$ solutions.

[b] Measured at 90 MHz.

[c] See also figure 2.5.

[d] For $^{117,119}Sn - {}^1H$ coupling constants see reference 127.

[e] See also figure 2.6.

[f] See also figure 2.4.

$^1$H NMR spectrum of the germanium compound <u>2.5</u>, (Figure 2.5) is the unsymmetrical collapse of the two olefinic resonances of δ6.10 and 4.75. As the temperature is lowered to *ca.*0°C, the signal centered at δ4.75 becomes extremely broad and at -60°C a new broad absorption is apparent at δ3.12 (Table 2.9), while the methyl resonance at δ2.08 shows little variation in either chemical shift or line width.

The $^{13}$C NMR spectrum of <u>2.5</u> (Figure 2.6), shows extensive changes between -50 and +50°C (see also Table 2.9) : thus signals at 49.0 128.0 and 134.0 ppm in the -50°C spectrum become broad at *ca.* 0°C, the low frequency signal having completely collapsed at *ca.*+50°C. By contrast, signals at *ca.* 15.5 and 141.2 ppm, assigned to $C^{Me}$ and $C^{\gamma}$ , show little variation in frequency or line width throughout the temperature range studied. These spectra differ from comparable data for $GeMe_3(\eta^1-C_5H_4CH_3)$,[94,95] in that:

(i) the -50°C spectrum for <u>2.5</u> has only one ring-methyl signal (at 15.3 ppm), while for $GeMe_3(\eta^1-C_5H_4CH_3)$ at -30°C there are two ring-methyl signals,

(ii) there is only one resonance due to a ring carbon bearing a methyl substituent, $C^{\gamma}$, (at 141.0 ppm) in the -50°C spectrum of <u>2.5</u>, while two such absorptions are present for $GeMe_3(\eta^1-C_5H_4CH_3)$, in the -30°C spectrum,

(iii) neither of the two signals due to $C^{\gamma}$ and $C^{Me}$ in the $^{13}$C NMR spectrum of <u>2.5</u> show any variation in frequency or

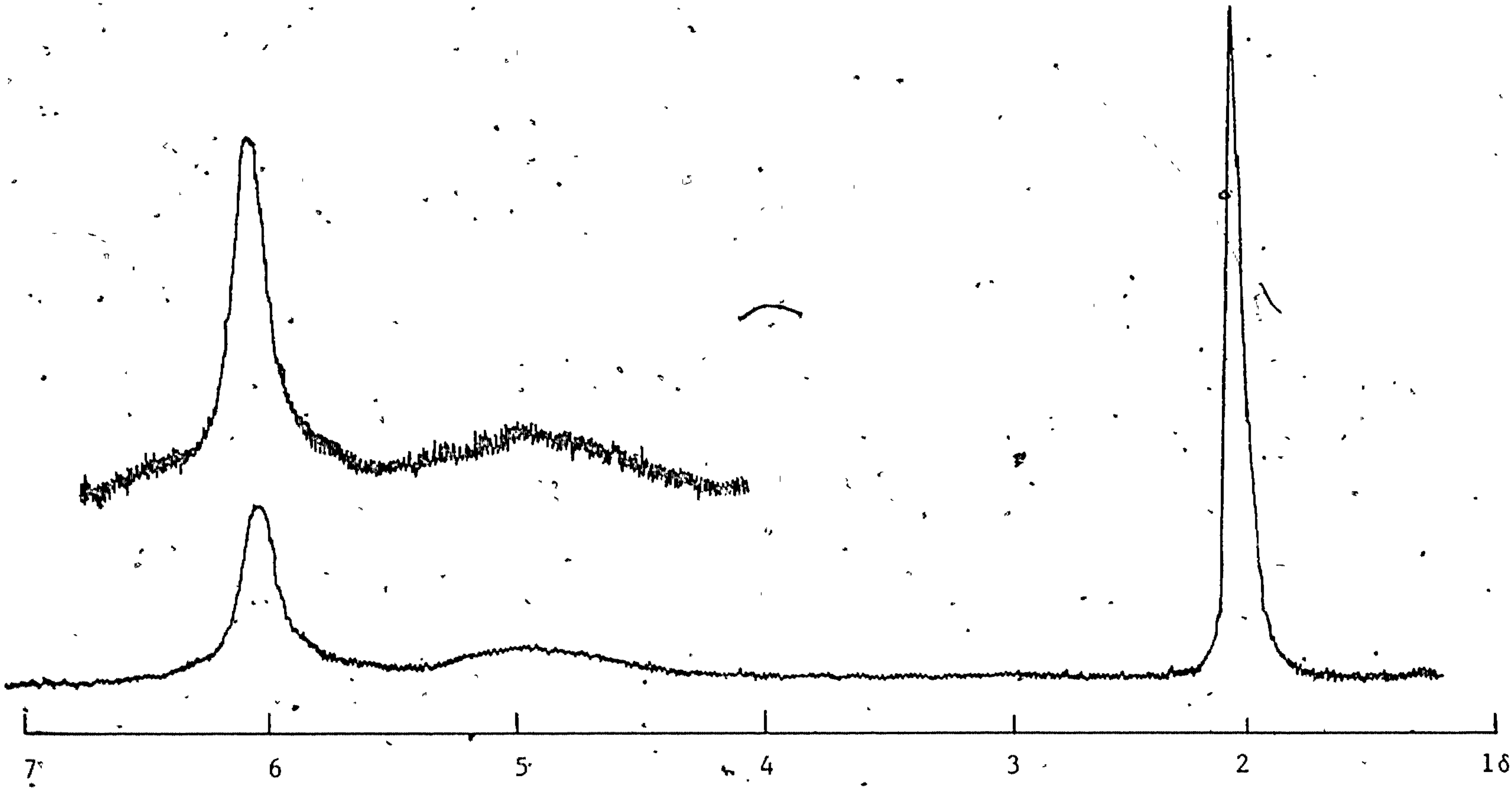


FIGURE 2.5. 90MHz $^1$H NMR spectrum of Ge($\eta^1$-$C_5H_4CH_3$)$_4$ at 27°C.

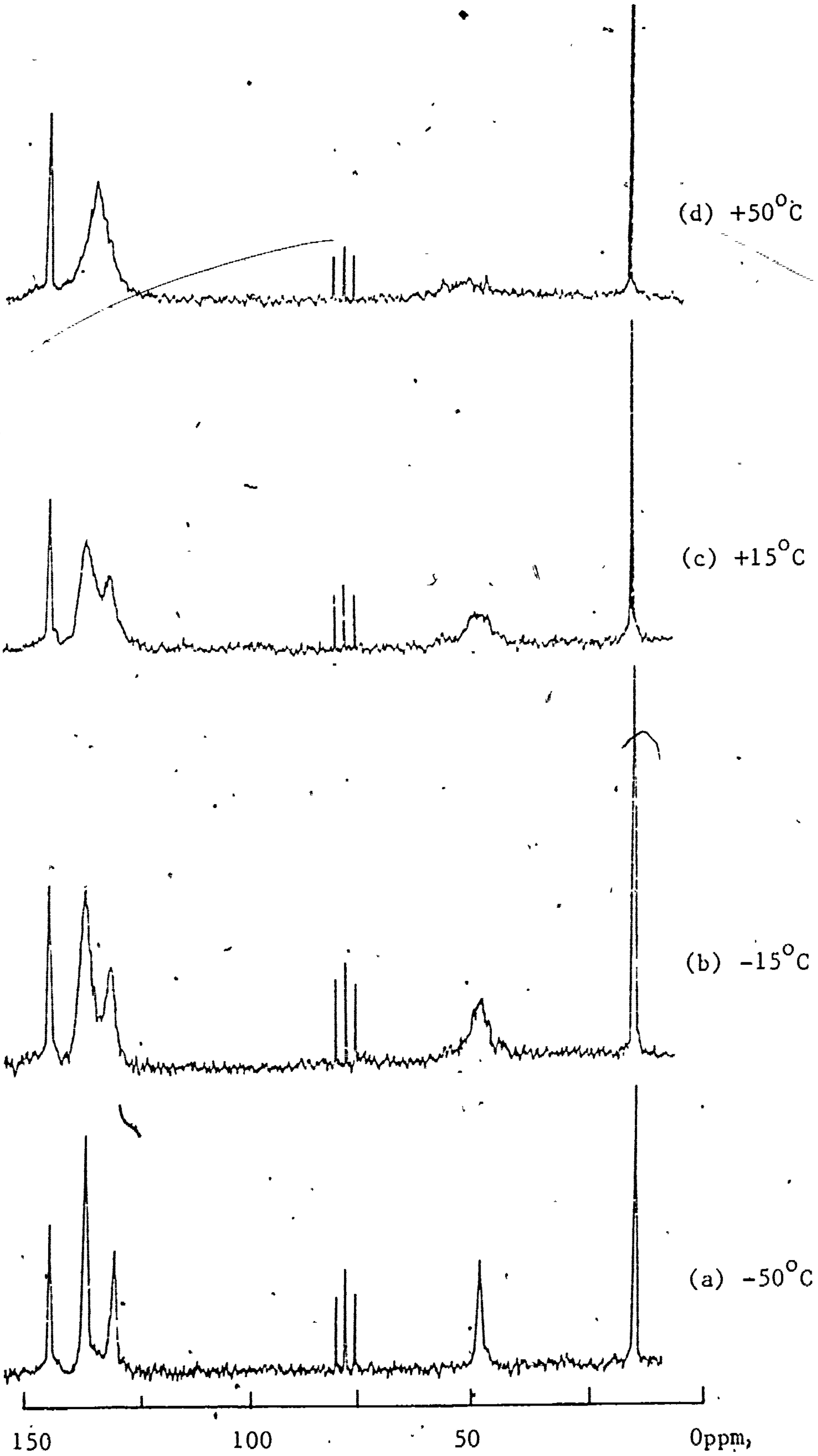
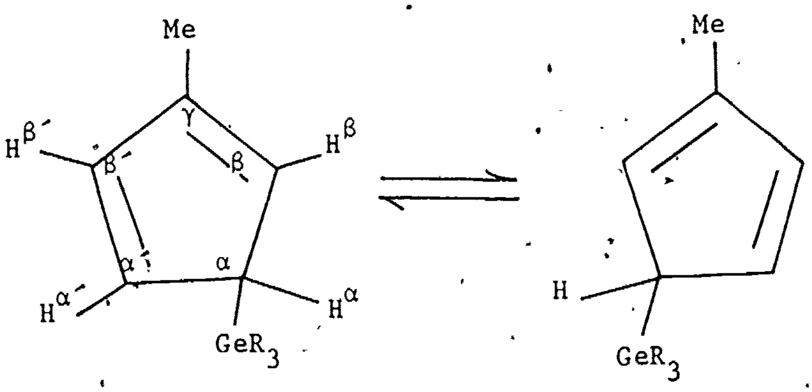


FIGURE 2.6. Variable temperature $^{13}$C NMR spectrum of Ge($\eta^1$-$C_5H_4CH_3$)$_4$.

line width during coalescence of the remaining portions of the spectrum while for $GeMe_3(\eta^1-C_5H_4CH_3)$, signals for $C^\gamma$ and $C^{Me}$ in the -30°C $^{13}C$ NMR spectrum broaden, eventually giving, at more elevated temperatures, a single line for each of $C^\gamma$ and $C^{Me}$.

These results show that while both isomer types A and B are present in significant (observable) concentrations for $GeMe_3(\eta^1-C_5H_4CH_3)$, for $Ge(\eta^1-C_5H_4CH_3)_4$, 2.5, there is only one major isomer present. This indicates that decreasing the size of the metal atom in $M(\eta^1-C_5H_4CH_3)_4$ results in only one ring configuration being detectable, steric constraints having increased the [A] : [B] ratio to a point where [B] can be neglected.

The rearrangement process taking place can then be formulated as the degenerate (*i.e.* fluxional) rearrangement shown in equation (4). This results in averaging of signals in the $^{13}C$ NMR



......(4)

spectrum due to $C^\alpha$, $(\nu_\alpha)$, and $C^{\alpha'}$, $(\nu_{\alpha'})$ and also $C^\beta$, $(\nu_\beta)$ and $C^{\beta'}$, $(\nu_{\beta'})$, while having no effect on resonances due to $C^\gamma$, $(\nu_\gamma)$ and $C^{Me}$. In fact the averaging process between $\nu_\alpha$ and $\nu_{\alpha'}$ (to give $\nu_1$) and $\nu_\beta$ and $\nu_{\beta'}$ (to give $\nu_2$) occurs at very different rates (because of the much larger frequency separation between the first pair), thus while $\nu_2$ is obvious at +40°C, $\nu_1$ is not apparent even at +65°C.

The $^1$H NMR spectrum can be analyzed in an exactly similar way . Thus the differential rate of collapse of resonances for the two pairs of ring protons results from the much larger frequency separation between the $H^1$ and $H^5$ resonances (assigned to lines at δ3.12 and 6.40 respectively in the -50°C spectrum), than for the $H^2$ and $H^4$ resonances (assigned to lines at δ6.25 and 5.90). This clearly identifies the low-field component of the fast-limiting spectrum with $H^{\beta,\beta'}$, a conclusion which has previously been reached [127] for $Sn(\eta^1\text{-}C_5H_4CH_3)_4$, from manipulation of ($^{117,119}$Sn - $^1$H) and ($^1$H - $^1$H) coupling constants.

These results also confirm conclusions reached by Stobart and Holmes-Smith [94] that a decrease in size of M in $MR_3(\eta^1\text{-}C_5H_4CH_3)$ or an increase in the steric requirements of the substituents R, will result in an increase on the relative concentration of isomer A.

The above discussion has treated the rearrangement behaviour of systems, represented by compounds 2.5 and 2.6, in terms of an approximate model ie that of a single ring attached to a metal center. Although this approach fully accounts for the experimental NMR data, it should be noted that if configuration B enters into the equilibrium, it would be present as part of a $GeA_3B$ molecule, and not, as may have been implied, a $GeB_4$

molecule. Also a $Ge\underline{A}_4$ molecule represents a more complex situation than has been assumed, in that the carbon atom $C^{\alpha}$ is asymmetric; thus $Ge\underline{A}_4$ in fact exists as a stereoisomeric mixture, a complication which gives rise to observable effects in several related systems as described in Chapters Three and Four. Possibly the fact that signals in a slow-limit $^{13}C$ NMR spectrum of compound $\underline{2.5}$ at -50°C, assigned to $C^{\alpha}$, $C^{\alpha'}$, $C^{\beta}$ and $C^{\beta'}$, and in the -60°C $^{1}H$ NMR spectrum for $H^{\alpha}$, $H^{\alpha'}$, $H^{\beta}$ and $H^{\beta'}$, are noticeably broad, may be due to unresolved chemical shift differences between resonances due to these nuclei in each of the different isomers.

## C. EXPERIMENTAL

General experimental information is contained in Chapter One.

Potassium-cyclopentadienide and -methylcyclopentadienide were prepared by literature methods.[138] Preparations of tetrakis($\eta^1$-cyclopentadienyl)- and tetrakis(methylcyclopentadienyl)-stannane have been published,[90] however both were prepared by the method described below for the germanium analogue, the properties of the products obtained corresponding exactly to those given in the literature preparations.

### (i) Tetrakis($\eta^1$-cyclopentadienyl)germane.

Germanium tetrachloride (3.56g., 16.5mmol) in benzene (30mL) was added slowly to a vigorously stirred suspension of potassium cyclopentadienide (8.6g, excess) in benzene (50mL), over a period of 0.5h. After stirring for a further 24h, the mixture was filtered and the filtrate concentrated *in vacuo*, leaving a yellow solid which was crystallized from diethyl ether (50mL) affording pure Ge($\eta^1$-$C_5H_5$)$_4$ (4.72g, 14.2mmol, 86%).

### (ii) Chlorotris($\eta^1$-cyclopentadienyl)germane.

A solution of germanium tetrachloride (3.56g, 16.5mmol) in benzene (20mL) was added slowly to a stirring slurry of potassium cyclopentadienide (5.21g, 49.5mmol) in benzene (100mL). The reaction mixture was stirred for 24h, the mixture filtered and the filtrate concentrated *in vacuo* to give a light yellow solid which was crystallized from diethyl ether (50mL) to give pure $Ge(\eta^1-C_5H_5)_3Cl$ (3.6g, 15.0mmol, 91%).

(iii) Tetrakis($\eta^1$-methylcyclopentadienyl)germane.

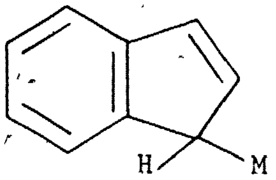
Germanium tetrachloride (5.40g, 2[illegible]0mmol) in benzene (50mL) was added slowly to a vigorously stirred suspension of potassium cyclopentadienide (12g, excess) in benzene (100mL) during 1h. The reaction mixture was stirred for 48h at room-temperature, giving a yellow gelatinous mixture. Hexane (25mL) was added and the mixture stirred for 0.5h, and then filtered, the filtrate being concentrated *in vacuo* leaving a viscous yellow oil. This was then dissolved in dry hexane, and the mixture filtered and pumped to remove the solvent. Repetition of this procedure followed by prolonged pumping (48h, $10^{-2}$mmHg) finally yielded $Ge(\eta^1-C_5H_4CH_3)_4$ as a viscous, air-sensitive, amber oil (7.2g, 18.5mmol, 74%).

# CHAPTER THREE

## METALLOTROPISM AND STEREOMUTATION IN POLY(INDENYL) DERIVATIVES OF GERMANIUM AND TIN.

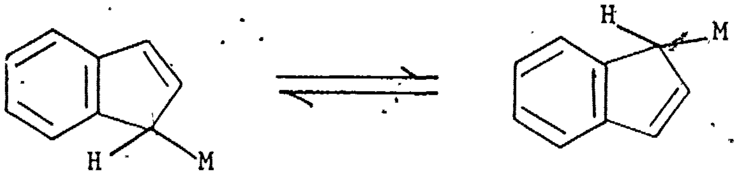
### A. INTRODUCTION.

The nature of the facile non-degenerate rearrangement occurring in metallocyclopentadienes is now believed to be well understood.[79] Examination of the non-rigid properties of related ring systems has resulted in the identification of rearrangement processes which have similar characteristics to those observed for the cyclopentadienyl derivatives.[24] In this context, the metallotropic properties of 1-metallo-indene-ring systems (1), were among the first to be studied in detail.[102,103]



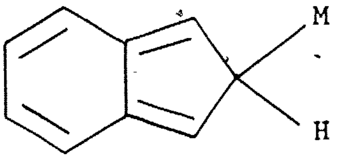
1

Davison and Rakita have shown[103,104] that the $^1$H NMR data obtained for $MMe_3(\eta^1\text{-}C_9H_7)$, M = Si, Ge, and Sn, are consistent with facile, 1,3 migration of the $MMe_3$ moiety across the indenyl ring (equation (1)). Cotton and Marks reached a similar conclusion[102]



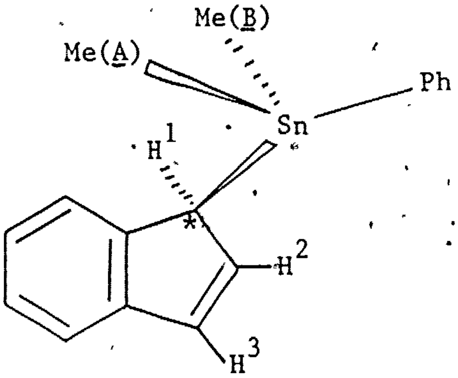
.......(1)

for $Hg(\eta^1-C_9H_7)_2$, based on a complete analysis of the variable temperature $^1$H NMR spectrum. These shifts have a substantially higher activation energy than related rearrangements observed for the cyclopentadienyl analogues[24] (*ca.* 30-40kJmol$^{-1}$ higher). Based on this observation and a variety of other experimental evidence[105,106,107] the *iso*-indene 2 has been proposed as an intermediate in the rearrangement process.



2

Analysis of the $^1$H DNMR spectrum of $SnMe_2Ph(\eta^1-C_9H_7)$, 3, has provided[103] some evidence for the effect of the rearrangement on the stereochemistry at the migrating center in such systems.



3

In 3 the two methyl groups (A) and (B) are magnetically inequivalent (diastereotopic) as a result of attachment of the $Me_2PhSn$ moiety to the chiral C$^*$ carbon atom of the indenyl ring. Migration of the $Me_2PhSn$ group from C$^1$ to C$^3$ was observed to be accompanied by averaging of resonances due to methyls (A) and (B). This indicates that the overall rearrangement process takes place with retention of configuration at the tin center, provided only suprafacial shifts are considered.

This chapter investigates the effects of degenerate and non-degenerate rearrangements in mono- and poly-indenyl derivatives of germanium and tin. The results of the solid state structure determination by X-ray crystallography of $Sn(\eta^1-C_9H_7)_4$, carried out by Professor J.L. Atwood and R.D. Rogers at the University of Alabama, are also discussed.

## B. RESULTS AND DISCUSSION.

Reactions of indenyllithium with germanium tetrachloride or suitably substituted tin(IV) halides, provide a convenient route to the compounds tetra(1-indenyl)germane (3.1),[139] triphenyl(1-indenyl)stannane (3.2),[140] diphenyldi(1-indenyl)stannane (3.3),[140] phenyltri(1-indenyl)stannane (3.4), n-butyltri(1-indenyl)-stannane (3.5), and tetra(1-indenyl)stannane (3.6);[141] all are white, crystalline materials which are air- and water-stable, compound 3.6 reportedly[141] being unchanged after refluxing in concentrated aqueous hydrochloric acid. Physical and analytical data for compounds 3.1 - 3.6 are given in Table 3.1.

### B.1. Mass Spectral Data.

The mass spectral data for compounds 3.1 - 3.6 are tabulated in Table 3.2. Molecular ions were observed for only two compounds, 3.2 and 3.6, both being of low abundance. The most abundant

## TABLE 3.1.

Physical and analytical data for compounds 3.1 - 3.6.

| Compound | %yield | M.Pt.(°C) | Analysis |  |  |  |
|---|---|---|---|---|---|---|
|  |  |  | Actual |  | Theoretical |  |
|  |  |  | %C | %H | %C | %H |
| $Ge(\eta^1-C_9H_7)_4$ 3.1 | 84 | 196-198 | 80.89 | 5.14 | 81.11 | 5.29 |
| $SnPh_3(\eta^1-C_9H_7)$ 3.2 | 95 | 129-130 | 69.78 | 4.87 | 69.71 | 4.77 |
| $SnPh_2(\eta^1-C_9H_7)_2$ 3.3 | 89 | 116-117 | 72.13 | 4.87 | 71.60 | 4.81 |
| $SnPh(\eta^1-C_9H_7)_3$ 3.4 | 51 | 153-154 | 73.91 | 4.98 | 73.23 | 4.84 |
| $Sn(Bu^n)(\eta^1-C_9H_7)_3$ 3.5 | 62 | 58 | 71.06 | 5.79 | 71.43 | 5.80 |
| $Sn(\eta^1-C_9H_7)_4$ 3.6 | 87 | 215 | 74.43 | 5.06 | 74.64 | 4.87 |

TABLE 3.2.

Mass spectral data[a,b], obtained for compounds <u>3.1</u> - <u>3.6</u>.

| Ion Family | $Ge(\eta^1-C_9H_7)_4$<br><u>3.1</u> | $SnPh_3(\eta^1C_9H_7)$<br><u>3.2</u> | $SnPh_2(\eta^1-C_9H_7)_2$<br><u>3.3</u> | $SnPh(\eta^1-C_9H_7)_3$<br><u>3.4</u> | $Sn(Bu^n)(\eta^1-C_9H_7)_3$<br><u>3.5</u> | $Sn(\eta^1-C_9H_7)_4$<br><u>3.6</u> |
|---|---|---|---|---|---|---|
| parent ion | n.o.[c] | 1.9 | n.o. | n.o. | n.o. | 0.1 |
| $M(\eta^1-C_9H_7)_3^+$ | 5.0 | | | n.o. | 0.5 | 0.6 |
| $MR(\eta^1-C_9H_7)_2^+$ | | | n.o. | 5.0 | 10.7 | |
| $MR_2(\eta^1-C_9H_7)^+$ | | 1.0 | 79.7 | | | |
| $MR_3^+$ | | 35.1 | | | | |
| $M(\eta^1-C_9H_7)_2^{+\cdot}$ | 1.4 | | 2.2 | 1.9 | 0.7 | 0.6 |
| $MR(\eta^1-C_9H_7)^{+\cdot}$ | | 0.4 | 1.1 | 3.0 | n.o. | |
| $MR_2^{+\cdot}$ | | | 0.6 | 2.9 | | |
| $M(\eta^1-C_9H_7)^+$ | 90.4 | 3.2 | 2.2 | 65.2 | 88.1 | 83.2 |
| $MR^+$ | | 28.9 | 14.2 | 22.0 | n.o. | |
| $M^{+\cdot}$ | 3.6 | 29.5 | n.o. | n.o. | n.o. | 15.5 |

---

[a] 70eV ionizing voltage.

[b] %metal containing ions summed within each family resulting from isotope distribution or hydrogen loss.

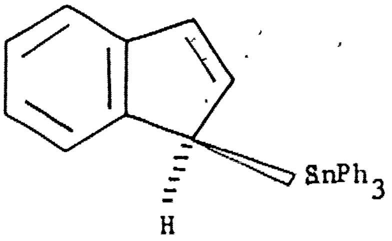
[c] Not observed.

ion in the mass spectra of compounds 3.1, 3.4, 3.5, and 3.6 is $M(C_9H_7)^+$, while for compounds 3.2 and 3.3, the major series of peaks correspond to the loss of one indenyl ring, *i.e.* $SnPh_3^+$ and $SnPh_2(C_9H_7)^+$ respectively. For the phenyl derivatives, 3.2, 3.3 and 3.4, the second most abundant ion corresponds to $SnPh^+$; however no obvious correlation between structure and relative intensity is apparent. Significantly, no carbon-carbon bond cleavage of the indenyl ring was observed, consistent with results obtained by Davison and Rakita[103] for the indenyls, $MMe_3(\eta^1-C_9H_7)$, M = Si, Ge, and Sn. Thus the main pathway for decomposition of $\eta^1$-indenyls is by breaking of the metal-carbon linkage, exactly paralleling the situation observed[128] for the cyclopentadienyl analogues.

### B.2. $^{13}C$ NMR Data.

### B.2.(i). $SnPh_3(\eta^1-C_9H_7)$, (3.2).

The $^{13}C$ NMR spectrum of $SnPh_3(\eta^1-C_9H_7)$, 3.2, at -30°C (Figure 3.1(a)), is consistent with the "rigid" structure 4, having a single resonance at 44.6ppm due to $C^1$, with further signals to higher frequency, the assignments for which are given



4

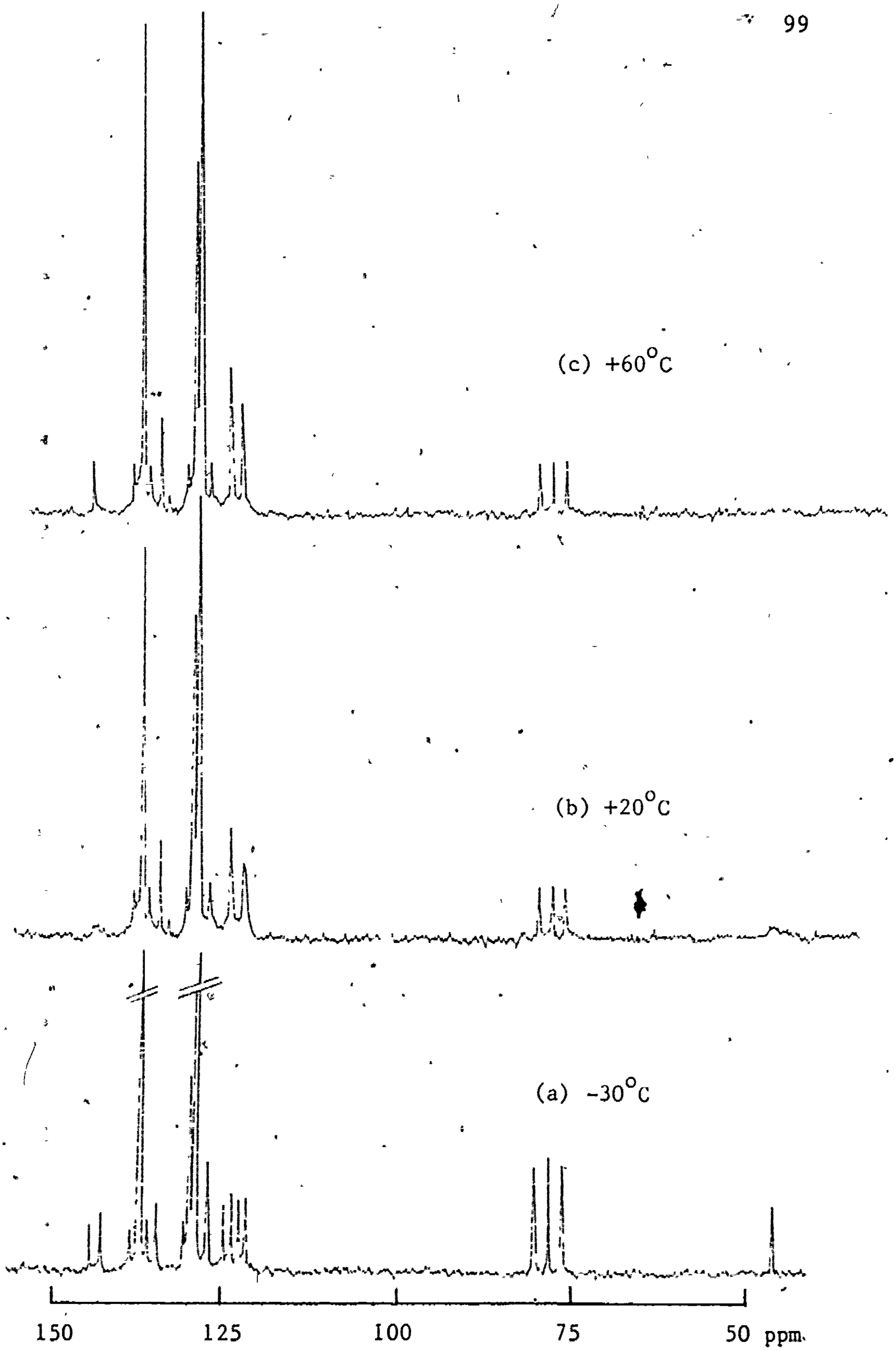
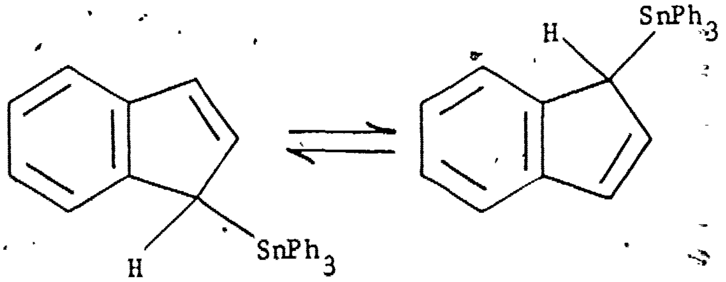


FIGURE 3.1. Variable temperature $^{13}$C NMR spectrum of SnPh$_3$($\eta^1$-C$_9$H$_7$), 3.2.

in Tables 3.3 -3.5. As the temperature is raised to *ca.*0$^{o}$C, signals at 142.8 and 144.3ppm, assigned to C$^{8,9}$, broaden, giving at *ca.*+60$^{o}$C (Figure 3.1(c)), a single resonance at 143.6ppm. Similarly resonances in the -30$^{o}$C spectrum at 121.5, 122.4,123.6 and 124.5ppm, assigned to C$^{4,5,6,7}$ are broad at *ca.*0$^{o}$C, giving at +60$^{o}$C two lines at 122.2 and 124.2ppm. Resonances for C$^{1}$ (44.6ppm) and C$^{3}$(126.9ppm) in the -30$^{o}$C spectrum have completely collapsed at *ca.*0$^{o}$C, however no absorption at the average of these two resonance positions is observed at +60$^{o}$C (Figure 3.1(c)). By contrast, the C$^{2}$ resonance (at 134.4ppm) shows no variation in chemical shift or line width throughout the temperature range studied. Similarly resonances due to the phenyl groups, at 137.0 (C$^{2,6}$), 129.5 (C$^{4}$) and 128.7ppm (C$^{3,5}$) (a resonance attributable to C$^{1}$ was not observed), are temperature independant.

These observations are consistent with a facile 1,3 migration of the metal substituent across the indenyl ring,$^{103}$ as shown in equation (2). Thus the pairs of resonances in the -30$^{o}$C



........(2)

spectrum, assigned to each of the pairs of carbon atoms, C$^{4,7}$, C$^{5,6}$ or C$^{8,9}$, average to give single resonances at *ca.*+60$^{o}$C. Resonances for C$^{1}$ and C$^{3}$ are averaged much more slowly because of the larger frequency separation between them, and hence a

TABLE. 3.3.

$^{13}$C NMR[a] resonances assigned to $C^1$, $C^2$, and $C^3$ of the indenyl rings in compounds 3.1 - 3.6.

| Compound | $C^1$ | $C^2$ | $C^3$ |
|---|---|---|---|
| $Ge(\eta^1-C_9H_7)_4$, 3.1 | 42.5, 43.2, 44.5, 44.7 | 134.8 | 130.0, 129.4, 129.1 |
| $SnPh_3(\eta^1-C_9H_7)$, 3.2 | 44.6 | 134.4 | 126.9 |
| $SnPh_2(\eta^1-C_9H_7)_2$, 3.3 | 43.8 | 134.0 | 127.0 |
| $SnPh(\eta^1-C_9H_7)_3$, 3.4 | 43.5, 44.6, 45.1 | 133.4, 133.7, 134.0 | 127.3 |
| $Sn(Bu^n)(\eta^1-C_9H_7)_3$, 3.5 | 44.0, 44.6, 44.9, 45.5 | 134.2, 133.8, 133.4 | 126.7, 126.2 |
| $Sn(\eta^1-C_9H_7)_4$, 3.6 | 44.2, 44.6, 45.7 | 133.2 | 127.5, 127.1 |

---

[a] $CDCl_3$ was used as solvent and internal reference; chemical shift values in ppm downfield from tetramethylsilane.

TABLE 3.4.

$^{13}$C NMR[a] resonances assigned to $C^{4,5,6,7}$ and $C^{8,9}$ of the indenyl rings in compounds 3.1 - 3.6.

| Compound | $C^{4,5,6,7}$ |  | $C^{8,9}$ |  |
|---|---|---|---|---|
|  | Slow limit | Fast limit | Slow limit | Fast limit |
| $Ge(\eta^1-C_9H_7)_4$, 3.1 | 121.9, 123.7, 123.9, 124.4, 126.0 | n.o.[b] | 144.8, 144.6, 144.2 | n.o.[b] |
| $SnPh_3(\eta^1-C_9H_7)$, 3.2 | 121.5, 122.4, 123.6, 124.5 | 122.2, 124.2 | 144.3, 142.8 | 143.6 |
| $SnPh_2(\eta^1-C_9H_7)_2$, 3.3 | 121.3, 122.3, 123.5, 124.5 | 122.1, 124.2 | 144.0, 142.5 | 143.7 |
| $SnPh(\eta^1-C_9H_7)_3$, 3.4 | 121.7, 122.5, 123.9, 124.9 | 122.0, 124.3 | 143.9, 143.6, 142.7 | 143.0 |
| $Sn(Bu^n)(\eta^1-C_9H_7)_3$, 3.5 | 121.7, 122.1, 123.8, 124.6 | 122.1, 124.3 | 144.3, 143.9 142.4 | 143.7 |
| $Sn(\eta^1-C_9H_7)_4$, 3.6 | 121.9, 122.6, 124.0, 125.2. | 122.4, 124.7 | 143.7, 143.4, 143.1 | 143.8 |

---

[a] $CDCl_3$ was used as solvent and internal reference; chemical shift values in ppm downfield from tetramethylsilane.

[b] Not observed.

TABLE 3.5.

$^{13}$C NMR[a] resonances for the phenyl groups of $SnPh_{4-n}(\eta^1-C_9H_7)_n$, n = 0, 1, 2, 3; and the n-butyl group of $Sn(Bu^n)(\eta^1-C_9H_7)_3$.

| Compound | $C^1$ | $C^{2,6}$ [b] | $C^{3,5}$ | $C^4$ |
|---|---|---|---|---|
| $SnPh_4$ | 138.0 | 137.3 | 129.1 | 128.6 |
| $SnPh_3(\eta^1-C_9H_7)$ | n.o.[c] | 137.0 | 128.7 | 129.5 |
| $SnPh_2(\eta^1-C_9H_7)_2$ | n.o.[c] | 136.4 | 128.3 | 129.3 |
| $SnPh(\eta^1-C_9H_7)_3$ | n.o.[c] | 136.2 | 128.2 | 129.4 |
| $Sn(Bu^n)(\eta^1-C_9H_7)_3$ | | 12.3, 13.5, 27.1, 28.1 | | |

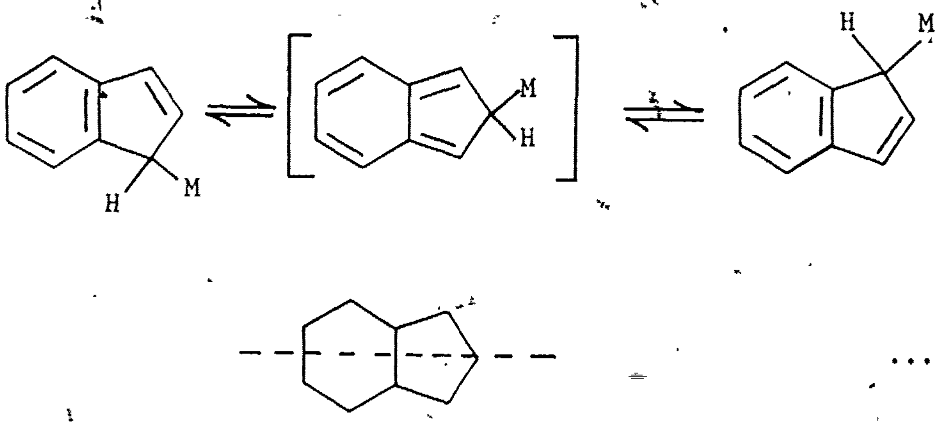
---

[a] $CDCl_3$ was used as solvent and internal reference; chemical shift values in ppm downfield from tetramethylsilane.

[b] Assignment of $C^{2,6}$ and $C^{3,5}$, see reference 142.

[c] Not observed.

coalesced signal is not observed in the +60°C spectrum. The magnetic environment of $C^2$ is not affected by the rearrangement process as indicated by equation(3); consequently the $C^2$ resonance is temperature independent.



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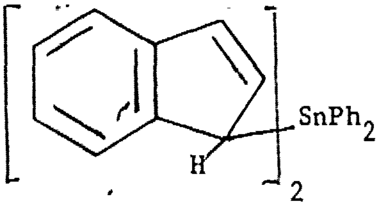
### B.2.(ii). $SnPh_2(\eta^1-C_9H_7)_2$ (3.3).

The -40°C $^{13}C$ NMR spectrum of compound 3.3 (Figure 3.2(a)), is consistent with the "static" structure shown in 5. As the temperature is raised many of the signals begin to broaden, with resonances at 43.8 and 127.0ppm, assigned to $C^1$ and $C^3$ respectively, doing so most rapidly. Signals at 142.5 and 144.0ppm, assigned to $C^{8,9}$ also broaden, giving at *ca.* +40°C, a single resonance at 143.7ppm. Similarly resonances at 121.3, 122.3, 123.5 and 124.5ppm assigned to $C^{4,5,6,7}$ coalesce to two lines centered



5

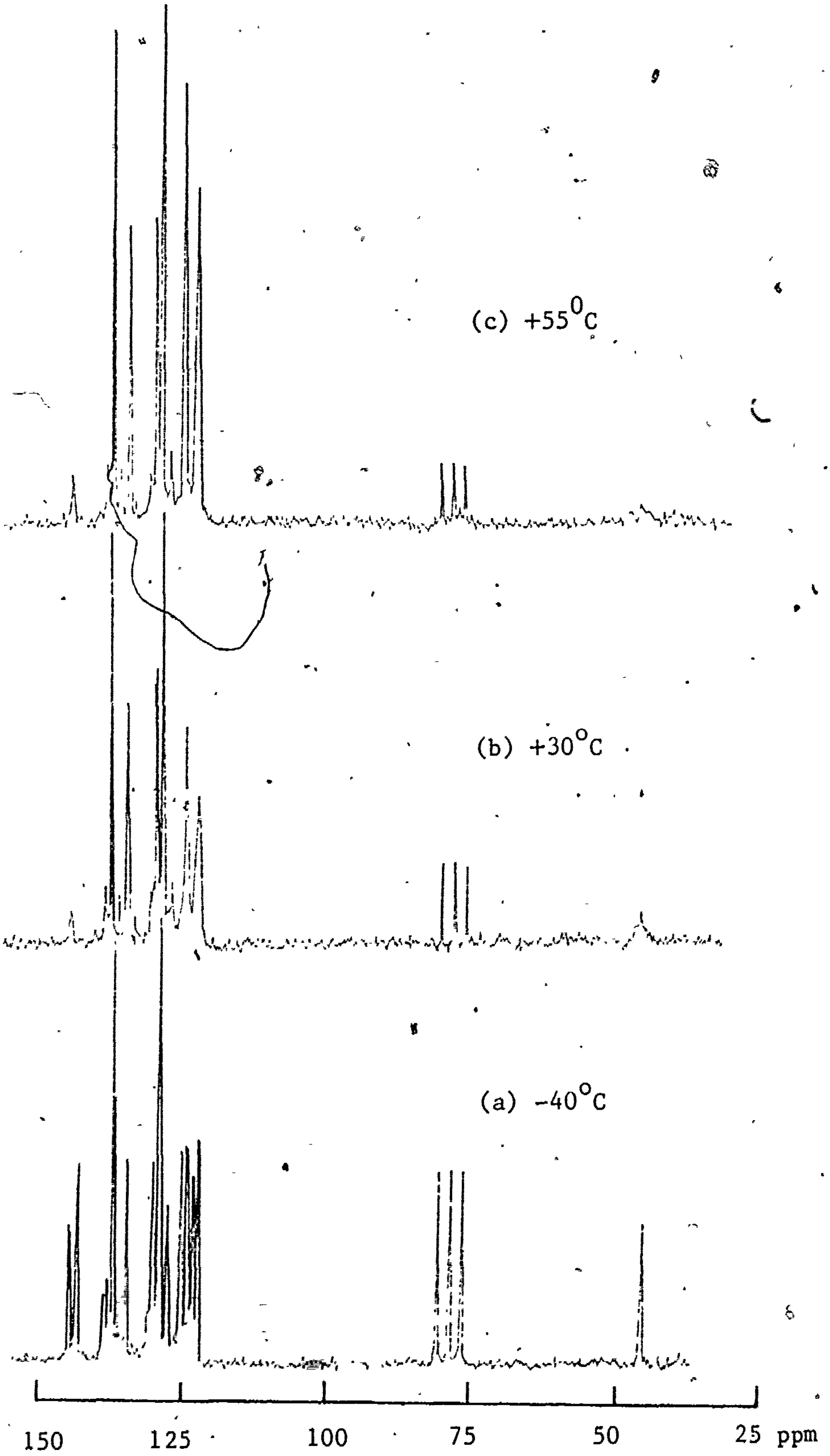
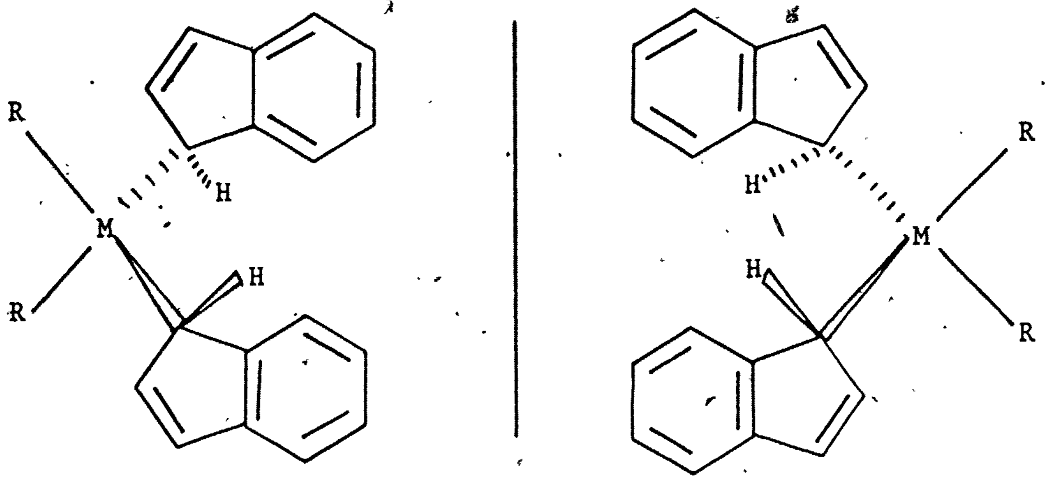


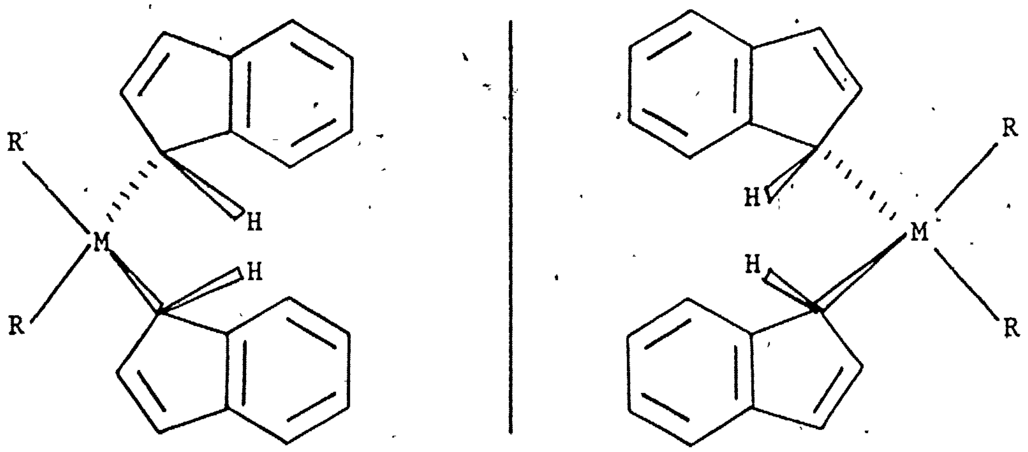
FIGURE 3.2. Variable temperature $^{13}C$ NMR spectrum of $SnPh_2(\eta^1-C_9H_7)_2$, 3.3.

at 121.1 and 124.2ppm at *ca.*+40°C. The signal at 134.0ppm, assigned to $C^2$, is temperature invariant, as are resonances at 128.3, 129.3, and 136.4ppm, assigned to $C^{3,5}$, $C^4$, $C^{2,6}$ respectively of the phenyl groups (no signal due to $C^1$ was observed).

Thus the variable temperature $^{13}C$ NMR spectrum of compound 3.3 is similar in many respects to that obtained for compound 3.2, and is consistent with a facile 1,3 migration of the tin moiety across each of the indenyl rings. Significantly, the indenyl carbon atom to which the metal is bound, $C^1$, is a chiral center, so that compound 3.3 exists as both enantiomorphic represented as (++,--) or (RR,SS) 6, and *meso*(R,S), 7 forms, (Figure 3.3). While the two enantiomers which constitute the pair 6 will have identical NMR properties, the *meso* form, 7, is a different compound (diastereoisomer), and will have different physical and chemical properties (*e.g.* NMR spectrum) from the enantiomeric pair 6. The slow-limit (-40°C) $^{13}C$ NMR spectrum of 3.3 might be expected to consist of a superimposition of the spectra of two similar, though distinct compounds (*i.e.* diastereoisomers). That this does not appear to be observed indicates that either the $^{13}C$ NMR spectra of pair 6 and isomer 7 are insufficiently diastereotopically shifted to be resolved, or that one isomer is overwhelmingly preferred with *ca.* 100% equilibrium concentration. A corresponding absence of diastereotopic effects in the $^1H$ NMR spectrum of the di-indenyl $Hg(\eta^1\text{-}C_9H_7)_2$ has been reported[102] by Cotton *et al.*



(++), (--) pair, 6: point group $C_2$



(+-) isomer, 7 (*meso*-): point group $C_s$

FIGURE 3.3. The possible isomers present in $MR_2(\eta^1\text{-}C_9H_7)_2$.

### B.2.(iii). $SnPh(\eta^1-C_9H_7)_3$ (3.4) and $SnBu^n(\eta^1-C_9H_7)_3$ (3.5).

The slow-limit $^{13}C$ NMR spectra of $SnPh(\eta^1-C_9H_7)_3$, 3.4, at -25°C, and $SnBu^n(\eta^1-C_9H_7)_3$, 3.5, at -60°C (Figure 3.4(a)), are complex; however a complete assignment for each is possible on the basis of temperature-dependent behaviour,(Tables 3.3 - 3.5). Raising the temperature above *ca.*0°C in either case results in averaging of resonances for $C^4$ and $C^7$, $C^5$ and $C^6$, and $C^8$ and $C^9$, such that single lines are observed for each of these pairs of nuclei at *ca.*+60°C. Resonances due to $C^1$ and $C^3$ also broaden on raising the temperature to *ca.*0°C, such that at +40°C these signals have completely collapsed; a coalesced peak is not observable at +60°C. Resonances for the phenyl group in compound 3.4 are temperature invariant, while in the spectrum of the butyl compound, 3.5, one of the four signals for the butyl group (at 12.3ppm) is broad at -60°C, and only becomes sharp above *ca.*0°C.

The complex, slow-limit spectra for both these compounds result from the existence for each of two diastereotopic pairs, 8 and 9, of enantiomorphs (Figure 3.5), In terms of stereochemical characteristics, these compounds are analogous to the isomers of tris-1-(2-methylnaphthyl)borane(Figure 3.6), which have been subjected to complete conformational analysis by Mislow *et al.*[143]

In pair 8 represented by (+++,---) or (RRR,SSS ) all asymmetric $C^1$ centers have the same relative configuration and are homotopic. The molecules in pair 9 (++-,--+) which contain one $C^1$ having the opposite configuration to that of the other two, belong to

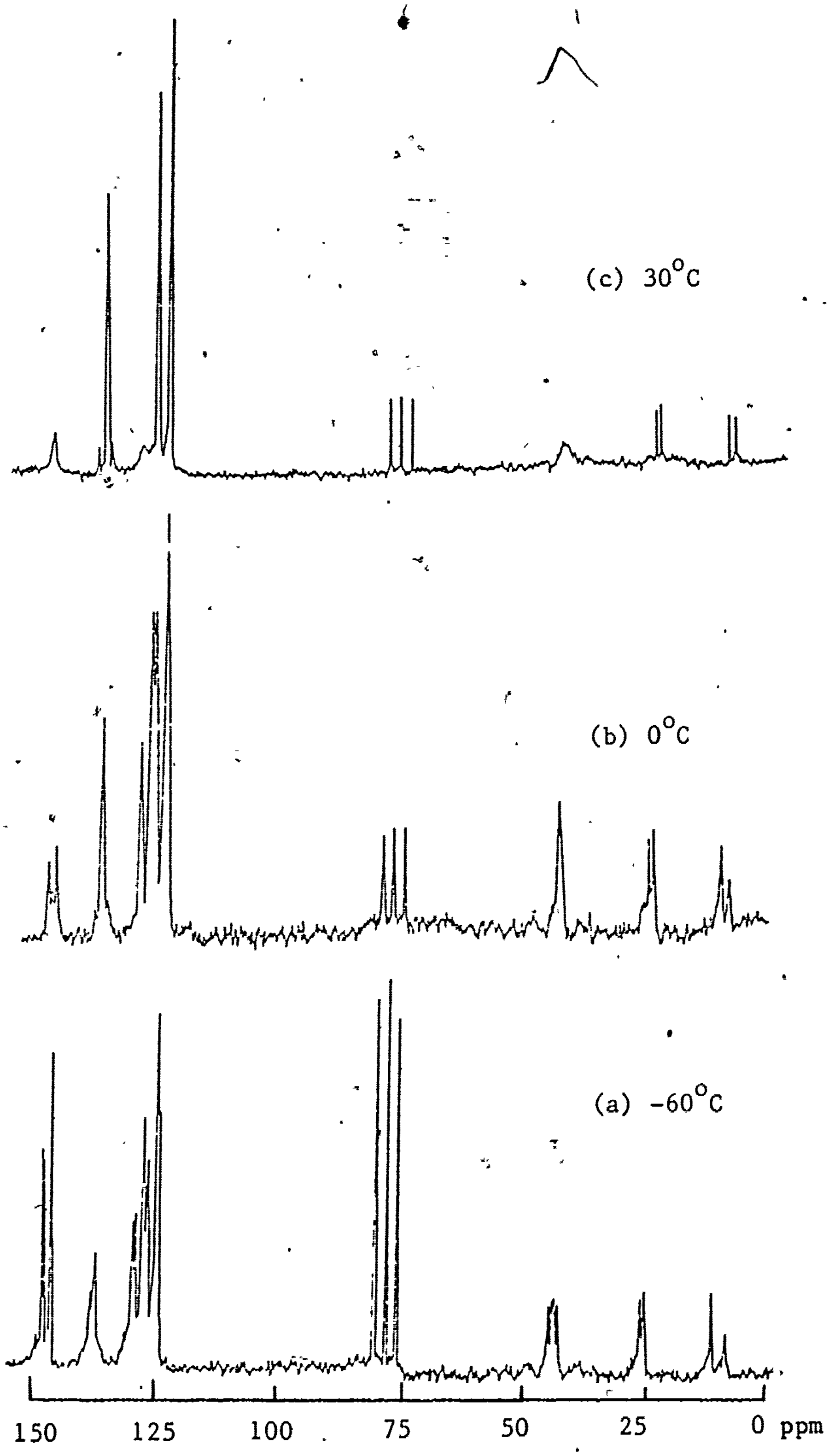
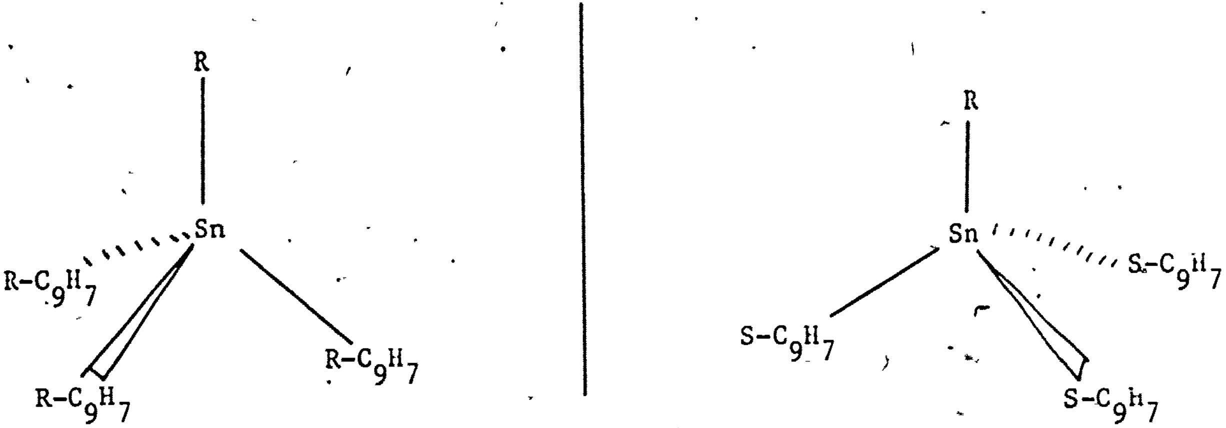
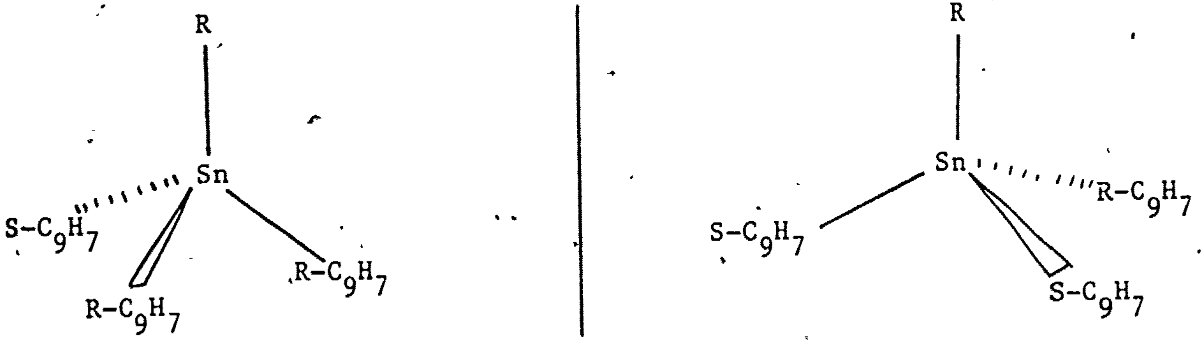


FIGURE 3.4. Variable temperature $^{13}C$ NMR spectrum of $Sn(Bu^{\underline{n}})(\eta^1-C_9H_7)_3$, 3.5.



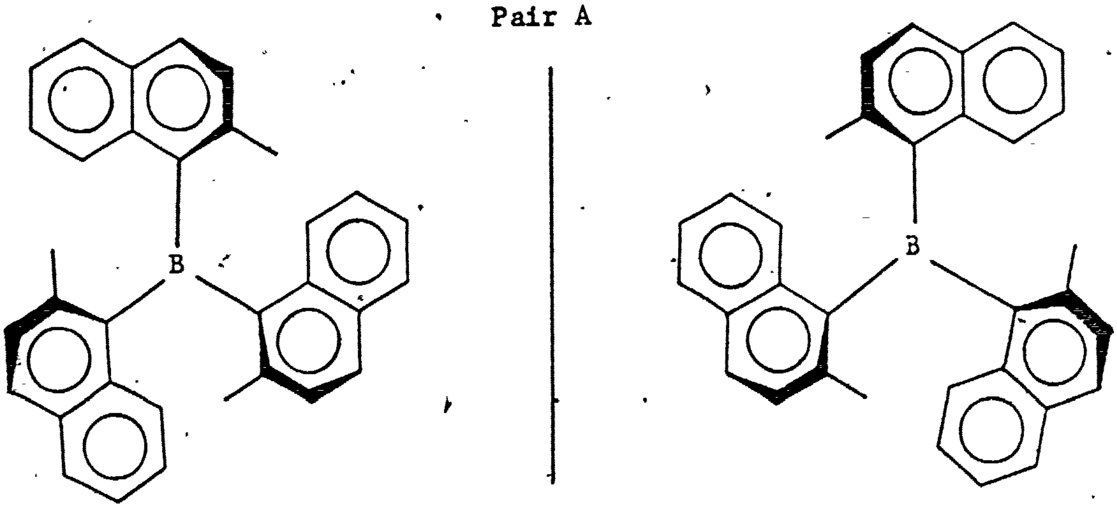
(+++),(---) pair, <u>8</u>; point group $C_1$



(++-), (+--) pair, <u>9</u>; point group $C_1$

FIGURE 3.5. The possible isomers present in $MR(\eta^1-C_9H_7)_3$, R = $Bu^{\underline{n}}$, Ph.

Pair A



Pair B

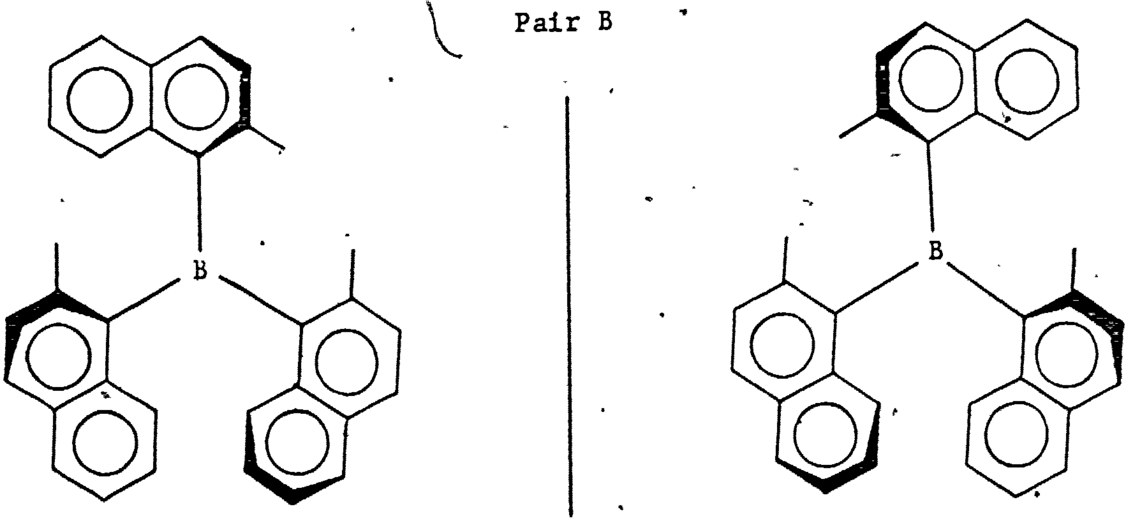


FIGURE 3.6. The possible isomers present in tris-1-(2-methylnaphthyl)borane.

the point group $C_1$ so that all three $C^1$ nuclei are magnetically inequivalent. Thus, in principle 8 and 9 together account for four anisochronous $C^1$ nuclei and in fact each appears to give rise to a separate resonance in the observed $^{13}C$ NMR spectrum of 3.5 at -60°C. The slow-limit spectrum of compound 3.4 at -25°C is also consistent with this interpretation if coincidence of two out of the four $C^1$ resonances is assumed. The near-equality in signal heights for the four components in the spectrum of compound 3.5, indicates that the equilibrium [8]:[9] ratio is approximately 1:3, *ie.* the statistical distribution, implying near-zero free energy difference in solution between the diastereoisomers. Diastereotopic splitting of resonances attributable to $C^2$, $C^3$, and $C^8$ in compounds 3.4 and 3.5 (by comparison with data for compound 3.2 and $SnMe_3(\eta^1-C_9H_7)$),[144] and to the n-butyl carbon bound to tin in 3.5, is also apparent in the slow-limit spectra.

On raising the temperature, collapse of these anisochronous effects accompanies coalescence behaviour characteristic of the non-degenerate rearrangement of compound 3.2, identifying the latter as the mechanism for interconversion between all the possible stereoisomers.

### B.2.(iv). $Sn(\eta^1-C_9H_7)_4$ (3.6) and $Ge(\eta^1-C_9H_7)_4$ (3.1).

An assignment of the complex slow-limit spectra obtained for $Sn(\eta^1-C_9H_7)_4$, 3.6, at -35°C (Figure 3.7(a)) and $Ge(\eta^1-C_9H_7)_4$, 3.1, at 25°C, is given in Tables 3.3 and 3.4. Raising the temperature

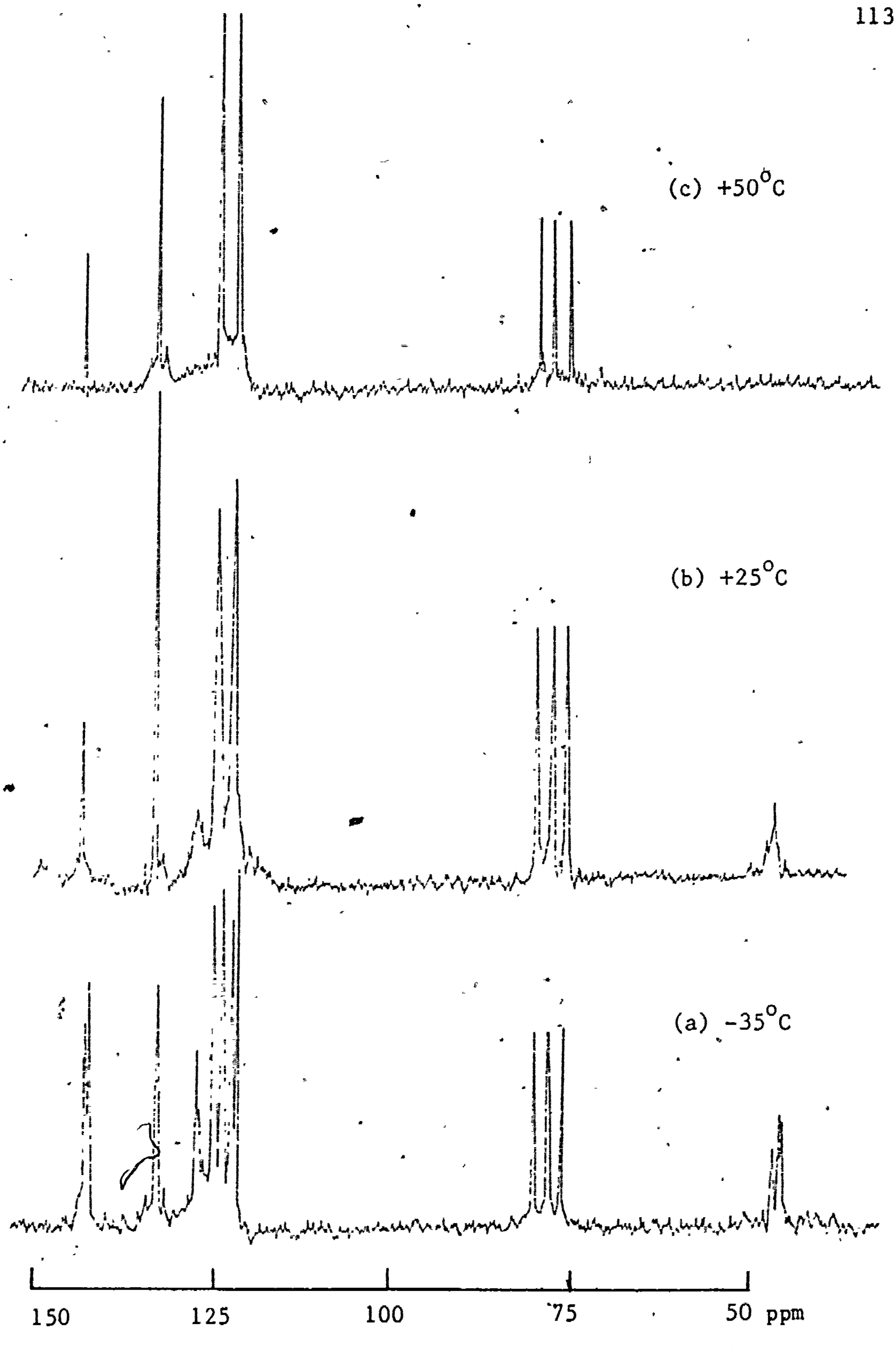
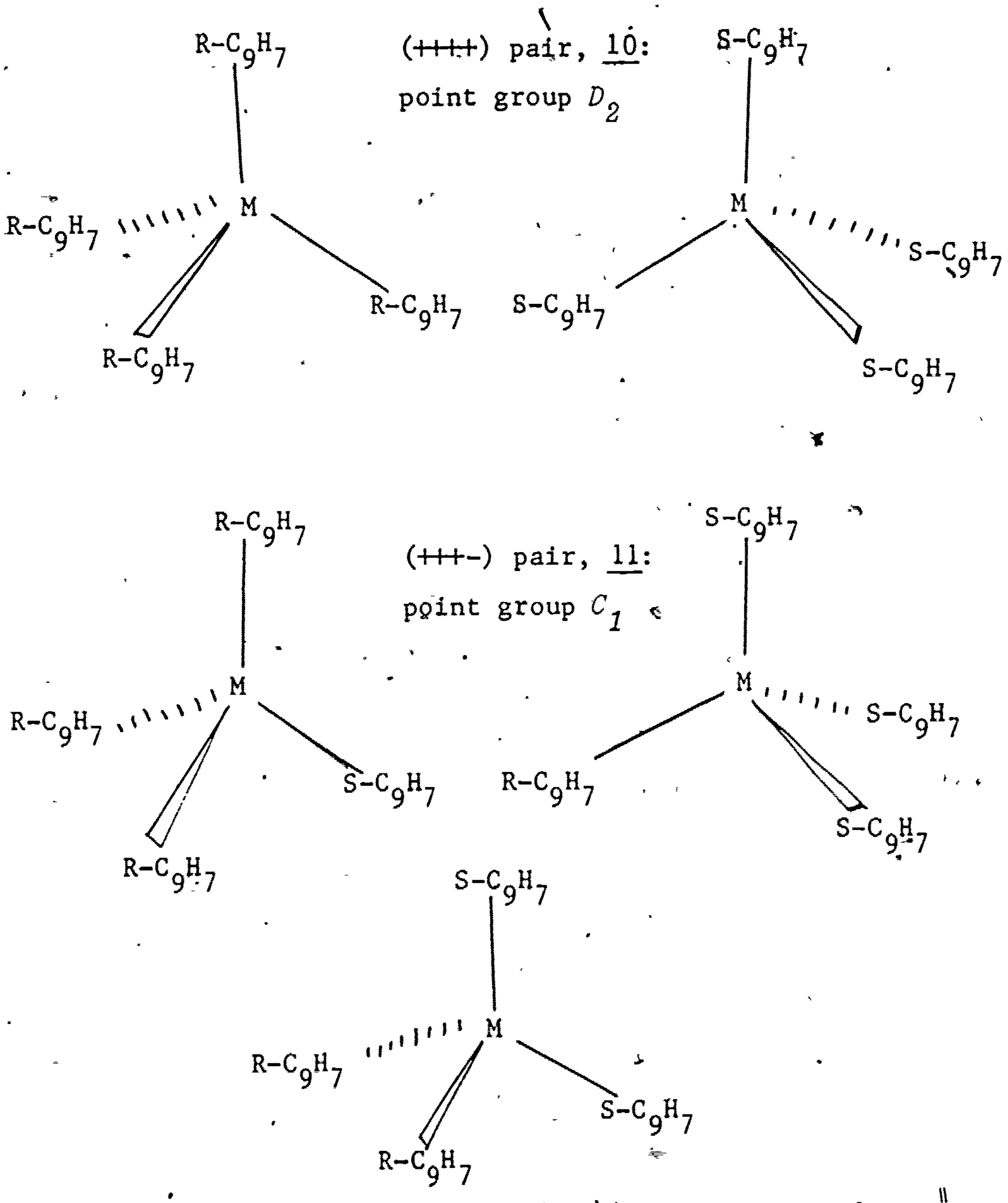


FIGURE 3.7. Variable temperature $^{13}$C NMR spectrum of $Sn(\eta^1-C_9H_7)_4$, 3.6.

for the tin compound 3.6 causes averaging between resonances for $C^{4,7}$ (and $C^{5,6}$ $C^{8,9}$ and $C^{1,3}$) while the $C^2$resonance at 133.2ppm is unchanged. Collapse of anisochronous effects present in the slow-limit spectrum occurs with the concomitant coalescent behaviour, in a way which parallels exactly that observed for the other tin indenyls studied (Sections B.2.(i)-(iii)). No corresponding changes in the appearance of the spectrum of the germane 3.1 was observed even at +90°C, a result consistent with the much higher activation energies for rearrangement of both indenyl- and cyclopentadienyl-germanium compounds compared with their tin analogues.

The complex slow-limit spectra of both these compounds are the result of each existing as two diastereomeric pairs 10 and 11 of enantiomorphs, along with a third stereoisomer, the *meso*-form 12 (Figure 3.8). In pair 10, which can be represented as (++++,----) or (RRRR,SSSS), in every molecule all four asymmetric $C^1$ centers have the same relative configuration and are homotopic. Pair 11, represented by (+++-,-+++) or (RRRS,SSSR), consists of molecules in which one $C^1$ has the opposite configuration from the other three and belongs to the point group $C_1$, however the unique $C^1$ center lies on a $C_3$ axis assuming free rotation about the Sn-$C^1$ bond and will contain only two distinct (diastereotopic) types of $C^1$ nuclei having a 3:1 distribution. The *meso*-isomer, 12 (++--) or (RRSS) belongs to the point group $S_4$ and contains four magnetically equivalent indenyl rings (homotopic $C^1$ nuclei).



(++++) pair, 10: point group $D_2$

(+++-) pair, 11: point group $C_1$

(++--) isomer 12 (*meso*): point group $S_4$

FIGURE 3.8. The possible isomers present in $M(\eta^1\text{-}C_9H_7)_4$, M = Ge, Sn.

Compounds 3.1 and 3.6, as equilibrium diastereoisomeric mixtures, will incorporate four anisochronous $C^1$ nuclei. (see Table 3.6). In a situation where there is no free energy difference between the ground states of these isomers, their equilibrium concentrations will be [10] : [11] : [12] = 1:4:3 : since isomer 11 has two anisochronous $C^1$ nuclei in a 3:1 ratio, resonant signals due to $C^1$ carbon nuclei in the $^{13}C$ NMR spectrum will therefore ideally appear as four lines of relative intensity 1:1:3:3. This is clearly the case for compound 3.1 (Figure 3.9), and is closely approximated to for 3.6 (Figure 3.7). It can thereby be concluded that the ground-state free energies of the three possible isomers are close to one another.

Resonances attributable to $C^1$ carbon nuclei in the slow-limit $^{13}C$ NMR spectra of compounds 3.1 - 3.6 are shown in Figure 3.9. The predicted number of such resonances for each possible isomer is given in Table 3.6 together with relative populations for each of the isomers assuming zero ground state free energy differences. The slow-limit spectra obtained for all the indenyl compounds investigated allow for the conclusion that the difference in ground state energy for the isomers of each of the polyindenyls studied is small.

### B.3. $^1H$ NMR Data.

The $^1H$ DNMR spectra of compounds 3.2 - 3.6 (Table 3.7, see also Figures 3.10, 3.11), are similar in many respects to those

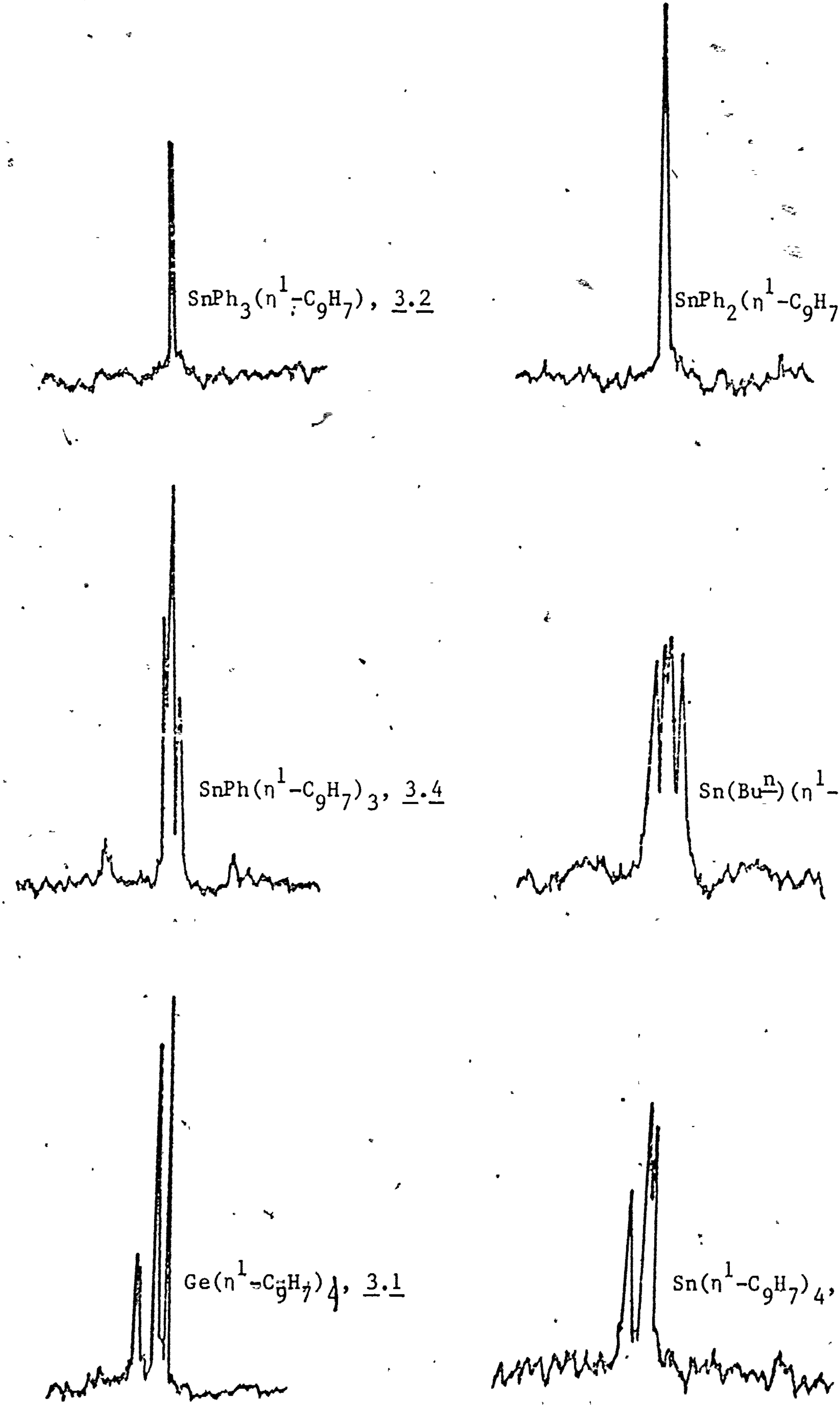
TABLE 3.6.

Stereoisomerism in polyindenyl derivatives.

| Compound | Isomer[a] | S[b] | Point Group | Mag.[c] | N[d] |
|---|---|---|---|---|---|
| $Ph_2Sn(ind)_2$ | (++)[e] | 1 | $C_2$ | H | 2 |
| | (+-)[f] | 1 | $C_s$ | H | 2 |
| $n\text{-}BuSn(ind)_3$ | (+++) | 1 | $C_1$ | H | 3 |
| | (++-) | 3 | $C_1$ | D | (1,1,1) |
| $Ge(ind)_4$ | (++++) | 1 | $D_2$ | H | 4 |
| | (+++-) | 4 | $C_1$ | D | (3,1)[g] |
| | (++--)[f,h] | 3 | $S_4$ | H | 4 |

---

[a] Each possible isomer for a given type is symbolized in terms of relative configuration + or - at an indenyl $C^1$ carbon center. [b] S represents the statistical distribution of the stereoisomers as listed in the preceding column. [c] Relationship between chemically equivalent nuclei in terms of magnetic properties H = homotopic, D = Diastereotopic. [d] N is the number of chemically equivalent nuclei per molecule sharing an identical magnetic environment *ie* which can be interchanged by some symmetry operation. [e] Racemic form. [f] *Meso*-isomer. [g] Reduces from(1,1,1,1) see text. [h] This notation (rather then(+-+-)) implies that the first two descriptions are related by an $S_4^2$ ($\equiv C_2$) rotation.



$SnPh_3(\eta^1-C_9H_7)$, 3.2

$SnPh_2(\eta^1-C_9H_7)_2$, 3.3

$SnPh(\eta^1-C_9H_7)_3$, 3.4

$Sn(Bu^n)(\eta^1-C_9H_7)_3$, 3.5

$Ge(\eta^1-C_9H_7)_4$, 3.1

$Sn(\eta^1-C_9H_7)_4$, 3.6

FIGURE 3.9. Comparison of $^{13}$C NMR signals attributable to indenyl-C$^1$ nuclei in compounds 3.1 -3.6.

TABLE 3.7.

$^1$H NMR data$^a$ for compounds 3.1 - 3.6.

| Compound | T °C | $H^{1\,b}$ | $H^{2\,d}$ |  | $H^{3\,d}$ | $H^{4,5,6,7}$ | R |
|---|---|---|---|---|---|---|---|
|  |  |  | Slow-limit | Fast-limit |  |  |  |
| $Ge(\eta^1-C_9H_7)_4$ | +25 | 3.71(3), 3.48(1) | 5.04–5.22,<br>5.83–5.93 | n.o.$^m$ | 6.58–6.92 | 6.98–7.62 |  |
| $SnPh_3(\eta^1-C_9H_7)$ | -60 | 4.62, $(102.6)^c$ | 6.89–7.09 | $6.93^g$ $(3.5)^h$ | $7.12–7.80^{f,e}$ | $7.12–7.80^f$ | $7.12–7.80^f$ |
| $SnPh_2(\eta^1-C_9H_7)_2$ | -50 | 4.29, $(101.7)^c$ | 6.38–6.48 | $6.58^i$ $(3.5)^h$ | $6.67–6.95^e$ | $6.92–7.65^f$ | $6.92–7.65^f$ |
| $SnPh(\eta^1-C_9H_7)_3$ | -50 | 3.89(1), 4.08(2)<br>4.16(1) | 6.04–6.36 | $6.57^j$ $(3.6)^h$ | $6.43–7.05^e$ | $6.82–7.80^f$ | $6.82–7.80^f$ |
| $Sn(Bu^n)(\eta^1-C_9H_7)_3$ | -60 | 3.51(1), 3.62(1),<br>3.72(1), 3.97(1) | 5.78–6.32 | $6.16^k$ $(3.4)^h$ | 6.52–6.91 | 6.91–7.90 | 0.31–1.35 |
| $Sn(\eta^1-C_9H_7)_4$ | -60 | 3.46(3), 3.61(3),<br>3.71(1), 3.78(1) | 4.81–5.11<br>5.58–5.97 | $5.79^l$ $(3.7)^h$ | 6.69–6.93 | 7.03–7.71 |  |

---

[a] $CDCl_3$ was used as solvent, TMS as internal reference, chemical shift values given in ppm downfield from TMS. [b] Values in brackets represent relative intensities. [c] $^2J(^{117,119}Sn-^1H)$ in Hz. [d] Multiplets, J values not determined. [e] Centered below phenyl resonances. [f] Resonances assigned to $H^{4,5,6,7}$ and phenyl protons overlap and were not resolved. [g] At +60°C. [h] $^3J(^{117,119}Sn-^1H)$. [i] +60°C. [j] +55°C. [k] +60°C. [l] +60°C. [m] Not observed.

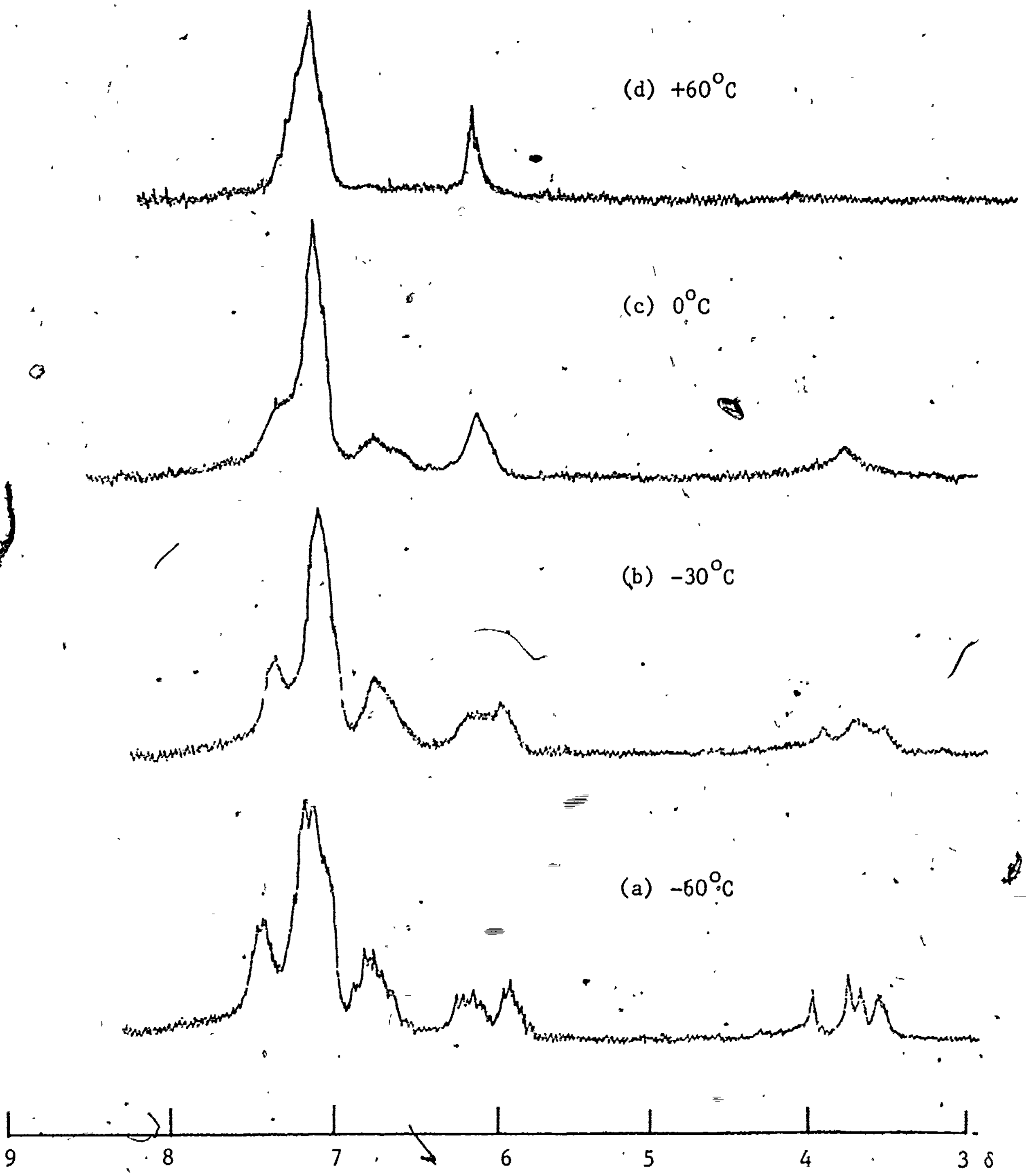


FIGURE 3.10. Variable temperature 90MHz $^1$H NMR spectrum of $Sn(Bu^{\underline{n}})(\eta^1-C_9H_7)_3$ in $CDCl_3$.

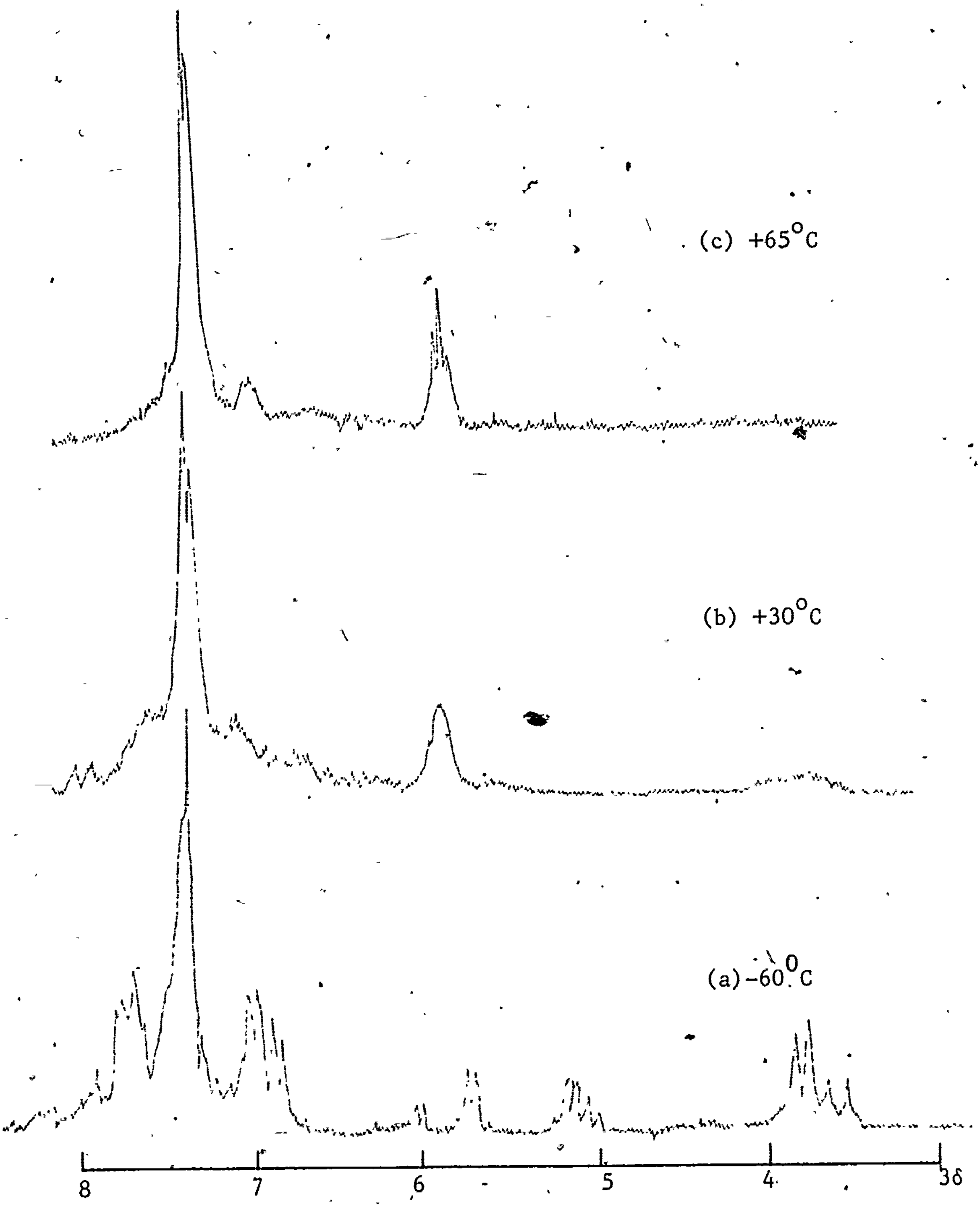


FIGURE 3.11. Variable temperature 90MHz $^{1}$H NMR spectrum of $Sn(\eta^{1}-C_9H_7)_4$ in $CDCl_3$.

reported for $SnMe_3(\eta^1\text{-}C_9H_7)$[103] and $Hg(\eta^1\text{-}C_9H_7)_2$[102]. Thus absorptions due to $H^1$ and $H^3$ in the slow-limit $^1H$ NMR spectrum (at *ca.*-30°C) broaden on increasing the temperature to *ca.*0°C, eventually giving, at temperatures above *ca.*120°C, a broad peak midway between the slow-limit $H^1$ and $H^3$ resonances. Resonances assigned to $H^2$ become broad at *ca.* 0°C, giving a well defined triplet above *ca.* 30°C, the coupling constants of which are given in Table 3.7. Resonances due to $H^{4,5,6,7}$ show some degree of broadening and spectral change throughout the temperature range studied (*ca.*-60 to +120°C).

The above data are consistent with an overall 1,3 migration of the metal across the indenyl ring, resulting in averaging of the resonances due to $H^1$ and $H^3$. Further $H^2$, which is strongly coupled to $H^3$,($^3J(H^2\text{-}H^3)$ = *ca.*7Hz), and only weakly coupled to $H^1$,($^3J(H^2\text{-}H^1)$ = *ca.* 0Hz),becomes broadened due to averaging between the two coupling constants $^3J(H^2\text{-}H^3)$ and $^3J(H^2\text{-}H^1)$, eventually becoming a triplet having

$$J_{av} = \frac{^3J(H^2\text{-}H^3) + {}^3J(H^2\text{-}H^1)}{2}$$

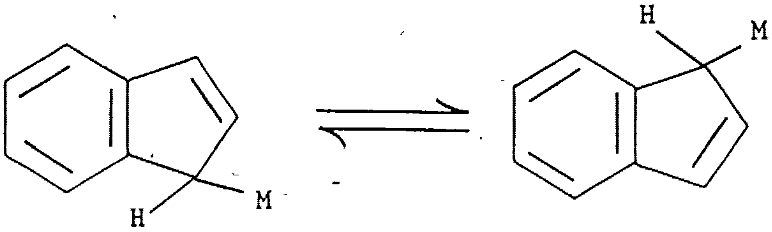
The $^1H$ NMR spectrum of compound <u>3.1</u> is slow-limiting, even at +100°C, further confirming that activation energies for rearrangement in indenylgermanes are significantly higher than those for tin analogues.

The slow-limit $^1H$ NMR spectra of compounds <u>3.1</u> and <u>3.4</u> - <u>3.6</u> are complex, not unexpectedly in the light of the foregoing discussion of the $^{13}$C NMR data. For all four compounds the absorptions due to $H^2$ and $H^3$ appear as overlapping multiplets, an analysis of which was not attempted. Since the $H^1$ nucleus for any particular indenyl ring is expected to give rise to a single although broadened absorption (through unresolved coupling to $H^2$ and to $H^3$), analysis of the appropriate spectral range (between δ3.0 and 4.0) should be possible.

In fact four distinct $H^1$ resonances of approximately equal intensity are observed for the butyl compound 3.5 (Figure 3.10), while three, in an *ca.* 1:2:1 ratio, are discernible for compound 3.4. The overall similarity of this portion of the spectrum to patterns encountered for $C^1$ nuclei in the slow-limit $^{13}$C NMR spectra of these compounds is striking. This again indicates the presence of four magnetically inequivalent indenyl rings in approximately equal ratio, and confirms that the relative concentrations of isomers 6 and 7 in both 3.4 and 3.5, are close to those calculated statistically.

While the region between δ3.0 and 3.5 is broad for the germane 3.1, four distinct absorptions are present for the tin compound 3.6 (Figure 3.11(a)) in an approximately 1:1:3:3 ratio, indicating the presence of four different $H^1$ sites and confirming the presence of the three possible isomers 8, 9 and 10 in close to statistical concentrations. Thus results derived from $^1$H NMR data are entirely consistent with conclusions reached on the basis of $^{13}$C NMR data.

Overall, these results establish that non-degenerate rearrangements occurring in mono-indenyl derivatives (equation (1)) are paralleled by the metallotropic shifts in poly-indenyl derivatives; and that in these latter this process also results in interconversion between all possible stereoisomers in each case, *i.e.* provides a facile mechanism for stereomutation.



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## G. THE CRYSTAL AND MOLECULAR STRUCTURE OF R,R,S,S-TETRA(1-INDENYL)STANNANE.

The X-ray crystal and molecular structure of R,R,S,S-Sn($\eta^1$-$C_9H_7$)$_4$, (<u>3.6</u>), was determined by Prof. J.L. Atwood and R.D. Rogers at the University of Alabama, using a sample provided by the author. The molecular structure is shown in Figure 3.12; pertinent bond lengths and angles are given in Tables 3.8 and 3.9 respectively. The geometry about the tin center is approximately tetrahedral, although there is some variation among the four (Sn-C) bond distances [2.202(8), 2.169(11), 2.182(10) and 2.202(9)Å]. These bond distances (mean 2.19 Å) are significantly shorter than the tin-carbon bond lengths determined[137] for Sn($\eta^1$-$C_5H_5$)$_4$, mean (Sn-C) = 2,27 Å. Related bond distances within each of the four indenyl rings are similar, being close to those expected for a

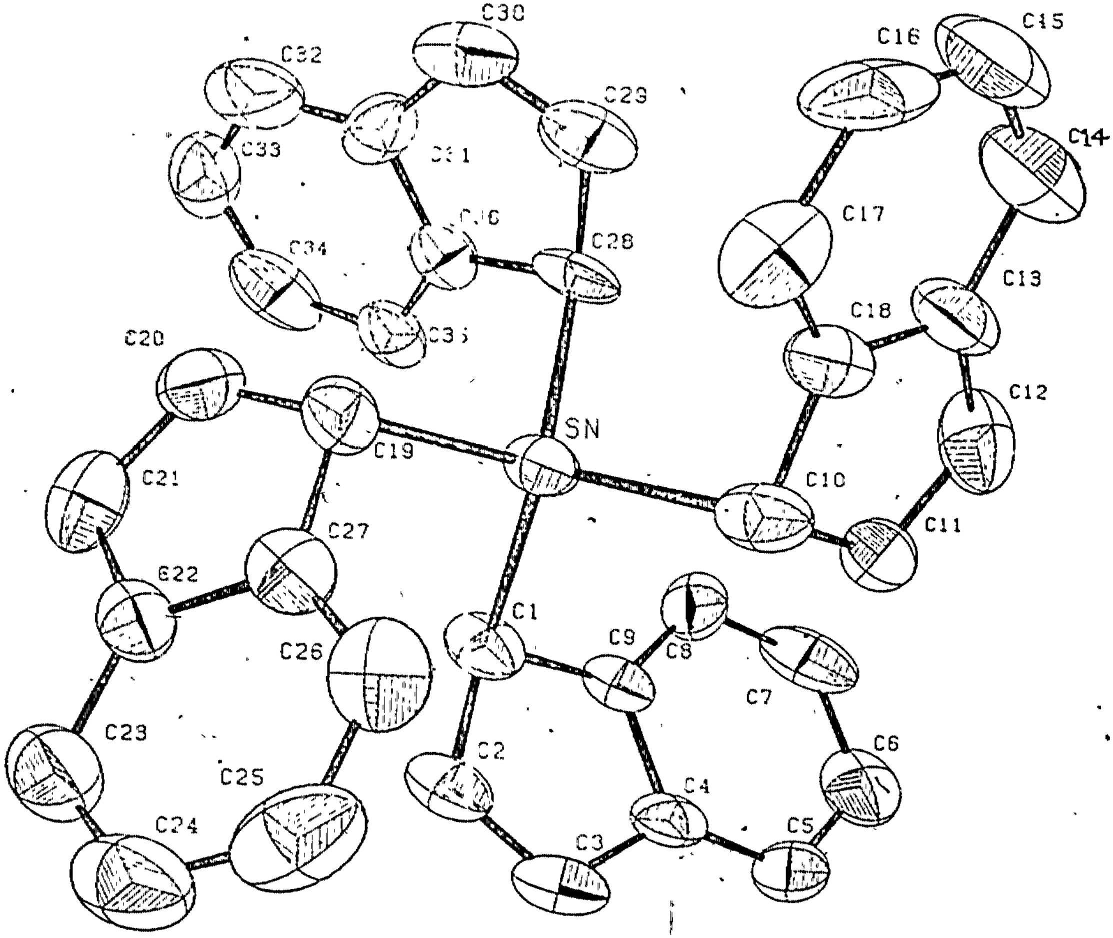


FIGURE 3.12. The molecular structure for R,R,S,S-tetra(1-indenyl)tin(IV).

TABLE 3.8.

Bond distances determined for R,R,S,S-tetra(1-indenyl)tin

(a)Tin-carbon bond distances.

| bond | length Å |
|---|---|
| Sn-C(1) | 2.202(8) |
| Sn-C(10) | 2.169(11) |
| Sn-C(19) | 2,182(10) |
| Sn-C(28) | 2.202(9) |

(b)Carbon-carbon bond distances.

| bond | length Å | bond | length Å | bond | length Å | bond | length Å |
|---|---|---|---|---|---|---|---|
| C(1)-C(2) | 1.51 | C(10)-C(11) | 1.47 | C(19)-C(20) | 1.45 | C(28)-C(29) | 1.51 |
| C(2)-C(3) | 1.34 | C(11)-C(12) | 1.33 | C(20)-C(21) | 1.36 | C(29)-C(30) | 1.33 |
| C(3)-C(4) | 1.46 | C(12)-C(13) | 1.44 | C(21)-C(22) | 1.43 | C(30)-C(31) | 1.33 |
| C(4)-C(5) | 1.36 | C(13)-C(14) | 1.36 | C(22)-C(23) | 1.40 | C(31)-C(32) | 1.40 |
| C(5)-C(6) | 1.39 | C(14)-C(15) | 1.36 | C(23)-C(24) | 1.37 | C(32)-C(33) | 1.37 |
| C(6)-C(7) | 1.40 | C(15)-C(16) | 1.37 | C(24)-C(25) | 1.39 | C(33)-C(34) | 1.40 |
| C(7)-C(8) | 1.35 | C(16)-C(17) | 1.42 | C(25)-C(26) | 1.39 | C(34)-C(35) | 1.39 |
| C(8)-C(9) | 1.40 | C(17)-C(18) | 1.38 | C(26)-C(27) | 1.40 | C(35)-C(36) | 1.37 |
| C(9)-C(1) | 1.48 | C(18)-C(10) | 1.51 | C(27)-C(19) | 1.51 | C(36)-C(28) | 1.48 |
| C(4)-C(9) | 1.41 | C(13)-C(18) | 1.41 | C(22)-C(27) | 1.39 | C(31)-C(36) | 1.40 |

## TABLE 3.9.

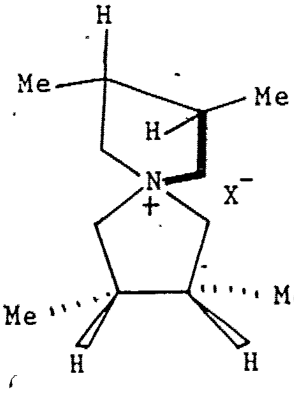
Bond angles determined for R,R,S,S-tetra(1-indenyl)tin.

| Bonds | Angle(deg) | Bonds | Angle(deg) |
|---|---|---|---|
| C(9)-C(1)-C(2) | 102 | C(18)-C(10)-C(11) | 104 |
| C(9)-C(2)-C(3) | 110 | C(10)-C(11)-C(12) | 110 |
| C(2)-C(3)-C(4) | 111 | C(11)-C(12)-C(13) | 110 |
| C(3)-C(4)-C(9) | 106 | C(12)-C(13)-C(18) | 108 |
| C(4)-C(9)-C(1) | 111 | C(13)-C(18)-C(10) | 107 |
| C(9)-C(4)-C(5) | 121 | C(18)-C(13)-C(14) | 121 |
| C(4)-C(5)-C(6) | 119 | C(13)-C(14)-C(15) | 118 |
| C(5)-C(6)-C(7) | 119 | C(14)-C(15)-C(16) | 123 |
| C(6)-C(7)-C(8) | 123 | C(15)-C(16)-C(17) | 121 |
| C(7)-C(8)-C(9) | 119 | C(16)-C(17)-C(18) | 116 |
| C(8)-C(9)-C(4) | 119 | C(17)-C(18)-C(13) | 121 |
| C(27)-C(19)-C(20) | 103 | C(36)-C(28)-C(29) | 104 |
| C(19)-C(20)-C(21) | 111 | C(28)-C(29)-C(30) | 109 |
| C(29)-C(21)-C(22) | 109 | C(29)-C(30)-C(31) | 110 |
| C(21)-C(22)-C(27) | 109 | C(30)-C(31)-C(36) | 110 |
| C(22)-C(27)-C(19) | 107 | C(31)-C(36)-C(28) | 107 |
| C(27)-C(22)-C(23) | 120 | C(36)-C(31)-C(32) | 117 |
| C(22)-C(23)-C(24) | 118 | C(31)-C(32)-C(33) | 123 |
| C(23)-C(24)-C(25) | 122 | C(32)-C(33)-C(34) | 118 |
| C(24)-C(25)-C(26) | 120 | C(33)-C(34)-C(35) | 122 |
| C(25)-C(26)-C(27) | 118 | C(34)-C(35)-C(36) | 118 |
| C(26)-C(27)-C(22) | 121 | C(35)-C(36)-C(31) | 123 |

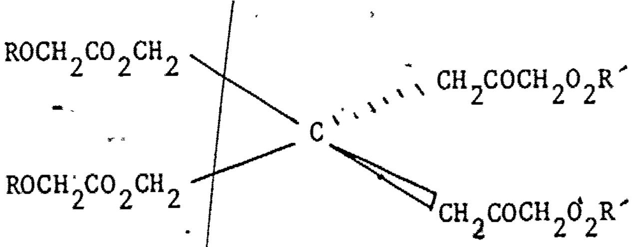
$\eta^1$-indenyl group.[145,146]

For each molecule there are two distinct types of indenyl substituent: two pairs of ring-systems each have opposite relative configurations at the $C^1$ carbon centers. Thus the crystal structure determined for $Sn(\eta^1-C_9H_7)_4$ contains only one of the five possible molecular units depicted in Figure 3.9 (*i.e.* structure <u>12</u>). This is the R,R,S,S -(++--) or *meso*-form, which is optically inactive, and belongs to the point group $S_4$.

Molecules possessing this kind of symmetry have been of interest since they where first discussed [147] in the literature by Mohr in 1903. McCasland and coworkers reported[148,149] the synthesis of the first two examples of such molecules (<u>13</u> and <u>14</u>), and both were indeed shown to have no observable optical rotation.



<u>13</u>



<u>14</u>

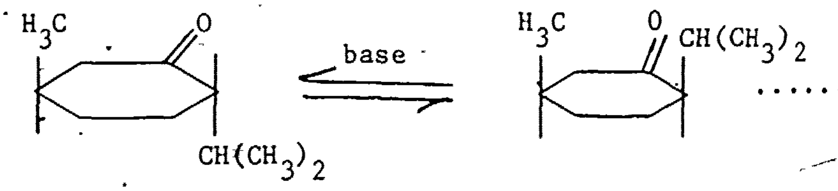
$R$ = (+) menthyl
$R'$ = (-) menthyl

These systems lack either a plane or center of symmetry, but do possess a fourfold alternating (improper) axis of rotation: any molecule containing this symmetry element (whether or not it contains other symmetry elements) is necessarily superimposable on its mirror image and is thus optically inactive.[150]

Although a variety of such molecules have now been prepared, there has been only one report in the literature of a structurally characterized example, the bis(N,N,N′,N′-tetrapropyl-*trans*-1,2-cyclohexylenedioxydiacetamido)manganese(II) cation.[151] The X-ray crystal structure of the bromide salt was published in 1977[151] and was subsequently recognized as a system for which the highest possible symmetry belongs to the point group $S_4$ by Professor Kurt Mislow, who kindly brought the paper to our attention. All other related structures result from conformational distortion of a higher symmetry configuration.[152] The *meso*-isomer, (RRSS)-form (isomer <u>11</u>) of tetra($\eta^1$-indenyl)tin(IV) thus represents only the second (first recognized as such[153]) example of this type of molecule for which X-ray data confirm the structure.

Because of the low barrier to stereomutation, a solution of tetra($\eta^1$-indenyl)tin(IV) represents a complex mixture of different molecules (diastereoisomers) whose relative concentrations are under thermodynamic control, (*i.e.* the concentrations of each of the diastereoisomers is determined by the relative values of their ground state free energies, differences in which have been shown to be negligibly small). Isolation in the crystalline state of only one of the five possible isomers can be interpreted in terms of crystal-lattice energy differences or lower solubility for the *meso*-form. The rapid equilibration between all of the isomers in solution provides a pathway for each of the molecules to convert to and crystallize as the *meso* diastereoisomer.

Interestingly every metallotropic shift of the metal-containing group across an indenyl ring effects inversion of the $C^1$ center of that ring and thus represents an extremely facile example of an epimerization process.[154] This process is also intramolecular while other, more familiar examples of epimerization processes are intermolecular *eg.* the base-catalysed epimerization of menthone and *iso*menthone.[154] (equation (4)).



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(-)-menthone (+)-*iso*menthone

## D. EXPERIMENTAL.

Indenyllithium was prepared by the literature method. Tetra($\eta^1$-indenyl)germane, 3.1,[139] triphenyl($\eta^1$-indenyl)stannane , 3.2,[140] diphenyldi($\eta^1$-indenyl)stannane, 3.3[140] and tetra($\eta^1$-indenyl)stannane, 3.6,[141] have been synthesized previously.

Phenyltri($\eta^1$-indenyl)tin(IV) (3.4).

A solution of $PhSnCl_3$ (2.26g, 7.5mmol) in hexane (20mL) was added dropwise over *ca.*0.5h to a stirring suspension of indenyllithium(3.0g, 25mmol) in hexane (50mL), the reaction mixture being maintained at 0°C throughout. After addition was complete, the mixture was allowed to warm to room-temperature, after which stirring was continued for an additional 24h. The mixture was filtered, the filtrate concentrated *in vacuo*, eventually giving a light yellow solid which was recrystallized from $Et_2O$/hexane (95/5) to give 2.1g of white crystalline 3.4.

*N*-Butyltri($\eta^1$-indenyl)stannane (3.5) was prepared by an exactly analogous procedure.

# CHAPTER FOUR

# CONSEQUENCES OF CHIRALITY AT TIN IN SOME STANNYLCYCLOPENTADIENE ANALOGUES.

## A. Introduction

The effect of stereoisomerism in non-rigid methylcyclopentadienyl -germanes and -stannanes was referred to very briefly in Chapter Two, and in Chapter Three the related stereochemical effects resulting from chirality within the $\eta^1$-indenyl framework were discussed at some length. Concurrently, chirality in the migratory group has been used by other workers in these laboratories (see Chapter One) to derive mechanistic information regarding fluxional rearrangements in cyclopentadienylsilanes and related compounds. Developing this approach into the context of related ring-systems (see Chapter One), three methyl(*iso*propyl)phenylstannyl derivatives, (the pentamethylcyclopentadiene; the methylcyclopentadiene; and the indene) have been prepared as part of the present work and have been examined in detail using variable-temperature $^1$H and $^{13}$C NMR spectroscopy.

## B. Results

Methyl(*iso*propyl)phenyl($\eta^1$-pentamethylcyclopentadienyl)stannane (4.2), methyl(*iso*propyl)phenyl($\eta^1$-methylcyclopentadienyl)stannane (4.3) and methyl(*iso*propyl)phenyl($\eta^1$-indenyl)stannane (4.4), none of which have been isolated previously, were prepared in high yield as yellow, volatile, air- and water-sensitive liquids, from the reaction of methyl(*iso*propyl)phenyltin bromide (4.1) with lithium pentamethylcyclopentadienide, potassium methylcyclopentadienide and indenyllithium respectively. Physical and analytical data for the new compounds, 4.2 - 4.4, are given in Table 4.1.

Sn(Me)(*i*-Pr)(Ph)(Br), 4.1, was prepared by the literature method[155] (Figure 4.1). This involved successive reactions of a triorganotin halide with the appropriate alkylmagnesium halide followed by either bromodemetallation (with $Br_2$) or protodemetallation (with HCl) of the tetraorganotin compound formed. Compounds isolated during the synthesis of compound 4.1 were characterized by IR, $^1H$ NMR, M S, and B.Pt., the observed properties agreeing exactly with these given in the literature.[155]

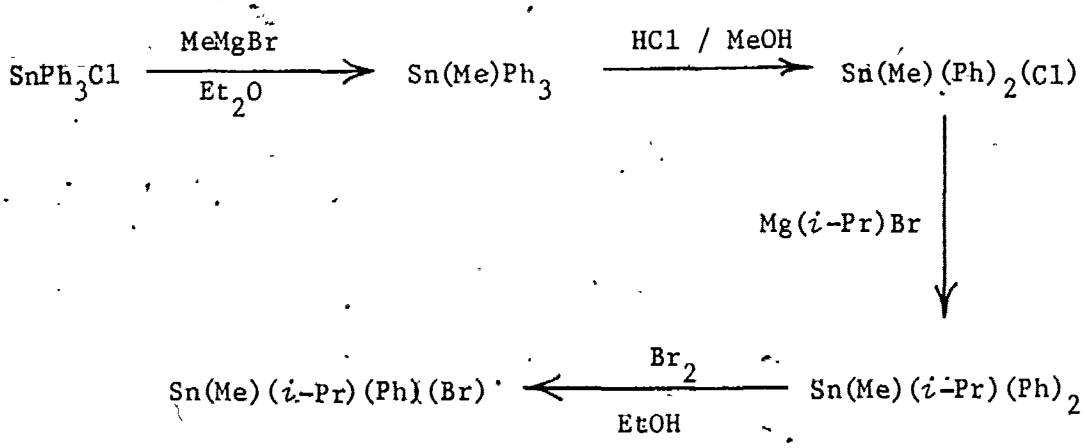

FIGURE 4.1. Synthetic scheme used to prepare Sn(Me)(*i*-Br)(Ph)(Br), 4.1.

TABLE 4.1.

Physical and analytical data for compounds 4.2 - 4.4.

| Compound | B.Pt. (°C/mmHg) | Analysis |  |  |  | % Yield |
|---|---|---|---|---|---|---|
|  |  | Theoretical |  | Actual |  |  |
|  |  | %C | %H | %C | %H |  |
| 4.2<br>$Sn(Me)(i\text{-}Pr)(Ph)[\eta^1\text{-}C_5(CH_3)_5]$ | 125-130°/$10^{-2}$ | 61.73 | 7.77 | 62.27 | 8.30 | 95 |
| 4.3<br>$Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_5H_4CH_3)$ | 115-125°/$10^{-2}$ | 58.08 | 6.87 | 57.72 | 6.66 | 55 |
| 4.4<br>$Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_9H_7)$ | 135-140°/$10^{-2}$ | 62.09 | 6.34 | 61.85 | 6.01 | 75 |

## B.1. Mass Spectral Data.

Mass spectral data for compounds 4.2 - 4.4 are listed in Table 4.2, and consist of a considerable range of ion families due to tin-containing fragments resulting from decomposition pathways involving the four different substituents on the metal. Molecular ions were observed for each compound, with the majority of the metal-containing ~~ion-current~~ being carried by the even electron ions (*i.e.* $SnR_1R_2R_3^+$ and $SnR^+$). No prominent peaks were attributed to fragmentation within the Cp′$^*$ substituent, indicative of monohapto-bonding between the metal and the Cp′-ring.[128]

## B.2. NMR Data

Compounds 4.2 - 4.4 are optically inactive, existing as racemic mixtures (equal proportion of the two enantiomorphs). Although such racemic mixtures differ from each of the optically pure enantiomers in their interaction with (a) polarized light, or (b) chiral substrates, they will possess NMR spectra (and IR, M S , *etc*) which are identical, and hence conclusions concerning the stereochemistry of the rearrangement behaviour may be adduced directly from the NMR data observed.

The $^1H$ and $^{13}C$ NMR spectra of the pentamethylcyclopentadiene, 4.2 (Figures 4.2 and 4.3), and the methylcyclopentadiene, 4.3

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* Cp′ = $C_5(CH_3)_5$, $C_5H_4CH_3$, $C_9H_7$ .

TABLE 4.2.

Mass spectral data[a] for compounds 4.2 - 4.4 ($Sn(Me)(i\text{-}Pr)(Ph)Cp'$).

| Ion Family/ Cp′ | Ion Abundance[b] | | |
|---|---|---|---|
| | $C_5(CH_3)_5$ | $C_5H_4CH_3$ | $C_9H_7$ |
| $Sn(Me)(Ph)(i\text{-}Pr)Cp'^{+\cdot}$ | 4 | 5 | 2 |
| $Sn(i\text{-}Pr)(Ph)Cp'^{+}$ | 1 | 2 | 1 |
| $Sn(Me)(Ph)Cp'^{+}$ | 16 | 5 | 12 |
| $Sn(Me)(i\text{-}Pr)Cp'^{+}$ | 13 | 7 | 7 |
| $Sn(Me)(i\text{-}Pr)(Ph)^{+}$ | 8 | 31[c] | 11 |
| $Sn(Me)(Ph)^{+\cdot}$ | 11 | 15 | 12 |
| $Sn(Me)(i\text{-}Pr)^{+\cdot}$ | 4 | 12 | 8 |
| $SnCp'^{+}$ | 13 | 31[c] | 14 |
| $SnPh^{+}$ | 24 | 13 | 27 |
| $SnMe^{+}$ | | 8 | 3 |
| $Sn^{+\cdot}$ | 7 | 2 | 3 |

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[a] 70eV ionizing voltage.

[b] % metal-containing ions, summed within each family resulting from isotope distribution and hydrogen loss.

[c] Peaks between m/e = 249 and 259 are assigned to both $Sn[C_5(CH_3)_5]^{+}$ and $Sn(Me)(i\text{-}Pr)(Ph)^{+}$.

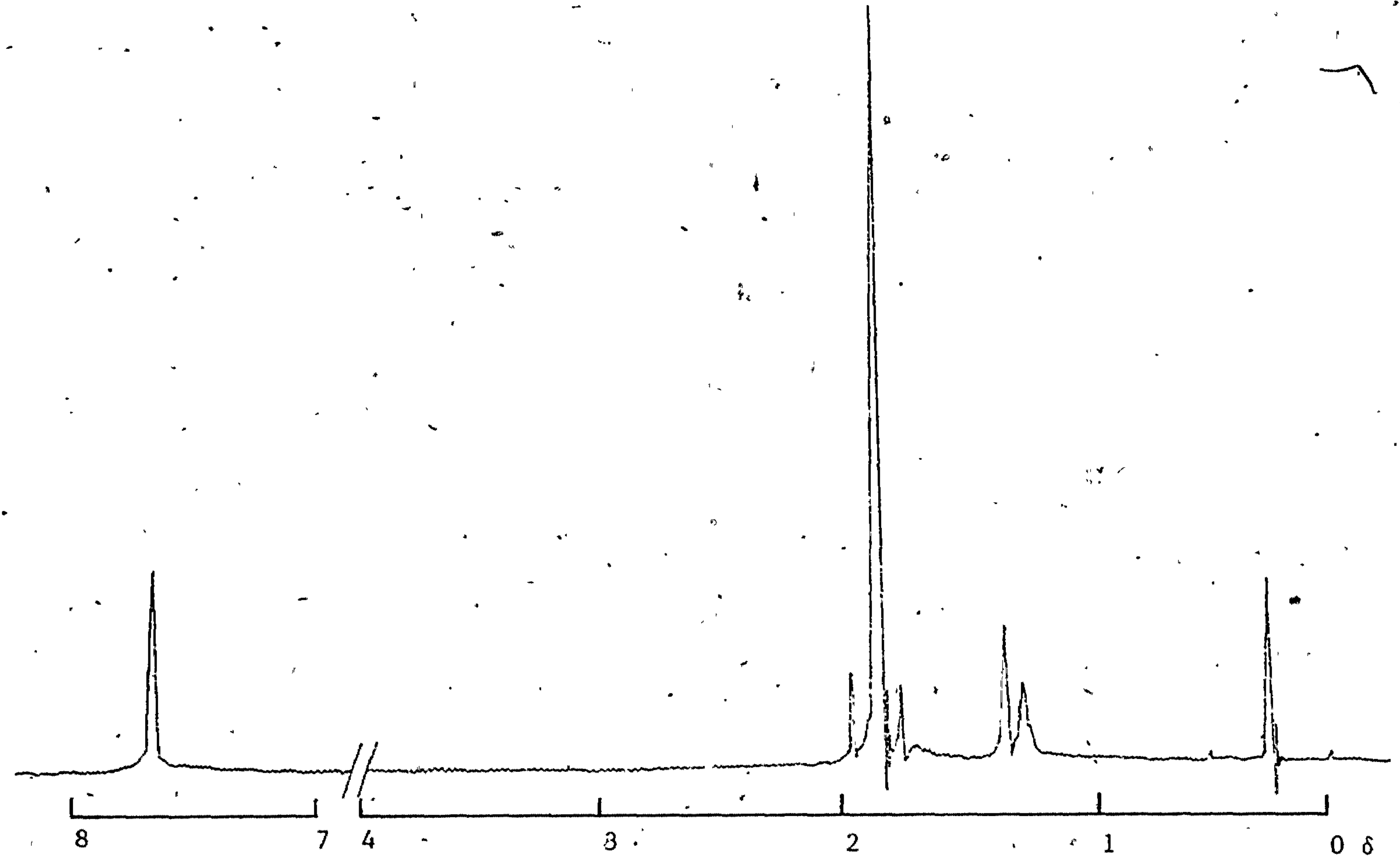

FIGURE 4.2. 90MHz $^{1}$H NMR spectrum of Sn(Me)(*i*-Pr)(Ph)[$\eta^{1}$-$C_5(CH_3)_5$], <u>4.2</u> at 27°C.

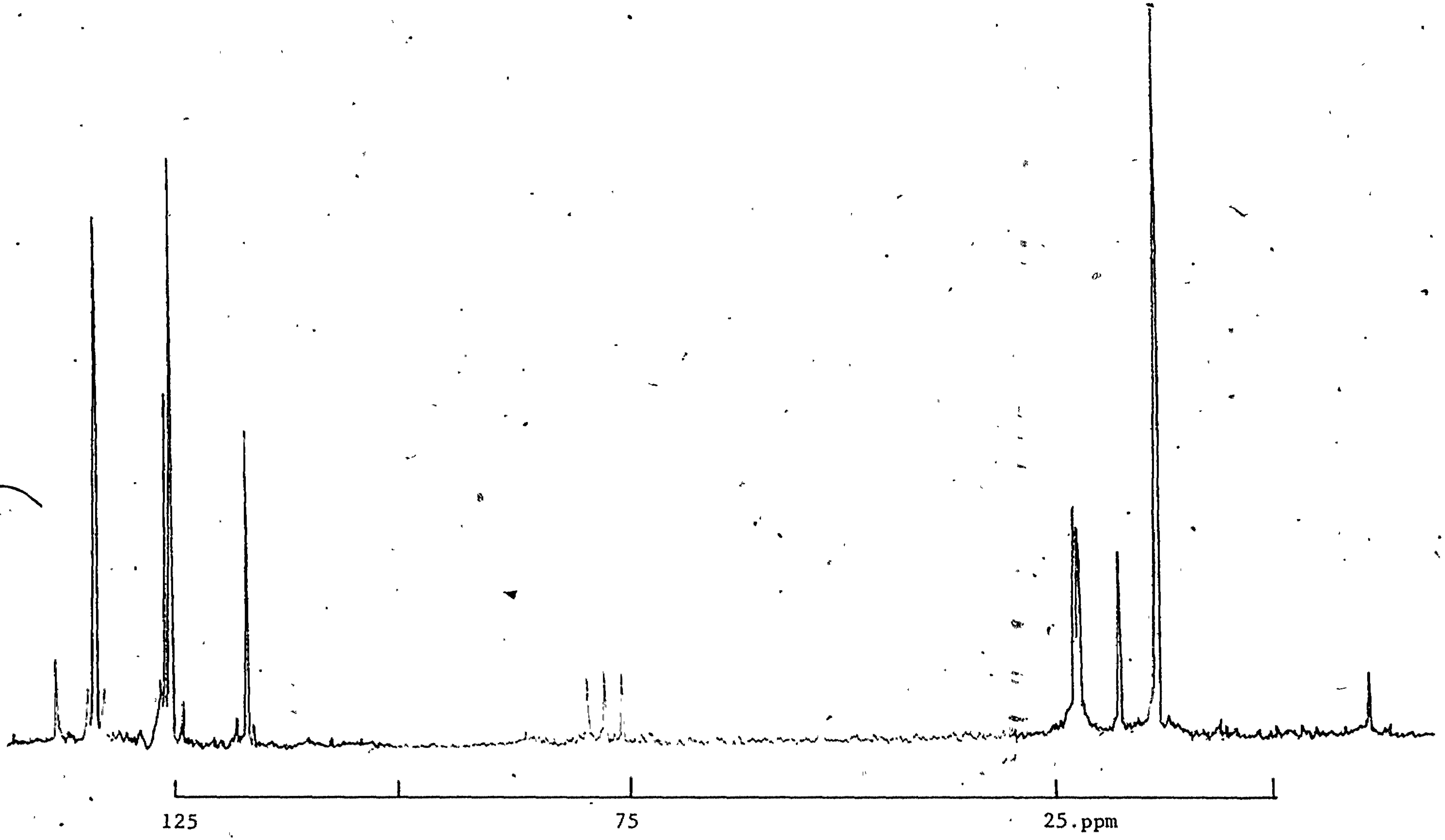

FIGURE 4.3. $^{13}$C NMR spectrum of Sn(Me)(*i*-Pr)(Ph)[$\eta^1$-$C_5(CH_3)_5$], 4.2.

(Figures 4.4 and 4.5), are temperature invariant, while corresponding spectra for the indene, 4.4 (Figures 4.6 and 4.7) are temperature dependent over the range studied (*ca.*-60° to +60°C), ( see also Tables 4.3 - 4.5).

### B.2.(i). Proton NMR data.

The $^1$H NMR spectra of compounds 4.2 and 4.3 each contain a single resonance ($\delta$ = 0.20, -0.16 respectively) due to the methyl group bound directly to tin, while the corresponding spectrum of compound 4.4 has two such signals at -60°C ($\delta$= -0.01, 0.05) which broaden on increasing the temperature through 0°C, giving at *ca.*+60°C a single resonance ($\delta$ = 0.04). Signals for the five phenyl protons appear as single absorptions at *ca.*δ7.7 for compounds 4.2 and 4.4 and as a broad multiplet centered at δ7.5 for compound 4.3.. The methyl groups of the *iso*propyl substituent give rise to two broad signals at δ1.22 and 1.30 for compound 4.2 while for compounds 4.3 and 4.4 (at -60°C) multiplets centered at δ1.2 are observed. For compound 4.4 these signals become broad at *ca.*0°C, sharpening again at *ca.*+60°C.

The pentamethylcyclopentadiene (4.2) has a single resonance at δ1.78 for the five methyl groups of the $C_5Me_5$ group. For the methylcyclopentadiene, (4.3) there is a single ring-methyl resonance at δ2.06, while three signals at δ5.52, 5.72 and 5.92 of relative intensity 2:1:1 are assigned to $H^{\alpha,\alpha'}$, $H^{\beta}$ and $H^{\beta'}$ respectively (*cf.*Figure 2.3).

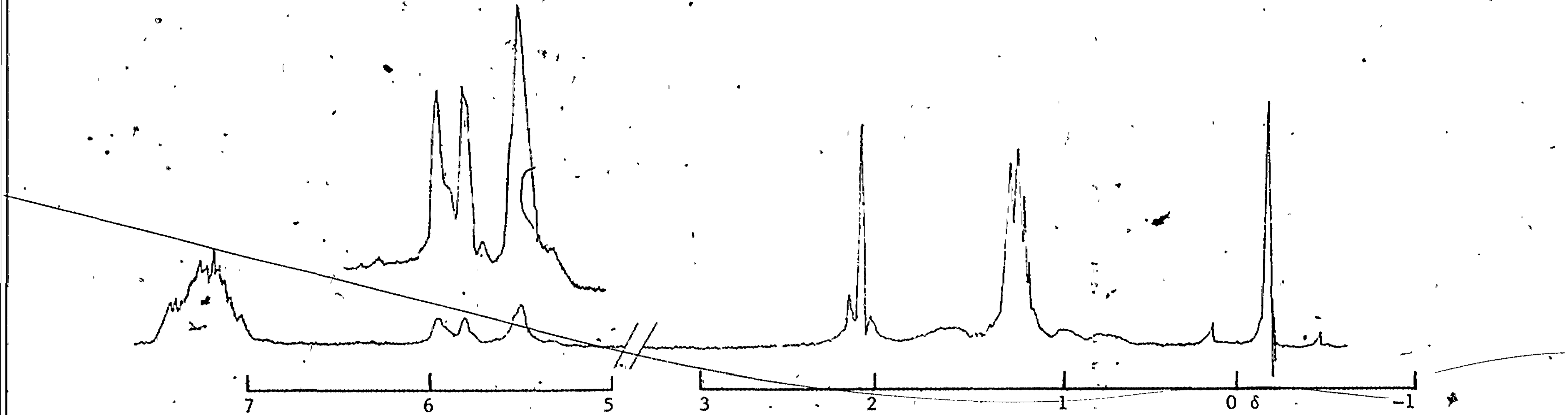

FIGURE 4.4. 90MHz $^{1}$H NMR spectrum of Sn(Me)(*i*-Pr)(Ph)($\eta^{1}$-$C_5H_4CH_3$), 4.3 at 27°C.

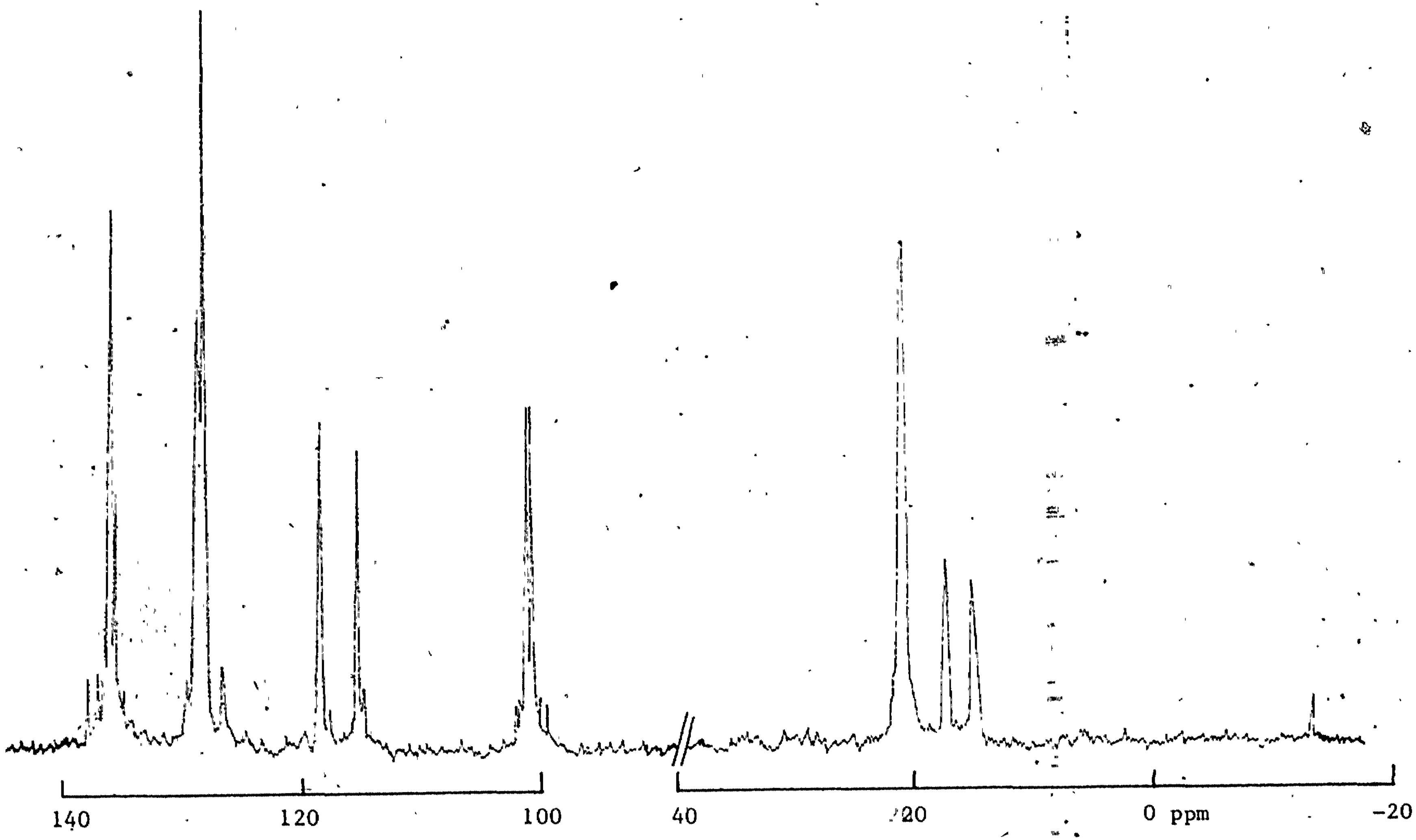

FIGURE 4.5. $^{13}$C NMR spectrum of Sn(Me)($i$-Pr)(Ph)($\eta^1$-$C_5H_4CH_3$), 4.3.

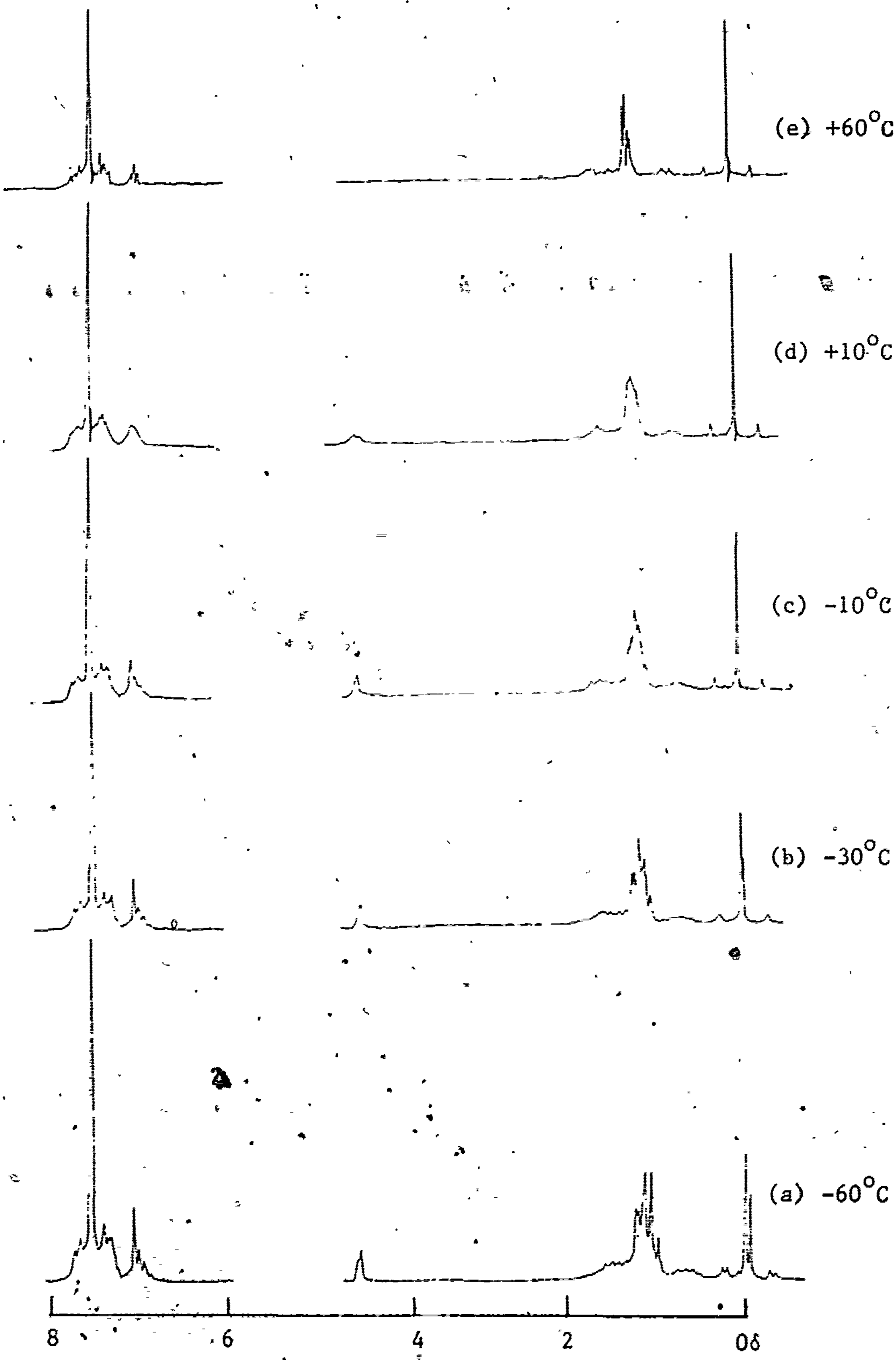

FIGURE 4.6. 90MHz variable temperature $^1H$ NMR spectrum of $Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_9H_7)$, 4.4.

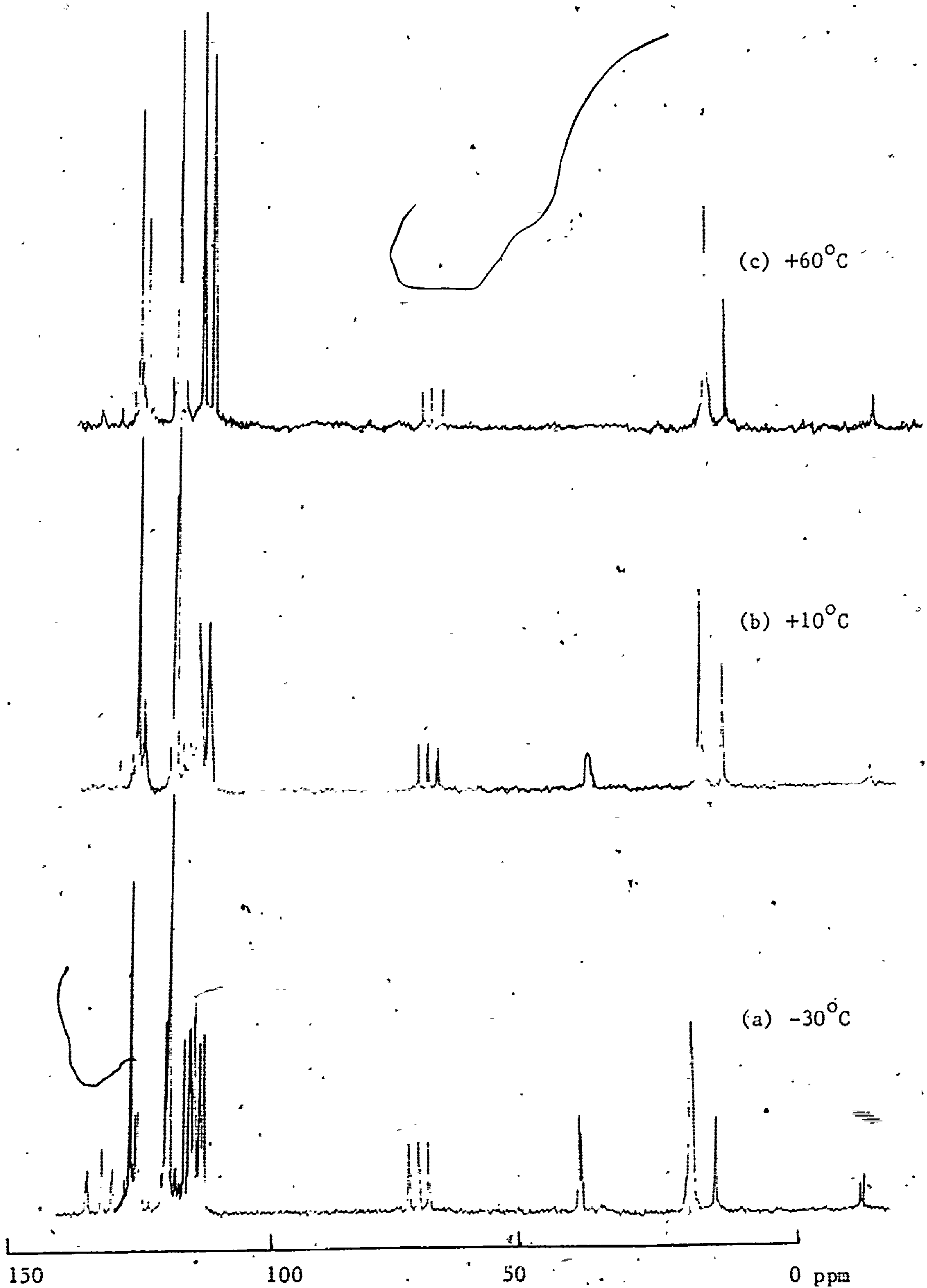

FIGURE 4.7. Variable temperature $^{13}$C NMR spectrum of Sn(Me)(*i*-Pr)(Ph)($\eta^1$-$C_9H_7$), 4.4.

## TABLE 4. 3.

NMR data[a] for the methylcyclopentadienyl, pentamethylcyclopentadienyl and indenyl groups of compounds 4.2–4.4.

| Compound | $^1$H NMR $C_5$–$C\underline{H}_3$ | $^1$H NMR $C_5$–$\underline{H}$ | $^{13}$C NMR $\underline{C}_5$–$CH_3$ | $C^{\gamma}$ | $C^{\alpha,\alpha'}$ | $C^{\beta,\beta'}$ |
|---|---|---|---|---|---|---|
| 4.2<br>$Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_5(CH_3)_5)$ | 1.78(19)$^d$ | | 15.4 | n.o.$^f$ | 100.6<br>101.1 | 115.4<br>118.8 |
| 4.3<br>$Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_5H_4CH_3)$ | 2.06(11)$^d$ | 5.52(2)$^e$<br>5.72(1)$^e$<br>5.96(1)$^e$ | 12.1 | | 119.3 | |

| Compound | | $C^1$ | $C^2$ | | $C^3$ | $C^{4,5,6,7}$ | | $C^{8,9}$ | |
|---|---|---|---|---|---|---|---|---|---|
| 4.4<br>$Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_9H_7)$ | $^{13}$C NMR | 43.9$^b$ | 134.7$^b$ | 134.9$^c$ | 125.2$^b$ | 121.2$^b$ | | 142.2$^b$ | |
| | | 44.4 | 135.4$^b$ | (7.1Hz)$^g$ | | 121.9 | 121.7$^c$ | 145.2 | 144.1$^c$ |
| | | | | | | 123.1 | | 145.5 | |
| | | | | | | 123.8 | 123.7 | | |

| | | $H^1$ | $H^2$ | $H^3$ | $H^{4,5,6,7}$ |
|---|---|---|---|---|---|
| | $^1$H NMR | 4.41$^b$ | 6.8–7.1$^b$ | 6.1–6.8$^b$ | 6.1–6.8$^b$ |
| | | 4.46 | 6.91(t)$^c$<br>($^3J(^1H\text{-}^1H)$ = 3.6Hz) | | |

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[a] Chemical shifts, ppm, measured positive downfield from $SiMe_4$ in $CDCl_3$. [b] Spectrum recorded at −60°C. [c] Spectrum recorded at 60°C. [d] $J(^1H\text{-}^{117,119}Sn)$, in Hz. [e] Relative intensity. [f] Not observed. [g] $^3J[(H^1/H^3)_{av.}\text{-}H^2]$.

TABLE 4.4.

$^1$H NMR data[a,b] for the methyl, *iso*propyl and phenyl groups of compounds 4.2 - 4.4.

| Compound | Sn-C$\underline{H}_3$ | $^2J(^{117,119}$Sn-$^1$H),(Hz) | -C$\underline{H}$(CH$_3$)$_2$ | -CH(C$\underline{H}_3$)$_2$ | C$_6\underline{H}_5$ |
|---|---|---|---|---|---|
| 4.2<br>Sn(Me)(*i*-Pr)(Ph)[$\eta^1$-C$_5$(CH$_3$)$_5$] | 0.20 | 45.0 | 1.4 - 1.9 | 1.22, 1.30 | 7.7[f] |
| 4.3<br>Sn(Me)(*i*-Pr)(Ph)($\eta^1$-C$_5$H$_4$CH$_3$) | -0.16 | 50.4 | 1.4 - 1.9[e] | 1.20, 1.23,<br>1.26, 1.30 | 7.8 - 7.2[e] |
| 4.4<br>Sn(Me)(*i*-Pr)(Ph)($\eta^1$-C$_9$H$_7$) | -0.01[c]<br>0.05[c]<br>0.04[d] | 48.7[c]<br>49.1[c]<br>49.1[d] | 1.4 - 1.9[e] | 1.0 - 1.4[c]<br>1.20, 1.23, 1.28, 1.31[d,e] | 7.7[f] |

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[a] Chemical chifts, ppm, measured positive downfield from SiMe$_4$ in 10% CDCl$_3$ solutions.

[b] Measured at 90MHz.

[c] Spectrum recorded at -30°C.

[d] Spectrum recorded at +60°C.

[e] Multiplet.

[f] Broad.

TABLE 4.5.

$^{13}C$ NMR data[a] for the methyl, *iso*propyl and phenyl groups of compounds 4.2 - 4.4.

| Compound | Sn-$\underline{C}H_3$ |  | Sn-*i*-Pr |  | Sn-$\underline{C}_6H_5$ |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | $\underline{C}H_3$ | $^1J(^{13}C-^{117,119}Sn)$[f] | $\underline{C}H(CH_3)_2$ | $CH(\underline{C}H_3)_2$ | $C^1$ | $C^{2,6}$[e] | $C^{5,3}$[e] | $C^4$ |
| 4.2<br>$Sn(Me)(i\text{-}Pr)(Ph)(n^1\text{-}C_5(CH_3)_5)$ | -12.9 | 129.9 | 16.9 | 21.7<br>22.0 | 141.4 | 136.8 | 127.9 | 128.4 |
| 4.3<br>$Sn(Me)(i\text{-}Pr)(Ph)(n^1\text{-}C_5H_4CH_3)$ | -13.4 | 130.4 | 17.7 | 21.7[b] | 141.4 | 136.4 | 128.4 | 128.8 |
| 4.4<br>$Sn(Me)(i\text{-}Pr)(Ph)(n^1\text{-}C_9H_7)$ | -13.9[c]<br>-13.2[c]<br>-13.2[d] | n.o. | 16.5 | 21.6[b] | 140.3 | 136.5 | 128.4 | 128.9 |

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[a] Chemical shifts, ppm, measured positive downfield from $SiMe_4$ in $CDCl_3$.

[b] Broad.

[c] Spectrum recorded at −30°C.

[d] Spectrum recorded at +60°C.

[e] Assignment as in reference 142.

[f] Values given in Hz.

At -60°C, the $^1$H NMR spectrum of compound 4.4 contains indenyl-H$^1$ resonances at δ4.41 and 4.46, a multiplet centered at δ6.95 due to H$^2$, with the other indenyl proton resonances forming a broad multiplet centered at δ6.5 which overlaps with resonances for the phenyl protons. Raising the temperature to *ca.* -10°C results in broadening of the H$^1$ and H$^2$ resonances, and at +60°C the H$^1$ resonances have completely collapsed while the H$^2$ resonance appears as a triplet. Signals due to H$^{4,5,6,7}$ show some spectral changes with temperature, but no detailed assignment was attempted.

B.2.(ii). Carbon-13 NMR data.

The $^{13}$C NMR spectrum of compounds 4.2 and 4.3 have methyl signals at -12.9 and -13.4ppm respectively due to the methyl group bound directly to tin. In contrast the -60°C spectrum of 4.4 contains two C$^{Me}$ resonances at -13.9 and -13.2ppm which broaden on increasing the temperature, giving at *ca.* +60°C a single resonance at -13.2ppm. Resonances at 127.9, 128.4, 136.8 and 141.4ppm for compound 4.2, at 128.4, 128.8, 136.4 and 141.4ppm for compound 4.3 and at 128.4, 128.9, 136.5 and 140.3ppm for compound 4.4 are attributed to C$^{3,5}$, C$^4$; C$^{2,6}$ and C$^1$ respectively of the substituent phenyl groups. The *iso*propyl group gives three signals at 16.9, 21.7 and 22.0ppm for compound 4.2, but only two signals for both compounds 4.3 (at 17.7 and 21.7ppm) and compounds 4.4 (at 16.5 and 21.6ppm), the high frequency signal for compounds 4.3 and 4.4 being broad.

For compound 4.2 the remaining resonances at 12.1 and 119.3ppm are due to the five methyl- and five ring-carbon atoms respectively of the pentamethylcyclopentadienyl ring. For the methylcyclopentadienyl compound 4.3, resonances at 15.4, 100.6, 101.1, 115.4 and 118.8ppm result from $C^{Me}$, $C^{\alpha}$, $C^{\alpha'}$, $C^{\beta}$ and $C^{\beta'}$ respectively of the methylcyclopentadienyl-ring (a signal corresponding to $C^{\gamma}$ was not observed).

In the indenyl, 4.4 the -30°C spectrum contains two $C^1$-indenyl resonances at 43.9 and 44.4ppm, the assignment of the remaining resonances, ascribed to the carbons of the indenyl ring are given in Table 4.3. At *ca.* 10°C, all the indenyl carbon resonances have broadened significantly and at *ca.* +60°C resonances due to $C^1$ (at 43.9 and 44.4ppm) and $C^3$ (125.2ppm) have completely collapsed, while slow-limit resonances at 121.2, 121.9, 123.1 and 123.8ppm due to $C^{4,5,6,7}$ have averaged to give two signals at 121.7 and 123.7ppm for $C^{4,7}$ and $C^{5,6}$ * in the +60°C spectrum. Similarly resonances at 142.2, 145.2 and 145.5ppm assigned to $C^{8,9}$ broaden, giving at *ca.* +60°C a single absorption at 144.1ppm, while $C^2$ signals at 134.7 and 135.4ppm are broad at *ca.* 0°C and at +60°C give a sharp resonance at 134.9ppm.

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* Order may be reversed.

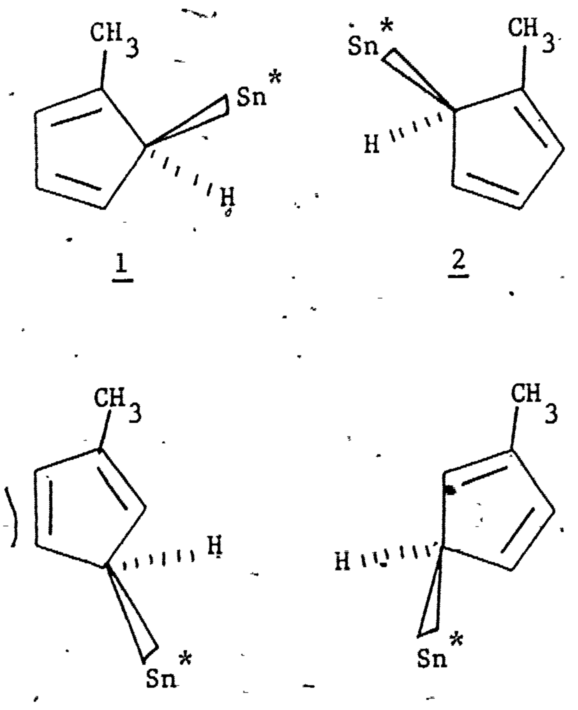
## C. DISCUSSION.

The NMR data obtained for the pentamethylcyclopentadiene $SnMe(\textit{i}\text{-}Pr)(Ph)[\eta^1\text{-}C_5(CH_3)_5]$ (4.2) are consistent with rapid migration of the tin moiety around the five carbon atoms of the $\eta^1$-$C_5$-ring, bringing about equivalence of the five ring carbons and also the five ring methyl groups on the NMR timescale, exactly paralleling the situation observed[92] for $SnMe_3[\eta^1\text{-}C_5(CH_3)_5]$. Thus only one signal is apparent in the $^1H$ NMR spectrum for the five methyl groups (Figure 4.2), while in the $^{13}C$ NMR spectrum the $C_5Me_5$ ring system gives rise to two singlets (Figure 4.3), one due to the five ring carbon atoms and the other to the five methyl groups. Although the rearrangement process has no effect on the resonances for the methyl, *iso*propyl or phenyl substituents, analysis of signals resulting from the *iso*propyl group is informative. In the $^{13}C$ NMR spectrum there are three distinct signals for the three carbon atoms of the *iso*propyl substituent, confirming magnetic non-equivalence of the two methyl groups. This observation at fast rates of intramolecular exchange establishes that the rearrangement process does not lead to averaging of the magnetic environments of the two methyl groups, and must therefore take place with retention of configuration at the tin center. By contrast, at 90 MHz the $^1H$ signals due to the β-protons of the *iso*propyl group show no resolvable splitting due to diastereotopic effects, appearing as a doublet through coupling to the single methine proton.

The appearance of the $^1$H and $^{13}$C NMR spectra (Figures 4.4 and 4.5 respectively) for the methylcyclopentadiene, SnMe(*i*-Pr)(Ph)($\eta^1$-$C_5H_4CH_3$)(4.3)is the result of facile sigmatropic migration of the tin-containing group around the methylcyclopentadienyl ring at a rate which is fast relative to the NMR timescale (see also Chapter Two). Thus the methyl group bound to the $C_5$-ring gives a single absorption in both the $^1$H and $^{13}$C NMR spectra. Diastereotopic splitting of resonances for the ring nuclei (see Chapter One, references 79 and 89) is also apparent, so that in the $^{13}$C NMR spectrum a signal arises for each of the ring carbons $C^{\alpha}$, $C^{\alpha'}$, $C^{\beta}$ and $C^{\beta'}$, while in the $^1$H NMR spectrum there are three broad lines at $\delta$5.52($H^{\beta}$), 5.72($H^{\beta'}$) and 5.96($H^{\alpha,\alpha'}$), in *ca* 1:1:2 intensity ratio.

In the $^1$H NMR spectrum the complexity of the multiplet centered at $\delta$1.25 attributable to the β-protons of the *iso*propyl substituent establishes magnetic non-equivalence between the two methyl groups to give a pattern resembling that expected for an $a_3b_3x$ spin system. By contrast, at 15.1 MHz the $^{13}$C NMR spectrum shows an unsplit signal for the two β-carbon atoms. Thus identification of magnetic non-equivalence of the two methyl groups at fast rates of rearrangement ($^1$H NMR data) leads to the conclusion that the sigmatropic migration occurs with retention of configuration at the migrating center. As Fabian and Labinger have noted[97] for a related iron system, the observation of diastereotopically shifted resonances for the carbons ($^{13}$C NMR) or protons ($^1$H NMR) of the methylcyclopentadienyl ring at fast rates of sigmatropic migration, is evidence for either (i) retention of configuration in a suprafacial process, or, (ii) inversion of configuration during an antarafacial process.

Thus the observed diastereotopic splitting of resonances for the methylcyclopentadienyl-ring nuclei, in conjunction with the above proof that rearrangement occurs with retention of configuration at the migrating center, leads to the conclusion that the rearrangement is suprafacial as anticipated. The rearrangement taking place can then be visualised as a rapid interconversion of the four isomers (1 - 4), Figure 4.8.



1 2

3 4

FIGURE 4.8. Isomers present in significant concentration in Sn(Me)(*i*-Pr)(Ph)($\eta^1$-$C_5H_4CH_3$), 4.3.

The complex slow-limit $^1$H (at -30°C) and $^{13}$C (at -60°C) NMR spectra observed for the indenyl 4.4 are the result of the presence in 4.4 of the diastereomeric pair, 5 and 6, of enantiomorphs (Figure 4.9).

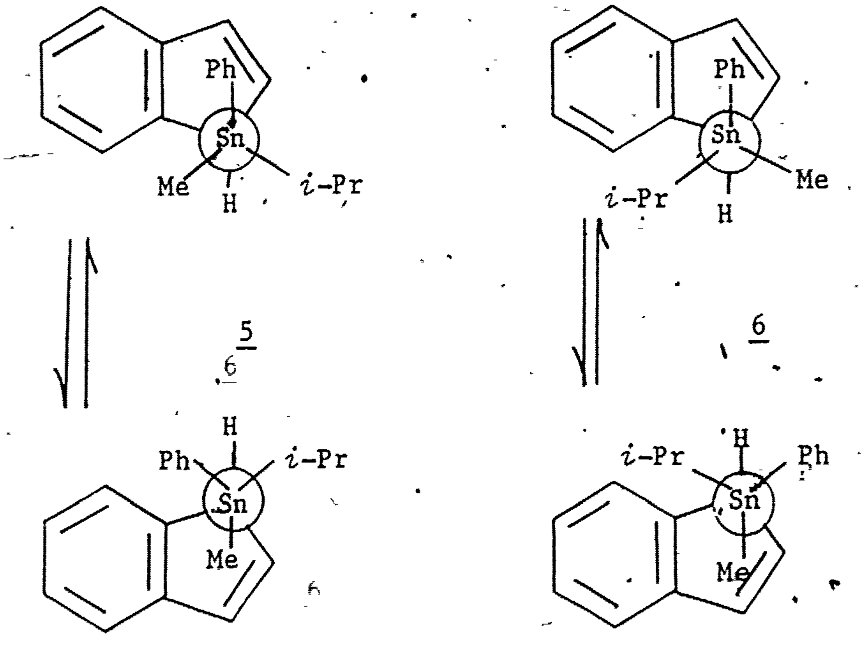
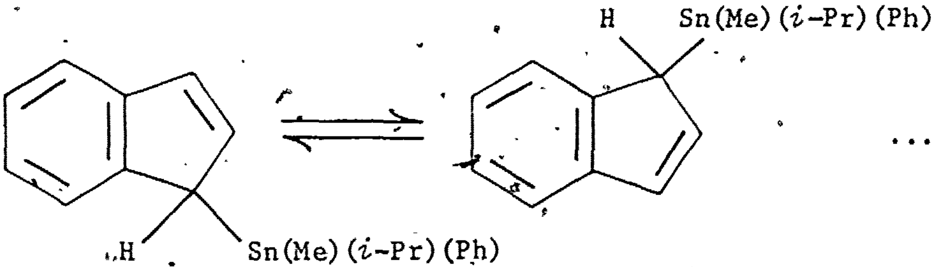


FIGURE 4.9. The diastereoisomers 5 and 6 present in $Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_9H_7)$, 4.4.

The enantiomeric pair 5 (and also the pair 6) have identical NMR spectra; but these two pairs are significantly different from one another and will give rise to different NMR spectra. Thus the methyl group bound directly to tin in each enantiomeric pair gives one signal in the $^{13}C$ NMR spectrum and in the $^{1}H$ NMR spectrum. Similarly there are two indenyl $C^1$ resonances in the $^{13}C$ NMR spectrum and two $H^1$ resonances in the $^{1}H$ NMR spectrum.

Raising the temperature results in an averaging of resonant positions for the indenyl ring nuclei, which is consistent with an overall 1,3 rearrangement of the tin moiety across the five membered ring of the indene framework (equation (1)).

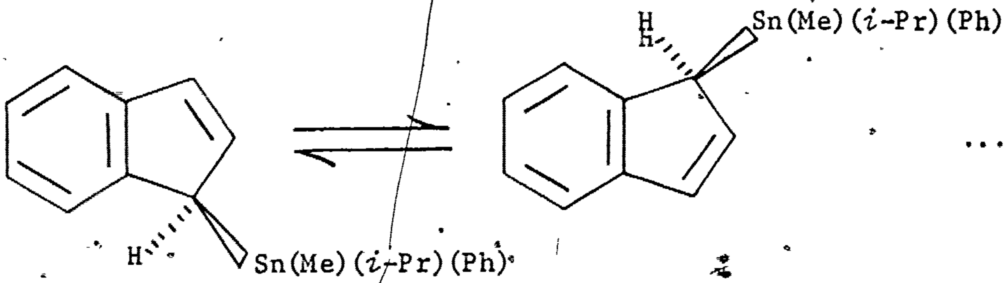


....(1)

Thus resonances assigned to $C^1$ and $C^3$ broaden at *ca.* 0°C and are completely collapsed at 20°C. Resonances for $C^{8,9}$ also broaden at *ca.* 0°C, giving a coalesced signal at *ca.* +60°C, as do resonances for $C^{4,7}$, and also for $C^{5,6}$. In the $^{1}H$ NMR spectrum $H^1$ and $H^3$ resonances broaden at *ca.* 0°C and completely collapse at *ca.* +30°C, while signals for $H^2$ broaden, giving a triplet at *ca.* +30°C, resulting from the averaging of the coupling constants $^{3}J(H^1-H^2)$ and $^{3}J(H^3-H^2)$.

The rearrangement process also averages resonances for the indenyl $C^2$ nuclei, and the tin-methyl groups in isomers 5 and 6, consistent with the metallotropic rearrangement bringing about interconversion between the two different isomer types 5 and 6.

A 1,3 suprafacial migration as depicted in equation (2) must necessarily involve a change in the configuration at $C^1$ of the indenyl ring; it follows that the observed interconversion between the two diastereoisomeric pairs 5 and 6 requires that the configuration at the tin center should remain invariant *i.e.* retention.



...(2)

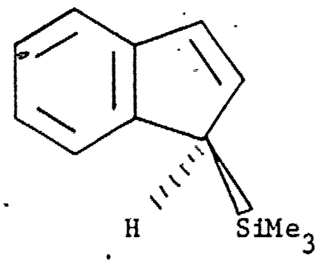
Resonances in the -30°C $^1$H NMR spectrum due to the methyl groups of the *iso*propyl substituent appear as a complex multiplet. This results from overlap of signals for the *iso*propyl group in diastereoisomers 5 and 6. Interconversion between 5 and 6 results in averaging of these resonances, so that the +60°C $^1$H NMR spectrum is consistent with the methyl groups of the *iso*propyl substituent maintaining magnetically distinguishable environments throughout the rearrangement process (*i.e.* resulting from an $a_3b_3x$ spin system). This is confirmatory evidence for retention of configuration at the migrating metal center.

These observations can be summarized as follows: Rearrangement of the indenyl (diastereoisomeric mixture 5:6) involves an overall 1,3 suprafacial migration of the metal, the configuration at which is unchanged by the metallotropic shift. Simultaneously this process interconverts the diastereoisomeric pairs 5 and 6 as shown in Figure 4.9.

Similarly the $^1$H NMR data obtained[103] for $SnMe_2Ph(\eta^1-C_9H_7)$

are consistent with exchange between the magnetic environments of the two methyl groups and support retention of configuration at the tin center in a suprafacial process (Chapter One and reference 103).

Rearrangement *via* an *iso*-indenyl intermediate is indicated by several compelling yet inconclusive experimental observations (see Chapter One). Thus in a number of instances[105,106] products have been isolated from the Diels-Alder reaction of metallo-1-indenes with dienophiles in which the migratory group is located at the 2-position. Thermolysis of trimethylsilyl($\eta^1$-indene), 7 yields[106,107] an equilibrium mixture of three compounds (7, 8, and 9), the presence of one of which (8) is consistent with the *iso*-indenyl intermediate. Site exchange between the two trimethylsilyl groups of 1,2-bis(trimethylsilyl)indene, 10, leads to only one methyl signal in the fast-limit $^1$H NMR spectrum.[104] This observation rules out the possibility of a concerted 1,3 migration; while it is consistent with the *iso*-indenyl intermediate an alternate process involving a pair of simultaneous,



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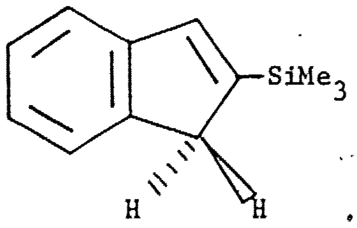

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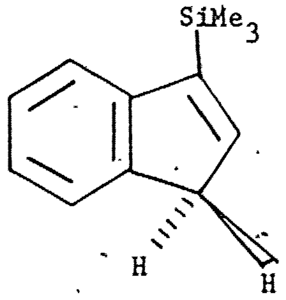

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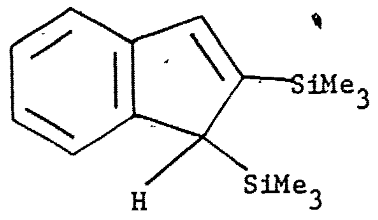
concerted 1,2 shifts (11) has also been proposed.[104]



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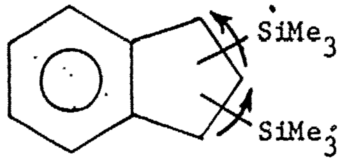

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The design of suitable experiments which will unambiguously assign this inherently-likely pathway (*ie.* overall 1,3 migration *via* successive 1,2 shifts) has not yet been achieved.

## D. EXPERIMENTAL.

Lithium pentamethylcyclopentadienide,[92] potassium methylcyclopentedienide,[138] indenyllithium[104] and methyl*iso*propylphenyltin bromide[155] were prepared by the literature methods.

### Methyl*iso*propylphenyl($\eta^1$-methylcyclopentadienyl)stannane

A solution of methyl*iso*propylphenyltin bromide (2.00g, 5.99mmol) in toluene (20mL) was added dropwise to a suspension of potassium cyclopentadienide (0.5g, 6.3mmol) in toluene (30mL) which was maintained at -78°C throughout the addition. The mixture was warmed to room-temperature and stirring continued for a further 12h. The mixture was then filtered, and the filtrate concentrated *in vacuo* leaving a light yellow oil. Sublimation *in vacuo* onto a -78°C (dry ice/acetone) probe gave pure liquid $Sn(Me)(i\text{-}Pr)(Ph)(\eta^1\text{-}C_5H_4CH_3)$ (1.10g, 3.31mmol, 55%).

Methyl*iso*propylphenyl($\eta^1$-pentamethylcyclopentadienyl)stannane and methyl*iso*propylphenyl($\eta^1$-indenyl)stannane were prepared in a similar manner.

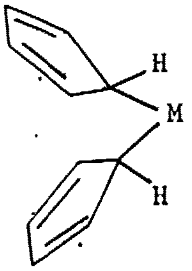
# CHAPTER FIVE

## SYNTHESIS AND PROPERTIES OF SOME BIVALENT DERIVATIVES OF GERMANIUM AND TIN.[43]

### A. INTRODUCTION:

While the organometallic chemistry of quadrivalent germanium, tin, and lead has been intensively investigated, related compounds in which the metal is in the bivalent state are much rarer and belong to a small number of specialized categories. Bis($\eta^5$-cyclopentadienyl) derivatives of tin(II) and lead(II),[20] are representative examples of one of those classes of accessible compounds in which a bivalent tin or lead atom is bound to carbon; these molecules have also been of interest because of the nature of the metal-to-ring interaction.

While it was initially assumed[20] that these compounds possessed the *sigma*-bonded structure shown in 1, Wilkinson *et al.* subsequently concluded [42] that in fact an angular π-bonded sandwich structure 2 was adopted on the basis of IR and dipole



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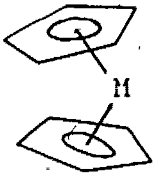

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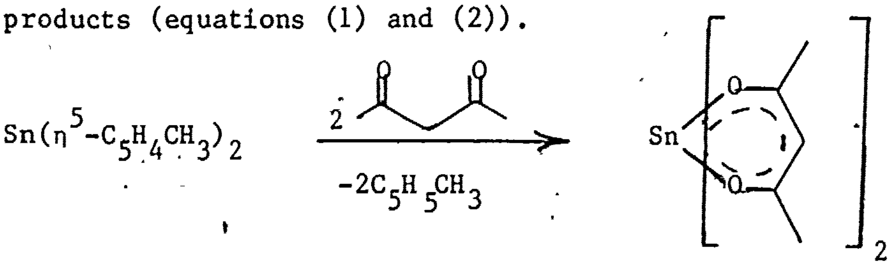
moment measurements. The existence of "sideways" rather than "end-on" bonding between the metal and the ring-system in these and related cyclopentadienyl derivatives has since been substantiated by electron diffraction [$\mathrm{Sn}(\eta^5\text{-}C_5H_5)_2$,[22] $\mathrm{Pb}(\eta^5\text{-}C_5H_5)_2$[22]] and X-ray crystallographic [$\mathrm{Sn}(\eta^5\text{-}C_5H_5)_2$,[23] $\mathrm{Pb}(\eta^5\text{-}C_5H_5)_2$,[44] $\mathrm{Sn}(\eta^5\text{-}C_5(CH_3)_5)_2$,[45] $\mathrm{Pb}(\eta^5\text{-}C_5(CH_3)_5)_2$,[23] $\mathrm{Sn}(\eta^5\text{-}C_5H_5)\,\mathrm{Cl}$,[47] $\mathrm{Sn}(\eta^5\text{-}C_5(CH_3)_5)\mathrm{BF}_4$[46]] studies.

Bis ($\eta^5$-cyclopentadienyl)- and bis($\eta^5$-methylcyclopentadienyl)-tin(II) have been shown[32,33,34] to be useful synthetic precursors to a variety of previously unknown or otherwise difficultly accessible derivatives of tin(II). Thus, in general, reactions with sources of acidic hydrogen give the corresponding tin(II) products (equations (1) and (2)).



......(1)

$$\mathrm{Sn}(\eta^5\text{-}C_5H_4CH_3)_2 \xrightarrow[-2C_5H_5CH_3]{2\mathrm{RSH}} \mathrm{Sn[SR]}_2 \quad \ldots\ldots\ldots\ldots(2)$$

A more limited range of related reactions of bis($\eta^5$-cyclopentadienyl)-lead(II) have been reported[156] by Puddephatt *et al*(equation (3)).

$$\mathrm{Pb}(\eta^5\text{-}C_5H_5)_2 + 2\mathrm{HA} \longrightarrow \mathrm{PbA}_2 + 2C_5H_6 \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

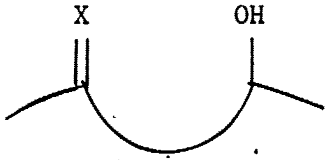
$\mathrm{A} = \mathrm{OR}^-,\ \mathrm{O_2CBu^{t}}^-,\ \mathrm{RCOCHCOR}^-$

The corresponding germanium chemistry has, until recently, been neglected due to a lack of convenient synthetic precursors.

Thus although bis($\eta^5$-cyclopentadienyl)germanium(II)[19] would appear to be a logical starting material, it has been reported to undergo rapid polymerization at room temperature (95%, 3h)[19], and, in fact, no detailed description of its reactions has appeared in the literature.

Organo-derivatives of bivalent germanium, tin, and lead have been shown to function as formal two-electron donors to low-valent transition metal centers. These types of complex have been referred to in Chapter One and their formation has been reviewed in the literature.[157]

This chapter reports the synthesis of the relatively thermally stable compound bis($\eta^5$-methylcyclopentadienyl)germanium(II) and describes its physical and chemical properties., Reactions with suitable protic reagents (particularly those of the general type 3) which might provide access to monomeric, intramolecularly associated germanium(II) containing products have been examined in some detail. An alternate synthetic route to some of these



X = O, N

3

germylenes, involving the reaction of a germanium(II) dihalide with the appropriate 1,3 ketoenolate and triethylamine has also been investigated. The reaction of bis(acetylacetonato)-germanium(II) and -tin(II) with tetrakis(triphenylphosphine)-

platinum(0) or bis(triphenylphosphine)(ethylene)platinum(0) is observed to give $Pt(PPh_3)_2[M(acac)_2]_2$, M = Ge, Sn. The crystal and molecular structure of the tin compound has been determined by Professor T.S. Cameron and Ms. E.T. Brennan at Dalhousie University and their results are commented upon.

## B. RESULTS AND DISCUSSION.

### B.1. Synthesis and Properties of bis($\eta^5$-methylcyclopentadienyl)germanium(II).

Bis($\eta^5$-methylcyclopentadienyl)germanium(II), 5.1 was conveniently prepared in high yield (>90%) as a light yellow oil by the reaction of germanium(II) diiodide with potassium methylcyclopentadienide in toluene at *ca.* 5°C. Reaction at temperatures above 10°C gave only low yields (<10%) of compound 5.1 together with a red insoluble gum. Attempts to prepare 5.1 from either $CsGeCl_3$ or $GeCl_2$.dioxan and potassium methylcyclopentadienide were not successful.

Compound 5.1 is a yellow liquid which is markedly air- and water-sensitive. It is soluble in most organic solvents (*eg.* hexane, benzene, ether, THF), but reacts rapidly with solvents containing protic hydrogen (*eg.* MeOH, EtOH) to give white insoluble solids (these reactions will be discussed later in this section). Attempts to crystallize or sublime the material *in vacuo* were unsuccessful; the yellow oil darkened in color after a few

TABLE 5.15

Physical and analytical data for compounds 5.1 and 5.3 - 5.12.

| Compound | Method of prep.[a] | %yield | Analysis |  |  |  | M.Pt(°C) /B.Pt(mmHg) |
|---|---|---|---|---|---|---|---|
|  |  |  | %C |  | %H |  |  |
|  |  |  | Actual | Theor. | Actual | Theor. |  |
| $Ge(\eta^5-C_5H_4CH_3)_2$, 5.1 | A | 85 | 62.45 | 61.92 | 5.92 | 6.07 | oil |
| $Ge(trop)_2$, 5.3 | B | 84 | 52.75 | 53.42 | 3.37 | 3.18 | 178°(dec) |
|  | C | 76 |  |  |  |  |  |
| $Ge(thuj)_2$, 5.4 | B | 86 | 60.61 | 60.23 | 5.82 | 5.52 | 137-139°(dec) |
|  | C | 79 |  |  |  |  |  |
| $Ge(oxine)_2$, 5.5 | B | 96 | 60.26 | 59.92 | 3.72 | 3.35[b] | 174° |
|  | C | 99 |  |  |  |  |  |
| $Ge(hyap)_2$, 5.6 | B | 73 | 56.56 | 56.05 | 4.04 | 4.12 | 250°(dec) |
|  | C | 55 |  |  |  |  |  |
| $Ge(acac)_2$, 5.7 | A | 55 | 43.79 | 44.35 | 5.49 | 5.21 | 25°($10^{-3}$mmHg)[c] |
|  | C | 90 |  |  |  |  |  |
| $Ge(piv)_2$, 5.8 | C | 85 | 59.76 | 60.17 | 8.94 | 8.72 | 110°($10^{-3}$mmHg) |
| Ge(benzac)Cl, 5.9 | C | 75 | 38.11 | 39.72 | [illegible].19 | 2.97 | 173°(dec) |
| $Ge(benzac)_2$, 5.11 | C | 98 | 60.45 | 60.82 | 4.79 | 4.59 | 137° |
| Ge(dibenz)Cl, 5.10 | C | 83 | d | 54.54 | d | 3.36 | 194°(dec) |
| $Ge(dibenz)_2$, 5.12 | C | 97 | 70.01 | 69.43 | 4.52 | 4.27 | 153-154° |

---

[a] A($R^-M^+ + GeX_2 \longrightarrow GeR_2$; M = $Li^+$, $Na^+$ or $K^+$; X = halogen),
B($(C_5H_4CH_3)_2Ge + HA \longrightarrow GeA_2$), C($GeX_2 + nHA + nNEt_3 \longrightarrow GeA_nX_{2-n}$).

[b] Analysis for N, actual 7.7[illegible]%, found 7.77%.

[c] Sublimed onto a water cooled probe over 24h.

[d] Suitable C, and H analysis could not be obtained.

minutes at +75°C, eventually giving a viscous, insoluble red gum. The undiluted liquid compound is also thermally unstable at room-temperature, forming over a period of several weeks, a clear yellow glass, insoluble in common organic solvents. The rate of polymerization is significantly reduced if compound 5.1 is stored as an *ca.* 5% solution in either hexane or toluene, but such solutions are significantly more air-sensitive that neat 5.1. Some physical and analytical data for compound 5.1 are given in Table 5.1.

TABLE 5.2.

Mass spectral data[a] for bis($\eta^5$-methylcyclopentadienyl)-germanium(II) and tin(II).

| Assignment | $Ge(\eta^5-C_5H_4CH_3)_2$ | $Sn(\eta^5-C_5H_4CH_3)_2$[b] |
|---|---|---|
| $M(C_5H_4CH_3)_2^{+\cdot}$ | 0.5 | 1.9 |
| $M(C_5H_4CH_3)^+$ | 74.1 | 84.0 |
| $MC_4H_n^+$ | 3.6 | n.o.[c] |
| $MC_2H_n^+$ | 7.7 | n.o.[c] |
| $M^{+\cdot}$ | 13.3 | 14.1 |

---

[a] 70eV ionizing voltage; %metal-containing ions, summed within each family resulting from isotope distribution and hydrogen loss.

[b] See reference 158.

[c] Not observed.

Mass spectral data for 5.1 together with those reported[158] for the tin analogue, $Sn(\eta^5-C_5H_4CH_3)_2$, are given in Table 5.2. Results for both compounds are similar with major metal-containing peaks corresponding to the parent ion and sequential loss of the two methylcyclopentadienyl rings. For compound 5.1 decomposition of the most abundant germanium containing ion, $Ge(C_5H_4CH_3)^+$, also occurs by carbon-carbon bond fission within the $C_5$-ring, resulting in significant abundances of the ions $GeC_4H_n^+$ and $GeC_2H_n^+$. Fragmentation of the cyclopentadienyl ring has also been reported for $Ge(\eta^5-C_5H_5)_2$[19] and $Sn(\eta^5-C_5H_5)_2$ but significantly it is not generally observed in the mass spectra of related monohaptocyclopentadienyls.[128]

TABLE 5.3.

NMR data[a] for compounds 5.1 and 5.2.

| | $^1H^b$ | | $^{19}F^c$ |
|---|---|---|---|
| | $H^{Me}$ | $H_{av}(C_5H_4CH_3)$ | |
| $Ge(\eta^5-C_5H_4CH_3)_2$, 5.1 | 2.08 | 5.72 | |
| $Ge(\eta^5-C_5H_4CH_3)_2BF_3$, 5.2 | 1.88 | 5.86 | -134.6 |

| | $^{13}C^b$ | | | |
|---|---|---|---|---|
| | $C^\gamma$ | $C^{\beta,\beta'}$ | $C^{\alpha,\alpha'}$ | $C^{Me}$ |
| 5.1 | 126.2 | 113.0 | 110.5 | 14.1 |

---

[a] All spectra were recorded in $CDCl_3$.

[b] ppm downfield from TMS.

[c] ppm upfield from $CFCl_3$.

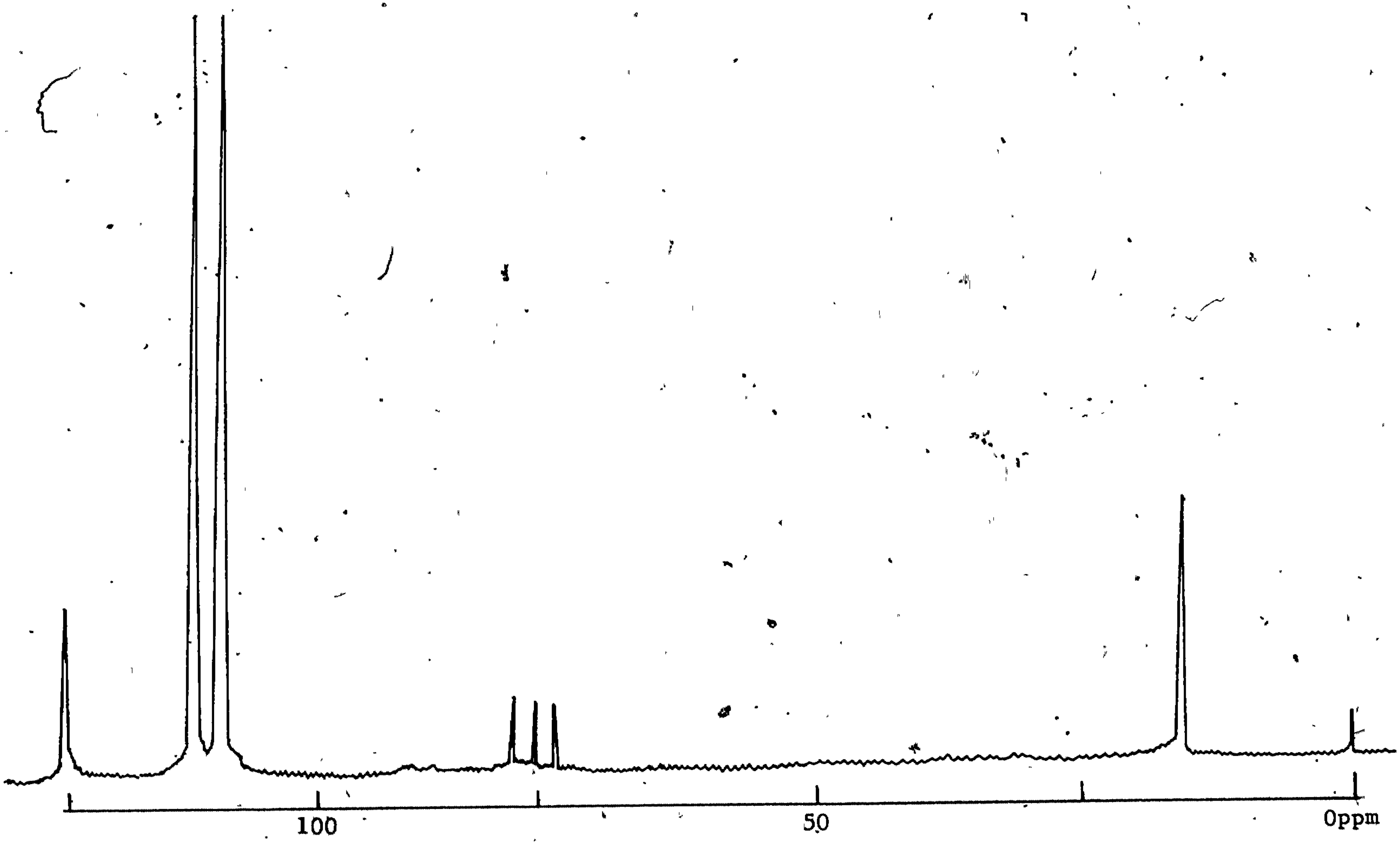
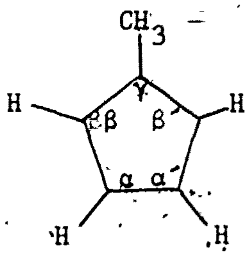
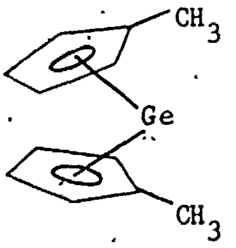


FIGURE 5.1. $^{13}$C NMR spectrum of bis($\eta^5$-methylcyclopentadienyl)germanium(II) at 25°C.

The $^1H$ and $^{13}C$ NMR spectra of compound 5.1 (see Table 5.3) are similar to those reported[43] for the tin and lead analogues. The $^1H$ NMR spectrum of compound 5.1 consists of a methyl signal at δ2.08 and a multiplet centered at δ5.72 for the four ring protons, while in the $^{13}C$ NMR spectrum (Figure 5.1) there is a methyl signal at 14.1ppm, with a further three absorptions at 110.5, 113.0 and 126.2ppm due to $C^{\alpha\alpha'}$, $C^{\beta\beta'}$ and $C^{\gamma}$ respectively.



These spectra are significantly different from the NMR spectra (described in Chapter Two) for tetrakis($\eta^1$-methylcyclopentadienyl)-germane (2.5) which are temperature dependent over the range studied (*ca.* -60°C to +60°C). The sharply contrasting spectra are the result of the different mode of bonding between the $C_5H_4CH_3$-ring and the germanium atom in 5.1 (4) and 2.5 (5).



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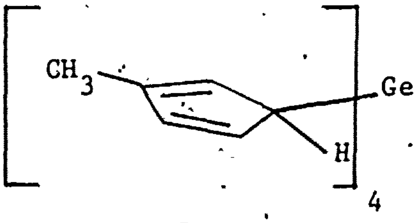

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Thus in the germane 2.5, the germanium atom is bound to a single aliphatic carbon atom of each of the four monohaptomethylcyclopentadienyl-rings. Migration of the germanium atom about the ($\eta^1$-$C_5H_4CH_3$)-rings results in averaging of the signals present in the slow-limit spectrum, however the rate is not sufficiently rapid for the spectrum to be fast-limiting at room temperature: thus broad absorptions are observed in both the $^1$H and $^{13}$C NMR spectra for the ring protons and the ring carbons, $C^{\alpha}$, $C^{\alpha'}$, $C^{\beta}$, $C^{\beta'}$ respectively.

By comparison, signals in the room-temperature $^1$H and $^{13}$C NMR spectra of compound 5.1 are sharp, the germanium atom being bound to two equivalent ($\eta^5$-$C_5H_4CH_3$)-rings to form the angular sandwich shown in 4.

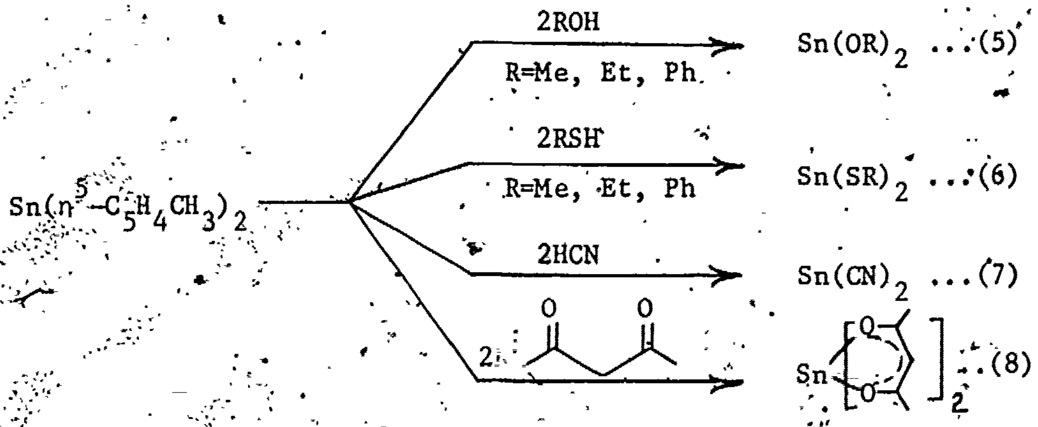
Reaction of compound 5.1 with MeI over a period of 1h at room-temperature yields a viscous yellow oil the $^1$H NMR and mass spectrum of which are indicative of the presence of a mixture of compounds of the type $Ge(Me)_m(\eta^1\text{-}C_5H_4CH_3)_nI_{4-m-n}$. By contrast, the reaction of $Sn(\eta^5\text{-}C_5H_5)_2$ with MeI has been reported to give the single product $Sn(Me)(\eta^1\text{-}C_5H_5)_2I$; this reaction is thought to proceed *via* a radical pathway, the following scheme having been proposed (equation (4)).[74]

$$\begin{tikzcd}
Sn(\eta^5\text{-}C_5H_5)_2 \arrow[r, "MeI"] & Sn(Me)(\eta^1\text{-}C_5H_5)_2I \arrow[r, shift left, "Sn(\eta^5\text{-}C_5H_5)_2"] & Sn(Me)(\eta^1\text{-}C_5H_5)_3 \arrow[l, shift left] \\
 & & + \\
 & & Sn(\eta^5\text{-}C_5H_5)I \arrow[uul, "Sn(Me)(\eta^1\text{-}C_5H_5)_3"]
\end{tikzcd} \qquad (4)$$

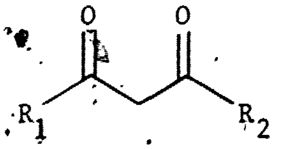
Similarly, $Sn(\eta^5-C_5H_5)_2$ reacts smoothly with an excess of $CH_2I_2$ to give $Sn(CH_2I)(\eta^1-C_5H_5)_2I$ [74] as the main product, while reaction using an excess of $Sn(\eta^5-C_5H_5)_2$ gives a series of products including $Sn(\eta^1-C_5H_5)_2(I)CH_2Sn(\eta^1-C_5H_5)_2I$, $Sn(\eta^1-C_5H_5)_3CH_2Sn(\eta^1-C_5H_5)_2I$ and $Sn(\eta^5-C_5H_5)I$.[74]

The presence of a non-bonding electron pair on the germanium atom allows compound 5.1 to function as a Lewis base; accordingly it reacts rapidly with boron trifluoride etherate at room-temperature to give the viscous red oil 5.2. Compound 5.2 is significantly more air-sensitive that 5.1, however $^1H$ and $^{19}F$ NMR spectral data were obtained (Table 5.3) and are consistent with the formulation $Ge(\eta^5-C_5H_4CH_3)_2BF_3$.

$Sn(\eta^5-C_5H_4CH_3)_2$ has been shown[32,33,34] to react with a wide variety of protic reagents to give the corresponding tin(II) derivative in high yield (*e.g.* equations (5) - (8)).



By contrast, although $Ge(\eta^1-C_5H_4CH_3)_2$, (5.1) did yield white solid precipitates with alcohols and azoles, analytical data supporting formulation as $GeY_2$ derivatives could not be obtained and the insolubility of these materials precluded convenient identification. Surprisingly no reaction was observed between $Ge(\eta^5\text{-}C_5H_4CH_3)_2$ and the β-diketones shown in 6 even after refluxing in toluene solution for several hours, the β-diketone being recoverable to *ca.* 90%.



6

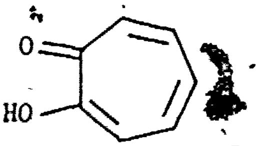
| $R_1$ | Me | Me | Ph | Me | $CF_3$ | $Bu^t$ |
|---|---|---|---|---|---|---|
| $R_2$ | Me | Ph | Ph | $CF_3$ | $CF_3$ | $Bu^t$ |

While the known chelated ketoenolate derivatives of Ge(II) were not produced from the reaction of $Ge(\eta^5\text{-}C_5H_4CH_3)_2$ and the corresponding β-diketone, rapid reaction was observed with some phenolic and related compounds capable of bidentate coordination at a germanium(II) center (equation (9)).

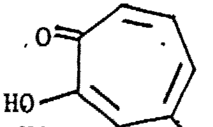
$$Ge(\eta^5\text{-}C_5H_4CH_3)_2 \xrightarrow[-2(C_5H_5CH_3)]{HA} GeA_2 \qquad (9)$$

Compound

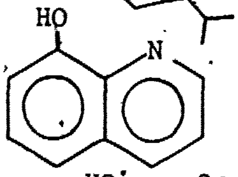
5.3 HA = tropolone (tropH)
(2-hydroxycyclohepta-2,4,6-trienone)



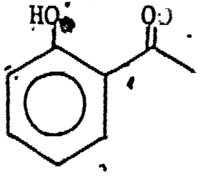
5.4 HA = thujaplicin (thujH)
(2-hydroxy-4-*iso*propylcyclohepta-2,4,6-trienone)



5.5 HA = 8-hydroxyquinoline (oxineH)



5.6 HA = *o*-hydroxyacetophenone (hyapH)



## TABLE 5.4.

Mass spectral data[a] for compounds 5.3 – 5.6.

Ge(trop)$_2$, 5.3

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_7H_5O_2)_2^{+\cdot}$ | 8.3 |
| $Ge(C_7H_5O_2)^+$ | 91.7 |
| $Ge^{+\cdot}$ | 0.0 |

Ge(thuj)$_2$, 5.4

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{10}H_{11}O_2)_2^{+\cdot}$ | 2.7 |
| $Ge(C_{10}H_{11}O_2)^+$ | 84.0 |
| $Ge(C_9H_8O_2)^{+\cdot}$ | 8.3 |
| $Ge(C_7H_5O_2)^+$ | 5.0 |
| $Ge^{+\cdot}$ | 0.0 |

Ge(oxine)$_2$, 5.5

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_9H_6NO)_2^{+\cdot}$ | 6.7 |
| $Ge(C_9H_6NO)^+$ | 93.3 |
| $Ge^{+\cdot}$ | 0.0 |

Ge(hyap)$_2$, 5.6

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_8H_7O_2)_2^{+\cdot}$ | 0.2 |
| $Ge(C_8H_7O_2)^+$ | 99.8 |
| $Ge^{+\cdot}$ | 0.0 |

---

[a] 70eV ionizing voltage; % metal-containing ions, summed within each family resulting from isotope distribution and hydrogen loss.

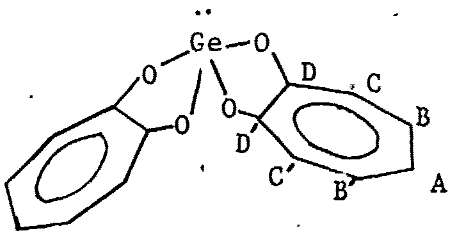
The synthetic procedures used to prepare each of these compounds were similar, involving addition at room-temperature of a toluene solution of the corresponding free hydroxo compound to a stirred toluene solution of Ge($\eta^5$-$C_5H_4CH_3$)$_2$. After *ca.*0.5h a precipitate started to form (see experimental), which gave, after work up, the pure Ge(II) derivative. These compounds are THF and chloroform soluble solids which are sufficiently volatile to allow for characterization by mass spectroscopy (see Table 5.4). Typically the most prominant peak in the mass spectra corresponds to loss of one chelate with the current carried by the molecular ion and $Ge^{+\cdot}$ being small. For the thujaplicinato derivative cleavage of the *iso*propyl group was also observed to give relatively intense germanium-containing ions.

TABLE 5.5.

Infrared carbonyl stretching frequencies for compounds 5.3, 5.5 and 5.6.

| Compound | ν(C=0) |
|---|---|
| Ge(trop)$_2$, 5.3 | 1590(v.s), 1570(m) |
| Ge(thuj)$_2$, 5.4 | 1583(m), 1569(s) |
| Ge(hyap)$_2$, 5.6 | 1580(m), 1635(m) |

The I R spectra of compounds 5.3, 5.4 and 5.6 show a significant reduction in frequency for bands due to ν(C=0) (Table 5.5) when compared to corresponding absorptions for the uncombined organic molecule, consistent with coordination of the oxygen atom of the carbonyl group and hence a four (*pseudo*-five) coordinate germanium atom (*eg.* 7 for Ge(trop)$_2$).



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NMR data obtained for compounds 5.3 - 5.6 are given in Tables 5.6 and 5.7, The $^1$H and $^{13}$C NMR spectra of compounds 5.4 - 5.6 are temperature invariant and confirm the proposed structure for each of the compounds. Surprisingly the $^1$H NMR spectrum of bis(tropolonato)germanium(II) is temperature dependent, the room-temperature spectrum consisting of two sharp lines centered at *ca.* δ7.55 and a multiplet at *ca.* δ7.00 in an intensity ratio of 4:1 respectively, while at lower temperatures the spectrum becomes significantly broadened. Analogous spectral changes have been reported for bis(tropolonato)tin(II), however these were not analyzed in detail.[159]

The $^{13}$C NMR spectra of these compounds are however less complex, each having four signals due to $C^A$, $C^{B,B'}$, $C^{C,C'}$, and $C^{D,D'}$. Further, spectra for both the germanium and tin compounds are temperature invariant, a result which would appear to preclude both inter- and intra-molecular rearrangement. Thus the spectral changes observed in the $^1$H NMR spectrum of both bis(tropolonato) -germanium(II) and -tin(II) most probably result from small changes in the chemical shifts of resonances for the

## TABLE 5.6.

NMR data[a] for compounds 5.3 and 5.4.

$^{1}H$ NMR Data[b]

| R | Compound | $\delta(H^{A,B,B',C,C'})$ | $\delta(C\text{-}\underline{H})$ | $\delta(CH(C\underline{H}_3)_2)$ |
|---|---|---|---|---|
| H | $Ge(trop)_2$ | 6.70-8.00[c] | | |
| Pr | $Ge(thuj)_2$ | 6.70-7.70 | 2.83(septet)[d] | 1.22 (d)[d] |

$^{13}C$ NMR Data

| | | | | | | | Pr | |
|---|---|---|---|---|---|---|---|---|
| R | Compound | $\delta(C^{D,D'})$ | $\delta(C^{C,C'})$ | $\delta(C^{A})$ | $\delta(C^{B})$ | $\delta(C^{B'})$ | $\delta(\underline{C}\text{-H})$ | $\delta(CH(\underline{C}H_3)_2)$ |
| H | $Ge(trop)_2$ | 176.6 | 139.6 | 129.0 | 126.8 | | | |
| Pr | $Ge(thuj)_2$ | 172.9[e] | 120.9, 122.2, 123.6,<br>135.1 | | | 157.8 | 39.6 | 23.6 |

---

[a] Chemical shifts, ppm, measured positive downfield from $SiMe_4$ of $CDCl_3$ solutions.

[b] Measured at 90MHz.

[c] Broad multiplet, not resolved.

[d] $^{3}J(^{1}H-^{1}H)$ = 6.1 Hz.

[e] Signals due to $C^1$ and $C^2$ were not resolved.

five ring protons and their respective coupling constants.

TABLE 5.7.

NMR data[a] for compounds <u>5.5</u> and <u>5.6</u>.

| | $^1$H NMR[b] | | $^{13}$C NMR |
|---|---|---|---|
| Compound | δ(ring-protons) | δ($CH_3$) | δ(ring carbons) |
| <u>5.5</u> | 8.81[c], 8.30[c] | | 113.6, 113.9, 121.6,<br>129.9, 137.9, 142.9 |
| <u>5.6</u> | 7.10[c] | 2,57 | n.o.[d] |

---

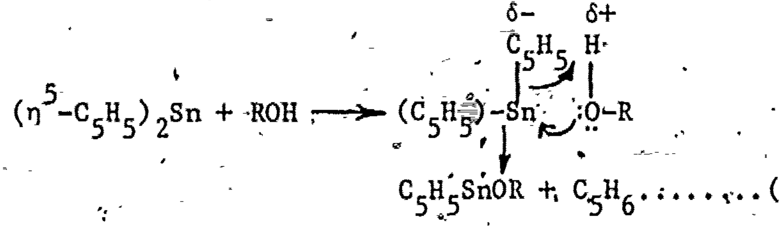
[a] Chemical shifts, ppm measured positive downfield from $SiMe_4$ on $CDCl_3$ solutions.

[b] Measured at 90MHz.

[c] Center of multiplet.

[d] Not observed.

Noltes *et al.*[74] have investigated the reaction of bis-($\eta^5$-cyclopentadienyl)tin(II) with protic reagents and concluded that the reaction rate is essentially independent of the $pK_a$ of the proton source, but depends on the ability of the atom to which the acidic hydrogen is bound to donate an electron pair to the tin center. Thus while reactions with ethanol ($pK_a$ = *ca.* 18) and phenol ($pK_a$ = *ca.* 10) are both fast, reaction with HCN ($pK_a$ = *ca.* 9.5) is slow and no reaction takes



$$(\eta^5\text{-}C_5H_5)_2Sn + ROH \longrightarrow (C_5H_5)\text{-}\overset{\overset{\delta-}{C_5H_5}}{Sn}\cdots\overset{\overset{\delta+}{H}}{\ddot{O}}\text{-}R \longrightarrow C_5H_5SnOR + C_5H_6 \quad \ldots\ldots\ldots(10)$$

place with malononitrile (NCCH$_2$CN; pK$_a$ = *ca.* 11). A mechanism for the reaction of Sn($\eta^5$-C$_5$H$_5$)$_2$ with alcohols (equation (10)), was also proposed. Thus nucleophilic attack by the oxygen atom at the tin center results in weakening of the tin-cyclopentadienyl linkage causing a significant negative charge to develop on the ring, while simultaneously the hydrogen atom on the oxygen becomes more acidic facilitating fast reaction.

Based on this mechanism, the difference in reactivity of bis($\eta^5$-methylcyclopentadienyl)-tin(II) and -germanium(II) with 1,3-diketoenolates of type <u>6</u> can be interpreted in terms of either the germylene being a poorer electron acceptor (*i.e.* the germanium atom to function as a Lewis acid) than the tin compound, or the significantly higher germanium-carbon bond strength relative to that for the corresponding tin-carbon bond may make the activation energy for cleavage of the germanium-carbon linkage prohibitively high.

## B.2. Synthesis and Properties of 1,3-Diketonato and Related Derivatives of Germanium(II).

The first ketoenolato derivatives of bivalent germanium were reported[30] by Rodgers and Stobart in 1976. These compounds were prepared in *ca.* 50% yield from reaction of GeI$_2$ or CsGeCl$_3$ with the sodium salt of the corresponding $\beta$-diketone. Related tin compounds have been synthesized by a variety of methods: for example Sn(acac)$_2$ has been prepared by (i) reaction of Na(acac) with SnCl$_2$[29], (ii) reaction of acacH with Sn($\eta^5$-C$_5$H$_4$CH$_3$)$_2$[29,34] and

(iii) refluxing acacH with $Sn(OMe)_2$.[34]

Alternatively we have found that reaction of $CsGeCl_3$ or $SnCl_2$ with two equivalents of Hacac and $NEt_3$ at room-temperature (see experimental) gives a convenient, high yield (*ca.*90%) route to $Ge(acac)_2$, 5.7, and $Sn(acac)_2$. Analogously, stirring solutions of $GeI_2$ with dipivaloylmethane or o-hydroxyacetophenone and $NEt_3$ at room-temperature for *ca.*18h gives good yields of the germanium(II) containing products bis(dipivaloylmethanato)germanium(II), 5.8 and bis(o-acetylphenoxy)germanium(II), 5.6 respectively.

Reactions at room-temperature of toluene solution of either benzoylacetone or dibenzoylmethane with germanium diiodide and triethylamine gave a mixture of 1,3-diketone, (1,3-diketonato)germanium(II) iodide and bis(1,3-diketonato)germanium(II), with the corresponding reactions using cesium trichlorogerminate also yielding a similar mixture of products. Attempts to improve the selectivity by varying the solvent, temperature and time of reaction were not successful, nor were attempts to purify the products by recrystallization or column chromatography. Reaction of $CsGeCl_3$ with one equivalent of β-diketone and a two-fold excess of $NEt_3$ does however give the pure (1,3-diketonato)germanium(II) chloride, [(benzoylacetonato)germanium chloride (5.9) and (dibenzoylmethanato)-germanium chloride (5.10)] in *ca.*90% yield. The subsequent reaction of the (1,3-diketonato)germanium(II) chloride with exactly one equivalent of the corresponding β-diketone and triethylamine gives the pure bis(1,3-diketonato)germanium(II) derivatives bis(benzoyl-

TABLE 5.8.

Mass spectral data[a] for compounds 5.7 - 5.12.

$Ge(acac)_2$, 5.7

| Assignment | Ion Abundance |
|---|---|
| $Ge(C_5H_7O_2)_2^{+\cdot}$ | 12.2 |
| $Ge(C_7H_{10}O_4)^{+\cdot}$ | 1.3 |
| $Ge(C_5H_7O_2)^+$ | 82.5 |
| $Ge(C_2H_3O_2)^+$ | 4.0 |
| $Ge^{+\cdot}$ | 0.0 |

$Ge(piv)_2$, 5.8

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{11}H_{19}O_2)_2^{+\cdot}$ | 0.2 |
| $Ge(C_{18}H_{29}O_2)^+$ | 1.8 |
| $Ge(C_{11}H_{19}O_2)^+$ | 94.0 |
| $Ge(C_{10}H_{15}O_2)^+$ | 0.3 |
| $Ge(C_9H_{13}O_2)^+$ | 3.7 |
| $Ge^{+\cdot}$ | 0.0 |

$Ge(benzac)_2$, 5.11

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{10}H_9O_2)_2^{+\cdot}$ | 1.2 |
| $Ge(C_{10}H_9O_2)^+$ | 98.8 |

$Ge(dibenz)_2$, 5.12

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{15}H_{11}O_2)_2^{+\cdot}$ | 2.3 |
| $Ge(C_{15}H_{11}O_2)^+$ | 97.2 |

Ge(benzac)Cl, 5.9

| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{10}H_9O_2)Cl^{+\cdot}$ | 1.3 |
| $Ge(C_{10}H_9O_2)^+$ | 93.1 |
| $GeCl^+$ | 5.6 |

Ge(dibenz)Cl, 5.10

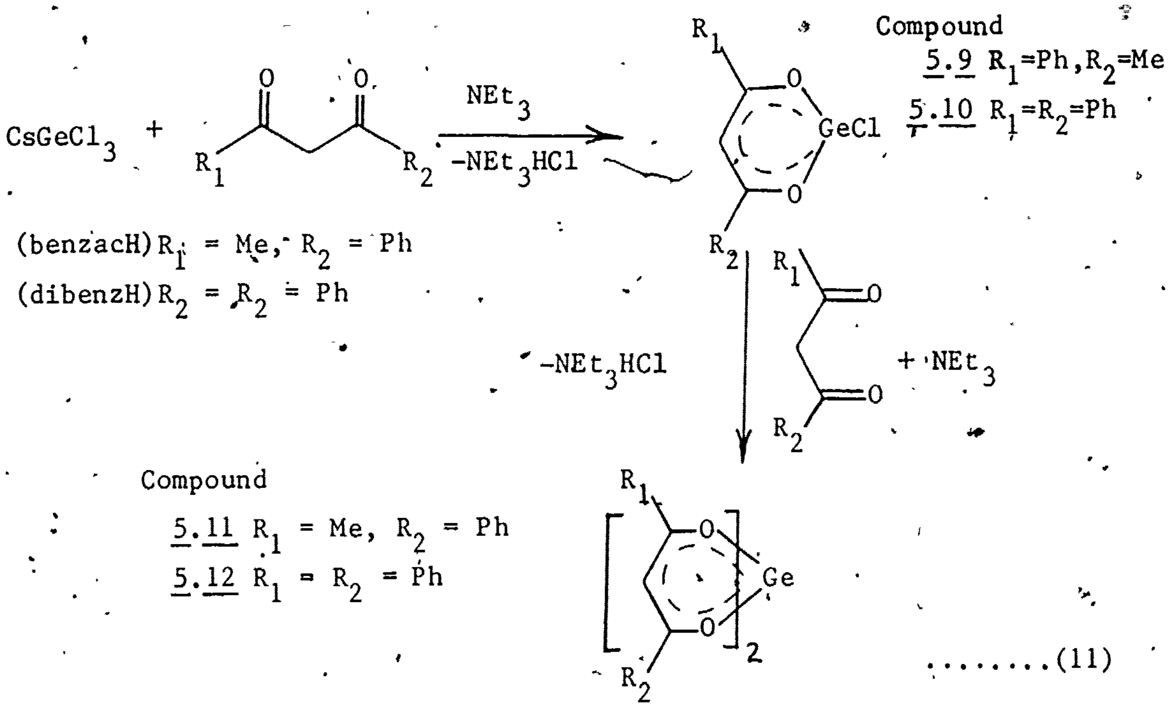
| Assignment | Relative Intensity |
|---|---|
| $Ge(C_{15}H_{11}O_2)Cl^{+\cdot}$ | 2.1 |
| $Ge(C_{15}H_{11}O_2)^+$ | 94.7 |
| $GeCl^+$ | 3.2 |

---

[a] 70eV ionizing voltage.

[b] % metal-containing ions, summed within each family resulting from isotope distribution and hydrogen loss.

acetonato)germanium(II), 5.11 and bis(dibenzoylmethanato)germanium(II), 5.12 in *ca* 95% yield (equation (11)).

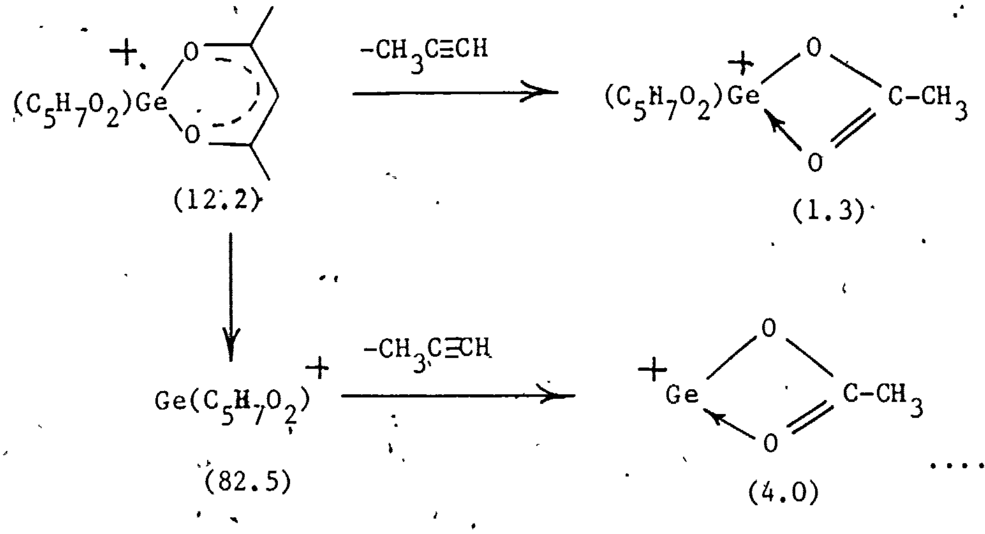


........(11)

Preparation of related germanium(II) derivatives of 1,1,1-trifluoroacetylacetone or 1,1,1,5,5,5-hexafluoroacetylacetone was not attempted by this method since these β-diketones are known[160] to form relatively stable complexes with bases such as triethylamine.

Compounds 5.3, 5.4 and 5.5 are apparently air-stable although contact with either air or water was avoided whenever possible, while compounds 5.6 - 5.12 are both air- and water-sensitive. Some physical and analytical data for compounds 5.6 - 5.12 are given in Table 5.1.

The mass spectral data for compounds 5.7 - 5.12 are tabulated in Table 5.8. These data are similar to those reported for the corresponding tin derivatives,[34,159] showing a weak molecular ion, with the most abundant metal containing ion corresponding to the loss of one chelate. Fragmentation within the organic portion of the molecule was observed for some compounds, thus bis(acetylacetonato)germanium(II) formally loses the acetylene $CH_3C\equiv CH$ (equation (12)),



....(12)

while bis(dipivaloylmethanato)germanium(II) has low abundance ions resulting from loss of a methyl radical and complete loss of a *tert*butyl group.

The I R spectra of compounds <u>5.7</u> - <u>5.12</u> (Table 5. 9) show a significant reduction in ν(C=O) compared

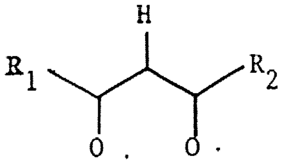
TABLE 5.9.

Infrared carbonyl stretching frequencies for compounds <u>5.7</u> - <u>5.12</u>.

| Compound | ν(C=O) |
|---|---|
| Ge(acac)$_2$, <u>5.7</u> | 1580(s), 1540(m) |
| Ge(piv)$_2$, <u>5.8</u> | 1570(s), 1539(m) |
| Ge(benzac)Cl, <u>5.9</u> | 1592(m), 1525(s) |
| Ge(dibenz) Cl, <u>5.10</u> | 1585(w), 1520(s) |
| Ge(benzac)$_2$, <u>5.11</u> | 1590(m), 1530(vs) |
| Ge(dibenz)$_2$, <u>5.12</u> | 1585(w), 1523(s) |

to corresponding absorptions for the free diketone indicative of intramolecular coordination involving the carbonyl oxygen atom. These spectra are also similar to those reported[34,159] for the corresponding tin compounds, consistent with germanium and tin analogues being isostructural.

The $^1$H and $^{13}$C NMR spectral data for compounds 5.7 - 5.12 are tabulated in Tables 5.10 and 5.11 (see also Figure 5.2 ). The results are consistent with both chelating ketoenolate substituents being equivalent (compounds 5.3 - 5.8, 5.11 and 5.12), and further when $R_1 = R_2$ (see 8), $R_1$ and $R_2$ being magnetically equivalent.



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This is good evidence for coordination of the carbonyl group to germanium (*ie.* intramolecular association). ~~For~~ compounds 5.6, 5.11 and 5.12, stepwise replacement of methyl by phenyl groups results in the deshielding of resonances for the methine proton [$\delta$(C<u>H</u>): 5.10 Ge(acac)$_2$, 6.01 Ge(benzac)$_2$, 6.76 Ge(dibenz)$_2$] with corresponding resonances in the $^{13}$C NMR spectrum for the C$^2$ carbons having much smaller shift differences.

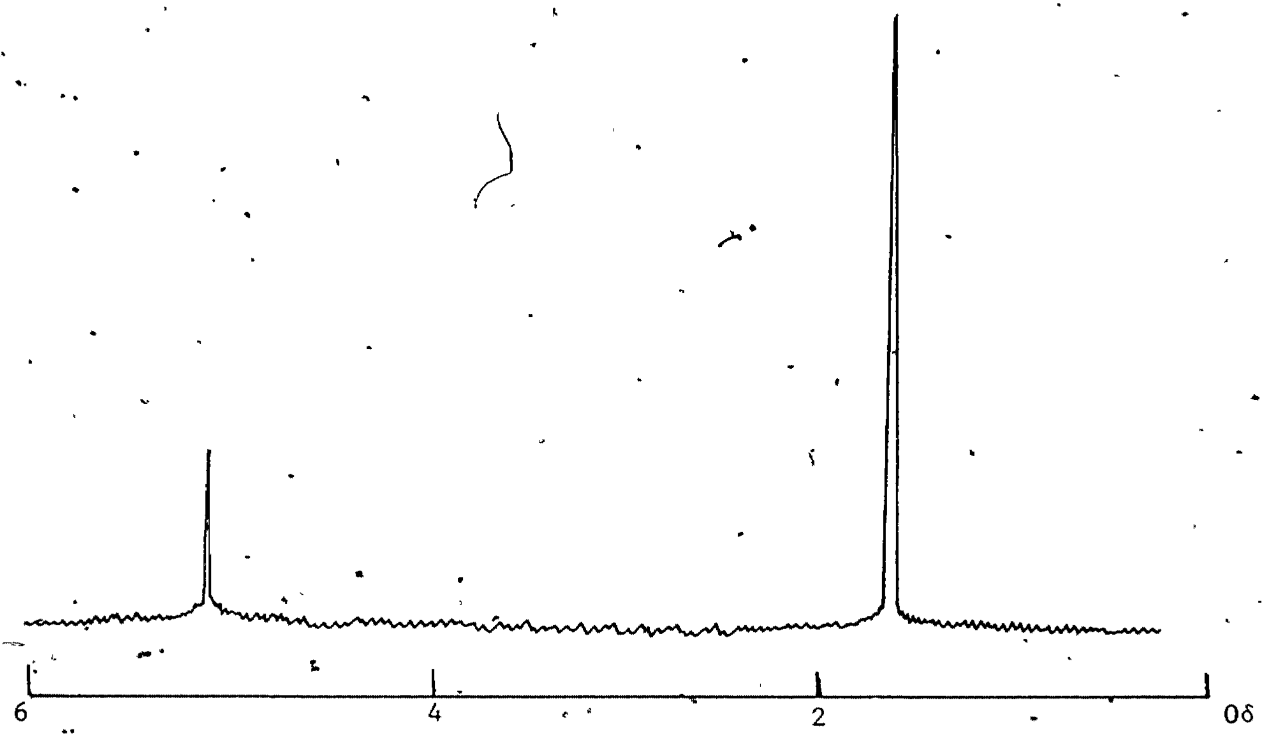


FIGURE 5.2. $^1H$ NMR spectrum of bis(acetylacetonato)germanium(II) in $CDCl_3$ at 27°C.

TABLE 5.10.

$^1$H NMR[a] data for compounds <u>5.7</u> - <u>5.12</u>.

| Compound | | | $R_1$ | $R_2$ | C – H |
|---|---|---|---|---|---|
| $R_1$ | $R_2$ | X | | | |
| Me | Ph | Cl | 2.30 | 7.22-8.07[b] | 6.52 |
| Me | Ph | | 2.08 | 7.08-7.93[b] | 6.01 |
| Ph | Ph | Cl | 7.30-8.21[b] | | 7.18 |
| Ph | Ph | | 7.12-8.10[b] | | 6.76 |
| Me | Me | | | 1.70 | 5.10 |
| t-Bu | t-Bu | | | 1.13 | 5.76 |

---

[a] $CDCl_3$ was used as solvent, TMS as internal reference, chemical shift values in ppm downfield from TMS.

[b] Multiplet.

TABLE 5.11.

$^{13}C$ NMR [a] spectral data for compounds 5.8 - 5.12.

| $R_1$ | $R_2$ | X | $C_1$ | $C_3$ | $C_2$ | $R=CH_3$ | Ph |  |  |  | t-Bu |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | $C_1$ | $C_{22}$ | $C_{33}$ | $C_4$ | $\underline{C}Me_3$ | $C-(\underline{C}H_3)_3$ |
| Me | Ph | Cl | 191.4 | 179.1 | 100.1 | 28.3 | 135.6 | 129.0 | 128.5 | 132.5 |  |  |
| Me | Ph |  | 192.2 | 181.1 | 98.3 | 28.6 | 137.7 | 128.5 | 127.7 | 131.8 |  |  |
| Ph | Ph | Cl | 183.0 |  | 96.9 |  | 136.3 | 129.1 | 128.6 | 134.0 |  |  |
| Ph | Ph |  | 183.7 |  | 95.3 |  | 135.9 | 128.7 | 127.5 | 133.2 |  |  |
| $Bu^{\underline{t}}$ | $Bu^{\underline{t}}$ |  | 201.5 |  | 90.8 |  |  |  |  |  | 41.0 | 27.6 |

---

[a] $CDCl_3$ was used as solvent and internal reference, chemical shift values in ppm downfield from TMS.

## B.3. Synthesis and Structure of Bis(triphenylphosphine)bis[bis(acetylacetonato)germylene]- and Bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene]-platinum(0).

Bis(triphenylphosphine)bis[bis(acetylacetonatogermylene)]platinum(0) (5.13) and bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene)]-platinum(0) (5.14) were prepared in almost quantitative yield from the room-temperature reaction of $Pt(PPh_3)_4$ with two equivalents of bis(acetylacetonato)-germanium(II) and -tin(II) respectively. Reaction of two equivalents of bis(acetylacetonato)tin(II) with $Pt(PPh_3)_2(\pi\text{-}C_2H_4)$ in toluene and subsequent addition of hexane afforded orange crystals of 5.14 suitable for X-ray diffraction. Significantly, no reaction takes place on stirring a toluene solution of $Pt(PPh_3)_4$ and $Sn(\eta^5\text{-}C_5H_4CH_3)_2$ at room-temperature over 6h. Related reactions of other organic germanium(II) and tin(II) derivatives with $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$ are currently underway in these laboratories.

Reaction of the tin derivative 5.14 with an excess (>3 equivalents) of $I_2$ results in cleavage of the tin-platinum linkage and formation of the corresponding tin(IV) and platinum(II) diiodides. A similar cleavage of the platinum-tin bond was observed in reactions of 5.14 with anhydrous HCl or MeI.

The IR spectra of compounds 5.13 and 5.14 (Table 5.12) both show bands near $1600cm^{-1}$ due to $\nu(C=O)$ in almost identical positions to those reported for the corresponding free germanium(II) (Table 5.9 ) and tin(II) derivatives. This indicates that coordination onto the Pt center does not affect the intramolecular coordination of the ketoenolate at the Ge or Sn center and thus these centers are probably five coordinate.

TABLE 5.12.

Infrared carbonyl stretching frequencies for compounds <u>5.13</u> and <u>5.14</u>.

| Compound | ν(C=O) |
|---|---|
| $Pt(PPh_3)_2[Sn(acac)_2]_2$ | 1575, 1530 |
| $Pt(PPh_3)_2[Ge(acac)_2]_2$ | 1570, 1532 |

The $^1H$ NMR spectra (Table.5.13) contain signals centered at *ca.* δ7.5 (15,m), 4,2 (2,s) and 1.3(12,s) attributable to $C_6\underline{H}_5$, $C\underline{H}$, and $C\underline{H}_3$ protons respectively, consistent with the presence of two $M(acac)_2$, M = Ge or Sn groups and two triphenylphosphine groups of Pt.

TABLE 5.13.

NMR data[a] for compounds <u>5.13</u> and <u>5.14</u>.

$^1H$ NMR[b]

| Compound | $C\underline{H}_3$ | $C\underline{H}$ | $C_6\underline{H}_5$ |
|---|---|---|---|
| <u>5.13</u> | 1.30 | 4.26 | 7.52[c] |
| <u>5.14</u> | 1.31 | 4.23 | 7.48[c] |

$^{31}P$ NMR[d]

| Compound | $^{31}P$ | $^1J(Pt\text{-}P)$ (Hz) | $^2J(^{117,119}Sn\text{-}P)$ (Hz) |
|---|---|---|---|
| <u>5.13</u> | 110.1 | 5252 | 445 |
| <u>5.14</u> | 116.0 | n.o.[e] | |

---

[a] All spectra recorded in $C_6D_6$. [b] ppm downfield from TMS. [c] Broad multiplet.
[d] Relative to TMP. [e] Not observed.

## TABLE 5.14.

Structural data for some platinum(0) complexes.

| Compound | (Pt – P) Å | (P – Pt – P)° | Reference |
|---|---|---|---|
| $Pt(PEtPh_2)_2(CO)_2$ | 2.360 (4) | 97.6 (2) | 161 |
| $Pt(PPh_3)_3(CO)$ | 2.340 (2) | 111.4 (1) | 162 |
| $Pt(PPh_3)_3SO_2$ | 2.348 (3) | 118.4 | 163,164 |
| (5.14) | 2.261 (4) | 120.1 (2) | this work |
| $Pt(PPh_3)_3$ | 2.265 | 122 | 165 |
| $Pt(PBu^t_2Ph)_2$ | 2.252 | 177 | 166 |

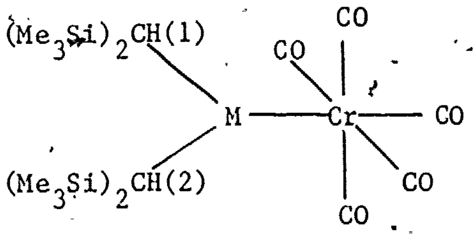
$^{31}P$ NMR data (Table 5.13) for the platinum compounds 5.13 and 5.14 consist of singlet resonances at 110.1 and 116.0 with that for the tin compound having satellite lines due to coupling to both $^{195}Pt(I = \frac{1}{2})$, ($^{1}J$ = 5252Hz) and $^{117,119}Sn(I = \frac{1}{2})$, ($^{2}J_{av}$ = 445Hz). The large value for $^{1}J(Pt-P)$ is indicative of a platinum(0) compound, being in fact somewhat larger than those reported for other zerovalent platinum complexes including $Pt(PPh_3)_n$ (n =2,3 or 4).

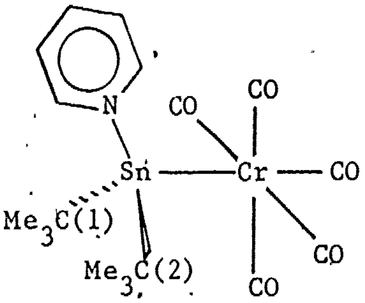
The crystal and molecular structure of bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene]platinum(0), 5.14 was determined by Ms. E.T. Brennan and Professor T.S. Cameron at Dalhousie University using X-ray crystallography. The molecular structure of compound 5.14 is shown in Figure 5.3. The two $PPh_3$ and the two $Sn(acac)_2$ units are disposed about the platinum center in a distorted tetrahedral arrangement with a wide (P-Pt-P) angle (120.1°), this despite the presence of the bulky tin containing ligands.

The Pt-P bond distance, 2.261(4) Å, is close to Pt-P bond distances which have been determined for $Pt(PPh_3)_3$[165] and $Pt(PBu^t_2Ph)_2$[166] (Table 5.14); however it is significantly shorter than those observed for some four-coordinate platinum(0) compounds. This is consistent with poor π-acceptor capability of the tin ligands resulting in enhanced π-donation of P. The short Pt-P bond lengths in $Pt(PPh_3)_3$ and $Pt(PBu^t_2Ph)_2$ have however been rationilized in terms of changes in hybridization at Pt rather than π-effects.[166]

Both tin centers have a distorted trigonal bipyramidal geometry with the platinum occupying one position in the equatorial plane (Figure 5. 4). This geometry is similar to that reported[61] for the uncomplexed Sn(benzac)$_2$* with values for corresponding bond distances and bond angles being almost identical.

Several structurally unrelated transition metal compounds in which a germanium(II) or tin(II) center functions as a two electron donor to the metal have previously been characterized. Thus the crystal structures of Cr(CO)$_5$M[CH(SiMe$_3$)$_2$]$_2$, M = Ge and Sn,[56,57] contain three coordinate germanium and tin atoms respectively (9), with the atoms C(1), C(2), M and Cr lying in approximately the same plane, a result attributed to back donation from Cr to M. Interestingly, the crystal structure of Cr(CO)$_5$Sn(Bu$^t$)$_2$(pyridine) (10)[58] has the tin atom out of the C(1), C(2), Cr plane reflecting a decrease in back donation from Cr to Sn upon incorporation of the pyridine molecule.





M = Ge, Sn

9

10

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* Benzac = benzoylacetonato.

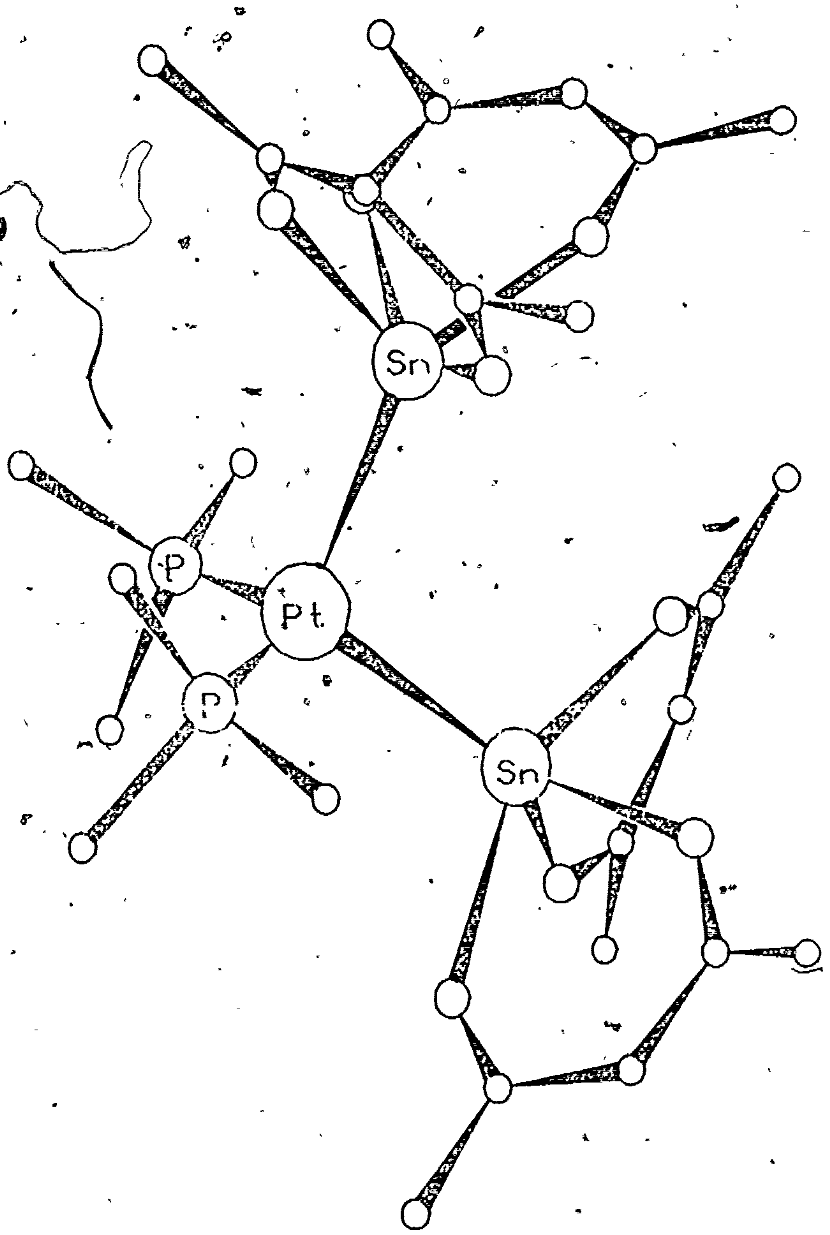

FIGURE 5.3. The molecular structure of 5.14,

bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene]platinum(0)

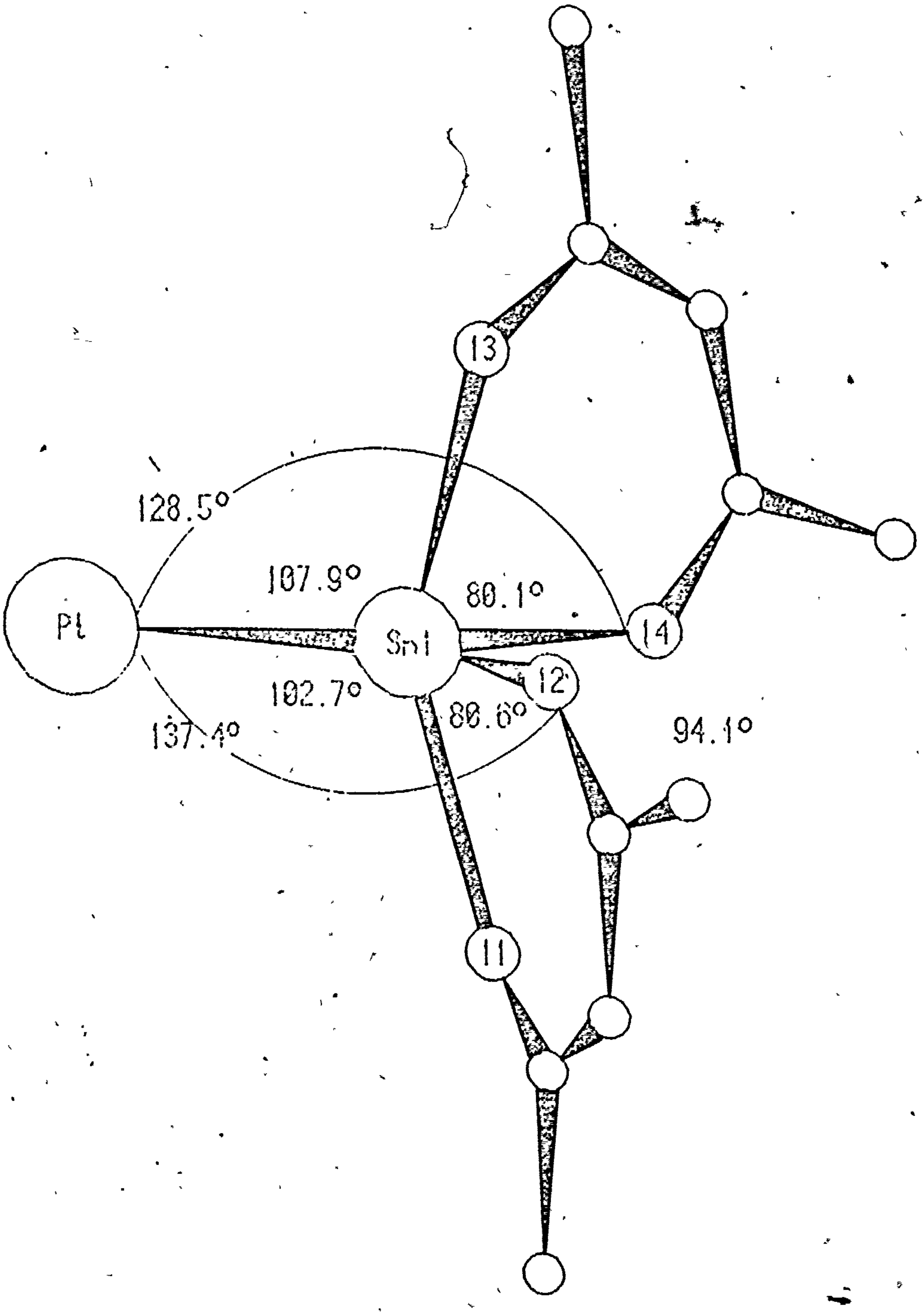

FIGURE 5.4. The local geometry about tin in 5.14, bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene]platinum(0).

## C. EXPERIMENTAL.

### Bis(η$^5$-methylcyclopentadienyl)germanium(II), 5.1.

A solution of $GeI_2$ (1.5g, 4.60mmol) in toluene (50mL) was added to a stirred slurry of $KC_5H_4CH_3$ (1.19g, 10mmol) in toluene (50mL) held at *ca.*5°C. The temperature of the reaction mixture was maintained at *ca.*5°C and stirring continued for 3h, and the solvent was then removed *in vacuo*. Addition of hexane (50mL) followed by filtration and concentration of the filtrate gave the product as a light yellow oil (0.92g, 3.91mmol, 85%). *Anal.* Calcd. for $C_{12}H_{14}Ge$ (calc. C 61.92, H 6.09; found C62.45, H5.92%).

### Reaction of bis(η$^5$-methylcyclopentadienyl)germanium(II) with methyl iodide.

To a stirring solution of $Ge(C_5H_4CH_3)_2$ (0.116g, 0.50mmol) in toluene ([illegible]mL) was added dropwise MeI (0.071g, 0.50mmol) in toluene (10mL) and stirring continued for a further 1h. Solvent was then removed by pumping *in vacuo* to give a viscous yellow oil (1.8g).

### Bis(methylcyclopentadienyl)(borontrifluoride)germanium(II), 5.2.

$BF_3.Et_2O$ (0.15g, 1.0mmol) in toluene (20mL) was added dropwise to a stirred solution of $Ge(C_5H_4CH_3)_2$(0.20g, 0.86mmol) in toluene (20mL). After *ca.*5 min a yellow oil separated at the bottom of the flask. The upper layer was syringed off and the yellow oil washed with hexane (3 x 20mL) to leave the yellow viscous air-sensitive product, 5.2 (0.23g, 0.78mmol, 91%).

### Attempted reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with benzoylacetone.

A solution of benzoylacetone (0.174g, 1.00mmol) in toluene (40mL) was added to a stirring solution of $Ge(C_5H_4CH_3)_2$ (0.116g, 0.50mmol) in toluene (20mL) and the solution refluxed for 6h. Removal of solvent *in vacuo* and addition of hexane (20mL) precipitated a white solid (0.16g) identified as benzoylacetone by $^1H$ NMR, I.R. and M.S.

### Reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with tropolone: synthesis of bis(tropolonato)germanium(II).

A solution of tropolone(1.21g, 10mmol) in $Et_2O$ (25mL) was added to a stirring solution of $Ge(C_5H_4CH_3)_2$ (1.16g, 5.0mmol) in hexane (20mL). The pale yellow solution slowly darkened, and after 0.5h, a yellow precipitate started to form. The reaction mixture was stirred for a further 1h, the precipitate allowed to settle, and the supernatant removed. The remaining solid was washed with $Et_2O$ (2 x 1[illegible]L), and dried *in vacuo* giving the product (1.23g, 4.2mmol, 84%) as a bright yellow solid.
*Anal*. Calcd. for $C_{14}H_{10}GeO_4$ (calc. C53.42, H3.18; found C52.75, H3.37%).

### Reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with 8-hydroxyquinoline(oxineH): synthesis of bis(oxine)germanium(II).

A solution of 8-hydroxyquinoline (1.45g, 10.0mmol) in $Et_2O$ (15mL) was added to a stirring solution of $Ge(C_5H_4CH_3)_2$ (1.16g, 5.0mmol) in hexane. The solution darkened, and after 1h a yellow precipitate started to form. The mixture was stirred for a further 3h, the precipitate allowed to settle and the supernatant removed. The remaining solid was washed with $Et_2O$ (2 x 10mL) and dried *in vacuo* giving the product (1.73g, 4.8mmol, 96%) as a yellow solid. *Anal.* for $C_{18}H_{12}GeN_2O_2$ (calc. C59.92, H3.35; found C60.26, H3.72%).

### Reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with o-hydroxyacetophenone (hyapH): synthesis of bis(hyap)germanium(II).

A solution of o-hydroxyacetophenone (1.36g, 10.0mmol) in hexane (25mL) was added to $Ge(C_5H_4CH_3)_2$, (1.16g 5.0mmol) in hexane (3 x 30mL) and dried *in vacuo* giving the product (1.25g, 3.65mmol, 73%) as a white solid. *Anal.* for $C_{16}H_{14}GeO_4$ (calc. C56.05, H4.12; found C56.56, H4.04%).

### Reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with methanol.

A solution of MeOH (0.064g, 2.0mmol) in toluene (20mL) was added dropwise to a stirring solution of $Ge(C_5H_4CH_3)_2$ (0.28g, 1.0mmol) in toluene, giving an immediate white precipitate. The solid was washed with toluene (3 x 25mL) to leave a white solid (0.3g). Similar reactions were observed on mixing toluene solutions of $Ge(C_5H_4CH_3)_2$ with EtOH and PhOH.

### Reaction of bis($\eta^5$-methylcyclopentadienyl)germanium(II) with pyrazole.

Pyrazole (0.14g, 2.0mmol) in toluene (30mL) was added dropwise to a stirring solution of $Ge(C_5H_4CH_3)_2$ (0.23g, 1.0mmol). After 3h the light yellow precipitate which had formed was allowed to settle and was washed with toluene (3 x 25mL) to give a light yellow solid (0.52g). Similar reactions were observed on mixing toluene solutions of Ge($C_5H_4CH_3$)$_2$ with 1,2,4-triazole and pyrrole.

Synthesis of bis(acetylacetonato)germanium(II).

$NEt_3$(2.02g, 2.78mL, 20.0mmol) in hexane (20mL) was added dropwise to a stirred mixture of $CsGeCl_3$ (3.12g, 10.0mmol) and acetylacetone (2.00g, 20mmol) in hexane (30mL). The mixture was stirred for 24h, then filtered, and the filtrate concentrated *in vacuo* giving a light yellow oil. Sublimation *in vacuo* onto a water cooled probe, maintaining the temperature of the sample at *ca.* 20°C, gave the pure product as a light yellow liquid (5.13g, 9.0mmol, 90%). *Anal.* Calcd. for $C_{10}H_{14}GeO_4$ (calc. C44.35, H5.21; found C43.79, H5.49%).

Synthesis of bis(dipivaloylmethanato)germanium(II).

$NMe_3$ (1.01g, 1.39mL, 10.0mmol) in hexane (20mL) was added dropwise to a stirred mixture of $CsGeCl_3$ (3.12g, 10.0mmol) and dipivaloylmethane (3.68g, 4.18mL, 20.0mmol) in hexane (30mL). The mixture was stirred for a further 18h, then filtered, and the resulting filtrate concentrated *in vacuo* giving a light yellow oil. Sublimation *in vacuo* at 110°C onto a -78°C (dry ice/acetone) probe followed by recrystallization from hexane at -30°C gave the pure product as a white crystalline solid (3.8g, 8.6mmol, 86%). *Anal.* calcd. for $C_{22}H_{38}GeO_4$ (calc. C60.17, H8.72; found C59.76, H8.94%).

Attempted synthesis of bis(benzoylacetonato)germanium(II).

$NEt_3$ (1.01g, 1.39mL,10.0mmol) in toluene (20mL) was added dropwise to a stirred mixture of $CsGeCl_3$ (1.56g,5.0mmol) and benzoylacetone (1.62g, 10mmol) in toluene (50mL). The mixture was stirred for 24h, then filtered, and the filtrate concentrated *in vacuo* giving a yellow oil. Dropwise addition of hexane (25mL) yielded a yellow solid which was washed with hexane (3 x 20mL) and dried *in vacuo* . The resulting yellow solid (1.9g) was shown by $^1$H NMR, IR and M.S. to be a mixture of three compounds, benzoylacetone, (benzoylacetonato)germanium(II)chloride and bis(benzoylacetonato)germanium(II).

Synthesis of (benzoylacetonato)germanium(II) chloride.

$NEt_3$ (1.09g, 1.39mL,10mmol) in toluene (20mL) was added dropwise to a stirred mixture of $CsGeCl_3$ (3.12g, 10mmol) and benzoylacetone (1.64g, 10mmol) in toluene (50mL). The mixture was stirred for 24h, then filtered, and the filtrate concentrated *in vacuo* giving a yellow solid which was washed with hexane (3 x 20mL) to give the pure product (2.27g, 7.5mmol, 75%). *Anal.* Calcd. for $C_{10}H_9ClGeO_2$ (cacl. C39.72, H2.97; found C38.11, H3.39%).

Synthesis of bis(benzoylacetonato)germanium(II).

$NEt_3$ (0.25g, 0.35mL, 2.5mmol) in toluene (20mL) was added dropwise to a stirred mixture of (benzoylacetonato)germanium chloride (0.76g, 2.5mmol) and benzoylacetone (0.41g, 2.5mmol) in toluene (50mL). The mixture was stirred for 24h, then filtered, and the filtrate concentrated *in vacuo* giving a bright yellow solid which was washed with hexane (3 x 20mL) to give the pure product (0.97g, 2.45mmol, 98%). *Anal.* calcd for $C_{20}H_{18}GeO_4$ (calc. C60.82, H 4.59; found C60.45, H4.79%). Exactly analogous reactions to the two described above using dibenzoylmethane in place of benzoylacetone gave pure (dibenzoylmethanato)germanium(II) chloride and bis(dibenzoylmethanato)germanium(II).

Synthesis of bis(triphenylphosphine)bis[bis(acetylacetonato)stannylene]platinum(0).

A solution of $Sn(acac)_2$ (0.105g, 0.33mmol) in toluene (15mL) was added dropwise to a stirred solution of $Pt(PPh_3)_4$ (0.20g, 0.16mmol) in toluene (25mL). The mixture was stirred for a further 3h, the volume reduced to *ca.* 5mL by pumping *in vacuo* and hexane (30mL) added. The resulting yellow solid was washed with hexane (3 x 30mL) and dried by pumping *in vacuo* to give the pure complex as a bright yellow solid (0.20g, 0.15mmol, 94%).

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Cyclopentadienyl and Related Derivatives of Germanium and Tin

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January, 14th, 1982
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