

COMPOUNDS CONTAINING
TIN - TRANSITION METAL BONDS

A Thesis presented for the
Degree of Doctor of Philosophy
in the
Faculty of Science

by

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University of Leicester
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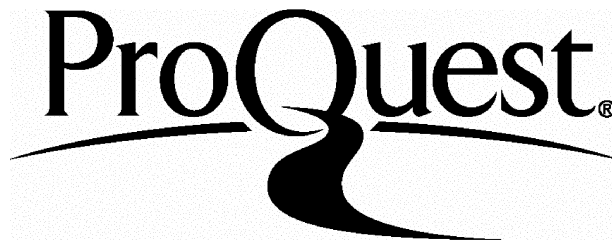
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** The author*

S T A T E M E N T

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1966 and September 1969. The work has not been presented and is not being concurrently presented for any other degree.

J. N. Crossley

September 1969

A C K N O W L E D G E M E N T S

I extend my sincere thanks to Dr. R.D.W. Kemmitt for his invaluable encouragement and advice in the supervision of this work, and to Dr. D.M. Adams for helpful discussions on vibrational spectroscopy.

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S U M M A R Y

The first chapter contains a review of compounds with tin-transition metal bonds, with the emphasis on recent results.

Some insertion reactions of stannous halides with compounds containing metal-metal and metal-halogen bonds have been investigated and found to produce compounds with metal-tin bonds. Many of the products from these reactions have not been previously reported.

The low-frequency infrared and Raman spectra of the trinuclear compounds $[\text{Co}(\text{CO})_4]_2\text{SnX}_2$, $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnX}_2$ and $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been obtained and assigned. The symmetric tin-metal stretching modes were found to be intense in the Raman spectra, and the antisymmetric modes to be strong in the infrared spectra.

The nature of the species present in an ethanolic solution of rhodium(III) chloride and stannous chloride has been investigated by Raman spectroscopy, and the reactions of this solution with a number of unsaturated organic compounds have been studied. The reaction of the rhodium(III)-tin(II)-chloride solution with 1,3-butadiene gives a product containing both co-ordinated butadiene and a rhodium-tin bond.

The synthesis of tin(II)-metal bonded complexes of

empirical formula $(L_nM)_2Sn$ has been attempted, but without success. The reactions of stannous chloride with a variety of transition metal carbonyl anions have been found to give tin(IV) compounds of the type $(L_nM)_2SnCl_2$ and $(L_nM)_3SnCl$.

To Kathleen with love.

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C H A P T E R 1

A Review of Compounds Containing

Tin - Transition Metal Bonds

The existence of a metal-metal interaction in, for example, the mercury(I) halides has been recognised for many years but it is only within the last two decades that the general importance of metal-metal bonding in transition metal chemistry has been established⁽¹⁾⁽²⁾⁽³⁾. The earlier work in this field was concerned mainly with bonding between two or more transition metals⁽¹⁾⁽²⁾⁽⁴⁾, but more recently there has been renewed interest in bonding between transition metals and main-group metals⁽⁵⁾. In the latter type of compound Group IVB metals seem to hold a unique position in terms of the number and variety of known compounds in which they are bonded to transition metals⁽⁶⁾, and, within this Group, tin is the element which shows the greatest ability to form such bonds.

1.1 Compound Types

The large and ever-increasing number of compounds with tin-transition metal bonds requires that some attempt be made to rationalise them by a system of classification into a number of types of compound. This will clarify the present position and also serve as a guide for future developments.

The general chemistry of tin is governed by its ability to exist with comparable ease in both the Sn(II) and Sn(IV) oxidation states⁽⁷⁾, and it is possible to divide the transition metal complexes of tin into those containing tin in a divalent state and those containing tin in a tetravalent state. Further subdivision of these two main types is then possible:-

A. Tetravalent Compounds

- i) Monosubstituted complexes R_3SnML_n
- ii) Disubstituted complexes $R_2Sn[ML_n]_2$
- iii) Trisubstituted complexes $RSn[ML_n]_3$
- iv) Tetrasubstituted complexes $Sn[ML_n]_4$

(R represents any monovalent group and ML_n represents a co-ordinated transition metal in which L may be more than one type of ligand.)

B. Divalent Compounds Containing $SnCl_2$

- i) Anionic complexes
- ii) Carbonyl and hydride complexes
- iii) Complexes with Group V ligands
- iv) Olefin complexes

A. Tetravalent Compounds

Simple covalent compounds of tin are well known in which the tin exists in the tetravalent state expected from its electronic configuration $[\text{Kr}]4d^{10}5s^25p^2$. In valence bond terms, typical SnX_4 compounds have four equivalent sp^3 -hybridised covalent bonds which give rise to a tetrahedral environment around the central atom and X-ray structure determinations have shown that this tetrahedral environment of tin(IV) is retained in its transition metal complexes, which may therefore be regarded as normal tetravalent compounds. (See section 1.3.1).

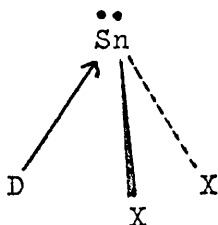
Tetravalent tin is the only Group IV element known to form stable compounds covering the complete range of compound types from R_3SnML_n to $\text{Sn}[\text{ML}_n]_4$. The mono- and di-substituted compounds are at present more numerous than the tri- and tetra-substituted ones, but this probably reflects the smaller amount of work done on the synthesis of the higher substituted compounds rather than any inherent lack of stability of such species.

B. Divalent Compounds

Simple divalent compounds of tin contain the so called 'inert pair' of valency electrons and the expected influence of these electrons on the stereochemistry and structure of tin(II) compounds has been confirmed. Thus an electron diffraction study on stannous halides⁽⁸⁾ in the gaseous phase has shown

that they have an angular structure which can be described in terms of sp^2 hybridisation. Such a description requires the presence of an empty p orbital on the tin atom, and so the formation of compounds of the type SnX_2Y would be expected, where Y is a species capable of acting as an electron donor towards the empty orbital on the tin atom. Addition compounds of tin (II) halides are now known⁽⁹⁾. Moreover the solubility of tin (II) compounds in oxygen-containing organic solvents may be attributed to the formation of solvent adducts.

The steric influence of the non-bonding electron pair in tin (II) compounds and the acceptor properties of the tin atom have been demonstrated in a number of crystal structure determinations⁽⁹⁾⁽¹⁰⁾⁽¹¹⁾. The basic structural unit in the solid state is the pyramidal structure:-



This may be regarded as a distorted tetrahedron based on sp^3 hybridisation of tin with the non-bonding electron pair occupying one directed hybrid orbital, and the donor species, such as halogen, oxygen or sulphur, providing the electron pair for another such orbital.

Halide species of the type SnX_3^- are known for all

halogens, as salts in the solid state and as the predominant species in solutions containing an excess of halide ion. The retention of the pyramidal configuration in solution has been shown by Raman spectroscopy for SnF_3^- (11), SnCl_3^- (12), and SnBr_3^- (12).

The existence of SnX_3^- species as pyramidal structures with a directed lone pair of electrons leads to the expectation that they will exhibit donor properties and so behave as co-ordinating ligands with transition metals. It is also feasible that the vacant d orbitals of tin will be energetically and sterically favourable for overlap with transition metal d orbitals, resulting in some $\text{d}\pi\text{-d}\pi$ back-bonding such as is found with tertiary phosphine, arsine and stibine ligands. These predictions are realised in the behaviour of SnCl_3^- (13)(14) and SnBr_3^- (24) as conventional donor ligands towards transition metals.

i) Anionic Complexes

The reactions of platinum metal salts with stannous chloride in hydrochloric acid to give intensely coloured solutions (15) have been known for many years and have been widely used for the detection and quantitative determination of the platinum metals, but only recently has the nature of the species present in these solutions been established.

Two species are present in the rhodium(III)-tin(II) - chloride system and the relative proportions depend on the

$\text{SnCl}_3^- : \text{Cl}^-$ ratio. At low concentrations of SnCl_3^- the binuclear anion $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ is precipitated on addition of a suitable large cation such as Et_4N^+ (14)(16). With a large excess of stannous chloride present, the ion $[\text{Rh}(\text{SnCl}_3)_4]^{3-}$ can be precipitated by $\phi_4\text{As}^+$ (14).

The composition of the palladium(II)-tin(II)-chloride system has, until recently, been less certain. A complex has been isolated⁽¹⁷⁾ and formulated as the palladium(I) species $[\text{PdCl}(\text{SnCl}_3)_2]_2^{4-}$, but this has since been shown⁽¹⁸⁾ to be $[\text{PdCl}(\text{SnCl}_3)_3]^{2-}$. Evidence has also been obtained⁽¹⁸⁾ for the existence of $[\text{Pd}(\text{SnCl}_3)_4]^{2-}$.

The platinum(II)-tin(II)-chloride system has yielded⁽¹⁴⁾ cis and trans isomers of $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ as the tetramethylammonium salts. In solutions where the Sn:Pt ratio is greater than five, a five co-ordinate species is formed and formulated as $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ (13)(14).

ii) Carbonyl and Hydride Complexes

Sodium chloroiridate(IV) and stannous chloride in alcohol undergo a reaction involving the solvent, reduction of which provides a source of carbon monoxide, with the eventual formation of $[\text{IrCl}_3(\text{SnCl}_3)_2(\text{CO})]^{2-}$ (20). Other known complexes of this type are $[\text{RuX}_2(\text{SnX}_3)_2(\text{CO})_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) (21)(22) and $[\text{RhCl}(\text{SnCl}_3)_2(\text{CO})]^{2-}$ (14). Addition of pyridine to solutions containing $[\text{RuX}_2(\text{SnX}_3)_2(\text{CO})_2]^{2-}$ gives $\text{Ru}(\text{SnCl}_3)_2(\text{CO})_2(\text{py})_2$ (23)

whereas addition of diethyl sulphide gives the complex

$[\text{Ru}(\text{SnCl}_3)(\text{CO})_2(\text{Et}_2\text{S})_3]\text{Cl}$ and addition of triphenylphosphine gives the product $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})(\text{P}\phi_3)_3(\text{acetone})_2$ (22).

Iridium salts in alcohols have a marked tendency to form hydride complexes in certain instances (20); for example, with triphenylphosphine and stannous chloride in ethanol the product is $\text{IrClH}(\text{SnCl}_3)(\text{P}\phi_3)_3$, while in 2-methoxy-ethanol the main product is the dihydride $\text{IrH}_2(\text{SnCl}_3)(\text{P}\phi_3)_3$.

Several platinum hydride complexes containing the SnCl_3^- ion are known and include $[\text{PtH}(\text{SnCl}_3)_4]^{3-}$ (19) and tertiary phosphine compounds such as $[\text{PtH}(\text{SnCl}_3)_2(\text{Et}_3\text{P})_2]^-$ (19) and cis and trans isomers of $\text{PtH}(\text{SnCl}_3)(\text{P}\phi_3)_2$ (25)(26).

iii) Complexes with Group V Ligands

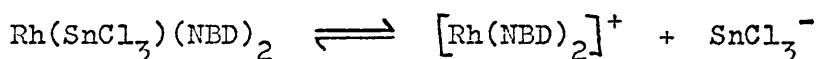
Addition of triphenylphosphine to an ethanolic solution of $\text{PtCl}_2(\text{SnCl}_2.\text{solvent})_2$ gives $\text{PtCl}(\text{SnCl}_3)(\text{P}\phi_3)_2$ (14). Two isomers of this compound have been isolated (26). The complex disproportionates reversibly in acetone to give $\text{PtCl}_2(\text{P}\phi_3)_2$ and free stannous chloride, thus confirming that tin is present in the divalent state in such complexes. The reaction is reversed by addition of excess stannous chloride.

Reflux of ethanolic $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2.\text{solvent})_4$ with triphenylphosphine gives $\text{Rh}(\text{SnCl}_3)(\text{P}\phi_3)_3$ (14).

iv) Olefin Complexes

The usual effect of addition of diolefins to ethanolic

$\text{Rh}_2\text{Cl}_2(\text{SnCl}_2\cdot\text{solvent})_4$ is formation of the well known dimeric $\text{Rh}_2\text{Cl}_2(\text{diolefin})_2$ by direct substitution of the tin groups, but with norbornadiene (NBD) the complex $\text{Rh}(\text{SnCl}_3)(\text{NBD})_2$ is obtained⁽¹⁴⁾. The divalent nature of the tin is again demonstrated by the equilibrium



in aqueous solution⁽¹⁴⁾. The analogous iridium compounds, $\text{Ir}(\text{SnCl}_3)(\text{diolefin})_2$, are formed with cyclo-octa-1,5-diene as well as norbornadiene⁽¹⁴⁾⁽²⁷⁾. In the rhodium compound one diolefin molecule can be displaced by two monodentate ligands, such as triphenylphosphine, or one bidentate ligand, such as bipyridyl, to give the compounds $\text{Rh}(\text{SnCl}_3)(\text{NBD})(\text{P}\phi_3)_2$ and $\text{Rh}(\text{SnCl}_3)(\text{bipy})(\text{NBD})$. The cyclo-octadiene complex of iridium, $\text{Ir}(\text{SnCl}_3)(\text{COD})_2$ (where COD = cyclo-octa-1,5-diene), behaves similarly but the norbornadiene complex $\text{Ir}(\text{SnCl}_3)(\text{NBD})_2$ is inert to substitution. The olefin complexes of rhodium will be discussed more fully in Chapter 5.

It is of interest to note that in all the compounds discussed above, and reasonably formulated as containing divalent tin, the tin atom, nevertheless, is always four - co-ordinate and acting as an electron donor as expected from the theoretical considerations given at the beginning of Section 1.1.B. With one notable and dubious exception⁽²⁸⁾⁽²⁹⁾, namely

$\text{Sn}[\text{Co}(\text{CO})_4]_2$ and its substitution product $\text{Sn}[\text{Co}(\text{CO})_3\phi_3]_2$, there have been no reports in the literature on the existence of simple covalent compounds of tin (II) which could, at least empirically, be formulated as $:\text{Sn}[\text{ML}_n]_2$. This point is considered in greater detail in Chapter 6.

1.2 Methods of Synthesis of Tin-Transition Metal Bonds

Some indication of the preparation of the complexes containing divalent tin has already been given in the preceding section. Generally speaking these species are simply the ones obtained on mixing solutions of transition metal salts and stannous halides, and the derivatives containing Group V ligands and olefins arise from the addition of suitable ligands to the resulting solutions.

In view of the large and increasing number of covalent transition metal complexes of tetravalent tin, it is fortunate that the syntheses of most of these compounds can be classified as belonging to one of six main types:-

- a) Metathetical reactions involving metal carbonyl anions.
- b) Metathetical reactions involving anionic tin species.
- c) Oxidative-addition reactions.
- d) Oxidative-elimination reactions.
- e) Reactions involving elimination of a neutral molecule.
- f) Insertion reactions.

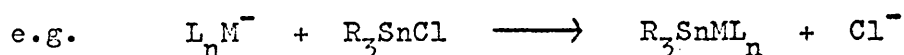
In the following summary of these types of reactions the examples given are taken from recently published work, since progress in this field up until 1967 has been comprehensively documented elsewhere⁽³⁾⁽⁵⁾⁽⁶⁾.

a) Metathetical reactions involving metal carbonyl anions

This type of reaction is the one that has been most widely used for the synthesis of tin-transition metal bonds. The most obvious reasons for this are:-

- i) The comparative ease of preparation of a wide range of suitable anions⁽³⁰⁾.
- ii) Mild reaction conditions, usually at or below room temperature.
- iii) Good yields of the required product.
- iv) Accurate control of the course of the reaction to give the desired product.

The metal carbonyl anion is allowed to react with a suitable halide or organometallic halide of tin to give the desired product.



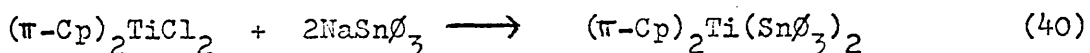
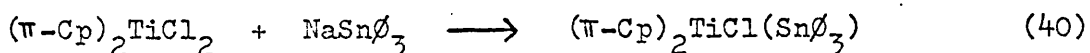
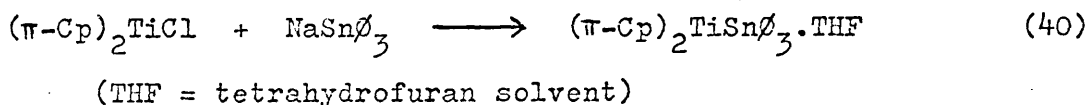
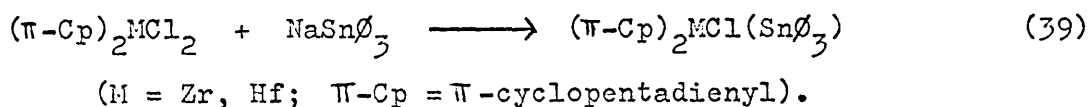
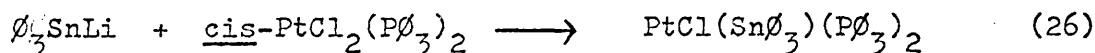
Some examples of this type of reaction which have appeared in the literature in the course of the last two years are collected in Table 1.1 .

TABLE 1.1. Recent Syntheses of Tin - Transition Metal
Bonds via Metal Carbonyl Anions

<u>Reactants</u>	<u>Major Product</u>	<u>Ref.</u>
$\text{Co}(\text{CO})_4^- + \text{Me}_3\text{SnCl}$	$\text{Me}_3\text{SnCo}(\text{CO})_4$	(29)
$\text{Co}(\text{CO})_4^- + \text{SnCl}_4$	$\text{SnCo}(\text{CO})_4$	(29)
$2\text{Co}(\text{CO})_4^- + \text{SnCl}_2$	$\text{Sn}[\text{Co}(\text{CO})_4]_2$	(29)
$2\text{Co}(\text{CO})_4^- + \text{SnCl}_3$	$\text{ClSn}[\text{Co}(\text{CO})_4]_2$	(29)
$\text{Co}(\text{CO})_4^- + (\text{acac})_2\text{SnCl}_2$	$(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$	(31)
$\text{Fe}(\text{CO})_4^{2-} + \text{MeSnCl}_3$	$[\text{Me}_2\text{SnFe}(\text{CO})_4]_2 +$ $\text{Me}_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$	(32)
$\text{Mn}(\text{CO})_5^- + \text{SnCl}_2$	$[\text{Mn}(\text{CO})_5]_4\text{Sn}$	(33)
$[\pi\text{-CpMo}(\text{CO})_2\text{P}(\text{OEt})_3]^- +$ Me_3SnCl	$\text{Me}_3\text{SnMo}(\text{CO})_2[\text{P}(\text{OEt})_3]\pi\text{-Cp}$	(34)
$[\pi\text{-CpMo}(\text{CO})_2\text{L}]^- + \text{SnCl}_4$	$\text{SnMo}(\text{CO})_2\text{L}\pi\text{-Cp}$	(35)
(L = CO, P(OEt) ₃ , P(OMe) ₃ , PPh ₃ , SbPh ₃).		
$[\text{Ir}(\text{CO})_3\text{PPh}_3]^- + \text{Me}_3\text{SnCl}$	$\text{Me}_3\text{SnIr}(\text{CO})_3\text{PPh}_3$	(36)
$[\text{Ir}(\text{CO})_3\text{PPh}_3]^- + \text{Me}_2\text{SnCl}_2$	$\text{Me}_2\text{Sn}[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$	(36)
$[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]^- + \text{Me}_3\text{SnCl}$	$\text{Me}_3\text{SnRh}(\text{CO})_2(\text{PPh}_3)_2$	(36)
$\text{Ru}(\text{CO})_4^{2-} + 2\text{Me}_3\text{SnCl}$	$(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4$	(37)
$3\pi\text{-CpMo}(\text{CO})_3^- + \text{SnCl}_4$	$\text{ClSn}[\text{Mo}(\text{CO})_3\pi\text{-Cp}]_3$	(38)
$3\pi\text{-CpMo}(\text{CO})_3^- + \text{SnCl}_3$	$\text{Sn}[\text{Mo}(\text{CO})_3\pi\text{-Cp}]_3$	(38)
$3\text{Mn}(\text{CO})_5^- + \text{SnCl}_4$	$\text{ClSn}[\text{Mn}(\text{CO})_5]_3$	(38)
$3\text{Mn}(\text{CO})_5^- + \text{SnCl}_3$	$\text{Sn}[\text{Mn}(\text{CO})_5]_3$	(38)

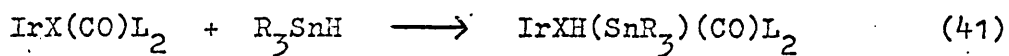
b) Metathetical Reactions Involving Anionic Tin Species

A comparatively recent method for the synthesis of tin-transition metal bonds involves the use of compounds which may be regarded as containing anionic tin species and are directly analogous to similar carbon compounds used widely in synthetic organic chemistry. Typical tin compounds of this type are R_3SnLi and R_3SnNa , and some recent examples of their use are:-



c) Oxidative - Addition Reactions

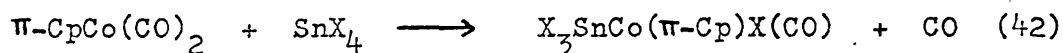
This type of reaction has been widely used in other fields of organometallic synthesis and to a lesser extent in the synthesis of tin - transition metal bonds. The primary requirement of the reaction is that the transition metal be capable of increasing both its oxidation state and co-ordination number at the same time. An example is :-



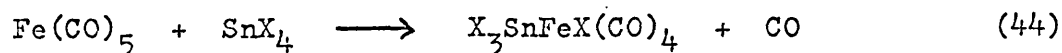
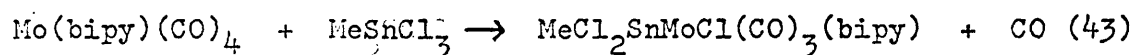
(L = $\text{P}\phi_3$, $\text{P}\phi_2\text{Me}$, $\text{P}\phi\text{Et}_2$; X = Cl, Br, I; R = ϕ , Me, Et.)

d) Oxidative - Elimination Reactions

Oxidative - elimination reactions are similar to oxidative - addition reactions in as much as a suitable tin compound adds to a transition metal complex and results in an increase in the oxidation state of the transition metal, but in the former type of reaction another ligand is removed from the complex in order to maintain the original co-ordination number. Kummer and Graham have published a series of recent papers on the use of oxidative - elimination reactions in the synthesis of compounds with metal-tin bonds:-



(X = Cl, Br, I.)

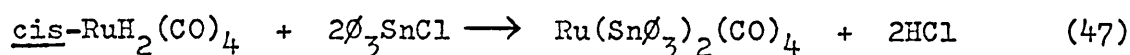
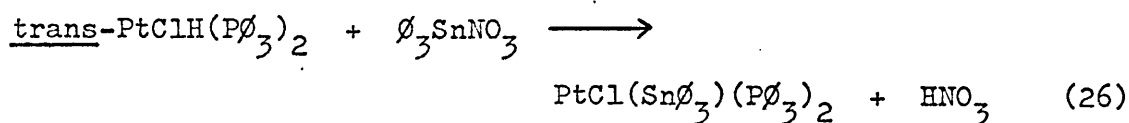
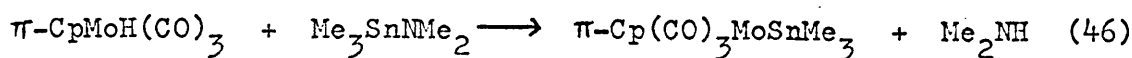


Reactions similar to the second one above have also been reported elsewhere⁽⁴⁵⁾.

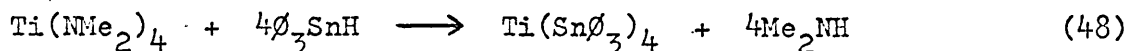
e) Reactions Involving Elimination of a Neutral Molecule

Most of the recent examples of this type of reaction involve, as one of the reactants, a metal hydride which may be a transition metal hydride complex or a stannane derivative.

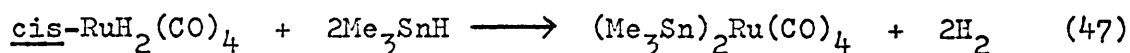
Examples in which a transition metal hydride is the hydride reactant are :-



There is one recent example in which the hydride reactant is a stannane derivative :-



There is also an example in which both reactants are hydrides :-



f) Insertion Reactions

The synthesis of transition metal - tin bonds by insertion of stannous halides into metal - metal and metal - halogen bonds will be discussed in detail in Chapters 2 and 3.

1.3 Structure and Bonding in Tin - Transition Metal Compounds

A variety of physical methods have now been used in the study of compounds with tin - transition metal bonds and in the following short review of these techniques the emphasis is, where possible, on the more recent results.

1.3.1. Structure Determination by X-Ray Crystallography

A considerable number of compounds containing tin - transition metal bonds have been the subject of crystal and molecular structure determinations⁽⁵⁾⁽⁶⁾ and several such studies have been published during the last two years⁽⁴⁹⁾⁻⁽⁵⁵⁾. Generally speaking the bonding of a tin moiety to a co-ordinated transition metal does not lead to any new or entirely unexpected stereochemistry around either the tin atom or the transition metal atom. It is the distortions of this stereochemistry and the lengths of the metal - metal bonds which provide useful information.

Significant deviations from regular tetrahedral co-ordination around the tin atom are usually observed. In many cases this distortion has been attributed to the mutual repulsion of the bulky transition metal groups, but in other instances it has been postulated that the tin - transition metal bond has some multiple bond character (arising from the donation of electron density from filled d orbitals on the transition metal to the empty 5d orbitals of the tin atom) and such multiple bonding would explain the observed distortions⁽⁵¹⁾⁽⁵⁶⁾.

The tin - transition metal bond lengths are usually significantly shorter than the values calculated from suitable covalent radii and this is taken as further evidence for multiple bonding. This idea is supported by the results from structure determinations of the two compounds $\phi_3\text{SnMn}(\text{CO})_5$ and $\phi_3\text{SnMn}(\text{CO})_4(\text{P}\phi_3)$

which have tin-manganese bond lengths of 2.674 ± 0.004 Å and 2.627 ± 0.01 Å respectively. The observed shortening of the metal - metal bond length can be ascribed to increased $d\pi-d\pi$ bonding in the compound in which a triphenylphosphine group is in a position trans to the Sn-Mn bond because this phosphine group would be expected to compete less readily than a carbonyl group for the d electrons on manganese and so allow an increase in tin - manganese $d\pi$ -bonding.

A very recent paper⁽⁵⁵⁾ has described the structures of $\pi\text{-CpFe(CO)}_2\text{SnCl}_3$ and $\pi\text{-CpFe(CO)}_2\text{SnBr}_3$ and there is evidence for free rotation about the Fe-Sn bond in these compounds. This is taken as evidence for the Fe-Sn bond being a pure σ -bond.

1.3.2. Nuclear Magnetic Resonance Spectra

Most of the NMR work which has yielded results on the nature of the tin - transition metal bond has been confined to methyl-tin derivatives and has been reviewed⁽⁶⁾. The main conclusions may be summarised as follows :-

a) The methyl resonances shift to lower field as the methyl groups in tetramethyl-tin are successively replaced by chlorine atoms because the methyl protons become less shielded as electrons are drawn towards the electronegative chlorine atoms. A similar result is obtained when the methyl groups are successively replaced by transition metal groups. It is considered that the

magnitude of these shifts does not depend solely on inductive effects because, in the silicon analogues, the shift is less when (p→d)π-bonding between silicon and chlorine is favoured, as would be expected if back-donation of electrons to the metal atom led to a greater shielding of the methyl protons. This idea, plus the fact that the shifts are less in the transition metal derivatives of tetramethyl-tin than in the analogous chlorine derivatives, is regarded as evidence for π-bonding in the tin - transition metal bond.

b) $J(^{119}\text{Sn-Me})$, the tin-proton coupling constant for the methyl protons, also decreases on successive replacement of methyl groups by transition metal groups in tetramethyl-tin. The values of such coupling constants can be related to the s-character of the tin - methyl bonds in that the magnitude of the coupling constant is increased as the s-character is increased. Thus the lower values observed in the transition metal derivatives imply that the remaining tin - methyl bonds have less s-character and consequently the tin - transition metal bonds have more s-character than the 25% expected for pure sp^3 hybridisation. This conclusion is supported by the structural determinations discussed in section 1.3.1., in which deviations from regular tetrahedral bond angles were observed.

A more recent paper⁽⁵⁹⁾ has argued along similar lines to explain the chemical shifts and coupling constants of the $\text{Me}_3\text{Sn-}$

group in a series of compounds $\text{Me}_3\text{SnFeL}_2\pi\text{-Cp}$ ($\text{L}_2 = 2\text{CO}$, CO and $\text{P}(\text{O}\phi)_3$, CO and $\text{P}\phi_3$, or $\phi_2\text{PCH}_2\text{CH}_2\text{P}\phi_2$). The chemical shift of the Me_3Sn group protons increases as the π -acceptor ability of L_2 decreases. This is interpreted as being due to an increase in $d\pi$ - $d\pi$ bonding between iron and tin as L_2 becomes less able to accept electron density from the iron atom. Moreover the tin-methyl proton coupling constant decreases as the π -acceptor ability of L_2 decreases and so it is considered that the increase in involvement of the d orbitals of tin results in a lowering of the s-character of the tin orbitals bonding to the methyl groups.

1.3.3. Infrared and Raman Spectra

Vibrations involving metal - metal bonds are expected to be at low frequencies, usually below 200 cm^{-1} . This is partly a mass effect and partly due to the low force constants of such bonds. The low-frequency vibrational spectra of compounds containing tin - transition metal bonds will be discussed in detail in Chapter 4, with particular emphasis on the metal - tin vibrations.

Tin - halogen vibrational frequencies are also important in understanding the nature of the tin - transition metal bond and several examples will be given and discussed in various parts of this work. Such vibrations are also of relatively low frequencies (below 400 cm^{-1}) but numerous examples have now been

reported and interpreted⁽⁶⁴⁾ for the SnCl_3^- ligand. The essential conclusion is that "For a ligand LX_n the L-X force constant will increase upon co-ordination of L to an electron acceptor if X is significantly more electronegative than L and it will decrease for the converse situation." Thus the tin - chlorine stretching frequencies in transition metal complexes such as L_nMSnCl_3 will be higher than the values of 297 and 250 cm^{-1} for the free SnCl_3^- ion⁽⁶⁵⁾ and the shift will be greatest for the complexes of the transition metal groups with the highest electron pair affinities.

Routine infrared spectra at higher frequencies, in the 'sodium chloride region' of 650-4,000 cm^{-1} , are now usually reported as a matter of course for most new compounds without any attempt at rigorous assignment or interpretation. The main purpose of such spectra is to enable use to be made of the group frequency concept to identify particular ligands and groups within the complex. However there are many exceptions to this general statement and careful measurements and interpretations of higher frequency infrared spectra of tin - transition metal complexes have been reported, usually in the carbonyl stretching frequency region⁽²⁹⁾⁽³³⁾⁽⁶⁶⁾⁻⁽⁷⁴⁾. Some of the earlier work on the infrared spectra of tin - transition metal complexes in the carbonyl stretching frequency region has been reviewed and discussed⁽⁶⁾. The main conclusion reached from these studies

is confirmation of the idea that appreciable π -bonding is present in the tin - transition metal bond.

1.3.4. Mass Spectrometry

Little mass spectral data have, as yet, been published for compounds with tin - transition metal bonds. Mass spectra of the compounds $\phi_3\text{SnMn}(\text{CO})_5$, $\phi_3\text{SnFe}(\text{CO})_2\pi\text{-Cp}$ and $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\pi\text{-Cp}]_2$ have been reported⁽⁶⁰⁾ but, although the peaks were identified, no other conclusions were drawn from the spectra. Other work⁽⁶¹⁾⁽⁶²⁾ has included mass spectra of the compounds $\text{RSn}[\text{Co}(\text{CO})_4]_3$ ($\text{R} = \phi, \text{CH}_3, \text{CH}_2=\text{CH}, \text{n-Bu}$) and $\text{XSn}[\text{Co}(\text{CO})_4]_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). These spectra have confirmed the correct formulation to be $\text{RSn}[\text{Co}(\text{CO})_4]_3$ and not $\text{RSn}[\text{Co}(\text{CO})_3]_3$ as was originally thought to be the case⁽⁶³⁾.

1.3.5. Mössbauer Spectra

Mössbauer spectroscopy is a comparatively new technique in chemistry⁽⁷⁵⁾ but has already yielded useful results on tin - transition metal complexes⁽⁷⁶⁾⁽⁷⁷⁾⁽⁷⁸⁾. The available data have been added to and interpreted⁽⁷⁹⁾ and the results compared with those from structural determinations and NMR spectra. The main conclusions are :-

- a) that there is enhanced s-character in the tin - transition metal bond;

b) that there is $d\pi-d\pi$ bonding in the tin - metal bond but that this does not predominate over other factors which influence electron distribution at the tin atom.

1.3.6. Conclusions on the Nature of the Tin - Transition Metal Bond

The overall physical evidence suggests that there is considerable π -bonding in the Sn-M bond as a result of overlap of filled d orbitals on M with empty d orbitals on Sn, but further work is needed before any conclusions can be made about the extent of such bonding.

Two classes of compounds are known with tin - transition metal bonds. With the platinum metals, stannous chloride forms SnCl_3^- complexes which, from chemical evidence, appear to contain formally divalent tin whereas the mono- and di-substituted compounds of the other transition metals behave as compounds of tin(IV). These facts are explicable in bonding terms by the following hypotheses :-

a) overlap of empty d orbitals of tin with filled d orbitals of the platinum metals are especially favoured and the resulting bond is mainly a π -bond with the lone-pair of electrons on tin remaining close to the parent atom in a very polar σ -bond;

b) with the other transition metals, d orbital overlap is less favourable or less d electrons are available and a stronger, less

polar, σ -bond is required to draw the atoms closer together to allow π -bond formation.

It would then be expected that reactions of the metal - metal bond would differ in the two cases; in the platinum metal complexes the tin atom would tend to retain its electron pair while in the other cases the bond would tend to split homolytically.

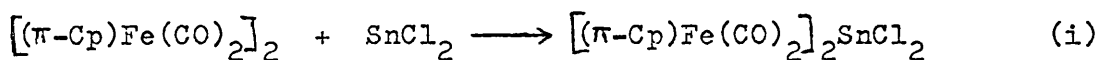
CHAPTER 2

CHAPTER 2

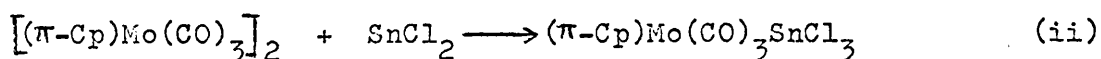
The Insertion of Stannous Halides into Metal-Metal Bonds

2.1. Introduction

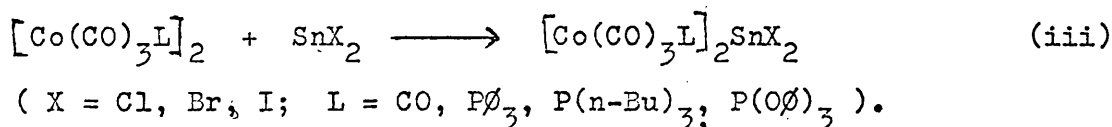
The first insertion reaction of a stannous halide into a metal-metal bond was reported in 1964⁽⁸⁰⁾. Stannous chloride was found to insert into the iron-iron bond of bis(π -cyclopentadienyl-dicarbonyliron), in refluxing methanol, according to the reaction :-



The unbridged metal-metal bond in decacarbonyldimanganese was shown to be unaffected by stannous chloride under similar conditions, and bis(π -cyclopentadienyltricarbonylmolybdenum) reacted but the product was trichloro(π -cyclopentadienyltricarbonylmolybdenum)tin :-

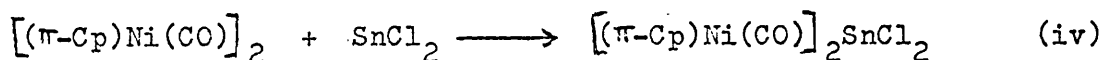


Octacarbonyldicobalt and some of its derivatives were found to undergo a similar insertion reaction with stannous halides⁽⁸²⁾⁽⁸³⁾ :-



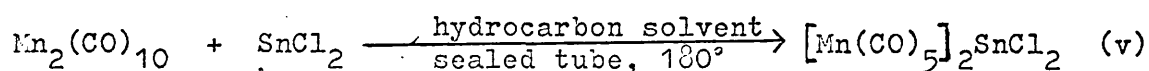
The ease of reaction with stannous chloride varied with change of ligand L and decreased in the order $(\text{n-Bu})_3\text{P} > \phi_3\text{P} > (\text{O}\phi)_3\text{P}$, which is the reverse order of π -acceptor ability for these ligands. This was considered to be possible evidence for electrophilic attack at the cobalt-cobalt bond by a carbene-like species : SnCl_2 .

The reaction of octacarbonyldicobalt with stannous halides was independently reported by other workers⁽⁸¹⁾, who also showed that bis(π -cyclopentadienyldicarbonyliron) would react with stannous bromide and stannous iodide in a manner similar to that given by reaction (i). Bis(π -cyclopentadienylcarbonylnickel) behaves similarly :-



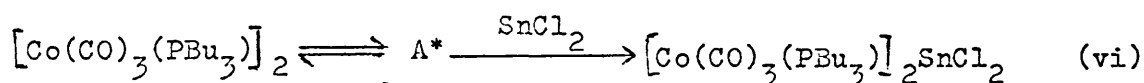
The lack of reaction of decacarbonyldimanganese was confirmed and this, and the anomalous reaction of bis(π -cyclopentadienyltricarboxymolybdenum), were suggested to be due to the lack of bridging carbonyl groups across the metal-metal bond in these compounds.

It is now known⁽⁸⁴⁾ that decacarbonyldimanganese will react with stannous chloride under very vigorous conditions to give the expected insertion product :-



This does not disprove the idea that bridging carbonyls are needed to allow insertion of stannous halides into metal-metal bonds under mild conditions but it would probably be more realistic to say that bridging carbonyls will in some way aid the insertion reaction rather than that their absence prevents the reaction. This view is borne out by the fact that the substituted cobalt carbonyls, $[\text{Co}(\text{CO})_3\text{L}]_2$, which contain an unsupported metal-metal bond with no bridging carbonyl groups⁽⁸⁹⁾, have been shown to react in the normal way⁽⁸²⁾.

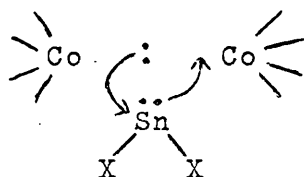
An investigation of the kinetics of the reactions of stannous chloride and stannous bromide with hexacarbonylbis(tri-n-butylphosphine)dicobalt has been reported⁽⁸⁶⁾. The thermal reaction at room temperature is very slow but the rate is greatly increased when the reaction mixture is exposed to light. For the thermal reaction with stannous chloride the evidence suggests that a reactive intermediate A^* is involved :-



For the thermal reaction with stannous bromide two mechanisms

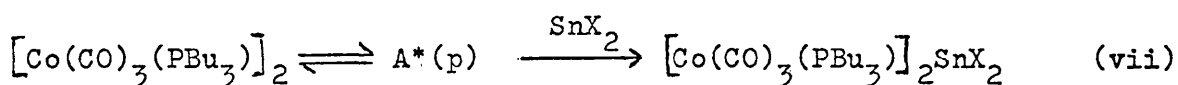
appear to be operating simultaneously :-

- a) a two-stage mechanism, as for the chloride;
- b) a bimolecular associative mechanism, which may be a concerted process and may be represented diagrammatically as



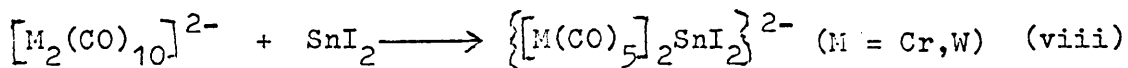
This is consistent with the higher polarisability of the bromide over the chloride.

For the photochemical reaction a two-step mechanism, similar to that for the thermal reaction, seems to be operating but with a photochemically produced reactive intermediate :-

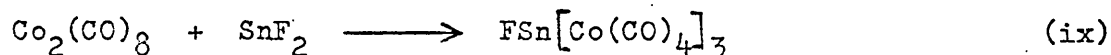


The photochemical reactions for the chloride and bromide have similar mechanisms.

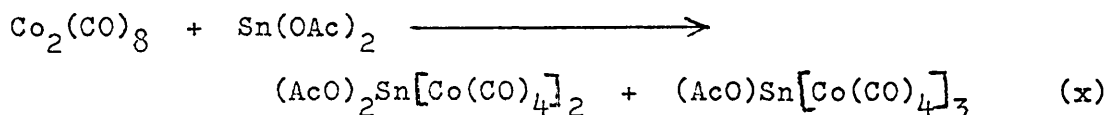
Anionic species containing metal-metal bonds have been shown to undergo insertion reactions with stannous iodide⁽⁸⁵⁾ :-



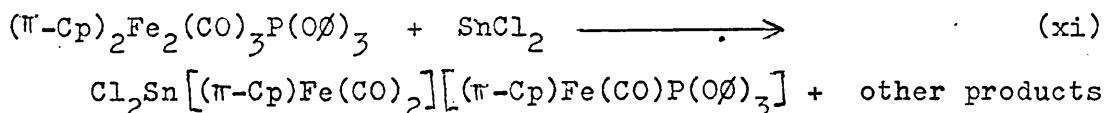
The insertion reactions of octacarbonyldicobalt have been extended to include reactions with stannous fluoride and stannous acetate⁽⁶⁸⁾. The product from reaction with stannous fluoride is unexpected :-



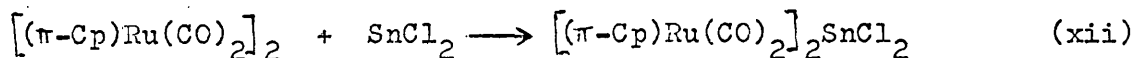
The reaction with stannous acetate gives a mixture of two products :-



The mono-substituted iron derivative bis(π -cyclopentadienyl)(tricarbonyl)(triphenylphosphite)diiron reacts with stannous chloride to give the expected insertion product but the reaction is complex and at least three other minor products are obtained, including dichlorobis(π -cyclopentadienyldicarbonyliron)tin⁽³⁷⁾ :-



Very recently⁽⁸⁸⁾ π -cyclopentadienyldicarbonylruthenium dimer has been shown to react with stannous chloride in a manner similar to that of the analogous iron compound :-



In this present work the scope of the insertion reaction as a preparative method has been extended and some unexpected results have been obtained from some of the reactions discussed above.

2.2 Reactions of Bis(π -cyclopentadienyltricarbonylmolybdenum) with Stannous Halides

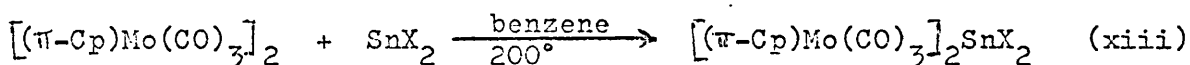
2.2.1 At High Temperatures in Non-Polar Solvents

An investigation of the reactions of bis(π -cyclopentadienyltricarbonylmolybdenum) with stannous halides under vigorous conditions was thought to be desirable because :-

a) the reaction with stannous chloride under mild conditions has been reported to give trichloro(π -cyclopentadienyltricarbonylmolybdenum)tin as the unexpected product⁽⁸⁰⁾;

b) decacarbonyldimanganese, which is inert to stannous chloride in refluxing methanol, reacts to give the expected insertion product under more vigorous conditions in hydrocarbon solvents⁽⁸⁴⁾.

Consequently, bis(π -cyclopentadienyltricarbonylmolybdenum) and stannous chloride, with benzene as solvent, were heated to 200° in a closed stainless steel reaction vessel. Under these conditions the reaction was found to give the simple insertion product dichlorobis(π -cyclopentadienyltricarbonylmolybdenum)tin. Stannous bromide and stannous iodide were found to react similarly :-

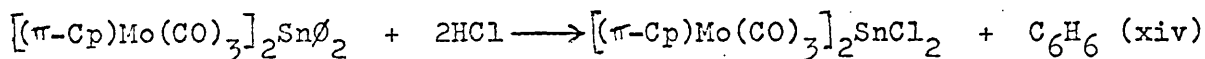


With stannous bromide, tribromo(π -cyclopentadienyltricarbonylmolybdenum)tin was also isolated as a minor product but no similar

side-reactions were detected with either the chloride or the iodide. This observation is consistent with similar anomalous reactions of stannous bromide and bis(π -cyclopentadienyldicarbonyliron) discussed later in section 2.4. It was also found that trichloro(π -cyclopentadienyltricarbonylmolybdenum)tin (the reported product from the reaction in refluxing methanol) could not be isolated from the reaction under vigorous conditions, even in the presence of lithium chloride as a source of extra chloride ion which might have assisted the formation of a trichlorotin species.

It is interesting to note that, even under similarly vigorous conditions, evidence could not be found for the insertion of lead(II) chloride into the molybdenum-molybdenum bond. (It has previously been reported⁽⁸⁰⁾ that lead(II) chloride will not insert into metal-metal bonds under mild conditions in refluxing methanol).

Dichlorobis(π -cyclopentadienyltricarbonylmolybdenum)tin has been briefly mentioned elsewhere⁽⁹⁰⁾, having been synthesised by the reaction :-

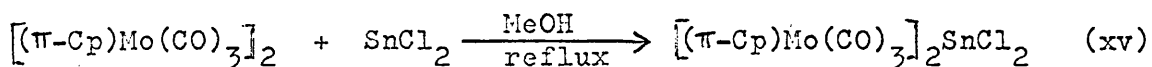


The dibromo- and diiodo-compounds have not been previously reported in the literature.

2.2.2 Under Mild Conditions

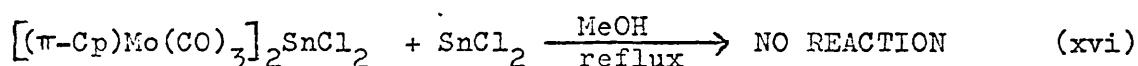
The reported reaction of bis(π -cyclopentadienyltricarbonylmolybdenum) with stannous chloride to give trichloro(π -cyclopentadienyltricarbonylmolybdenum)tin⁽⁸⁰⁾ (reaction (ii) of section 2.1) is somewhat surprising in view of the fact that all the other reactions of stannous halides with compounds containing metal-metal bonds have given the simple insertion product. This present work has now shown that it is possible to obtain the insertion product, dichlorobis(π -cyclopentadienyltricarbonylmolybdenum)tin, even under the relatively mild conditions of reflux of low-boiling solvents.

Thus, the dimeric molybdenum compound was found to react with anhydrous stannous chloride in dry methanol at reflux temperature to give the insertion product :-



The identical product was obtained with ethanol and acetone as solvents. Even a series of similar reactions under conditions identical to those originally reported⁽⁸⁰⁾, using hydrated stannous chloride, have been found to give the simple insertion product as the major product, but on one occasion trichloro-(π -cyclopentadienyltricarbonylmolybdenum)tin was isolated as the sole product. These results verify that the original report was a correct one but that it is more usual for the reaction to

result in a simple inserion of stannous chloride into the molybdenum-molybdenum bond. It is not, as yet, possible to explain this variation in the result under apparently identical conditions, but it seems that reaction time is not important since it has been found that the insertion product does not react further with an excess of stannous chloride under the usual reaction conditions :-



It has been found that products could not be isolated from the reactions of stannous bromide or stannous iodide with bis(π -cyclopentadienyltricarbonylmolybdenum) in refluxing methanol or THF. The usual result was the formation of unstable green solids.

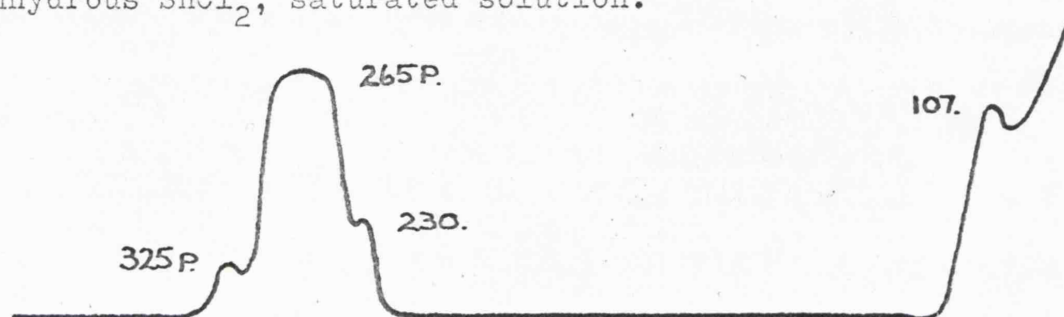
2.3 Raman Spectra of Stannous Chloride in Methanol

In an attempt to understand the inconsistencies discussed in the preceding section, the Raman spectra of methanolic solutions of anhydrous and hydrated stannous chloride were investigated. The resulting spectra are reproduced diagrammatically in Figure 2.1.(Page 32).

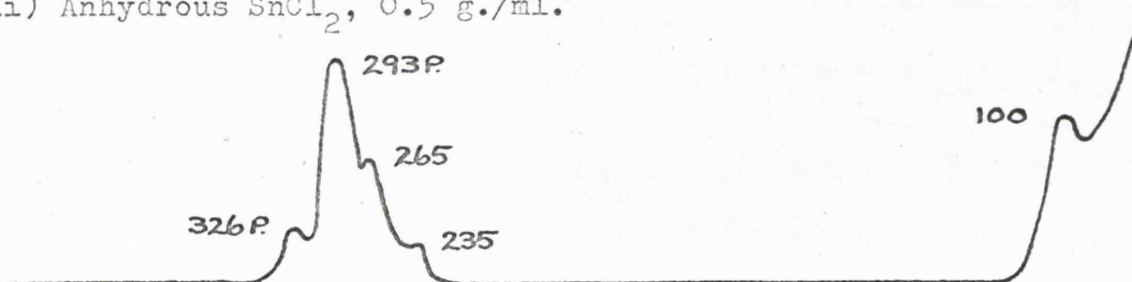
The essential result is that, at the concentrations used during the reactions, the same species are present in solution for both anhydrous and hydrated stannous chloride. Therefore

FIGURE 2.1 Raman Spectra of Methanolic Solutions of Anhydrous
Stannous Chloride and Stannous Chloride Dihydrate

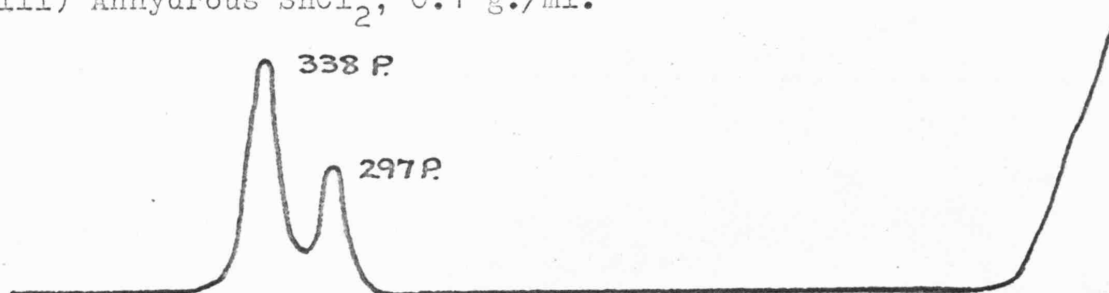
i) Anhydrous SnCl_2 , saturated solution.



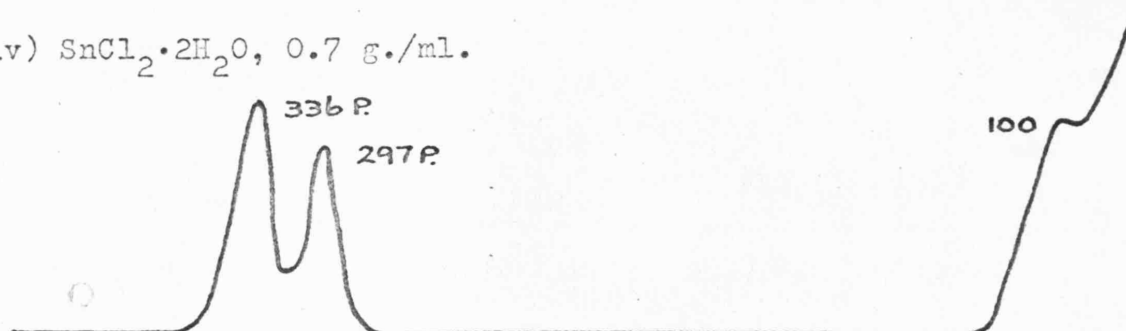
ii) Anhydrous SnCl_2 , 0.5 g./ml.



iii) Anhydrous SnCl_2 , 0.1 g./ml.



iv) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 0.7 g./ml.



Frequency shifts are given in cm^{-1} .

P = polarised.

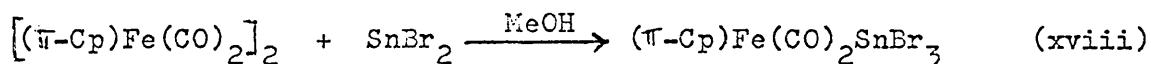
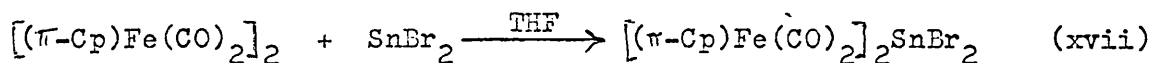
it is not possible to make any conclusions about the inconsistencies of the reaction from these spectra. The main species present in the more dilute solutions are probably of the type $\text{SnCl}_2 \cdot \text{MeOH}$ or $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and it is then reasonable to assign the strong bands at 336 cm^{-1} and 297 cm^{-1} to the symmetric tin-chlorine stretching mode and the tin-oxygen stretching mode respectively because both these bands are polarised.

An interesting feature of these spectra is the variation with concentration for the anhydrous compound. The strong band at about 265 cm^{-1} observed for the saturated solution shifts to higher frequency on dilution. This fact has been briefly mentioned elsewhere⁽⁹¹⁾. A likely explanation is that the chain-polymer structure of the solid⁽¹⁰⁾ is retained in saturated solutions and the spectral change on dilution is due to the gradual depolymerisation of $(\text{SnCl}_2)_n$ with the eventual formation of discrete molecules of the form $\text{SnCl}_2 \cdot (\text{solvent})$. This effect is probably not relevant to the reactions discussed in section 2.2.2 because, at the concentrations used in these reactions, the Raman spectra indicate that the depolymerisation process is complete.

2.4 Reactions of Bis(π -cyclopentadienyldicarbonyliron) with Stannous Halides

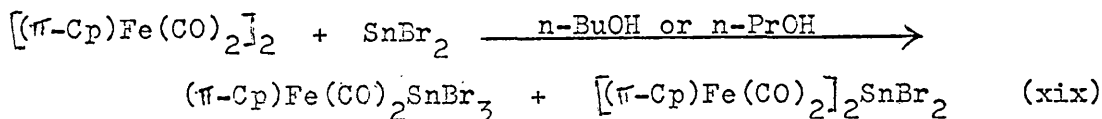
The reaction of bis(π -cyclopentadienyldicarbonyliron) with

stannous chloride in methanol has been found to give the expected insertion product⁽⁸⁰⁾ and stannous iodide has been found to react similarly in THF (as previously reported⁽⁸¹⁾) and also in methanol. However, stannous bromide has been found to behave in a somewhat unexpected manner. In THF the expected insertion product was obtained, but in methanol the sole product was tribromo(π -cyclopentadienyldicarbonyliron)tin :-

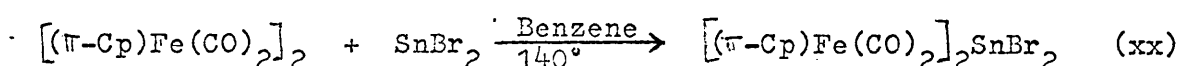


This result is particularly surprising in view of the fact that none of the trichloro-compound could be isolated from the reaction with stannous chloride, even in the presence of hydrochloric acid when it is reasonable to suppose that a species such as SnCl_3^- would be present in high concentration at the start of the reaction⁽⁶⁵⁾.

The reaction with stannous bromide has also been investigated in ethanol, n-propanol, and n-butanol and it was found that in n-propanol and n-butanol a mixture of products was obtained :-



The reaction was also carried out in benzene under vigorous conditions, similar to those used for the molybdenum compounds (section 2.2.1), and it was found to give the insertion product in high yield with no evidence for the formation of the tribromo-compound :-



The results for the reaction of stannous bromide with bis(π -cyclopentadienyldicarbonyliron) are summarised in Table 2.1 (page 36). This table shows that the proportion of dibromobis(π -cyclopentadienyldicarbonyliron)tin formed in the reaction increases as the reaction temperature is increased, but it is not possible to comment on the reasons for this without further evidence.

It is noteworthy that similar anomalous reactions of stannous bromide, as compared with the chloride and iodide, have been observed in the reactions of stannous halides with compounds containing transition metal-mercury bonds but no explanations were proposed⁽⁹²⁾.

2.5 The Raman Spectra of Stannous Bromide in Various Solvents

The variations in the reaction of stannous bromide with bis(π -cyclopentadienyldicarbonyliron) in different solvents might be explained if it could be shown that different species were

TABLE 2.1 Reactions of Stannous Bromide with
Bis(π -cyclopentadienyldicarbonyliron)
in Various Solvents

Solvent	Reaction Temp. °C	Approximate Relative Percentages of Products	
		$(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{SnBr}_3$	$[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnBr}_2$
MeOH	64	100	0
EtOH	78	100	0
n-PrOH	97	80	20
n-BuOH	117	70	30
Benzene	140	0	100

present in the various reaction solvents. Therefore the Raman spectra of stannous bromide solutions were investigated for a variety of solvents. These spectra are reproduced diagrammatically in Figure 2.2 and show that, at room temperature, the same species are present in solution in the various solvents and so no further conclusions may be drawn about the observed differences in reaction.

2.6 The Reactions of Octacarbonyldicobalt with Stannous Halides

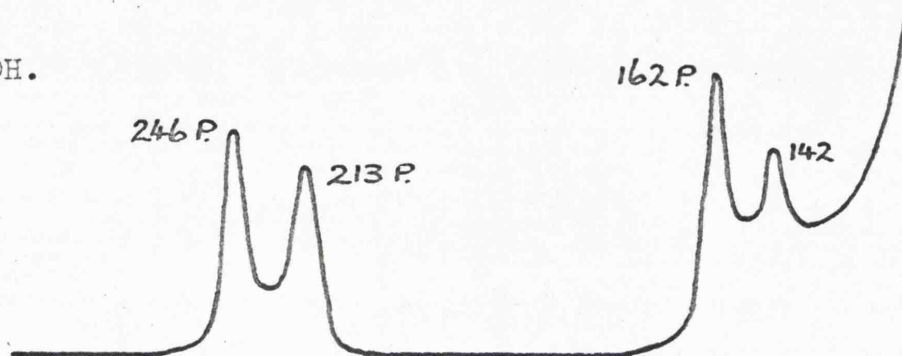
The insertion reactions of stannous halides with octacarbonyldicobalt have been repeated and the expected insertion products were obtained in each case⁽⁸¹⁾⁽⁸²⁾⁽⁸³⁾.

2.7 Conclusions

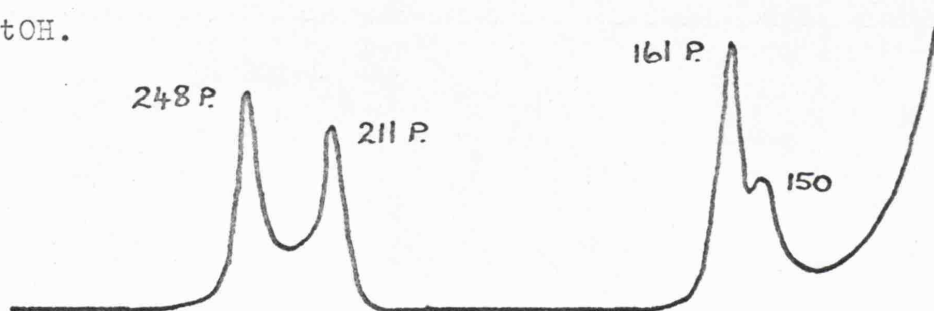
The insertion reactions of stannous halides with compounds containing homonuclear metal-metal bonds have been extended and, in some cases, re-examined. The essential result is that in all cases, under suitable conditions, it is possible to obtain compounds of the type $[L_nM]_2SnX_2$ and that the formation of compounds of the type L_nMSnX_3 is exceptional for these reactions. The factors which govern the formation of the trihalo-tin compounds in preference to the dihalo-tin compounds in certain instances are, as yet, undetermined.

FIGURE 2.2 Raman Spectra of Stannous Bromide Dihydrate
in Various Solvents

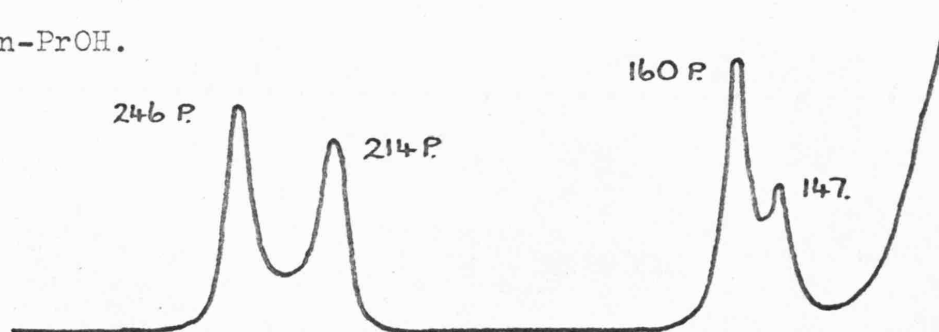
i) In MeOH.



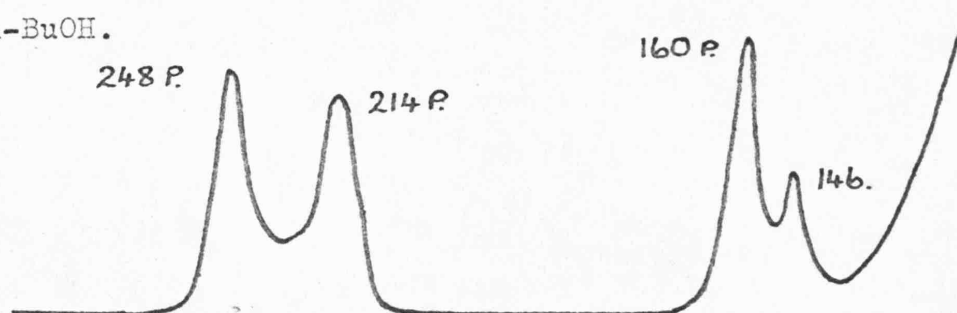
ii) In EtOH.



iii) In n-PrOH.



iv) In n-BuOH.



Frequency shifts are given in cm.⁻¹.

P = polarised.

2.8 Experimental

Raman spectra were obtained on a Coderg PH O instrument with a Ferranti LR 50 helium-neon laser as the exciting source. Infrared spectra were obtained on a Perkin Elmer 225 instrument with the samples mounted as Nujol mulls on potassium bromide ($4,000 - 400 \text{ cm}^{-1}$) and polythene ($400 - 200 \text{ cm}^{-1}$) plates.

Microanalyses were carried out by Dr. F. Pascher, Mikroanalytisches Laboratorium, 53 Bonn, Burchstrasse 54, W. Germany, and by Rapid Elemental Analysis, 6, Burkes Parade, Beaconsfield, Buckinghamshire.

Melting points (designated m.p.) were determined on a Kofler hot-stage apparatus and are uncorrected.

All reactions, except those at high temperatures in closed reaction vessels, were carried out under an inert atmosphere of dry nitrogen.

Reagent grade and 'Analar' grade solvents were used without further purification with the exception of THF, which was distilled, in a dry nitrogen atmosphere, from sodium wire and then from lithium aluminium hydride.

$[(\eta\text{-Cp})\text{Fe}(\text{CO})_2]_2$ and $[(\eta\text{-Cp})\text{Mo}(\text{CO})_3]_2$ were purchased from Alfa Inorganics Inc. and used without further purification. $\text{Co}_2(\text{CO})_8$ was prepared according to the published method⁽⁹³⁾.

A. High Temperature Reactions

i) Synthesis of Dichlorobis(π -cyclopentadienyltricarbonylmolybdenum)tin

A mixture of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (1.0 g), excess anhydrous stannous chloride (1.0 g), and benzene (15 ml.) were sealed in a stainless steel high-pressure reaction vessel and heated to 200° for 24 hr. The resulting yellow solution was filtered and evaporated to dryness to give a yellow solid. This solid was recrystallised from benzene-petroleum spirit to give yellow crystals of the product (0.91 g., 65%), m.p. 200-201°, (Lit. value, ⁽⁹⁰⁾ 200-201°). (Found: C, 27.9; H, 1.52; Cl, 11.1%. Calc. for $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{Mo}_2\text{O}_6\text{Sn}$: C, 28.3; H, 1.49; Cl, 10.4%).

The reaction was repeated under identical conditions except that lithium chloride (1.0 g.) was added to the reaction mixture. The yellow product (0.85 g.) was purified as described above and shown by m.p. 200° and infrared spectrum (400-200 cm^{-1}) to be $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2$.

ii) Synthesis of Dibromobis(π -cyclopentadienyltricarbonylmolybdenum)tin

$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (1.0 g.), excess hydrated stannous bromide (1.5 g.), and benzene (15 ml.) were sealed in the steel reaction vessel and heated to 190° for 24 hr. The resulting yellow solution was evaporated to dryness at the rotary evaporator and the

yellow solid so obtained was redissolved in boiling methanol to give an orange solution. Filtration and cooling gave orange crystals of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnBr}_2$ (0.69 g., 44%), m.p. 211-212°. (Found: C, 24.6; H, 1.28; Br, 23.1%. Calc. for $\text{C}_{16}\text{H}_{10}\text{Br}_2\text{Mo}_2\text{O}_6\text{Sn}$: C, 25.0; H, 1.32; Br, 20.8%).

Evaporation of the filtrate to small bulk and cooling gave orange crystals of $(\pi\text{-Cp})\text{Mo}(\text{CO})_3\text{SnBr}_3$ (0.2 g., 8.2%), m.p. 158°. (Found: C, 15.9; H, 0.75; Br, 43.9%. Calc. for $\text{C}_8\text{H}_5\text{Br}_3\text{MoO}_3\text{Sn}$: C, 15.9; H, 0.83; Br, 39.8%).

iii) Synthesis of Diiodobis(π -cyclopentadienyltricarbonylmolybdenum)tin

$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (1.0 g.), excess hydrated stannous iodide (1.5 g.), and benzene (15 ml.) were sealed in the steel reaction vessel and heated to 175° for 24 hr. The resulting orange-red solution was evaporated to dryness at the rotary evaporator and the orange solid so obtained was recrystallised from methylene chloride-methanol to give orange-red crystals of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnI}_2$ (0.9 g., 51%), m.p. 201-203°. (Found: C, 21.8; H, 1.15; I, 28.6%. Calc. for $\text{C}_{16}\text{H}_{10}\text{I}_2\text{Mo}_2\text{O}_6\text{Sn}$: C, 22.3; H, 1.17; I, 29.4%).

iv) Attempted Reaction of Bis(η -cyclopentadienyltricarbonylmolybdenum) and Lead(II) Chloride

$[(\eta\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (1.0 g.), excess lead(II) chloride (1.0 g.) and benzene (15 ml.) were sealed in the steel reaction vessel and heated to 180° for 24 hr. Only unchanged starting materials could be isolated from the reaction mixture.

v) Synthesis of Dibromobis(η -cyclopentadienyldicarbonyliron)tin

$[(\eta\text{-Cp})\text{Fe}(\text{CO})_2]_2$ (1.0 g.), excess hydrated stannous bromide (1.5 g.), and benzene (15 ml.) were sealed in the steel reaction vessel and heated to 140° for 24 hr. The resulting orange solution was evaporated at the rotary evaporator and the orange solid so obtained was recrystallised from boiling methanol to give needle-like orange crystals of $[(\eta\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnBr}_2$ (0.3 g., 45%), m.p. $186\text{--}189^\circ$ (Lit. values, $168\text{--}171^\circ$ ⁽⁸¹⁾ and $177\text{--}179^\circ$ ⁽⁹²⁾). (Found: C, 26.6; H, 1.54; Br, 24.8%. Calc. for $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{Fe}_2\text{O}_4\text{Sn}$: C, 26.6; H, 1.6; Br, 25.3%).

B. Reactions in Refluxing Solvents

i) Reaction of Bis(η -cyclopentadienyltricarbonylmolybdenum) and Anhydrous Stannous Chloride

$[(\eta\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (0.3 g.), and anhydrous stannous chloride (1.1 g.) in 'Analar' grade methanol (50 ml.) were refluxed for

three days to give a clear orange solution. Evaporation of this solution to small bulk gave orange crystals which were recrystallised boiling methanol as orange-yellow, needle-like crystals of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2$ (0.2 g., 48%), identified by m.p. $199\text{--}205^\circ$ and infrared spectrum ($400\text{--}200\text{ cm}^{-1}$).

Similar reactions, using acetone and absolute ethanol as solvents, gave essentially the same result.

ii) Reaction of Bis(π -cyclopentadienyltricarbonylmolybdenum) and Hydrated Stannous Chloride

$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (0.3 g.) and stannous chloride dihydrate (1.2 g.) in reagent grade methanol were refluxed for three days. The resulting orange solution was evaporated to small bulk and cooled to give an orange solid. This was recrystallised from boiling methanol to give orange-yellow crystals of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2$ (0.13 g., 43%), identified by m.p. $198\text{--}199^\circ$ and infrared spectrum ($400\text{--}200\text{ cm}^{-1}$).

The reaction was repeated twice more to give essentially the same result, but on another occasion the product was found to crystallise less readily from the reaction solvent and only after standing in the refrigerator for 15 hr. were yellow crystals obtained (0.12 g.). These were shown to be the trichloro-compound $(\pi\text{-Cp})\text{Mo}(\text{CO})_3\text{SnCl}_3$ by m.p. 161° (dec.) (Lit. value⁽⁸⁰⁾, 164° (dec.)), and infrared spectrum ($400\text{--}200\text{ cm}^{-1}$).

iii) Reaction of Dichlorobis(π -cyclopentadienyltricarbonyl-molybdenum)tin and Hydrated Stannous Chloride

$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2$ (0.4 g.) and excess stannous chloride dihydrate (0.5 g.) in reagent grade methanol (50 ml.) were refluxed for two days. The hot reaction solution was filtered and allowed to cool to room temperature to give orange crystals of starting material, $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2$.

iv) Reactions of Bis(π -cyclopentadienyltricarbonylmolybdenum) With Stannous Bromide and Stannous Iodide

$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (0.5 g.) and excess hydrated stannous bromide (2.0 g.) in reagent grade methanol (40 ml.) were refluxed for five days. The hot reaction solution was filtered and placed in the refrigerator. After two hours purple-red crystals had separated and were shown, by infrared spectrum, to be the starting material $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$. The filtrate was evaporated to very small bulk and left in the refrigerator for two days but other products were not obtained.

The reaction was repeated with THF as solvent and after refluxing for twelve hours the solution had become deep green in colour. Removal of the solvent at the rotary evaporator left a green solid which immediately decomposed to a black solid on exposure to the atmosphere.

Similar results were obtained when $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ and

hydrated stannous iodide were refluxed in methanol and THF.

v) Reaction of Bis(π -cyclopentadienyldicarbonyliron) and Hydrated Stannous Chloride in Methanol

The reaction was carried out as previously described⁽⁸⁰⁾ to give the expected product $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ (yield, 63%), identified by m.p. $165\text{-}167^\circ$ (Lit. value, $166\text{-}168^\circ$) and infrared spectrum.

vi) Reaction of Bis(π -cyclopentadienyldicarbonyliron) and Hydrated Stannous Chloride in Methanol in the Presence of Hydrochloric Acid

$[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ (1.25 g.), stannous chloride dihydrate (2.5 g.), and 2N hydrochloric acid (5 ml.) in reagent grade methanol (60 ml.) were refluxed for five hours to give a clear orange solution containing some orange crystals. These crystals were filtered off, washed quickly with cold methanol, and dried in air; (yield, 0.21 g.). The filtrate was cooled in ice to give a second crop of orange crystals which were washed and dried similarly; (yield, 1.03 g.). Both products were shown by m.p. $166\text{-}167^\circ$ and infrared spectrum ($400\text{-}200\text{ cm}^{-1}$) to be $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ (total yield, 65%).

vii) Reactions of Bis(π -cyclopentadienyldicarbonyliron) and
Stannous Bromide in Various Alcohols

- a) In MeOH:- $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ (0.5 g.) and hydrated stannous bromide (1.5 g.) in reagent grade methanol (20 ml.) were refluxed for three hours to give an orange solution. This solution was filtered while hot and then cooled in ice to give orange-yellow crystals of $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{SnBr}_3$ (0.52 g., 34%), m.p. 172° (Lit. value, $170\text{--}171^\circ$ ⁽⁹⁴⁾). (Found: C, 15.3; H, 0.96; Br, 38.5%. Calc. for $\text{C}_7\text{H}_5\text{Br}_3\text{FeO}_2\text{Sn}$: C, 15.7; H, 0.93; Br, 44.8%).
- b) In EtOH:- Quantities used were as in a) except that absolute ethanol (25 ml.) was used as solvent. The reaction seemed to be complete (as estimated from the colour of the solution) in about 90 min. Orange-yellow crystals (0.56 g., 37%) separated from the solution on cooling in ice and were shown to be $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{SnBr}_3$ by m.p. 171° and infrared spectrum ($1000\text{--}200\text{ cm}^{-1}$)
- c) In n-PrOH:- Quantities used were as in a) except that n-propanol (25 ml.) was used as solvent. The reaction was complete in 10 min. Evaporation to small bulk and cooling of the solution gave orange crystals (yield, 0.62 g.). The crystals were shown by infrared spectrum ($1,000\text{--}200\text{ cm}^{-1}$) to be a mixture of $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{SnBr}_3$ and $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnBr}_2$ and the approximate relative proportions of these compounds were estimated from the intensities of bands in the spectrum.

d) In n-BuOH:- Quantities used were as in a) except that n-butanol (25 ml.) was used as solvent. The reaction was complete in 2-3 minutes. The reaction solution was evaporated to small bulk and cooled to room temperature to give orange crystals (0.59 g.) which were shown by infrared spectrum (1,000-200 cm^{-1}) to be a mixture of $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{SnBr}_3$ and $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnBr}_2$. The relative proportions of these two products were estimated as in c).

viii) Reaction of Bis(π -cyclopentadienyldicarbonyliron) and Stannous Bromide in THF

The reaction was carried out in a manner similar to the one reported previously⁽⁸¹⁾. $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ (1.8 g.) and hydrated stannous bromide (1.6 g.) in THF (100 ml.) were refluxed for 20 hr. Solvent was removed at the rotary evaporator and the residue was washed with pentane to remove unchanged $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$. The remaining solid was then crystallised from boiling methanol to give yellow crystals of $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnBr}_2$ (0.9 g., 28%), m.p. 170° (dec.), (Lit. value $168\text{-}171^\circ$ ⁽⁸¹⁾).

ix) Reaction of Bis(π -cyclopentadienyldicarbonyliron) and Stannous Iodide in Methanol

$[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ (1.0 g.) and hydrated stannous iodide

(4.0 g.) in reagent grade methanol (100 ml.) were refluxed for 2 hr. to give an orange-red solution. This solution was filtered while hot, evaporated to small volume, and cooled in ice to give red crystals of $[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnI}_2$ (1.3 g., 63%), m.p. 185° (dec.) (Lit. value⁽⁸¹⁾, 180° (dec.)). (Found: C, 23.2; H, 1.34%. Calc. for $\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{I}_2\text{O}_4\text{Sn}$: C, 23.2; H, 1.40%).

x) Reactions of Octacarbonyldicobalt with Stannous Halides

The previously reported reactions of octacarbonyldicobalt with stannous chloride⁽⁸¹⁾, stannous bromide⁽⁸²⁾ and stannous iodide⁽⁸²⁾ were repeated and only the expected products were isolated. The results are summarised in the following table:-

Reactants	Product
$\text{Co}_2(\text{CO})_8$ (3.0 g.) + SnCl_2 (1.7 g.)	$[\text{Co}(\text{CO})_4]_2\text{SnCl}_2$ (1.5 g.)
$\text{Co}_2(\text{CO})_8$ (2.0 g.) + $\text{SnBr}_2 \cdot 2\text{H}_2\text{O}$ (1.9 g.)	$[\text{Co}(\text{CO})_4]_2\text{SnBr}_2$ (1.6 g.)
$\text{Co}_2(\text{CO})_8$ (1.9 g.) + $\text{SnI}_2 \cdot x\text{H}_2\text{O}$ (3.0 g.)	$[\text{Co}(\text{CO})_4]_2\text{SnI}_2$ (0.73 g.)

Compound	Yield	M.p.	Lit.value m.p.
$[\text{Co}(\text{CO})_4]_2\text{SnCl}_2$	33 %	108°	106°
$[\text{Co}(\text{CO})_4]_2\text{SnBr}_2$	44 %	$112-114^\circ$	115°
$[\text{Co}(\text{CO})_4]_2\text{SnI}_2$	18 %	$86-90^\circ$	ca. 105°

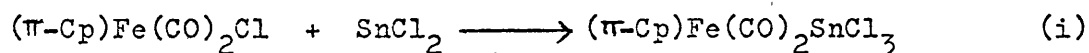
CHAPTER 3

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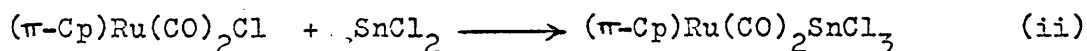
The Insertion of Stannous Halides Into Transition Metal-Halogen Bonds

3.1 Introduction

The first example of an insertion reaction of a stannous halide into a transition metal-halogen bond was reported in 1964⁽⁸⁰⁾, when it was found that chloro(π -cyclopentadienyl)-(dicarbonyl)iron would react with stannous chloride to give the insertion product:-

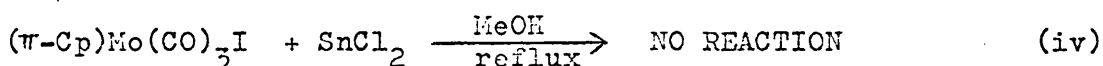
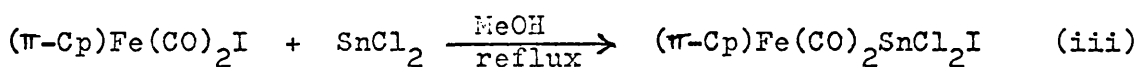


More recently, the ruthenium analogue has been shown to react similarly⁽⁸⁸⁾:-



Kinetic studies of the mechanisms of such reactions have

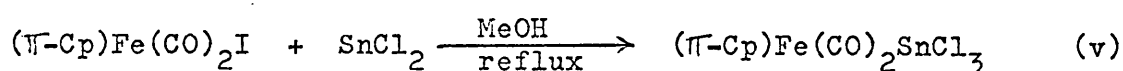
not been reported and so the term 'insertion reaction' has no mechanistic implications and is merely descriptive of the overall reaction. A preparative approach to the determination of the mechanism has been attempted⁽⁹⁵⁾; it was found that stannous chloride would insert into the iron-iodine bond of iodo(π -cyclopentadienyl)(dicarbonyl)iron to give a mixed-halide complex, but that iodo(π -cyclopentadienyl)(tricarbonyl)molybdenum would not react under the same conditions:-



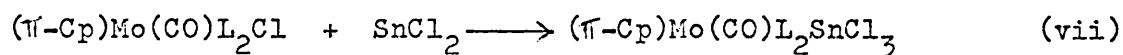
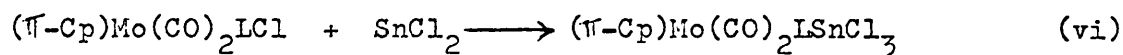
From these results it was postulated that the reaction involved initial co-ordination of stannous chloride to the central atom followed by migration of iodine from iron to tin; the lack of reactivity of the molybdenum compound could then be ascribed to the difficulty of formation of the necessary eight-co-ordinate intermediate.

It has not been possible to confirm these results in this present work, and a very recent paper has also suggested that a preparative approach to the determination of the mechanisms of such reactions is unlikely to be successful⁽⁹⁶⁾. Thus it was found⁽⁹⁶⁾ that the only product which could be isolated from the reaction of iodo(π -cyclopentadienyl)(dicarbonyl)iron and

stannous chloride was trichlor(π -cyclopentadienyldicarbonyl-iron)tin:-

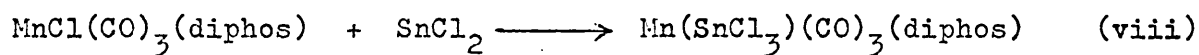


The postulate that the lack of reactivity of the molybdenum compound was due to steric effects was also shown to be unsatisfactory by the fact that some tertiary phosphine derivatives of the compound would react in the normal way⁽⁹⁶⁾⁽⁹⁷⁾:-



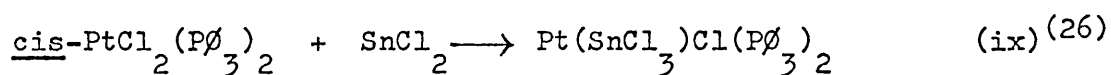
(L = P(OMe)₃ or P(O $\emptyset$)₃)

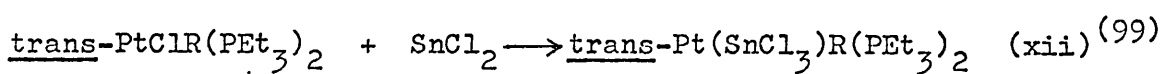
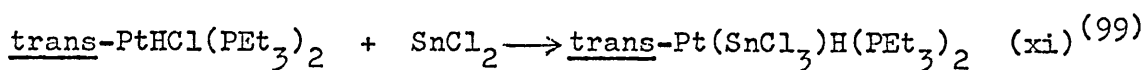
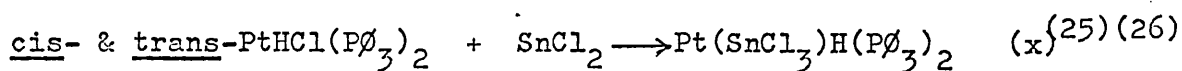
Similarly, chloropentacarbonylmanganese does not react with stannous chloride⁽⁸⁰⁾ but, under similar conditions, tertiary phosphine derivatives react to give the insertion product⁽⁹⁸⁾:-



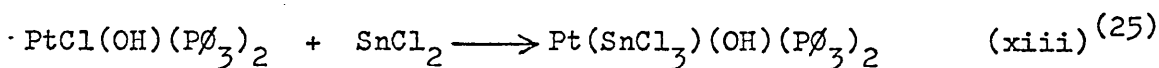
(diphos = $\emptyset_2\text{PCH}_2\text{CH}_2\text{P}\emptyset_2$)

Stannous chloride has been shown to react with several compounds containing platinum-chlorine bonds:-

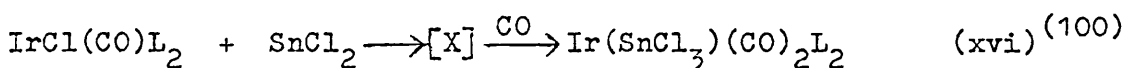
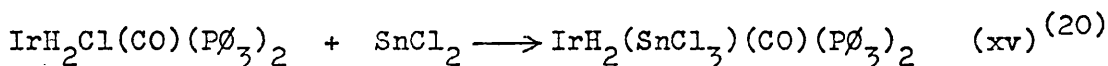
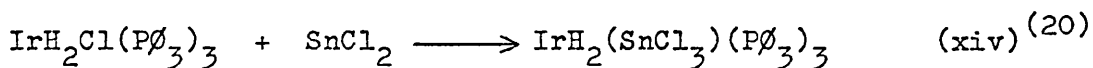




(R = meta- and para-fluorophenyl groups)

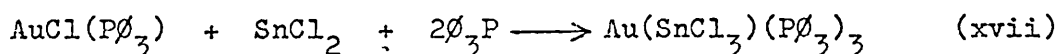


The insertion of stannous chloride into iridium-chlorine bonds is also well established:-



(L = P ϕ_3 or P(n-Bu)₃; [X] = intermediate)

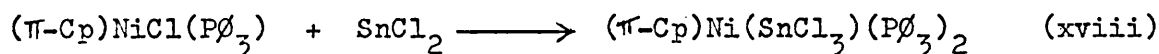
An interesting feature of the final product of reaction (xvi) is that it contains five-co-ordinate iridium(I) rather than the more usual square-planar geometry of metal ions with the d⁸ configuration. An unexpected co-ordination number is also found for gold(I) in the product from the reaction of chloro(triphenylphosphine)gold(I) with stannous chloride⁽¹⁰¹⁾:-



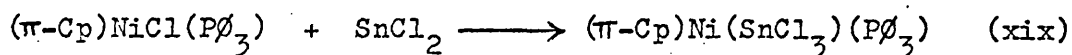
This, together with other evidence⁽⁹⁹⁾⁽¹⁹⁾, indicates that the

trichlorostannate ligand is able to stabilise co-ordination numbers greater than those usually found for a particular metal in a given oxidation state. This may be due to the weak σ -donor and strong π -acceptor properties of the ligand, which thus prevent excessive build-up of electron density at the central metal atom in the compounds with higher co-ordination numbers. Such an explanation is reasonable in the case of the trichlorostannate ligand, but it should be noted that five-co-ordinate iridium(I) complexes are known⁽³⁶⁾ with ligands such as hydride, iodide and acetyl groups for which a similar hypothesis is untenable.

An unusual example of the insertion of stannous chloride into a metal-chlorine bond has been reported for the reaction with chloro(π -cyclopentadienyl)(triphenylphosphine)nickel(II) in THF⁽¹⁰²⁾:-



The product was obtained in only 30 % yield, but addition of one equivalent of triphenylphosphine to the reaction solution increased this yield to 80%. The compound was shown to be ionic and was formulated as $[(\pi\text{-Cp})\text{Ni}(\text{P}\phi_3)_2]^+[\text{SnCl}_3]^-$. The same reaction was reinvestigated with acetone as solvent⁽¹⁰³⁾ and it was found that the major product was a molecular complex containing a nickel-tin bond:-



An ionic complex, identical to the one previously described, was also obtained as a minor product from the reaction in acetone and the yield of this ionic compound was again found to increase on addition of one equivalent of triphenylphosphine to the reaction mixture.

In the following sections of this chapter some new work on the insertion reactions of stannous halides with compounds containing transition metal-halogen bonds is described. The products from these reactions include new compounds, and known compounds which have been prepared by other reactions.

3.2 The Reaction of Iodo(π -cyclopentadienyl)(dicarbonyl)iron with Stannous Chloride

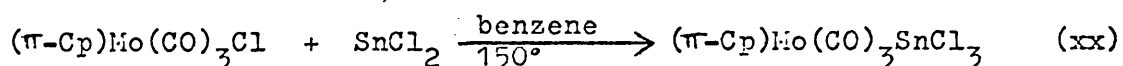
The earlier work on this reaction⁽⁹⁵⁾ has already been mentioned in the preceeding section. It was stated that the reaction was carried out in methanol with a ten-fold excess of stannous chloride, but other experimental details were not given. In this present work it was found that heating the reaction mixture under reflux resulted in rapid decomposition to give a brown, insoluble solid; if the reaction mixture was left at room temperature for several days, an orange-coloured solution was obtained but subsequent work-up yielded only orange oils and a

pure product could not be isolated. Thus it has not been possible to repeat the original reaction and this is in agreement with a later report⁽⁹⁶⁾ which was published after the completion of this present work.

3.3 The Reaction of Chloro(π -cyclopentadienyl)(tricarbonyl)-molybdenum with Stannous Chloride

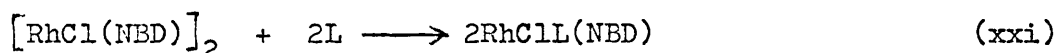
It has been reported that iodo(π -cyclopentadienyl)(tricarbonyl)molybdenum does not react with stannous chloride in refluxing methanol⁽⁹⁵⁾ and, in agreement with this, it has now been found that chloro(π -cyclopentadienyl)(tricarbonyl)molybdenum is similarly inert under these conditions.

In view of the successful insertion of stannous halides into metal-metal bonds under vigorous conditions (as described in Chapter 2), it was considered to be worthwhile to investigate the reaction of chloro(π -cyclopentadienyl)(tricarbonyl)molybdenum with stannous chloride under similarly vigorous conditions. Consequently the reactants, with benzene as solvent, were heated to 150° in a closed reaction vessel for several hours, after which time it was found that the desired insertion reaction had taken place to give trichloro(π -cyclopentadienyltricarbonylmolybdenum)tin:-



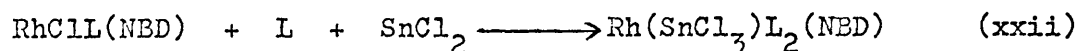
3.4 The Insertion of Stannous Chloride into the Rhodium-Chlorine Bond of Compounds of the Type RhClL(NBD)

Bis(μ -chloronorbornadienerrhodium(I)) will undergo a bridge-splitting reaction with a variety of ligands⁽¹⁰⁴⁾:-



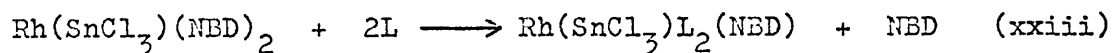
(NBD = bicyclo-2,2,1-hepta-2,5-diene; L = *p*-toluidine, $\phi_3\text{P}$, $\phi_2\text{MeP}$, $\phi_3\text{As}$, $\phi_3\text{Sb}$).

It has now been found that the products from such reactions will react with stannous chloride at room temperature in the presence of one equivalent of L, with insertion of stannous chloride into the rhodium-chlorine bond and formation of a five-co-ordinate complex of rhodium(I):-



(L = $\phi_3\text{P}$, $\phi_3\text{As}$, $\phi_3\text{Sb}$, (n-Bu) $_3\text{P}$, $\phi_2\text{MeP}$ & Et $_3\text{As}$).

The products with L = (n-Bu) $_3\text{P}$, $\phi_2\text{MeP}$ and Et $_3\text{As}$ are new compounds, but the ones with L = $\phi_3\text{P}$, $\phi_3\text{As}$ and $\phi_3\text{Sb}$ have been prepared previously by reaction of the appropriate ligand with trichlorostannatobis(norbornadiene)rhodium(I)⁽¹⁴⁾:-



The ability of the trichlorostannate ligand to stabilise high co-ordination numbers is again shown in compounds of this type.

Evidence for the formation of four-co-ordinate compounds of the type $\text{Rh}(\text{SnCl}_3)\text{L}(\text{NBD})$ could not be obtained, even when the reactions were carried out without the one equivalent excess of ligand in the reaction mixture.

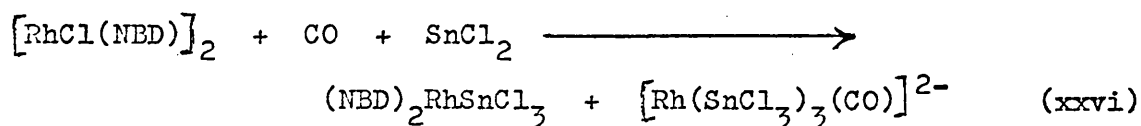
The reaction with triphenylphosphite as ligand, L, did not give the expected product and only orange oils could be isolated from the reaction mixture. This result is probably related to the fact that triphenylphosphite will displace the di-olefin from $\text{bis}(\mu\text{-chlorocycloocta-1,5-diene})\text{rhodium}$ rather than react to split the halogen bridge.

The results described in this section are the first examples of the simple insertion of stannous chloride into a rhodium-chlorine bond.

3.5 The Reaction of $\text{Bis}(\mu\text{-chloronorbornadiene})\text{rhodium}$ with Carbon Monoxide and Reaction of the Product with Stannous Chloride

The reaction of $\text{bis}(\mu\text{-chloronorbornadiene})\text{rhodium}$ with a variety of Group V donor ligands was mentioned in the previous section (reaction xxi), but such a reaction with carbon monoxide as the ligand has not been reported. An insertion reaction with stannous chloride, similar to that given by reactions (xxi) and (xxii), was therefore attempted with carbon monoxide as the ligand, L. The surprising result was that two compounds were

obtained, namely (trichlorostannato)bis(norbornadiene)rhodium(I) and the tris(trichlorostannato)(carbonyl)rhodium di-anion which was isolated as its tetraethylammonium salt. The overall reaction may be written as:-

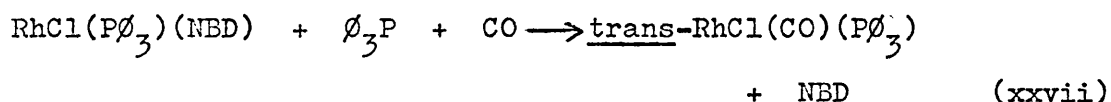


The notable feature of this reaction is the transfer of a norbornadiene ligand between two rhodium atoms.

In view of the unexpected nature of this reaction it was considered to be worthwhile to investigate the reaction of bis(μ -chloronorbornadiene)rhodium(I) with carbon monoxide alone. The infrared spectrum of the crude product obtained by bubbling carbon monoxide through a solution of the dimer showed the presence of a mixture of the starting material and a small amount of a carbonyl-containing species with two $\nu(\text{CO})$ frequencies at ca. 2095 cm^{-1} and ca. 2050 cm^{-1} . Although it was possible to separate the starting material from this mixture, a pure sample of the carbonyl compound could not be isolated. The two carbonyl frequencies might be due to a species such as $(\text{CO})_2\text{RhCl}_2\text{Rh}(\text{NBD})$, which could be readily envisaged as reacting with stannous chloride and the free norbornadiene to give trichlorostannato-bis(norbornadiene)rhodium(I) and the dichlorodicarbonylrhodium(I) di-anion. This di-anion would then react readily with excess

stannous chloride to give $[\text{Rh}(\text{SnCl}_3)_3(\text{CO})]^{2-}$ (113).

The ease with which carbon monoxide will displace norbornadiene from its complexes with rhodium was demonstrated by the reaction of carbon monoxide with chloro(triphenylphosphine)(norbornadiene)rhodium(I) in the presence of one equivalent of triphenylphosphine to give trans-chloro(carbonyl)bis-(triphenylphosphine)rhodium(I):-



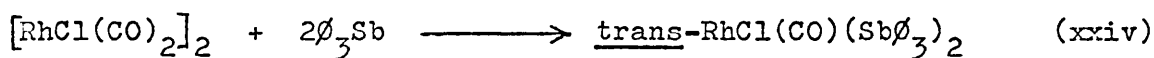
This reaction provides some evidence for the feasibility of a reaction mechanism such as the one tentatively postulated above to explain reaction (xxvi).

3.6 The Insertion of Stannous Chloride into the Rhodium-Chlorine Bond of Compounds of the Type $\text{RhCl}(\text{CO})\text{L}_2$

trans-chloro(carbonyl)bis(triphenylphosphine)rhodium(I) has been found to be inert to stannous chloride in solvents such as THF and methylene chloride and the starting materials could be recovered in quantitative yields from such mixtures. It has been briefly mentioned elsewhere⁽¹⁰⁶⁾ that a reversible reaction occurs between trans-chloro(carbonyl)bis(triphenylphosphine)-rhodium(I) and stannous chloride, but the product was not characterised and details of the reaction conditions were not

given.

The triphenylstibine analogue of trans-chloro(carbonyl)-bis(triphenylphosphine)rhodium(I) has been prepared but its correct formulation is still in some doubt. It was originally reported⁽¹⁰⁷⁾ that triphenylstibine would react with bis(chlorodicarbonylrhodium(I)), in a manner similar to that for triphenylphosphine and triphenylarsine, to give trans-chloro(carbonyl)bis(triphenylstibine)rhodium(I):-

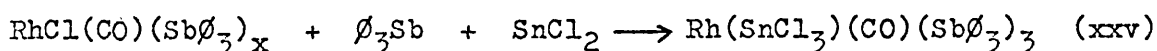


Other results⁽¹⁰⁸⁾ have suggested that the product from this reaction is the tris(triphenylstibine) compound, $\text{RhCl}(\text{CO})(\text{SbPh}_3)_3$, and later work⁽¹⁰⁹⁾ has indicated that both the previously reported products of the reaction should, in fact, have been formulated as the tetrakis(triphenylstibine) compound, $\text{RhCl}(\text{CO})(\text{SbPh}_3)_4$. An apparently similar compound has been prepared from the reaction of heptaldehyde with chlorotris(triphenylstibine)rhodium(I)⁽¹¹⁰⁾, but a formulation was not given for the product because analytical results were unsatisfactory.

In this present work the reaction of triphenylstibine with bis(chlorodicarbonylrhodium) was repeated as originally described⁽¹⁰⁷⁾, and a compound was obtained with the same colour and melting point as the reported product⁽¹⁰⁷⁾. The analytical results were inconclusive but favoured formulation as

$\text{RhCl}(\text{CO})(\text{Sb}\phi_3)_2$ rather than as the tri- or tetrakis-triphenylstibine compound. The far-infrared spectrum, on the other hand, provides evidence for a co-ordination number greater than four; the spectrum shows a strong band at 272 cm.^{-1} with shoulders at 267 cm.^{-1} and 263 cm.^{-1} and it is reasonable to assign one of these bands to the rhodium-chlorine stretching frequency because these are the only bands in the region where $\nu(\text{Rh-Cl})$ is expected to occur for compounds of rhodium(I)⁽¹¹¹⁾. Whichever of these bands is due to $\nu(\text{Rh-Cl})$ it is at an appreciably lower frequency than those due to $\nu(\text{Rh-Cl})$ in $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ and $\text{RhCl}(\text{CO})(\text{As}\phi_3)_2$, which are at 309 cm.^{-1} and 300 cm.^{-1} respectively⁽¹¹¹⁾. This lowering of the rhodium-chlorine stretching frequency may be due to an increased co-ordination number about rhodium in the triphenylstibine compound, since it is recognised that, in the absence of other effects, an increase in co-ordination number will result in a lowering of a given metal-chlorine stretching frequency⁽¹¹²⁾.

The exact formulation of the triphenylstibine compound is still, therefore, uncertain but its reaction with stannous chloride in the presence of one equivalent of free triphenylstibine has been found to give the five-co-ordinate compound, (trichlorostannato)(carbonyl)tris(triphenylstibine)rhodium(I):-

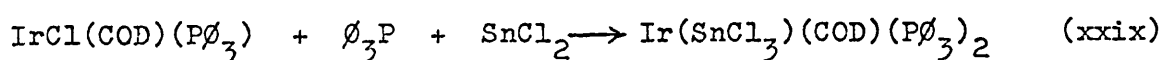
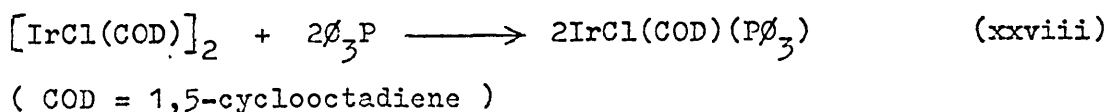


Excellent analytical data have been obtained for this product and there is no reason to doubt that the given formulation is a correct one.

3.7 The Insertion of Stannous Chloride into the Iridium-Chlorine Bond of Chloro(1,5-cyclooctadiene)(triphenylphosphine)-iridium(I)

From the successful insertion reactions of stannous chloride into rhodium-chlorine bonds (as described in section 3.4) it follows that a similar reaction with an iridium complex would be worthy of investigation. Such a reaction is of interest because it has been found⁽²⁰⁾ that reactions of stannous chloride with certain compounds containing iridium-chlorine bonds have resulted in the formation of iridium hydride complexes.

Thus μ -chloro(1,5-cyclooctadiene)iridium(I) dimer was treated with triphenylphosphine to give chloro(1,5-cyclooctadiene)-(triphenylphosphine)iridium(I), and this was found to react readily with stannous chloride in the presence of one equivalent of free triphenylphosphine to give the insertion product, (trichlorostannato)(1,5-cyclooctadiene)bis(triphenylphosphine)iridium:-



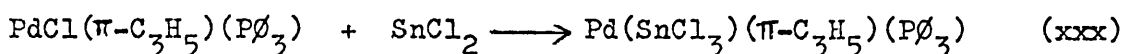
There was no infrared spectral evidence for the formation of an iridium hydride species.

The product from reaction (xxix) has been made previously by the reaction of triphenylphosphine with (trichlorostannato)bis-(1,5-cyclooctadiene)iridium(I)⁽¹⁴⁾.

3.8 The Insertion of Stannous Chloride into the Palladium-Chlorine Bond of Compounds of the Type $\text{PdCl}(\pi\text{-allyl})\text{L}$

Until very recently⁽⁵²⁾⁽¹¹⁴⁾ neutral compounds containing a palladium-tin bond were unknown. Therefore the reaction of stannous chloride with chloro(π -allyl)(triphenylphosphine)-palladium(II) was investigated in the expectation that the stannous chloride would insert into the palladium-chlorine bond and form a palladium-tin bond. The reaction was found to take place readily at room temperature in methanol solvent and the crude product could be readily recrystallised from benzene-petroleum spirit to give a yellow crystalline material. A nuclear magnetic resonance (NMR) spectrum of this compound indicated the presence of benzene as solvent of crystallisation, and this was confirmed by elemental analysis results. A further recrystallisation of the compound from toluene-petroleum spirit gave a product which did not contain solvent of crystallisation and excellent analytical data enabled the compound to be formulated as $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$. Therefore the expected

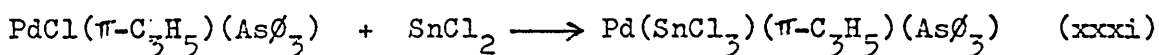
insertion reaction had taken place and may be written as:-



The room-temperature NMR spectrum of this product strongly suggests that the allylic ligand is symmetrically π -bonded and tentative assignments are given in Table 3.1 (page 65). The observed chemical shifts are very similar to those found for $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2^{(115)}$ but the doublets due to the terminal protons in the dimeric compound have become broad singlets in the tin-containing compound. Later work⁽⁵²⁾ has shown that these signals remain broad at -40° , and this suggests that the broadening is due to coupling with other nuclei rather than to an exchange phenomenon such as is observed in $\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)^{(116)(117)}$.

Since the completion of this present work, the symmetrical nature of the π -bonded allylic ligand has been confirmed by an X-ray structure determination⁽⁵²⁾ and such symmetry implies that the trans-directing effects of the trichlorostannate and triphenylphosphine ligands are very similar.

Chloro(π -allyl)(triphenylarsine)palladium(II) has been found to react readily with stannous chloride in a similar manner to the triphenylphosphine analogue:-



The product was again readily recrystallised from benzene-

TABLE 3.1 Room Temperature NMR Spectra of
 $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ and $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)\text{L}$

Compound	τ_5	$\tau_{1,4}$	$\tau_{2,3}$
$[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2^{(115)}$	4.57	5.93(d) ($J_{4,5} = 6.9$)	6.91(d) ($J_{3,5} = 12.0$)
$\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$	4.47(qui)	5.4(s,b)	6.6(s,b)
$\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3)$	ca.4.5(m)	5.4(s,b)	6.5(s,b)

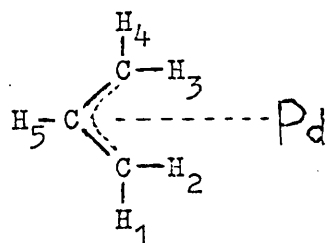
J = coupling constant in cycles/sec.

Spectrum measured at 60 Mc/sec. in CDCl_3 as solvent.

Chemical shifts (τ) are relative to Me_4Si as internal standard.

s = singlet, d = doublet, qui = quintet, m = unresolved multiplet,

b = broad. Protons are numbered as follows:-



petroleum spirit and was found to contain solvent of crystallisation. Elemental analysis indicated the correct formulation to be $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ and recrystallisation from toluene-petroleum spirit gave a similar compound containing toluene as solvent of crystallisation. The NMR spectrum of this product was similar to that of the triphenylphosphine compound discussed above, (see Table 3.1)

A related product could not be isolated from the reaction of stannous chloride with the triphenylstibine analogue, $\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{Sb}\phi_3)$.

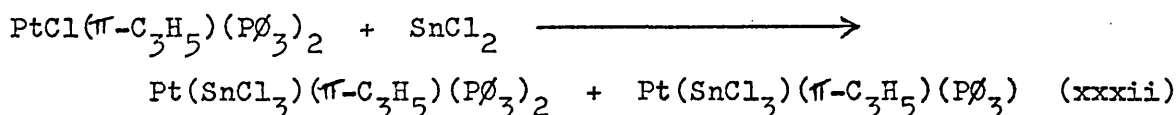
3.9 The Reaction of Stannous Chloride with Chloro(π -allyl)bis-(triphenylphosphine)platinum(II)

A platinum analogue of chloro(π -allyl)(triphenylphosphine)-palladium(II) is not known, but chloro(π -allyl)bis(triphenylphosphine)platinum(II) has been synthesised⁽¹¹⁸⁾⁽¹¹⁹⁾. This platinum complex has a conductivity in nitromethane which is typical of a 1:1 electrolyte and so may be formulated as $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]^+\text{Cl}^-$, but other evidence⁽¹²⁰⁾ suggests that the compound is five-co-ordinate in the solid state and in chloroform solution.

Chloro(π -allyl)bis(triphenylphosphine)platinum(II) was found to react readily with stannous chloride in methylene chloride-methanol solution to give two products. The major product (I) was recrystallised from benzene-petroleum spirit as

yellow crystals and identified by elemental analysis, NMR spectrum (Table 3.2, page 68), and infrared spectrum as (trichlorostannato)-(π-allyl)bis(triphenylphosphine)platinum(II), $\text{Pt}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2$. A minor product (II), isolated as orange crystals from methylene chloride-methanol, was identified by elemental analysis and infrared spectrum as (trichlorostannato)-(π-allyl)(triphenylphosphine)platinum(II), $\text{Pt}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$. An NMR spectrum of (II) could not be obtained, presumably because the signals were broad and of low intensity.

The overall reaction may be written as:-



This reaction is clearly very similar to the one between stannous chloride and chloro(π-cyclopentadienyl)(triphenylphosphine)nickel which was discussed in section 3.1 (reactions xviii and xix).

The far-infrared spectrum of (I) has two bands at 293 cm.^{-1} and 259 cm.^{-1} which may be assigned to the tin-chlorine stretching frequencies of a virtually unco-ordinated SnCl_3^- group (c.f. $\phi_4\text{AsSnCl}_3$ with $\nu(\text{SnCl}_3)$ at 289 cm.^{-1} and 252 cm.^{-1} and free SnCl_3^- with $\nu(\text{SnCl}_3)$ at 297 cm.^{-1} and 256 cm.^{-1} (65)). Moreover, the NMR spectra of (I) and $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{Cl}^{(121)}$ are almost identical (see Table 3.2, page 68) and so it is reasonable to formulate (I) as $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]^+\text{SnCl}_3^-$.

TABLE 3.2 Room Temperature NMR Spectra of
 $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{X}$ (X = Cl & SnCl_3)

Compound	τ_5	$\tau_{1,2,3,4}$
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{Cl}^a$	4.31(qui)	6.58 (4 bands) $(J_{(1,2,3,4)-5} = 11;$ $J_{(1,2,3,4)-^{195}\text{Pt}} = 22).$
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{SnCl}_3$	ca.4.32(m)	6.56 (4 bands) $(J_{(1,2,3,4)-5} = 11;$ $J_{(1,2,3,4)-^{195}\text{Pt}} = 22).$

J = coupling constant in cycles/sec.

Spectrum measured at 60Mc./sec. in CDCl_3 as solvent.

Chemical shifts (τ) are relative to Me_4Si as internal standard.

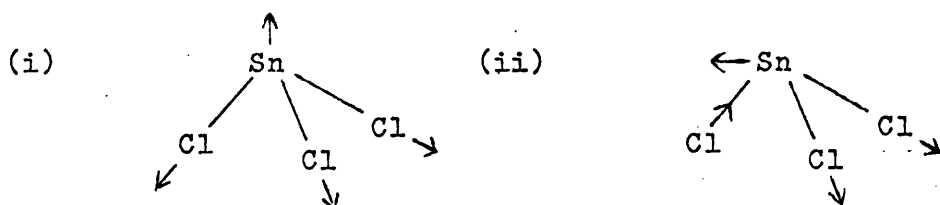
qui = quintet, m = unresolved multiplet. a = see refs. (118)(121)

Protons numbered as in Table 3.1.

The far-infrared spectrum of (II), on the other hand, has tin-chlorine stretching frequencies at 354 cm.^{-1} and 325 cm.^{-1} which are typical of an SnCl_3 group co-ordinated to platinum⁽⁹⁹⁾. Far-infrared spectra thus provide an excellent means for the differentiation of compounds of these two types.

3.10 Infrared Spectra of Compounds Containing the Trichlorostannato Ligand

The trichlorostannato ligand in a metal complex may be considered as having local C_{3v} symmetry. Using this approximation, theory predicts two infrared-active tin-chlorine stretching vibrations ($A_1 + E$), which correspond to the totally symmetric vibration (i) and the doubly degenerate antisymmetric vibration (ii) :-



It has been suggested⁽⁹⁹⁾ that a doublet at 330 cm.^{-1} in the infrared spectrum is typical of complexes containing the SnCl_3^- ligand and this doublet may be assigned to the tin-chlorine stretching vibrations. Later work⁽⁶⁴⁾ has included a more systematic study of the far-infrared spectra of such compounds and some useful correlations have been made.

Thus the SnCl_3^- ion, as its tetraphenylarsonium salt, has

bands at 289 cm.^{-1} and 252 cm.^{-1} which can be assigned to the symmetric and antisymmetric tin-chlorine stretching frequencies respectively, while in MeSnCl_3 the corresponding bands are at 384 cm.^{-1} and 366 cm.^{-1} . The tin-chlorine stretching frequencies in transition metal complexes of SnCl_3^- would then be expected to fall between these two extremes, with the highest such frequencies in complexes of metals of the greatest electron-pair affinity, since co-ordination of SnCl_3^- would result in an increase in the positive charge on tin and so increase the $\text{Sn}^{\delta+}-\text{Cl}^{\delta-}$ restoring force. It has been found that the lowest tin-chlorine stretching frequencies occur in free SnCl_3^- , with higher frequencies in complexes of metals in the +1 oxidation state and still higher frequencies in complexes of metals in the +2 oxidation state.

The infrared spectra (from $400\text{--}200\text{ cm.}^{-1}$) of all the complexes mentioned in this chapter are given in Table 3.3 (page 71), and it is found that, in general, the expected correlations are observed. Thus for complexes of metals in the +2 oxidation state the symmetric tin-chlorine stretching frequencies lie in the range $354\text{--}327\text{ cm.}^{-1}$ with the antisymmetric frequencies in the range $325\text{--}316\text{ cm.}^{-1}$, while for metals in the +1 oxidation state the corresponding ranges are $321\text{--}302\text{ cm.}^{-1}$ and $300\text{--}273\text{ cm.}^{-1}$ respectively. The platinum complex formulated as $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]^+\text{SnCl}_3^-$ has bands at 293 cm.^{-1} and

TABLE 3.3 Far Infrared Spectra (400-200 cm.⁻¹) of
Trichlorostannato-Transition Metal Complexes

Compound	$\nu(\text{Sn-Cl})_{\text{sy}}$	$\nu(\text{Sn-Cl})_{\text{as}}$	Other bands
$\text{Cl}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	337(s)	320(s)	382(w) 370(w)
$\text{Cl}_3\text{SnPd}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$	335(m)	325(s) 320(sh)*	297(vs)*
$\text{Cl}_3\text{SnPd}(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3)$	335(m)	325(s) 317(s)*	297(vs)* 342(m)
$\text{Cl}_3\text{SnPt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$	354(m)	325(s, br)	-
$\text{Cl}_3\text{Sn Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2$	293(m)	259(s)	-
$\text{Cl}_3\text{SnRh}(\text{NBD})_2$	314(s)	299(s) 281(s)*	-
$\text{Cl}_3\text{SnIr}(\text{COD})_2$	316(s)	299(s) 290(s)*	265(w) 255(w) 246(m)
$\text{Cl}_3\text{SnIr}(\text{COD})(\text{P}\phi_3)_2$	308(s)	290(m) 279(sh)	-
$\text{Cl}_3\text{SnRh}(\text{NBD})(\text{P}\phi_3)_2$	305(s)	280(s)	-
$\text{Cl}_3\text{SnRh}(\text{NBD})(\text{As}\phi_3)_2$	307(s)	284(s)	331(m) 323(sh)
$\text{Cl}_3\text{SnRh}(\text{NBD})(\text{Sb}\phi_3)_2$	311(s)	296(s)	277(m) 267(m) 261(sh) 254(w)
$\text{Cl}_3\text{SnRh}(\text{NBD})(\text{Pn-Bu})_2$	302(s)	278(s)	-

Continued.....

TABLE 3.3 (Continued)

Compound	$\nu(\text{Sn-Cl})_{\text{sy}}$	$\nu(\text{Sn-Cl})_{\text{as}}$	Other Bands
$\text{Cl}_3\text{SnRh(NBD)(PMe}\phi_2)_2$	306(s)	287(s) 273(m)*	-
$\text{Cl}_3\text{SnRh(NBD)(AsEt}_3)_2$	305(s)	295(s) 276(s)	-
$\text{Cl}_3\text{SnRh(CO)(Sb}\phi_3)_3$	321(s)	300(s)	279(s) 269(s) 264(sh)
$(\text{Et}_4\text{N})_2[\text{Rh(SnCl}_3)_3(\text{CO})]$	312(s)	297(sh)	348(m)
$[\text{As}\phi_4]^+[\text{SnCl}_3]^-$	289(ms)	252(s)	-

sy = symmetric, as = antisymmetric.

s = strong, m = medium, w = weak, br = broad, sh = shoulder.

* = see text.

259 cm.^{-1} which are very near to those observed in $(\text{As}\phi_4)^+\text{SnCl}_3^-$.

It should be noted that several of the assignments given in Table 3.3 are somewhat tentative. The spectra of the compounds $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$ and $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3)$ are particularly difficult to assign; the assignments given in the table arise from a comparison with related compounds but the spectra of both compounds have a very strong band at 297 cm.^{-1} , the intensity of which would suggest that it is also due to a tin-chlorine stretching mode. The crystal structure determination of the triphenylphosphine compound⁽⁵²⁾ did not provide an explanation for the surfeit of bands in the tin-chlorine stretching frequency region. Several of the other compounds listed in Table 3.3 are shown as having two bands assignable to the antisymmetric stretching vibration. It is reasonable to assume that, in such cases, the degeneracy of this vibrational mode might be lifted by the influence of the site symmetry in the crystal.

3.11 Experimental

Elemental analyses, infrared spectra, and melting points were obtained as described in Chapter 2. Proton NMR spectra were obtained in deuteriochloroform solvent, with tetramethylsilane as internal standard, on a Varian Associates A60 spectrometer operating at 60Mc/sec.

The following compounds were prepared by literature methods :- iodo(π -cyclopentadienyl)(dicarbonyl)iron⁽¹²²⁾, chloro(π -cyclopentadienyl)(tricarbonyl)molybdenum⁽¹²³⁾, bis(μ -chloronorbornadienerhodium)⁽¹²⁴⁾, chloro(carbonyl)bis(triphenylphosphine)rhodium⁽¹²⁵⁾, bis(μ -chlorocycloocta-1,5-diene-iridium)⁽¹²⁶⁾, tetrakis(triphenylphosphine)platinum⁽¹²⁷⁾, bis(μ -chloro(π -allyl)palladium)⁽¹²⁸⁾, and chloro(π -allyl)(ligand)-palladium⁽¹¹⁶⁾ (where ligand is triphenyl-phosphine, -arsine and -stibine).

All the reactions described below were carried out under an atmosphere of dry nitrogen.

i) Reaction of Iodo(π -cyclopentadienyl)(dicarbonyl)iron with Stannous Chloride

(π -Cp)Fe(CO)₂I (0.3 g.) and a ten-fold excess of stannous chloride (1.9 g.) in methanol (30 ml.) were heated under reflux. After 30 min. a brown insoluble solid had formed and was filtered off, washed with methanol and dried in air. This product was

insoluble in all common solvents and its far infrared spectrum did not show any bands assignable to a tin-chlorine stretching vibration.

The reaction was repeated with similar quantities of reactants and the reaction mixture was left to stand at room temperature for three days to give a clear, orange-coloured solution. Work-up of this solution gave only orange-yellow oils which could not be identified.

ii) Reaction of Chloro(π -cyclopentadienyl)(tricarbonyl)molybdenum with Stannous Chloride

a) Under reflux:- (π -Cp)Mo(CO)₃Cl (0.3 g.) and excess stannous chloride (0.5 g.) in methanol (30 ml.) were refluxed for eight days without any obvious signs of reaction. The starting material was recovered in somewhat less than quantitative yield but other products could not be isolated.

b) At high temperature:- (π -Cp)Mo(CO)₃Cl (0.2 g.), excess stannous chloride (0.5 g.) and benzene (20 ml.) were heated to 150° in a sealed, stainless steel reaction vessel for twenty hours. The resulting solution was filtered to give a clear yellow solution to which was added petroleum spirit (boiling range 100-120°), and rotary evaporation of the mixture gave yellow crystals of (π -Cp)Mo(CO)₃SnCl₃ (0.15 g., 45%), m.p. 160-163° (lit. value, 164° (80)). The compound was further

characterised by comparison of its infrared spectrum ($400-200\text{ cm.}^{-1}$) with that of a genuine sample prepared by the reaction of $\text{Hg}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ and stannous chloride⁽⁹²⁾.

iii) Reaction of Stannous Chloride with Compounds of the Type $\text{RhClL}(\text{NBD})$

The reaction was attempted with $\text{L} = \text{P}\phi_3$, $\text{As}\phi_3$, $\text{Sb}\phi_3$, $\text{P}(\text{n-Bu})_3$, $\text{PMe}\phi_2$, AsEt_3 and $\text{P}(\text{O}\phi)_3$. The same method was used in each case and, as an example, the one with $\text{L} = \text{P}\phi_3$ is described. Thus $[\text{RhCl}(\text{NBD})]_2$ (0.23 g.) and four equivalents of triphenylphosphine (0.5 g.) were dissolved in 20 ml. of a solvent consisting of equal volumes of methylene chloride and methanol to give a clear orange solution. To this solution was added excess stannous chloride (0.4 g.) and after shaking for a few minutes orange crystals of the product separated. The crystals were filtered off, washed with methanol and dried in vacuo. Some of the other products were more soluble than the one with $\text{L} = \text{P}\phi_3$ and it was necessary to evaporate the solvent to small volume to induce crystallisation in these cases.

The yields, analytical data and melting points of all the compounds prepared by this reaction are given in Table 3.4.

TABLE 3.4 Yields, Melting Points and Analytical Data
For the Compounds $\text{Cl}_3\text{SnRh(NBD)L}_2$

L	% Yield	m.p. ^o	Found			Required		
			C%	H%	Cl%	C%	H%	Cl%
$\text{P}\phi_3$	82	145-147	54.4	3.84	12.2	54.7	4.0	11.3
$\text{As}\phi_3$	70	178-180 ^a	50.6	3.78	9.7	50.0	3.7	10.3
$\text{Sb}\phi_3$	72	ca.200 ^a	45.1	3.40	9.4	45.8	3.40	9.5
$\text{P}(\text{O}\phi)_3^*$	0	-	-	-	-	-	-	-
$\text{P}(\text{n-Bu})_3$	76	140-142	45.1	7.25	12.3	45.2	7.58	12.9
$\text{PMe}\phi_2$	72	163-165	47.9	4.31	13.9	48.3	4.17	13.0
AsEt_3	68	144	30.8	5.17	14.3	30.7	5.15	14.3

^a = with decomposition

* It was not possible to isolate a crystalline product from the reaction with $\text{L} = \text{P}(\text{O}\phi)_3$.

iv) Reaction of Bis(μ -chloronorbornadienerhodium) with Carbon Monoxide and Reaction of the Product with Stannous Chloride

$[\text{RhCl}(\text{NBD})]_2$ (0.4 g.) was dissolved in methylene chloride-methanol to give a clear orange solution. Carbon monoxide was bubbled into this solution for fifteen minutes and then excess stannous chloride (0.8 g.) in methylene chloride-methanol solvent was added to give a deep red solution. Carbon monoxide was bubbled into the solution for a further 2-3 hours and, as the methylene chloride was driven off, yellow crystals formed in the solution. These were filtered off, washed with methanol and dried in vacuo to give yellow crystals of $\text{Cl}_3\text{SnRh}(\text{NBD})_2$, m.p. 170° (dec.) (lit value, $170-177^\circ$ dec.⁽¹⁴⁾). (Found: C, 33.2; H, 3.01; Cl, 20.8%. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_3\text{RhSn}$: C, 32.9; H, 3.14; Cl, 20.8%).

Tetraethylammonium chloride (0.5 g.) in methanol was added to the deep red filtrate to give an immediate orange precipitate of $(\text{Et}_4\text{N})_2[\text{Rh}(\text{SnCl}_3)_3(\text{CO})]$ (Found: C, 20.0; H, 4.04; Cl, ~~20.4~~^{23.9}; N, 2.73%. Calc. for $\text{C}_{17}\text{H}_{40}\text{Cl}_9\text{N}_2\text{ORhSn}$: C, 19.3; H, 3.79; Cl, 29.9; N, 2.63%).

v) Reaction of Bis(μ -chloronorbornadienerhodium) with Carbon Monoxide

$[\text{RhCl}(\text{NBD})]_2$ (0.3 g.) was dissolved in methylene chloride-methanol and carbon monoxide was bubbled through this solution

for $1\frac{1}{2}$ hr. A slight colour change (from orange to orange-yellow) was observed. Rotary evaporation of the solution to very small volume gave an orange solid. An infrared spectrum of this crude product showed it to consist mainly of unchanged $[\text{RhCl}(\text{NBD})]_2$ together with a small amount of a carbonyl compound. The crude product dissolved in hot petroleum spirit (boiling range $60-80^\circ$) and crystals of pure $[\text{RhCl}(\text{NBD})]_2$ separated from this solution on cooling to room temperature. The crystals were filtered off but other products could not be isolated from the filtrate.

vi) Reaction of Bis(μ -chloronorbornadienerhodium) with Triphenylphosphine and Carbon Monoxide

$[\text{RhCl}(\text{NBD})]_2$ (0.2 g.) and triphenylphosphine (0.3 g.) were dissolved in methylene chloride-methanol (20 ml.) to give a solution of $\text{RhCl}(\text{NBD})(\text{P}\phi_3)$. Carbon monoxide was bubbled through this solution and after a few minutes pale yellow crystals were deposited from the solution. These crystals were filtered off, washed with methanol, dried in vacuo and shown by infrared spectrum and m.p. $195-200^\circ$ to be identical to a genuine sample of trans- $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$.

vii) Attempted Reaction of trans-chloro(carbonyl)bis(triphenylphosphine)rhodium with Stannous Chloride

trans- $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ (0.69 g.) and triphenylphosphine

(0.26 g.) were dissolved in warm THF (30 ml.) and to the resulting pale yellow solution was added excess stannous chloride (0.5 g.) in a minimum amount of the same solvent. The mixture was refluxed for 3 hr. without any apparent change in colour. Rotary evaporation of the solution to dryness and washing of the crude solid with ethanol gave pure trans- $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ in quantitative yield.

A similar procedure with methylene chloride-methanol as solvent gave the same negative result.

viii) Preparation of $\text{RhCl}(\text{CO})(\text{Sb}\phi_3)_2$

Excess triphenylstibine (1.8 g.) was added to a solution of $[\text{RhCl}(\text{CO})_2]_2$ (0.3 g.) in benzene (25 ml.). The initially orange solution immediately became deep red and gas was evolved. After one hour the solution was evaporated to small bulk on the rotary evaporator and addition of ethanol gave a red precipitate. This precipitate was filtered off, washed with ethanol and recrystallised from methylene chloride-methanol as deep red crystals (0.8 g.), m.p. $156-158^\circ$ dec. (lit value, $151-153^\circ$ dec.⁽¹⁰⁷⁾). (Found: C, 51.8; H, 2.87; Cl, 7.71%. Calc. for $\text{C}_{37}\text{H}_{30}\text{ClORhSb}_2$: C, 50.9; H, 3.46; Cl, 4.07%).

ix) Reaction of $\text{RhCl}(\text{CO})(\text{Sb}\phi_3)_x$ with Stannous Chloride

$\text{RhCl}(\text{CO})(\text{Sb}\phi_3)_x$ (0.44 g.) and triphenylstibine (0.18 g.) were dissolved in methylene chloride-methanol (25 ml.) to give a deep red solution. To this solution was added an excess of stannous chloride (0.3 g.) in a minimum amount of the same solvent with an immediate reaction to give a clear orange solution. Methanol (25 ml.) was added and, on standing, orange crystals separated from the reaction solution. These crystals were filtered off, washed with methanol and dried in vacuo to give pure (trichlorostannato)(carbonyl)tris(triphenylstibine)rhodium, $\text{Rh}(\text{SnCl}_3)(\text{CO})(\text{Sb}\phi_3)_3$, (0.48 g.), m.p. 186° dec. (Found: C, 46.2; H, 3.19; Cl, 7.90%. Calc. for $\text{C}_{55}\text{H}_{45}\text{Cl}_3\text{ORhSb}_3\text{Sn}$: C, 46.7; H, 3.22; Cl, 7.53%).

x) Reaction of Chloro(cycloocta-1,5-diene)(triphenylphosphine)-iridium with Stannous Chloride

$[\text{IrCl}(\text{COD})]_2$ (40 mg.) and triphenylphosphine (70 mg.) were dissolved in methylene chloride-methanol (15 ml.) to give a deep red solution. Addition of a solution of excess stannous chloride (0.2 g.) in methanol produced an immediate orange colouration and addition of methanol and rotary evaporation to small volume gave orange crystals of $\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}\phi_3)_2$ (0.1 g., 80%), m.p. $164\text{--}166^\circ$ dec. (lit. value, $127\text{--}130^\circ$ dec.⁽¹⁴⁾). The product was identified by comparison of its infrared spectrum with that

of an authentic sample prepared by the literature method⁽¹⁴⁾.

The melting point of this authentic sample was found to be 163-167° dec.

xi) Reaction of Chloro(π -allyl)(triphenylphosphine)palladium with Stannous Chloride

A methanolic solution of excess stannous chloride (1.0 g.) was added to a solution of $\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$ (1.0 g.) in warm methanol (25 ml.) to give a dark coloured precipitate. This precipitate was filtered off and treated with hot benzene to give a yellow solution and leave a small quantity of a purple oil. Addition of petroleum spirit (boiling range 100-120°) to the filtered benzene solution and evaporation to small volume gave pale yellow crystals of $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3) \cdot \text{C}_6\text{H}_6$ (0.9 g., 56%), m.p. 134-135° dec. (Found: C, 44.8; H, 3.57; Cl, 12.8%. Calc. for $\text{C}_{27}\text{H}_{26}\text{Cl}_3\text{PPdSn}$: C, 45.5; H, 3.67; Cl, 14.9%).

Recrystallisation of this product from toluene-petroleum spirit gave very pale yellow crystals of $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$ m.p. 138-140° dec. (Found: C, 40.2; H, 3.25; Cl, 16.7%. Calc. for $\text{C}_{21}\text{H}_{20}\text{Cl}_3\text{PPdSn}$: C, 39.7; H, 3.18; Cl, 16.8%).

xii) Reaction of Chloro(π -allyl)(triphenylarsine)palladium
with Stannous Chloride

To a solution of $\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3)$ (0.5 g.) in methylene chloride-methanol (15 ml.) was added an excess of stannous chloride (0.5 g.) in a minimum amount of the same solvent to produce an immediate purple-red colouration. After 30 min. the solution was evaporated to small volume to give an impure solid. This solid redissolved in hot benzene to give a pale yellow solution. The solution was filtered and addition of petroleum spirit followed by evaporation to small volume gave pale yellow crystals. A further recrystallisation from benzene-petroleum spirit gave off-white crystals of $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (0.5 g., 68%), m.p. 142-144° dec. (Found: C, 40.0; H, 3.19; Cl, 15.5%. Calc. for $\text{C}_{24}\text{H}_{23}\text{AsCl}_3\text{PdSn}$: C, 40.2; H, 3.22; Cl, 14.8%).

Recrystallisation of this product from toluene-petroleum spirit gave pale yellow crystals of $\text{Pd}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{As}\phi_3) \cdot \frac{1}{2}\text{C}_7\text{H}_8$ m.p. 145-147° dec. (Found: C, 40.3; H, 3.23; Cl, 15.8%. Calc. for $\text{C}_{24.5}\text{H}_{24}\text{AsCl}_3\text{PdSn}$: C, 40.6; H, 3.34; Cl, 14.7%).

xiii) Reaction of Chloro(π -allyl)(triphenylstibine)palladium
with Stannous Chloride

$\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{Sb}\phi_3)$ (0.5 g.) in methylene chloride-methanol was treated with excess stannous chloride (0.5 g.) in the same solvent to give a deep red solution but subsequent work-up

failed to give any crystalline products.

xiv) Synthesis of Chloro(π -allyl)bis(triphenylphosphine)platinum

This method is a modification of the one given in the literature⁽¹¹⁹⁾. Allyl chloride (1 ml.) was added to a stirred solution of $\text{Pt}(\text{P}\phi_3)_4$ (4.0 g.) in benzene (60 ml.) to give a pale yellow solution. Stirring was continued for a few minutes and the solution was then left to stand. After 2-3 hr. white crystals had formed and the supernatant liquid was a deeper yellow colour. The crystals were filtered off and washed with benzene and methanol to leave white crystals of the required product $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{Cl}$ (2.7 g.) m.p. $194\text{--}198^\circ$ dec., (lit. value $195\text{--}200^\circ$ dec.⁽¹¹⁹⁾). (Found: C, 59.5; H, 4.40; Cl, 4.45%. Calc. for $\text{C}_{39}\text{H}_{35}\text{ClP}_2\text{Pt}$: C, 58.8; H, 4.43; Cl, 4.45%).

The yellow filtrate was evaporated to dryness and the residue crystallised from methylene chloride-methanol to give white crystals of cis- $\text{PtCl}_2(\text{P}\phi_3)_2$, m.p. $\text{ca. } 265^\circ$ dec. (Found: C, 54.2; H, 3.82; Cl, 9.32%. Calc. for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pt}$: C, 54.7; H, 3.82; Cl, 9.0%).

xv) Reaction of Chloro(π -allyl)bis(triphenylphosphine)platinum with Stannous Chloride

$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{Cl}$ (0.9 g.) was dissolved in methylene chloride-methanol to give an almost colourless solution. To

this stirred solution was added excess stannous chloride (1.2 g.) in methanol with the immediate formation of an orange colour. Stirring was continued for 30 min. without any further change taking place. The solution was then evaporated to small volume at the rotary evaporator to give an orange solid. This solid was filtered off and washed with methanol. Treatment of the crude product with cold benzene gave a pale yellow solution and left a small amount of an insoluble orange solid. Addition of petroleum spirit (boiling range 100-120°) to the benzene solution and rotary evaporation to small volume gave yellow crystals of $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)_2]\text{SnCl}_3$, m.p. 165° dec. (Found: C, 48.0; H, 3.61; Cl, 11.7%. Calc. for $\text{C}_{39}\text{H}_{35}\text{Cl}_3\text{P}_2\text{PtSn}$: C, 47.6, H, 3.58; Cl, 10.8%).

Recrystallisation of the orange solid from methylene chloride-methanol gave a small yield of orange micro-crystals of $\text{Pt}(\text{SnCl}_3)(\pi\text{-C}_3\text{H}_5)(\text{P}\phi_3)$, m.p. 155-165° dec. (Found: C, 35.7; H, 2.86; Cl, 13.7%. Calc. for $\text{C}_{21}\text{H}_{20}\text{Cl}_3\text{PPtSn}$: C, 35.0; H, 2.80; Cl, 14.7%).

CHAPTER 4

C H A P T E R 4

Low-Frequency Vibrational Spectra of Compounds Containing Tin-Transition Metal Bonds

4.1 Introduction

Vibrational modes which lead to a change in dipole moment in a molecule are expected to be infrared active, while vibrational modes which lead to a change in polarisability in a molecule are expected to be Raman active. From these selection rules it has been suggested⁽¹³⁰⁾ that Raman spectroscopy would be particularly useful for the detection of metal-metal stretching modes, $\nu(\text{M-M})$, because of the large change in polarisability when a covalent bond between two atoms of high atomic number is deformed, and it was found that high Raman intensity is characteristic of $\nu(\text{M-M})$. On the other hand it was thought that $\nu(\text{M-M})$ might prove difficult to detect by infrared spectroscopy, especially in binuclear M-M systems when the metal-metal stret-

ching vibration would not lead to a change in dipole moment. Later work⁽¹³¹⁾ has shown that binuclear Sn-M systems can be usefully studied by far-infrared spectroscopy and that $\nu(\text{Sn-M})$ is often of medium or strong intensity in the infrared.

The increasing availability of far-infrared and Raman instruments has resulted, in recent years, in a number of reports of $\nu(\text{M-M})$ frequencies⁽¹²⁹⁾. Many such frequencies are known in which tin is one of the metals and these results are collected in Table 4.1 (page 88). An inspection of this table leads to two main conclusions:-

a) almost all the reported $\nu(\text{Sn-M})$ frequencies have been for binuclear compounds with a single Sn-M bond;

b) the overall shift of $\nu(\text{Sn-M})$ in such compounds is relatively small and falls in the range $165\text{-}235\text{ cm.}^{-1}$.

In this present work the low-frequency infrared and Raman spectra have been obtained and assigned for three series of trinuclear compounds containing the M_2SnX_2 group ($\text{M} = (\pi\text{-Cp})\text{Fe}(\text{CO})_2$, $\text{Co}(\text{CO})_4$ and $(\pi\text{-Cp})\text{Mo}(\text{CO})_3$; $\text{X} = \text{Cl, Br, I}$). These spectra contain the first reported examples of $\nu(\text{Sn-M})$ for trinuclear compounds of the type $(\text{L}_n\text{M})_2\text{SnX}_2$.

4.2 The M_2SnX_2 Skeleton

The M_2SnX_2 skeleton has C_{2v} "local" symmetry and the $3n - 6 = 9$ vibrational modes span the representation

TABLE 4.1 Tin-Transition Metal Stretching Frequencies

<u>Compound</u>	<u>$\nu(\text{Sn-M})$ cm.⁻¹</u>		<u>Reference</u>
	<u>Raman</u>	<u>i.r.</u>	
Sn_2Me_6	190	-	(130)
Sn_2O_6	208	-	"
$\text{Sn}(\text{SnO}_3)_4$	207	-	"
$\text{O}_3\text{SnMn}(\text{CO})_5$	174	-	"
$\text{O}_3\text{SnSnEt}_3$	-	208	(131)
$\text{Et}_3\text{SnSnBu}_3$	-	199	"
$\text{O}_3\text{SnSnMe}_3$	-	194	"
$\text{Me}_3\text{SnGeO}_3$	-	225	"
$\text{Et}_3\text{SnGeO}_3$	-	230	"
$\text{O}_3\text{SnGeBu}_3$	-	235	"
$\text{Me}_3\text{SnMn}(\text{CO})_5$	179	182	"
$\text{O}_3\text{SnMn}(\text{CO})_5$	174	174	"
$\text{Me}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	172	"
$\text{O}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	169	"
$\text{Me}_3\text{SnFe}(\text{CO})_2(\pi\text{-Cp})$	-	185	"
$\text{O}_3\text{SnFe}(\text{CO})_2(\pi\text{-Cp})$	-	174	"
$\text{Me}_3\text{SnCo}(\text{CO})_4$	-	176	"
$\text{Me}_3\text{SnMn}(\text{CO})_5$	-	182	(132)
$\text{Me}_2\text{ClSnMn}(\text{CO})_5$	-	197	"

Continued.....

TABLE 4.1 (Continued)

<u>Compound</u>	$\nu(\text{Sn-M}) \text{ cm.}^{-1}$		<u>Reference</u>
	<u>Raman</u>	<u>i.r.</u>	
$\text{MeCl}_2\text{SnMn}(\text{CO})_5$	-	201	(132)
$\text{Cl}_3\text{SnMn}(\text{CO})_5$	-	201	"
$\phi_3\text{SnMn}(\text{CO})_5$	-	175	"
$\text{Me}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	172	"
$\text{Me}_2\text{ClSnMo}(\text{CO})_3(\pi\text{-Cp})$	-	186	"
$\text{MeCl}_2\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	195	"
$\text{Cl}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	190	"
$\phi_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	-	169	"
$\text{Me}_3\text{SnW}(\text{CO})_3(\pi\text{-Cp})$	-	169	"
$\text{Me}_2\text{ClSnW}(\text{CO})_3(\pi\text{-Cp})$	-	175	"
$\text{Me}_2\text{BrSnMn}(\text{CO})_5$	-	191	"
$\text{Me}_2\text{ISnMn}(\text{CO})_5$	-	178	"
$\text{Me}_2(\text{CF}_3)\text{SnMn}(\text{CO})_5$	-	189	"
$\text{Me}_3\text{SnFe}(\text{CO})_2(\pi\text{-Cp})$	-	208 or 186	"
$\phi_3\text{SnFe}(\text{CO})_2(\pi\text{-Cp})$	-	209 or 174	"
$\text{Me}_3\text{SnCo}(\text{CO})_4$	-	176	"
$\text{Me}_3\text{SnCo}(\text{CO})_4$	172	-	(133)
$\text{Cl}_3\text{SnCo}(\text{CO})_4$	204	204	(134)

Continued.....

TABLE 4.1 (Continued)

<u>Compound</u>	$\nu(\text{Sn-M}) \text{ cm.}^{-1}$		<u>Reference</u>
	<u>Raman</u>	<u>i.r.</u>	
$\text{Br}_3\text{SnFe}(\text{CO})_2(\pi\text{-Cp})$	198	198	(135)
$\text{Cl}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$	190	190	"
$\text{Cl}_3\text{SnIr}(\text{COD})_2$	165	-	"
$\text{Cl}_3\text{SnRh}(\text{NBD})_2$	165	-	"
$(\text{Et}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$	-	209	(139)
$(\text{Et}_4\text{N})_4[\text{Rh}_2\text{Br}_2(\text{SnBr}_3)_4]$	-	217	"
$(\text{Et}_4\text{N})_3[\text{Pt}(\text{SnCl}_3)_5]$	-	210	"
$(\text{Et}_4\text{N})_3[\text{Pt}(\text{SnBr}_3)_5]$	-	207, 193	"

$4A_1 + A_2 + 2B_1 + 2B_2$. Two modes ($A_1 + B_2$) which are approximately described as $\nu(\text{Sn-X})$ vibrations are both infrared and Raman active and, similarly, two modes ($A_1 + B_1$) which approximate to $\nu(\text{Sn-M})$ vibrations are to be expected in both the infrared and Raman spectra. Clearly, there will be some interaction between these modes in the A_1 symmetry species (see below).

4.3 The Compounds $X_2\text{Sn}[\text{Co}(\text{CO})_4]_2$

The solid-state vibrational spectra, and their assignments, for the compounds $X_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ ($X = \text{Cl}, \text{Br}, \text{I}$) and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ are given in Table 4.2 (page 92). Bands arising from the $\text{Co}(\text{CO})_4$ moiety in the compounds $X_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ are readily identified by comparison with $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and $\nu(\text{Sn-X})$ modes can be easily assigned as they shift progressively to lower frequency in the expected order $X = \text{Cl} > X = \text{Br} > X = \text{I}$. Metal carbonyl residues do not absorb in the region $300\text{--}150\text{ cm.}^{-1}$, with $\nu(\text{M-CO})$ and $\delta(\text{MCO})$ above 300 cm.^{-1} and $\delta(\text{CMC})$ below 150 cm.^{-1} (112), and these facts further simplify the task of assignment of these spectra.

For the compound with $X = \text{Cl}$ the bands near 200 cm.^{-1} can be confidently assigned to metal-metal bond stretching modes. The symmetric SnCo_2 stretch is found to be intense in the Raman spectrum and the antisymmetric stretch is similarly prominent in the infrared spectrum. One of the $\nu(\text{Sn-X})$ modes and one of

TABLE 4.2 Vibrational Frequencies (cm.⁻¹) of the Solid
Compounds X[Co(CO)₄]₂ (X = Hg, Cl₂Sn, Br₂Sn, I₂Sn)

X = Hg	X = Cl ₂ Sn	X = Br ₂ Sn	^a X = I ₂ Sn	
I.r. Raman	I.r. Raman	I.r. Raman	I.r.	Assignments
545s	537vs 542vw	536vs	540vs	δ(CoCo)
531s	500m	504m	504m	"
499m	488m	483m	492sh	"
475m	461s	462s	469s	"
414w 418vs	406w 412w	404w 410w	405w-m	ν(Co-CO)
368w 364w	365w-m 364vw	361w-m	372w-m	"
196vs	213s 214w-m	210m-s*	190sh*	ν(MCo ₂)asym
165w 164vs	172w 174vs	168vs*		ν(MCo ₂)sym
84vw	82vw			δ(CCoC)
	332s 332w	234m-s 234w	178vs*	ν(SnX ₂)
	322s 320w-m	222s		"
	138vw	183wm*		Others
	108vs			

* See text.

^a This compound failed to yield a Raman spectrum.

the $\nu(\text{Sn-Co})$ modes are of the same symmetry (A_1) and so there is the possibility of interaction between them. This is found to be the case for $\text{Br}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ in which the $\nu(\text{Sn-Br})$ modes fall near the unperturbed (as estimated from the chloride) $\nu(\text{Sn-Co})$ modes and causes the observed shift to lower frequency. There also seems to be some sharing of intensity in these bands. The Raman spectra of these compounds do not show nearly as many lines as are predicted by theory. This is particularly obvious in the $\delta(\text{MCO})$ region where there are several lines in the infrared (of a characteristically high intensity expected from the large dipole changes associated with such deformations) but with relatively few bands in the Raman spectra in this region.

4.4 The Compounds $\text{X}_2\text{Sn}[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$

The solid-state vibrational spectra of the compounds $\text{X}_2\text{Sn}[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), together with their assignments, are given in Table 4.3 (page 94). This series of compounds yielded better Raman spectra than the cobalt series discussed in section 4.3. The infrared and Raman spectra of some simpler, related compounds have also been obtained (Table 4.4) and used as an aid to the assignments of the spectra of the trinuclear compounds.

Bands in the $\nu(\text{M-C})/\delta(\text{MCO})$ region of $(\pi\text{-Cp})\text{Fe}(\text{CO})_2\text{I}$ have been assigned previously⁽¹³⁶⁾ and similar assignments for this

TABLE 4.3 Vibrational Frequencies (cm.⁻¹) and Assignments
for X₂Sn[(π -Cp)Fe(CO)₂]₂ in the Solid State

X = Cl		X = Br		X = I		Assignment
I.r.	Raman	I.r.	Raman	I.r.	Raman	
627vs	626w	624s	N.i.	626vs	N.i.	δ (FeCO)
596m	599w-m		"	596m	"	"
	584vw	574vs	"	574vs	"	"
504s	506w	504m	508w	505s		ν (Fe-CO)
456m	454w	452w	453w	454m	452w	"
393vs	393w-m	387m		390m		ν (Fe-Cp)
370s	371m	372m	374m	370m	371m	"
286vs	287w-m		182sh		177w-m	ν (SnX ₂) asym.
				167s	167m	ν (SnX ₂) sym.
233s	234w	235s	234w-m	232s	233m	ν (SnFe ₂) asym.
	196vs	201s	197vs	196m	198s	ν (SnFe ₂) sym
155m ^a	155s ^a		149w	143w		Others
123sh ^b					121vs	"
114m ^b						"
	106vs		109s			"

^a δ (SnCl₂). ^b SnCl₂ twist and wag.

N.i. = not investigated in this region.

TABLE 4.4 Vibrational Frequencies (cm.⁻¹) and Assignments
for (π-Cp)Fe(CO)₂X in the Solid State

X = Cl ^a	X = I ^a	X = SnBr ₃		
I.r.	I.r.	I.r.	Raman	Assignment
600s	605s	611s		δ(FeCO)
565s	564s	577s		"
530s	542s	560s		"
478wm	486w	501m		ν(Fe-CO)
437w	436w	444m		"
351w	358w	377wm	379s	ν(Fe-Cp)
302s	137m	198s	198vs	ν(Fe-X)
162m	153w	161wm		Ring tilt
		248s	246w	ν(SnBr ₃)
		229s	227w	"
		93s		δ(SnBr ₃)
	118wm	137wm		Others
	103wm			

^a These compounds failed to yield Raman spectra.

group of bands are given here. Similar bands are to be found in all compounds of this type. The Fe-(π -Cp) stretching modes may be readily assigned as in tables 4.3 and 4.4 since many other monocyclopentadienyl compounds are known to have such a vibration in the same region⁽¹¹²⁾.

The Fe-Sn stretching modes are assigned to the intense Raman lines at about 200 cm.⁻¹ and to the strong infrared bands in the same region. There is an intense Raman line at about 110 cm.⁻¹ in the spectra of the trinuclear compounds and it might be argued that this is the ν (Fe-Sn) mode with the bands around 200 cm.⁻¹ being due to the ring tilt vibration (a tilt of the cyclopentadienyl ring with respect to the rest of the molecular framework). However, it is considered that the feature at 110 cm.⁻¹ is probably due to a skeletal deformation such as δ (CFeC) (which is often strong in the Raman effect) or possibly due to δ (FeSnFe). The shift to 120 cm.⁻¹ in the iodide may be due to interaction with Sn-I deformation modes, which will undoubtedly be below 80 cm.⁻¹.

The Raman spectra of the three trinuclear compounds have also been examined in acetone and methylene chloride solutions (Table 4.5, page 97). These solution spectra were of relatively poor quality when compared with those obtained from the solid compounds and several of the weaker bands in the solid-state spectra could not be observed in the solution spectra. This was

TABLE 4.5 Raman Frequencies (cm.⁻¹) and Assignments for
X₂Sn[(π -Cp)Fe(CO)₂]₂ in Solution

X = Cl ^a	X = Cl ^b	X = Br ^b	Assignment
435w	512w 432w	513w	$\nu(\text{Fe-CO})$ "
378s(P)	374s(P)	373s(P)	$\nu(\text{Fe-Cp})$
301m(P)	S	213w	$\nu(\text{SnX}_2)$
291w	S		"
230w	231w		$\nu(\text{SnFe}_2)$ asym.
201vs(P)	200vs(P)	189vs(P)	$\nu(\text{SnFe}_2)$ sym.

^a In acetone solvent. ^b In methylene chloride solvent.

S = obscured by solvent bands.

(P) = polarised

The compound with X = I failed to yield a spectrum.

more noticeable in the bromide than the chloride and the iodide failed to give a solution spectrum. Nevertheless, the intense band near 200 cm.^{-1} , assigned to $\nu(\text{SnFe}_2)_{\text{sym.}}$, was readily observed in the solution spectra of the chloride and bromide and found to be polarised, as would be expected for an A_1 mode.

4.5 The Compounds $\text{X}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$

The solid-state infrared and Raman spectra of the compounds $\text{X}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$ ($\text{X} = \text{Cl, Br}$) are assigned in Table 4.6 (page 99). The bands due to $\delta(\text{MoCO})$, $\nu(\text{Mo-C})$ and $\nu(\text{Mo-Cp})$ occur in the expected regions of the spectra⁽¹¹²⁾ and the $\nu(\text{SnX}_3)$ modes are readily identified by their shifts on going from $\text{X} = \text{Cl}$ to $\text{X} = \text{Br}$. The bands due to the $\nu(\text{Sn-Mo})$ mode are found to be very intense in the Raman spectra and of medium to strong intensity in the infrared spectra.

4.6 The Compounds $\text{X}_2\text{Sn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$

The solid-state vibrational spectra of the compounds $\text{X}_2\text{Sn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ ($\text{X} = \text{Cl, Br, I}$) were recorded and are assigned in Table 4.7 (page 100). Comparison of these spectra with those of the compounds $\text{X}_3\text{SnMo}(\text{CO})_3(\pi\text{-Cp})$ (section 4.5) allows assignments to be made for the $\delta(\text{MoCO})$, $\nu(\text{Mo-C})$ and $\nu(\text{Mo-Cp})$ vibrational modes. The halogen-sensitive $\nu(\text{SnX}_2)$ modes are again readily identified, at least for the chloride and

TABLE 4.6 Vibrational Frequencies (cm.⁻¹) and Assignments
for X₃SnMo(CO)₃(π -Cp) in the Solid State

X = Cl		X = Br		Assignment
I.r.	Raman	I.r.	Raman	
564vs	565w	564vs	N.i.	$\delta(\text{MoCO})$
543vs	543w	542vs	"	"
473vs	468w-m	474s	"	$\nu(\text{Mo-C})$
454s		454s	"	"
382w	383sh	378w		$\nu(\text{Mo-Cp})$
370w	370s	373w	375m	"
		368w	364s	"
337vs	339s	239vs	235m-s	$\nu(\text{SnX}_3)$
320vs	321m	224vs	223m	"
190vs	190vs	171m	168vs	$\nu(\text{Sn-Mo})$
142vs				$\delta(\text{SnCl}_3)$
133sh	124vw			"
103w			107w	Others
89w				"

TABLE 4.7 Vibrational Frequencies (cm.⁻¹) and Assignments
for X₂Sn[(π -Cp)Mo(CO)₃]₂ in the Solid State

X = Cl		X = Br		X = I		Assignment
I.r.	Raman	I.r.	Raman	I.r.	Raman	
576vs		576vs		574s		$\delta(\text{MoCO})$
563s	562m	563s	562m	562s	561m	"
553vs		552vs		552vs		"
490s		492s		498s		$\nu(\text{Mo-CO})$
459m	462m	459m-s	459m	464s	461m	"
442w-m	451w	447m	449s	449s	445m-s	"
	420m		419m		416m	"
			410m			"
	374m				366m	$\nu(\text{Mo-Cp})$
	363s		361s		350s	"
	350vs		348vs		339m	"
294s	290m	239m-s		171s	171s	$\nu(\text{SnX}_2)$
279m-s	276w-m	223m-s				"
		205s	204m			"
195s	193m	190s	188m	189s	183m	$\nu(\text{SnMo}_2)\text{asym.}$
166w-m	161s	162w-m	158vs			$\nu(\text{SnMo}_2)\text{sym.}$
132w-m				141w		Others
114w-m			117w		101s	"
		88w				"

bromide, and for these two compounds the bands near 190 cm.^{-1} and 160 cm.^{-1} may be reasonably assigned to the antisymmetric and symmetric $\nu(\text{Sn-Mo})$ modes respectively. The assignments for the iodide in this region are more tentative as there seems to be some mixing, and sharing of intensities, of the $\nu(\text{SnI}_2)$ and $\nu(\text{SnMo}_2)$ modes. The very intense Raman band at about 160 cm.^{-1} , which might otherwise be expected for the symmetric $\nu(\text{Sn-Mo})$ mode, was not observed in the iodide.

The Raman spectra of acetone solutions of the three trinuclear compounds were also examined, with the results recorded in Table 4.8 (page 102). The iodide did not give a satisfactory spectrum, probably because it underwent some decomposition in the laser beam and so caused the solution to become cloudy. An acetone solution of the bromide appeared to fluoresce and a spectrum above 180 cm.^{-1} could not be recorded. Nevertheless, a relatively intense band at 163 cm.^{-1} was observed and shown to be polarised, thus supporting the assignment of the corresponding band in the solid-state spectrum to the symmetric $\nu(\text{Sn-Mo})$ mode. A better spectrum was obtained for the chloride, and this spectrum showed a very intense band at 161 cm.^{-1} which was again found to be polarised, as would be expected for a band assignable to the symmetric $\nu(\text{Sn-Mo})$ vibration.

TABLE 4.8 Raman Frequencies (cm.⁻¹) for X₂Sn[(π -Cp)Mo(CO)₃]₂
in Acetone Solution

X = Cl	X = Br *	Assignment
563w-m(P)		$\delta(\text{MoCO})$
461w		$\nu(\text{Mo-CO})$
432m		"
361sh		$\nu(\text{Mo-Cp})$
351s(P)		"
340sh		"
300m		$\nu(\text{SnX}_2)$
285m		"
196w		$\nu(\text{SnMo}_2)\text{asym.}$
161vs(P)	163s(P)	$\nu(\text{SnMo}_2)\text{sym.}$

* Fluoresces above 180 cm.⁻¹

The compound with X = I failed to give a spectrum.

4.7 Discussion

There is a significant difference in $\nu(\text{Sn-M})$ and $\nu(\text{Sn-Cl})$ frequencies between the cobalt and iron complexes, with $\nu(\text{Sn-Fe})$ at appreciably higher frequency than $\nu(\text{Sn-Co})$ while $\nu(\text{Sn-Cl})$ is at lower frequency in the iron compound than in the cobalt compound. This is consistent with X-ray work on the compound $\text{Cl}_2\text{Sn}[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2$ ⁽¹³⁷⁾ in which it was found that the Fe-Sn bond is "shorter than any previously reported tin to transition metal atom bond", while the Sn-Cl bond is longer than in such compounds as Me_2SnCl_2 . That the difference between $\nu(\text{Sn-Fe})$ and $\nu(\text{Sn-Co})$ is not simply a mass effect is demonstrated by writing the complexes as Cl_2SnM_2 and noting that the masses of the M groups in the two cases are almost the same, i.e. $\text{Co}(\text{CO})_4 = 171$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2 = 177$.

It is reasonable to suppose that, due to the presence of the π -cyclopentadienyl ring, the iron atom will have more electron density associated with it than will the cobalt atom, and this is confirmed by the $\nu(\text{CO})$ frequencies for the two compounds (Table 4.9, page 104). The $\nu(\text{CO})$ frequencies are considerably higher in the cobalt compound than the iron compound, thus suggesting that there is more π -type back-bonding from the metal to the carbonyl groups in the iron compound, as would be expected for higher electron density at the central metal atom. Therefore the iron atom can reduce its electronegativity by donating more

TABLE 4.9 Carbonyl Stretching Frequencies (cm.⁻¹) in the
Infrared Spectra of the Compounds [Co(CO)₄]₂SnCl₂,
[(π -Cp)Fe(CO)₂]₂SnCl₂ and [(π -Cp)Mo(CO)₃]₂SnCl₂

$[\text{Co}(\text{CO})_4]_2\text{SnCl}_2^{\text{a}}$	$[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]_2\text{SnCl}_2^{\text{b}}$	$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2\text{SnCl}_2^{\text{c}}$
2114w	2026vs	2030s
2097s	2000s	2008m
2056ms	1975s	1959s
2052sh	1956m	1938m
2040s		1914w
2023m		
2016sh		

^a In cyclohexane solution, ref. (29).

^b In cyclohexane solution, ref. (138).

^c In benzene solution, this work.

charge towards the tin atom, thus strengthening the Fe-Sn bond and weakening the Sn-Cl bond. A similar effect would be expected to operate in the corresponding molybdenum compound and this seems to be the case. Thus the $\nu(\text{CO})$ frequencies for the molybdenum compound have similar values to those of the iron compounds (Table 4.9, page 104) and the $\nu(\text{Sn-Cl})$ frequencies are appreciably lower in the molybdenum compound than in the cobalt compound. On the other hand, $\nu(\text{Mo-Sn})$ is at lower frequency than $\nu(\text{Co-Sn})$ but this can be attributed to a mass effect, with $\text{Co}(\text{CO})_4 = 171$ and $(\pi\text{-Cp})\text{Mo}(\text{CO})_3 = 245$.

4.8 Conclusion

From this study it may be concluded that, for compounds of the type $(\text{L}_n\text{M})_2\text{SnX}_2$, the symmetric stretching frequencies of the tin-transition metal bond are intense in the Raman spectra, while the antisymmetric modes are strong in the infrared and may also be detected in the Raman spectra. For the compounds studied the symmetric tin-metal bond stretching frequencies lie in the range $201\text{-}158\text{ cm.}^{-1}$, while the corresponding antisymmetric stretching frequencies lie in the range $235\text{-}183\text{ cm.}^{-1}$.

4.9 Experimental

The compounds were prepared by the methods described in Chapter 2 and Chapter 3. Solid-state Raman spectra were obtained with a Cary 81 laser (6328 Å) Raman instrument using powdered specimens and solution spectra were obtained with a Coderg PH 0 laser (6328 Å) Raman instrument. Solid-state infrared spectra (Nujol mulls) were obtained with RIIC FS-520, RIIC FS-620 and Perkin-Elmer 225 infrared spectrometers.

CHAPTER 5

CHAPTER 5

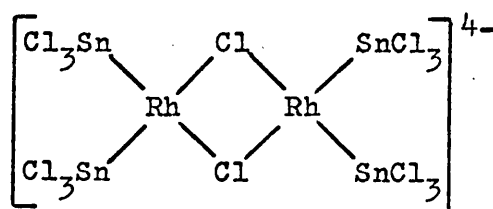
Some Reactions of Unsaturated Organic Compounds with the Ethanolic Rhodium(III)-Tin(II)-Chloride Solution

5.1 Introduction

Although an ethanolic solution of rhodium(III) chloride and tin(II) chloride will react with diolefins such as cyclo-octa-1,5-diene, 4-vinylcyclohexene and dicyclopentadiene to form dimeric compounds of the general type $\text{Rh}_2\text{Cl}_2(\text{diolefin})_2$, with norbornadiene as the diolefin the only product is the five-co-ordinate complex $\text{Rh}(\text{SnCl}_3)(\text{NBD})_2^{(14)}$; this compound contains a rhodium-tin bond. In this present work the reactions of the ethanolic rhodium(III)-tin(II)-chloride solution with some simple unsaturated organic compounds have been further investigated and, in at least one case, it has been possible to isolate a rhodium complex containing both co-ordinated double bonds and a rhodium-tin bond.

5.2 The Nature of the Rhodium(III)-Tin(II)-Chloride Solution

Treatment of a solution of rhodium(III) chloride in dilute hydrochloric acid with stannous chloride gives a deep red solution and it has been suggested⁽¹⁴⁾ that the complex anion present in this solution may be formulated as a rhodium(I) complex:-



A similar species is thought to be present in the ethanolic solution of rhodium(III) chloride and tin(II) chloride, but with the SnCl_3^- group replaced by solvated SnCl_2 groups to give a neutral species. Treatment of both the aqueous and ethanolic solutions with tetramethylammonium chloride results in the precipitation of $(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$; the far-infrared spectrum of this solid has been reported⁽¹³⁹⁾ and is given in Table 5.1 (page 109). This spectrum is entirely consistent with the dimeric halogen-bridged structure. The Raman spectrum of the solid has now been examined (Table 5.1) and confirms the assignments made for the infrared spectrum. This Raman spectrum has a strong band at 168 cm.^{-1} , assigned to the symmetric $\nu(\text{Rh-Sn})$ mode, which had not been observed in the infrared spectrum although its existence had been predicted⁽¹³⁹⁾. In this present work the Raman spectrum of the actual rhodium(III)-tin(II)-

TABLE 5.1 Vibrational Frequencies (cm^{-1}) of the Complex Anion
Derived from Rhodium(III) Chloride and Tin(II) Chloride

Me_4N^+ salt (solid) ^a I.r.	Et_4N^+ salt (solid) ^a I.r.	Me_4N^+ salt (solid) ^b Raman	Et_4N^+ salt (solid) ^b Raman	$\text{RhCl}_3/\text{SnCl}_2$ in EtOH^c Raman	Assignment
363	361	360m	360m	368s(P)	$\nu(\text{SnCl}_3)$
336	334	332w-m	331w-m	347sh	"
		314sh	310sh	309w	
288	288	287w	287w		$\nu(\text{Rh-Cl})$ (bridge)
267	272			264vw	
		240w	241w	245w	
210	209	209m	210m	209w	$\nu(\text{Rh-Sn})$ asym.
		168s	169s	172s(P)	$\nu(\text{Rh-Sn})$ sym.
		146w	146w		$\delta(\text{Sn-Cl})$

^a Reference (139). ^b D.M. Adams, unpublished work.

^c This work. (P) = polarised.

chloride solution has been recorded and is assigned in Table 5.1. This spectrum is very similar to the ones obtained for the tetra-alkylammonium salts and so suggests that a species such as $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ is the dominant one in solution. There is a small difference between the values of $\nu(\text{Sn-Cl})$ for the solids and solution, with the ones in the latter being at slightly higher frequencies. This may be due to the fact that the species present in ethanolic solution is a neutral one, as previously suggested⁽¹⁴⁾, with the SnCl_3^- groups replaced by solvated SnCl_2 groups.

5.3 Reaction of Ethanolic Rhodium(III)-Tin(II)-Chloride with 1,3-butadiene

Using standard vacuum-line techniques, ethanolic rhodium (III)-tin(II)-chloride solution and 1,3-butadiene were allowed to react in a sealed glass tube at room temperature. The initially deep red solution became orange in colour and pale-coloured crystals were formed, isolated as buff-coloured crystals and shown by elemental analysis to have the formula $\text{Rh}(\text{SnCl}_3)(\text{C}_4\text{H}_6)_2$. The infrared spectrum of this product is given in Table 5.2 (page 111) and compared with that of free 1,3-butadiene⁽¹⁴⁰⁾. The far-infrared spectrum ($400\text{-}200\text{ cm.}^{-1}$) confirms the presence of the Rh-SnCl_3 group, with $\nu(\text{SnCl}_3)$ at 328 cm.^{-1} and 303 cm.^{-1} and a band at 209 cm.^{-1} which has been tentatively assigned to the

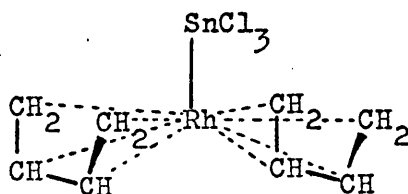
TABLE 5.2 Vibrational Frequencies (cm.⁻¹) of Free 1,3-butadiene
and Infrared Spectrum of Rh(SnCl₃)(C₄H₆)₂

1,3-butadiene ^a		Rh(SnCl ₃)(C ₄ H ₆) ₂	Assignment
Raman	I.r.	I.r.	
3101	3100	3076sh	$\nu(\text{CH})$
	3060	3059m	"
3014	3000	3050sh	"
		3004w	"
1643	1599		$\nu(\text{C}=\text{C})$
1442	1484	1478m	CH ₂ deformation
		1425s	$\nu(\text{C}=\text{C})$ co-ord.
1302	1379	1377ms	CH rocking
1279	1290	1226w	CH ₂ rocking
1205		1209w	$\nu(\text{C}-\text{C})$
	1014	1187wm	CH wagging
911	909	910m	CH ₂ wagging
890		775m	CH wagging
686	520	485m	CH ₂ torsion
		434m	$\nu(\text{Rh}-\text{C})$
^a Reference (140)		376m	"
		328s	$\nu(\text{SnCl}_3)$
		303s	"
		209m	$\nu(\text{Rh}-\text{Sn})$

$\nu(\text{Rh-Sn})$ mode. The values for $\nu(\text{SnCl}_3)$ are typical of those for SnCl_3^- co-ordinated to rhodium(I) (see Chapter 3, section 3.10).

Vibrational frequencies due to the co-ordinated butadiene molecules are assigned and, although some of these assignments are uncertain, it is clear that the band near 1600 cm.^{-1} due to $\nu(\text{C}=\text{C})$ in free butadiene has shifted to lower frequency upon co-ordination. Such a result is expected and has been reported for many metal-olefin complexes⁽¹¹²⁾. The absence of a band near 1600 cm.^{-1} confirms that both double bonds of the butadiene molecule are co-ordinated to rhodium.

The infrared spectrum of the complex in the region $1500-1350 \text{ cm.}^{-1}$ is very similar to that reported for chlorobis(butadiene)rhodium(I)⁽¹⁴¹⁾ and it is reasonable to assume that the two compounds will have similar structures. The structure of $\text{RhCl}(\text{C}_4\text{H}_6)_2$ has been determined by X-ray methods⁽¹⁴²⁾ and so it is likely that trichlorostannatobis(butadiene)rhodium(I) has the related structure:-



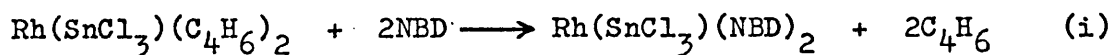
Such a structure requires that each butadiene molecule contributes four electrons to rhodium in the complex and so rhodium

attains the rare-gas configuration.

Chlorobis(butadiene)rhodium(I) is sensitive to air and only stable under nitrogen below 40° . The trichlorostannato complex, on the other hand, can be kept in air for several months without apparent change and only undergoes thermal decomposition above 150° . This marked difference in the stabilities of the two compounds may be related to the π -acceptor properties of the SnCl_3^- ligand, whereby excessive electron density can be removed from the rhodium atom.

5.4 Reaction of Trichlorostannatobis(butadiene)rhodium(I) with Norbornadiene

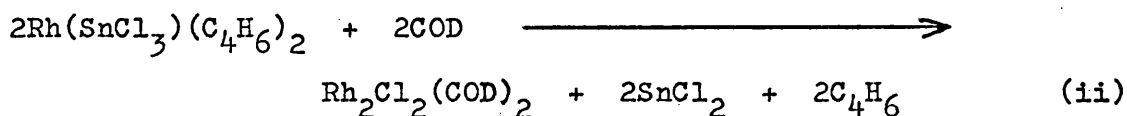
Trichlorostannatobis(butadiene)rhodium(I) was found to react rapidly with excess norbornadiene to give a quantitative yield of trichlorostannatobis(norbornadiene)rhodium(I) :-



Such a reaction, in which co-ordinated butadiene is displaced by another diolefin to give a known product, serves to confirm that the formulation given in section 5.3 for the butadiene complex is a correct one.

5.5 Reaction of Trichlorostannatobis(butadiene)rhodium(I) with Cycloocta-1,5-diene

In view of the success of the reaction of trichlorostannatobis(butadiene)rhodium(I) with norbornadiene (section 5.4), it was thought that a similar reaction with cycloocta-1,5-diene might result in the formation of the new compound trichlorostannatobis(cycloocta-1,5-diene)rhodium(I). (The reaction of the rhodium(III)-tin(II)-chloride solution with cycloocta-1,5-diene gives $\text{Rh}_2\text{Cl}_2(\text{COD})_2^{(14)}$). However, it was found that the butadiene complex reacted with cycloocta-1,5-diene to give $\text{Rh}_2\text{Cl}_2(\text{COD})_2$ as the only product :-



There is not an obvious route to the synthesis of the compound $\text{Rh}(\text{SnCl}_3)(\text{COD})_2$ because the preferential formation of the very stable dimer, $\text{Rh}_2\text{Cl}_2(\text{COD})_2$, seems to be the dominant factor.

5.6 Reaction of Ethanolic Rhodium(III)-Tin(II)-Chloride with Ethylene

Ethylene was found to react with ethanolic rhodium(III)-tin(II)-chloride solution, under conditions similar to those used for the butadiene reaction (section 5.3), but the only

product was the well-known, halogen-bridged dimer, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2^{(143)}$, which was isolated in high yield. This reaction is, in fact, a useful method of preparation of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ since it has been found to give a higher yield of the product than previously reported syntheses⁽¹⁴³⁾⁽¹⁴⁴⁾ from rhodium(III) chloride alone.

5.7 Reaction of Ethanolic Rhodium(III)-Tin(II)-Chloride with Cyclooctene

Ethanolic rhodium(III)-tin(II)-chloride solution reacts with cyclooctene very slowly at room temperature and orange crystals separate in very small yield after about four weeks. Melting point and analysis of this product indicate that it is the known compound $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2^{(141)}$.

5.8 Reaction of Ethanolic Rhodium(III)-Tin(II)-Chloride with Acrylonitrile

Ethanolic rhodium(III)-tin(II)-chloride solution reacts readily with acrylonitrile at room temperature and a yellow powder separates from the reaction mixture. This product is completely insoluble in all common solvents and so could not be purified by recrystallisation. Therefore the elemental analysis results must be interpreted with caution but do, in fact, correspond to the empirical formula $\text{Rh}(\text{SnCl}_3)(\text{C}_3\text{H}_3\text{N})_{2.4}$. The

infrared spectra of the complex and free acrylonitrile⁽¹⁴⁵⁾ are given in Table 5.3 (page 117). In the spectrum of the complex there is a band at 1610 cm.^{-1} which indicates that the C=C double bond is not co-ordinated to rhodium, and also a band at 2262 cm.^{-1} which shows that acrylonitrile is probably bonded to the metal through the nitrogen atom⁽¹⁴⁶⁾. These facts are consistent with the presence of a grouping such as $\text{CH}_2=\text{CHC}\equiv\text{N}:\rightarrow\text{Rh}$ in the complex, but further speculation on the structure is not possible.

5.9 Reactions of Ethanolic Rhodium(III)-Tin(II)-Chloride with Methyl Vinyl Ketone, Allyl Acetate and Allyl Chloride

Methyl vinyl ketone, allyl acetate and allyl chloride all react slowly with ethanolic rhodium(III)-tin(II)-chloride solution on standing at room temperature for several days. In each case a gradual change of colour was observed, but it was not possible to isolate a pure product from any of the mixtures; work-up usually yielded orange oils or brown, insoluble solids.

5.10 Conclusions

It has been found that the dimeric, halogen-bridged species which is formed in an ethanolic solution of rhodium(III) chloride and stannous chloride will react with a number of simple, unsaturated organic compounds. With 1,3-butadiene the product is $\text{Rh}(\text{SnCl}_3)(\text{C}_4\text{H}_6)_2$, and this compound contains a rhodium-tin bond.

TABLE 5.3 Infrared Frequencies (cm.⁻¹) of Free Acrylonitrile
and of the Product from Rhodium(III)-Tin(II)-Chloride
Solution and Acrylonitrile

Acrylonitrile ^a	Complex	Assignment
3114s	3020m	CH stretch
3068s		"
3033s		"
2228s	2262s	C≡N stretch
1609s	1610m-s 1620sh	C=C stretch
1415s	1458m 1409m 1360m	CH ₂ deformation
1288m	1190m	CH rock
1094s	1082m, br	CH ₂ rock
960-980vs	965w-m, br	CH ₂ =C wag
871m	776w, br	C-C stretch
690s	332m-s, br 303sh	SnCl ₃ stretch "

^a Reference (145)

However, with ethylene and cyclooctene the chloro-tin groups in the complex are displaced by the olefins to give compounds of the type $\text{Rh}_2\text{Cl}_2(\text{olefin})_4$. A product has also been isolated from the reaction with acrylonitrile and, although this compound has not been fully characterised, it probably contains both an SnCl_3^- group and acrylonitrile groups co-ordinated to rhodium.

5.11 Experimental

The Raman spectrum of the rhodium(III)-tin(II)-chloride solution in ethanol was obtained using a Coderg PH 0 instrument with a Ferranti LR 50 helium-neon laser as the exciting source. Infrared spectra were recorded on a Perkin-Elmer 225 instrument with samples in the form of Nujol and hexachlorobutadiene mulls mounted on potassium bromide ($4,000-400\text{ cm.}^{-1}$) and polythene ($400-200\text{ cm.}^{-1}$) plates. Melting points were determined on a Kofler hot-stage apparatus and microanalyses were obtained as described in Chapter 2. Rhodium(III) chloride trihydrate was purchased from Johnson, Matthey & Co. Ltd.

i) Reaction of Rhodium(III) Chloride, Tin(II) Chloride and 1,3-butadiene

A cylinder of 1,3-butadiene (supplied by Air Products) was attached to a vacuum line and the gas (ca. 2 ml.) was condensed into a trap cooled with liquid nitrogen. This trap was then allowed to warm slowly to room temperature and the 1,3-butadiene to distil into a thick-walled glass tube (120 ml. capacity), cooled in liquid nitrogen and containing rhodium(III) chloride (0.3 g.), stannous chloride (0.8 g.) and absolute ethanol (20 ml.). The tube was sealed, allowed to warm to room temperature, shaken mechanically for one hour and then left to stand overnight. The initially deep red solution became pale orange in colour and buff-

coloured crystals were formed. These were filtered off, washed with ethanol and dried in vacuo (0.45 g., 90%), m.p. 150-160° dec. (Found: C, 21.3; H, 2.92; Cl, 25.8%. Calc. for $C_8H_{12}Cl_3RhSn$: C, 22.0; H, 2.78; Cl, 24.4%).

ii) Reaction of $Rh(SnCl_3)(C_4H_6)_2$ and Norbornadiene

A suspension of $Rh(SnCl_3)(C_4H_6)_2$ (0.1 g.) in methylene chloride (10 ml.) was treated with norbornadiene (0.5 ml.) and the mixture left to stand, with occasional shaking. Over a period of about one hour the suspension gradually dissolved and a clear yellow solution was formed. Methanol was added to this solution and the mixture was then evaporated to small volume at the rotary evaporator to give yellow crystals (0.12 g.), m.p. >120° dec. The crystals were identified as $Rh(SnCl_3)(NBD)_2$ by infrared spectrum (1,000-200 cm^{-1}).

iii) Reaction of $Rh(SnCl_3)(C_4H_6)_2$ and Cycloocta-1,5-diene

A suspension of $Rh(SnCl_3)(C_4H_6)_2$ (0.1 g.) in methylene chloride (10 ml.) was treated with cycloocta-1,5-diene (0.5 ml.) and the mixture left to stand, with occasional shaking, for 90 min. After this time an orange solution, containing a slight precipitate, had formed. The solution was filtered, treated with methanol, evaporated to small volume and left to stand overnight.

Yellow crystals formed and were filtered off, washed with methanol and dried in vacuo. The crystals (0.04 g.), m.p. ca. 235° dec., were shown by infrared spectrum (1,000-200 cm.⁻¹) to be $\text{Rh}_2\text{Cl}_2(\text{COD})_2$.

iv) Reaction of Rhodium(III) Chloride, Tin(II) Chloride and Ethylene

Using a technique similar to that described in i) above, ethylene (ca. 2 ml.) was sealed into a thick-walled glass tube (120 ml. capacity) containing rhodium(III) chloride (0.3 g.), tin(II) chloride (0.8 g.) and absolute ethanol (20 ml.). The tube was allowed to warm to room temperature and after a short time orange-red crystals separated from the reaction solution. The mixture was left to stand for two days and the crystals filtered off (0.20 g., 90%) and shown by m.p. 115-125° dec. and far-infrared spectrum (400-200 cm.⁻¹) to be identical to a genuine sample of $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$, prepared according to the literature method⁽¹⁴³⁾.

v) Reaction of Rhodium(III) Chloride, Tin(II) Chloride and Cyclooctene

To a solution of rhodium(III) chloride (0.3 g.) and tin(II) chloride (0.8 g.) in absolute ethanol (20 ml.) was added cyclooctene (1 ml.). The mixture was left to stand at room temper-

ature under an atmosphere of nitrogen for three weeks and then reduced to small volume at the rotary evaporator and left for a further two days. Orange crystals separated from the mixture in very small yield (<0.05 g.) and were filtered off and dried in vacuo. M.p. 132° dec., (lit. value for $\text{Rh}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$, 140° dec.⁽¹⁴¹⁾). (Found: C, 52.2; H, 7.66; Cl, 9.45%. Calc. for $\text{C}_{32}\text{H}_{56}\text{Cl}_2\text{Rh}_2$: C, 53.5; H, 7.95; Cl, 9.89%).

vi) Reaction of Rhodium(III) Chloride, Tin(II) Chloride and Acrylonitrile

To a solution of rhodium(III) chloride (0.4 g.) and stannous chloride (1.0 g.) in absolute ethanol (40 ml.) was added acrylonitrile (2 ml.). After standing overnight the solution had lost its deep red colour and contained a yellow precipitate. Filtration, washing with ethanol and ether, and drying in air gave a yellow powder (0.3 g.), melting over a wide range above 160° with decomposition. (Found: C, 19.9; H, 2.31; Cl, 23.3; N, 7.48%. Calc. for $\text{C}_{7.2}\text{H}_{7.2}\text{Cl}_3\text{N}_{2.4}\text{RhSn}$: C, 19.0; H, 1.58; Cl, 23.4; N, 7.38%).

vii) Reaction of Rhodium(III) Chloride, Tin(II) Chloride and

a) Methyl Vinyl Ketone, b) Allyl Acetate, c) Allyl Chloride

a) With methyl vinyl ketone:- to a solution of rhodium (III) chloride (0.4 g.) and stannous chloride (1.0 g.) in

absolute ethanol (40 ml.) was added methyl vinyl ketone (2 ml.). On standing for several days the solution became red-brown in colour and subsequent work-up yielded only brown oils.

b) With allyl acetate:- as in a) but with allyl acetate (2 ml.). After several days the solution had become orange in colour but subsequent work-up persistently yielded orange oils.

c) With allyl chloride:- as in a) but with allyl chloride (2 ml.). After standing for several days the solution had become orange-red in colour but a pure product could not be isolated.

CHAPTER 6

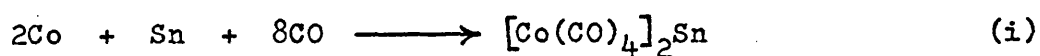
CHAPTER 6

The Reactions of Tin(II) Chloride with Transition Metal Carbonyl Anions

6.1 Introduction

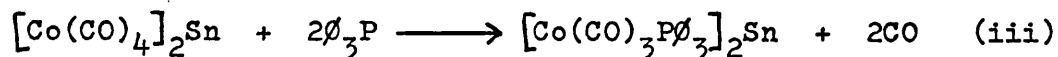
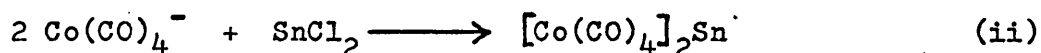
Compounds with tin-transition metal bonds containing tin in a formally divalent state are well known (see Chapter 1, section 1.1.B), but tin(II) compounds of empirical formula $(L_nM)_2Sn$ have been only briefly mentioned in the literature and have not been well characterised⁽²⁸⁾⁽¹⁴⁶⁾.

Early work on compounds with metal-metal bonds⁽²⁸⁾ included a report that intimate mixtures of cobalt and tin metal powders would react with carbon monoxide under conditions of high temperature and pressure (200°, 200 atmospheres) to give bis(tetracarbonylcobalt)tin(II) :-



More recently, it has been stated that this reaction could not be repeated⁽²⁹⁾.

The reaction between stannous chloride and the tetracarbonylcobalt anion has been reported to give bis(tetracarbonylcobalt)tin(II) and this product was found to react with triphenylphosphine⁽¹⁴⁶⁾ :-



It might be expected that other transition metal carbonyl anions would react with tin(II) halides to give compounds of the type $(\text{L}_n\text{M})_2\text{Sn}$, and in this present work several such reactions have been investigated. The reported syntheses of bis(tetracarbonylcobalt)tin(II) and bis(tricarbonyltriphenylphosphinecobalt)tin(II) by the methods described above have also been re-examined.

6.2 Reaction of Cobalt Powder and Tin Powder with Carbon Monoxide

Several attempts have been made to repeat the reaction of cobalt and tin powders with carbon monoxide, but without success. Cobalt and tin metal powders were intimately mixed before use, and temperatures as high as 250° and pressures of carbon monoxide up to 350 atmospheres were used, but on each occasion there

there was no indication that any reaction had taken place.

6.3 Reactions of Transition Metal Carbonyl Anions with Stannous Chloride in Tetrahydrofuran Solvent

A convenient method for the formation of transition metal carbonyl anions is the reaction of sodium with a suitable dimeric compound containing a metal-metal bond⁽³⁰⁾. Such a reaction requires the use of a solvent which does not react with sodium, and tetrahydrofuran (THF) is the one which is commonly used. Several transition metal carbonyl anions have been generated in THF solution by this and related methods, and their reactions with stannous chloride have been investigated.

a) Mn(CO)_5^-

Decacarbonyldimanganese in THF reacted with sodium amalgam to give a solution of the pentacarbonylmanganese anion⁽¹⁴⁷⁾. This solution was found to react rapidly with a solution of stannous chloride in THF, and vacuum sublimation of the crude product gave a small yield of orange-red crystals. These crystals were identified by melting point and infrared spectrum as chlorotris(pentacarbonylmanganese)tin, $\text{ClSn}[\text{Mn(CO)}_5]_3$. The formation of a formally tin(IV) compound by the reaction of tin(II) chloride with Mn(CO)_5^- is in agreement with a recent report⁽³³⁾ that tin(II) chloride will react with excess Mn(CO)_5^- in THF at 0°

to give tetrakis(pentacarbonylmanganese)tin, $[\text{Mn}(\text{CO})_5]_4\text{Sn}$.

b) $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ and $(\pi\text{-Cp})\text{W}(\text{CO})_3^-$

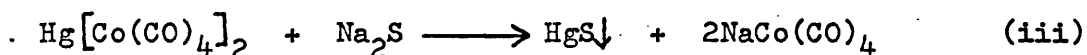
The anions were generated in THF solution by the reaction of sodium cyclopentadienide with the metal hexacarbonyl⁽¹⁴⁸⁾. Both anions were found to react rapidly with stannous chloride to give intensely coloured solutions, but pure products could not be isolated from the reaction mixtures. Vacuum sublimation of the crude mixtures gave very small yields of $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ and $[(\pi\text{-Cp})\text{W}(\text{CO})_3]_2$, but these compounds were formed by thermal decomposition of the initial products during the sublimation process and not by direct reaction of the anions with stannous chloride.

c) $\text{Co}(\text{CO})_4^-$

Octacarbonyldicobalt reacted with sodium amalgam in THF to give the tetracarbonylcobalt anion⁽³⁰⁾. This solution was found to react rapidly with a solution of stannous chloride in THF with the formation of an intense red colouration. Vacuum sublimation of the crude product gave a small yield of dichlorobis(tetracarbonylcobalt)tin, $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. This compound sublimes at low temperatures (30-35°) and so is probably a genuine product of the initial reaction and not the result of thermal decomposition during the sublimation.

6.4 Reactions of Transition Metal Carbonyl Anions with Stannous Chloride in Methanol Solvent

Bis(tetracarbonylcobalt)mercury will react with sodium sulphide to give mercuric sulphide and sodium tetracarbonylcobaltate⁽¹⁴⁹⁾:-



This reaction provides a novel method for the formation of the anion in aqueous and alcoholic solvents.

In this present work it has been found that other compounds containing mercury-transition metal bonds will react with sodium sulphide. Using this reaction, the transition metal carbonyl anions $(\pi\text{-Cp})\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Cr}, \text{Mo}$) have been generated in methanol solvent for the first time. The reactions of these methanolic solutions with stannous chloride have been investigated.

a) $\text{Co}(\text{CO})_4^-$

The tetracarbonylcobalt anion, in methanolic solution, has been reported to react with stannous chloride to give bis(tetracarbonylcobalt)tin(II), and this product was reported to react with excess triphenylphosphine to give bis(tricarbonyltriphenylphosphinecobalt)tin(II)⁽¹⁴⁶⁾. These reactions have now been repeated and a triphenylphosphine-substituted product has been obtained which is similar in appearance to that of the

reported product. It has not been possible to identify this product and variable elemental analysis results have been obtained for the products from separate preparations. The analysis results do not correspond to the formula $[\text{Co}(\text{CO})_3\text{P}\phi_3]_2\text{Sn}$ and show that the product contains chlorine. The presence of chlorine in the compound suggests that the tin may be present in a formally quadrivalent state and this idea is supported by the results from the related reaction with $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ and stannous chloride (see c) below).

b) $(\pi\text{-Cp})\text{Cr}(\text{CO})_3^-$

$\text{Hg}[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]_2$ was found to react with sodium sulphide in methanol to give a black precipitate of mercuric sulphide and a pale yellow solution of the anion $(\pi\text{-Cp})\text{Cr}(\text{CO})_3^-$. The filtered solution reacted rapidly with a solution of stannous chloride in methanol and a deep red solid was isolated from the reaction mixture. This compound was unstable in air and rapidly decomposed to a green solid, but it appeared to remain unchanged over a period of several weeks if sealed in an ampoule under an inert atmosphere. Analytical results for the red solid were not reproducible and did not correspond to the formula of the tin(II) compound, $[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]_2\text{Sn}$.

c) $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$

$\text{Hg}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ reacted rapidly with sodium sulphide in methanol to give a black precipitate of mercuric sulphide and a very pale yellow solution of the anion $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$. The filtered solution reacted with a solution of stannous chloride in methanol to give a deep red colouration. Two pure products were isolated from this solution and shown conclusively to be the tin(IV) compounds $\text{ClSn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_3$ and $\text{Cl}_2\text{Sn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$.

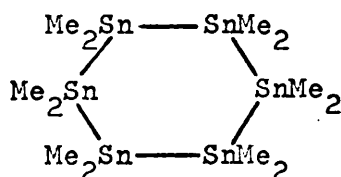
6.5 Discussion and Conclusions

Despite several attempts, it has not been possible to repeat the reaction of cobalt and tin metal powders with carbon monoxide to give $[\text{Co}(\text{CO})_4]_2\text{Sn}$. In view of this, and the fact that other workers⁽²⁹⁾ have also been unable to repeat the reaction, it is reasonable to suppose that the original report was in error.

It has been found that although the reaction between $\text{Co}(\text{CO})_4^-$ and stannous chloride, followed by treatment with triphenylphosphine, gave a product which was similar in appearance to the one originally described, this product contains chlorine and so cannot be formulated as $[\text{Co}(\text{CO})_3\text{P}\phi_3]_2\text{Sn}$. In most of the other reactions between transition metal carbonyl anions and stannous chloride which have been studied, it has only been possible to isolate compounds of tin(IV) of the type $(\text{L}_n\text{M})_2\text{SnCl}_2$

and $(L_nM)_3SnCl$. Therefore it seems that in these reactions the formation of compounds of tin(IV) is preferred to the formation of compounds of tin(II) and that a different approach is required for the successful synthesis of compounds of the type $(L_nM)_2Sn$.

Many organotin compounds which were originally formulated as simple derivatives of tin(II) (e.g. Et_2Sn , ϕ_2Sn , Me_2Sn) have now been identified as either cyclic or chain compounds which approximate to the composition R_2Sn but do, in fact, contain tin in a formally quadrivalent state⁽¹⁵⁰⁾. For example, dimethyl tin, Me_2Sn , is more correctly named as dodecamethylcyclohexastannane and has the structure:-



The existence of a similar situation in the field of tin-transition metal compounds is possible, and the results discussed above certainly indicate that the formation of compounds of tin(IV) is the preferred result in reactions in which it might be expected that tin(II) compounds would be the products. If, at some future date, the synthesis of compounds of empirical formula $(L_nM)_2Sn$ is achieved, it is likely that such compounds will have polymeric structures in which each tin atom is bonded to four nearest neighbours in a tetrahedral environment.

6.6 Experimental

Microanalyses, melting points and infrared spectra were obtained as described in Chapter 2. Tetrahydrofuran was purified immediately before use by distillation, under an atmosphere of dry nitrogen, from sodium wire and then from lithium aluminium hydride. All solvents were de-gassed before use by boiling for several minutes, and then saturated with nitrogen by bubbling the gas rapidly into the solvent. All the transition metal carbonyl anions are extremely air-sensitive and all preparations, manipulations and reactions were carried out under an atmosphere of dry nitrogen.

Cobalt and tin metal powders (5N grade), molybdenum hexacarbonyl and tungsten hexacarbonyl were purchased from Koch-Light Laboratories, Ltd. Decacarbonyldimanganese and chromium hexacarbonyl were purchased from Alfa Inorganics, Inc. The following compounds were prepared by literature methods: $\text{Co}_2(\text{CO})_8$ ⁽⁹³⁾, $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ⁽¹⁵¹⁾, $\text{Hg}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ ⁽¹⁵⁵⁾ and $\text{Hg}[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]_2$ ⁽¹⁵⁴⁾.

i) Reaction of Cobalt and Tin Powders with Carbon Monoxide

In a typical reaction cobalt powder (2.0 g.) and tin powder (2.0 g.) were intimately mixed and sealed into a stainless steel autoclave. Carbon monoxide was compressed into the autoclave to an initial pressure of 215 atmospheres and the autoclave

was heated to 200° to give a final pressure of 350 atmospheres. These conditions were maintained while the reaction vessel was rocked for 48 hr. After cooling and venting, the autoclave was opened and found to contain only the unreacted metal powders. Similar results were obtained on several occasions when different reaction conditions were used.

ii) Reaction of Mn(CO)_5^- and Stannous Chloride in THF

An amalgam of mercury (5 ml.) and freshly cut sodium (0.45 g.) was stirred for two hours and then excess amalgam was removed with a syringe. The green solution of Mn(CO)_5^- was treated with stannous chloride (1.6 g.) in THF (20 ml.) to give an immediate colour change to yellow-brown. After stirring for one hour solvent was removed at the rotary evaporator to leave an orange-brown solid. This solid was transferred to a water-cooled sublimation apparatus and this apparatus was then evacuated to about 0.1 mm. of mercury. On heating to 100° an orange sublimate collected on the probe. This sublimate was identified as $\text{ClSn[Mn(CO)}_5\text{]}_3$ by melting point 178°, (lit. value, 175-176°⁽¹⁵²⁾) and infrared spectrum.

iii) Reaction of $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ and Stannous Chloride in THF

$(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ in THF solution was prepared by the reported method⁽¹⁴⁸⁾ from sodium cyclopentadienide and hexacarbonylmolybdenum (2.7 g.). To the resulting solution was added a solution of stannous chloride (0.95 g.) in THF (25 ml.) with the immediate formation of a red colour. The solution was filtered and evaporated to dryness at the rotary evaporator to give a dark red solid. This solid dissolved in methylene chloride to give an orange solution but pure products could not be isolated from this solution. The bulk of the red solid was sublimed in vacuo at 120° to give a small quantity of a purple-red solid on the probe. This solid was identified by analysis and infrared spectrum as $[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ ⁽¹²³⁾. (Found: C, 38.6; H, 2.44%. Calc. for $\text{C}_{16}\text{H}_{10}\text{Mo}_2\text{O}_6$: C, 39.4, H, 2.31%).

iv) Reaction of $(\pi\text{-Cp})\text{W}(\text{CO})_3^-$ and Stannous Chloride in THF

$(\pi\text{-Cp})\text{W}(\text{CO})_3^-$ in THF solution was prepared in a manner similar to the one used for the analogous molybdenum compound from sodium cyclopentadienide and hexacarbonyltungsten (7.7 g.). To the resulting yellow solution was added a solution of stannous chloride (2.1 g.) in THF (20 ml.) with the immediate formation of a deep red colour. The mixture was stirred for one hour and then solvent was removed at the rotary evaporator to leave a purple-red solid. Vacuum sublimation of this solid at 80° gave

a white solid on the probe and this was shown by infrared spectrum to be unchanged hexacarbonyltungsten. Sublimation of the residue at 170° produced a purple-red solid which was identified by analysis and infrared spectrum as $[(\pi\text{-Cp})\text{W}(\text{CO})_3]_2$ ⁽¹⁵³⁾.
(Found: C, 29.3; H, 2.01%. Calc. for $\text{C}_{16}\text{H}_{10}\text{O}_6\text{W}_2$: C, 28.9; H, 1.50%).

v) Reaction of $\text{Co}(\text{CO})_4^-$ and Stannous Chloride in THF

$\text{Co}(\text{CO})_4^-$ was generated in THF solution by stirring a solution of $\text{Co}_2(\text{CO})_8$ (1.7 g.) in THF (50 ml.) with an amalgam of sodium (0.3 g.) and mercury (2.3 ml.) for three hours. Excess amalgam was removed by a syringe, and to the remaining solution was added a solution of stannous chloride (0.95 g.) in THF (15 ml.) with the immediate formation of a deep red colour. Stirring was continued for one hour and solvent was then removed at the rotary evaporator to leave a purple-red solid. Vacuum sublimation of this crude product at 35° produced an orange, crystalline sublimate which was identified by analysis and infrared spectrum as $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. (Found: C, 18.4; H, 0.0%. Calc. for $\text{C}_8\text{Cl}_2\text{Co}_2\text{O}_8\text{Sn}$: C, 18.1; H, 0.0%).

vi) Reaction of $\text{Co}(\text{CO})_4^-$ and Stannous Chloride in Methanol

Addition of methanol to a mixture of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ (1.0 g.) and hydrated sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, (0.5 g.) produced an immediate black precipitate of mercuric sulphide. The mixture was shaken mechanically for three hours and then filtered to give a pale yellow solution of $\text{NaCo}(\text{CO})_4$. This solution was added to a solution of stannous chloride (0.35 g.) in methanol (10 ml.) with the immediate formation of a purple-red colouration. After standing for 30 min. the solution was evaporated to dryness at the vacuum line to leave a purple solid. This solid was re-dissolved in benzene and the filtered solution added to a solution of triphenylphosphine (1.5 g.) in benzene. After standing overnight the initially purple solution had changed to a deep red colour. The benzene was removed in vacuo to leave a red crystalline residue which was washed thoroughly with several portions of ether to give a rust-coloured solid, m.p. $142-145^\circ$ dec. (Found: C, 50.8; H, 3.60; Cl, 10.2; Co, 12.3; Sn, 12.1%).

vi) Reaction of $(\pi\text{-Cp})\text{Cr}(\text{CO})_3^-$ and Stannous Chloride in Methanol

Methanol (50 ml.) was added to a mixture of $\text{Hg}[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]_2$ (1.2 g.) and hydrated sodium sulphide (0.48 g.) with the immediate formation of a black precipitate of mercuric sulphide. The mixture was shaken mechanically for three hours and then filtered to give a yellow solution of $\text{Na}[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]$.

(The presence of the anion was confirmed by treatment of a small portion of this solution with mercuric cyanide and subsequent isolation of $\text{Hg}[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]_2$. This product could not be isolated from a portion of the solution which had not been treated with mercuric cyanide). The yellow solution was added to a solution of stannous chloride (0.38 g.) in methanol (15 ml.) to give a slight brown precipitate and an orange-red solution. The solution was filtered and evaporated to dryness in vacuo to leave a red solid. This solid was redissolved in benzene and the resulting solution filtered and evaporated to dryness in vacuo to leave a red crystalline mass. This product decomposed to a green solid on exposure to air for a few hours but remained unchanged if stored under an atmosphere of dry nitrogen. Variable analysis results were obtained for this product, presumably because of the rapid decomposition in air. (Found: C, 23.2; H, 4.34%. Found: C, 31.2; H, 2.98%).

vii) Reaction of $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ and Stannous Chloride in Methanol

A pale yellow solution of $(\pi\text{-Cp})\text{Mo}(\text{CO})_3^-$ in methanol was generated from $\text{Hg}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$ (1.3 g.) and hydrated sodium sulphide (0.5 g.) in a manner similar to that used for the chromium analogue. (The presence of the anion was again confirmed by reaction with mercuric cyanide). The yellow solution of the anion was added to a solution of stannous chloride (0.38 g.) in

methanol (10 ml.) with the formation of a brown precipitate and an orange-red solution. This solution was filtered and left to stand overnight, after which time red crystals had formed in the solution. These crystals were filtered off and identified as $\text{ClSn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_3$ by analysis and m.p. 157° , (lit. value, 160° ⁽³⁸⁾). (Found: C, 32.2; H, 1.81%. Calc. for $\text{C}_{24}\text{H}_{15}\text{ClMo}_3\text{O}_9\text{Sn}$: C, 32.4; H, 1.70%).

The filtrate was evaporated to dryness in vacuo to leave an orange-red solid which was recrystallised from methylene chloride-petroleum spirit as golden-yellow crystals of $\text{Cl}_2\text{Sn}[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]_2$, m.p. 196° , (lit. value, 201° ⁽⁹⁰⁾). (Found: C, 28.0; H, 1.75%. Calc. for $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{Mo}_2\text{O}_6\text{Sn}$: C, 28.3; H, 1.49%).

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