AN INVESTIGATION INTO THE SYNTHESIS AND CATALYTIC HYDROGENATION ACTIVITY OF RHODIUM - STANNOUS - CHLORIDE COMPLEXES

By

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We accept this thesis as conforming to the required standard

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RhCl$_3$$\cdot$3H$_2$O in 3M HCl or ethanol was treated with various amounts of SnCl$_2$$\cdot$2H$_2$O and R$_4$NC1 (R = Me, Et) or [Et$_4$N][SnCl$_3$]. Kinetic products obtained include [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ and the new complex [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{3-}$. At longer reaction times [RhCl(SnCl$_3$)$_5$]$^{3-}$, [RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ and [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{5-}$, amongst other uncharacterised complexes, were found. The relative proportions of the complexes formed were dependent on the use of aerobic or anaerobic conditions, temperature, reaction time, precipitant and light. The products were characterised using UV-VIS and infrared spectroscopy and where possible by elemental analysis, conductance and tin Mössbauer spectroscopy. Based on the variability of product mixture under different synthetic conditions, a Rh(I) catalysed substitution at Rh(III) centres is believed to afford the initial Rh(III) anionic complexes. Other Rh(I) products form via reduction of Rh(III) to Rh(I) by Sn(II). Thermodynamic products result from slow equilibration of the initial product mixture. The anionic products obtained were found to be light-sensitive in solution.

A preliminary study of similar complexes, formed in situ, as catalyst precursors for the hydrogenation of fumaric and maleic acids was undertaken. In 3M HCl (or 3M DC1/D$_2$O) at 80° C and under 450 mmHg of H$_2$ (or D$_2$) the most catalytically active systems were those containing Sn(II) and Rh(III) with a ten-fold excess of olefin over Rh(III). An increase to thirty-fold excess of olefin markedly decreased activity although activity was independent of the
presence of Sn(II). A stoichiometric reduction by Sn(II), or rhodium-tin chloride complexes plus two protons, was found to compete with the catalytic processes. Deuterium scrambling was observed for both catalytic and stoichiometric systems. In the absence of Rh, this suggested the intermediacy of tin hydrides formed via β-elimination of tin-alkyl intermediates. As a working hypothesis, a conventional catalytic mechanism is proposed to operate via a 'hydride route' involving rhodium mono-hydrides formed by heterolytic splitting of H₂ (or D₂). Evidence also suggests that stoichiometric reduction of the olefin by a rhodium(I)-tin chloride complex resulting in oxidation of Rh(I) to Rh(III) may be coupled to the hydrogen reduction of Rh(III) to Rh(I) in the most active hydrogenation system.
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ABBREVIATIONS

The following list of abbreviations, most of which are commonly adopted in chemical literature, will be employed in this thesis.

A absorbance
$A_0$ " at time = zero
$A_{\infty}$ " " " = 'infinity'
$A_{\text{obs}}, A_{\text{calc.}}$ " : observed value, calculated value
aq. aqueous
br,s broad and strong
But tertiary butyl
calc. calculated
cat. catalyst
$[\cdot]_0$ concentration at time = zero
COD cyclooctadiene
COT cyclooctene
$\delta$ chemical shift
DMA N,N-dimethylacetamide
DMSO dimethyl sulfoxide
diphos 1,2-diphenylphosphinoethane
dipy 2,2'-dipyridyl
E non-metal atom
$\varepsilon$ extinction coefficient
eq'n. equation
Et ethyl
en ethylenediamine
fig. figure
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>F.I.D.</td>
<td>Free Induction Decay</td>
</tr>
<tr>
<td>FA</td>
<td>fumaric acid</td>
</tr>
<tr>
<td>I</td>
<td>spin or intensity</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>I.S.</td>
<td>Isomer Shift</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
<td>ln</td>
<td>natural logarithm</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
<tr>
<td>λ\text{max}</td>
<td>&quot; at maximum absorbance</td>
</tr>
<tr>
<td>m</td>
<td>medium</td>
</tr>
<tr>
<td>MA</td>
<td>maleic acid</td>
</tr>
<tr>
<td>MLA</td>
<td>malic acid</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>M</td>
<td>Molar or metal atom</td>
</tr>
<tr>
<td>M.O.</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>μ-</td>
<td>chemical formula prefix for a bridging atom</td>
</tr>
<tr>
<td>ν</td>
<td>frequency</td>
</tr>
<tr>
<td>nbd</td>
<td>norbornadiene</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PPh₃</td>
<td>triphenylphosphine</td>
</tr>
<tr>
<td>PMePh₂</td>
<td>methyldiphenylphosphine</td>
</tr>
<tr>
<td>press.</td>
<td>pressure</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>Q.S.</td>
<td>Quadrupole Splitting</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>R</td>
<td>alkyl</td>
</tr>
<tr>
<td>rel.</td>
<td>relative</td>
</tr>
<tr>
<td>r</td>
<td>correlation coefficient</td>
</tr>
<tr>
<td>s</td>
<td>strong</td>
</tr>
<tr>
<td>sec.</td>
<td>section</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>S/N</td>
<td>signal to noise ratio</td>
</tr>
<tr>
<td>sol'n</td>
<td>solution</td>
</tr>
<tr>
<td>SA</td>
<td>succinic acid</td>
</tr>
<tr>
<td>t₀</td>
<td>time zero</td>
</tr>
<tr>
<td>t₁/₂</td>
<td>half-life</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>X_{Sn} or x_{Sn}</td>
<td>mole fraction of Sn</td>
</tr>
<tr>
<td>w</td>
<td>weak</td>
</tr>
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</table>
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I wish to thank Professor B. R. James for his encouragement and helpful discussions throughout the course of this work.

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Synthesis of organics using soluble transition metal catalysts is industrially important. Recent production in the U.S. is over 10,000,000 tons /annum. Although not large relative to heterogeneously catalysed production, it is of relatively high dollar value. Principal processes and key transition metals include hydroformylation (Co, Rh), carbonylation (Co, Rh), hydrocarbon oxidation (Co, V, Cu, Mn, Pd, Mo), polymerization (Cu, Co, Mn, Zn, Ti, Sb, Ni, V), olefin/diene reactions (Ni, Rh, Ti, Cu), hydrogenation (Rh, Ni) and, addition of HCN (Ni). Cobalt-based processes are most common in terms of numbers and tonnage. Rhodium is dominant among second-row transition-metals. The most important processes are the Wacker (hydrocarbon oxidation, eq'n 1.1), vinyl acetate (hydrocarbon oxidation, eq'n 1.2), Oxo (hydroformylation, eq'n 1.3), methanol carbonylation (eq'n 1.4) and Ziegler-Natta polymerization (eq'n 1.5).

\[ \text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{PdCl}_2/\text{CuCl}_2(\text{aq})} \text{CH}_3\text{CHO} \] (1.1)

\[ \text{C}_2\text{H}_4 + \frac{3}{2} \text{O}_2 + \text{CH}_3\text{CO}_2\text{H} \xrightarrow{\text{PdCl}_2/\text{CuCl}_2(\text{aq})} \text{CH}_3\text{CO}_2\text{CH} = \text{CH}_2 + \text{H}_2\text{O} \] (1.2)

\[ \text{RCH} = \text{CH}_2 + \text{CO} + \text{H}_2 \xrightarrow{\text{HCo(CO)}_4 \text{ (organic sol'n)}} \xrightarrow{\text{RhCl(CO)(PPh}_3)_2 \text{ (organic sol'n)}} \text{RCH}_2\text{CH}_2\text{CHO} + \text{RCH}_3\text{CHO} \] (1.3)
\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{RhCl(CO)(PPh}_3)_2/\text{CH}_3\text{I promoter}} \text{aqueous or organic solution} \xrightarrow{} \text{CH}_3\text{CO}_2\text{H} \tag{1.4}
\]

\[
\text{C}_2\text{H}_4 \xrightarrow{\text{a-TiCl}_3(\text{s}) + \text{Al(C}_2\text{H}_5)_2\text{Cl}} \xrightarrow{} 1/n(\text{C}_2\text{H}_4)_n \tag{1.5a}
\]

\[
\text{C}_3\text{H}_6 \xrightarrow{\text{ditto}} 1/n(\text{C}_3\text{H}_6)_n \tag{1.5b}
\]

Despite a vast literature, hydrogenation is not as important on an industrial scale as other processes, except for the synthesis of optically active amino acids using a rhodium catalyst with chiral phosphine ligands (eq'n 1.6).

\[
\text{RCH}^+\text{CO}_2\text{H} \xrightarrow{\text{chiral cat., H}_2} \text{RCH}^+\text{CH}^+\text{NH}_2 \xrightarrow{\text{NHCOR}} \text{RCH}^+\text{CH}^+\text{CO}_2\text{H} \tag{1.6}
\]

As indicated by the equations above, reactants include small molecules such as CO, H\text{2}, O\text{2} and olefins combined in a gas-liquid process. Conditions are mild, typically at 70-150°C and \sim 20 atm., potentially leading to greater selectivity. \text{ }^6 For industrial catalytic processes, practical ranges of temperature and pressure are generally 20-500°C and up to hundreds of atmospheres, so homogeneous systems can also offer savings in energy costs. While no a priori guidelines for choosing between heterogeneous and homogeneous catalytic processes exist, selectivity, thermal control and effective utilization of catalytic sites are usually advantageous in homogeneous systems. On the other hand, catalyst expense, product separation, catalyst loss,
corrosion and mass-transfer problems are often disadvantageous\textsuperscript{2, 3, 6}.

This thesis is concerned with homogeneous catalytic hydrogenation of unsaturated dicarboxylic acids using rhodium-tin(II) chloride catalyst precursors. While no unified theory of catalysis exists\textsuperscript{2}, some catalytic hydrogenation reaction pathways have been firmly established\textsuperscript{3}. The essential steps (see below) are activation of H\textsubscript{2} and substrate, hydrogen transfer to olefin and release of the reduced product. The hydrogen transfer and product release steps are usually stereospecific, resulting in overall cis-addition of H\textsubscript{2} to the substrate.

1.1 Mechanisms of olefin hydrogenation\textsuperscript{7}

The transition-metal centre plays a key role in mediating the addition of H\textsubscript{2} to an olefin. Concerted cis-addition to double bonds is symmetry forbidden in the ground-state (fig. 1.1), although thermodynamically favourable\textsuperscript{8, 9}. Step-wise addition of H atoms is unfavourable since homolytic

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure1.png}
\caption{Symmetry forbidden addition of hydrogen to a C=C bond.}
\end{figure}
Cleavage of H$_2$ is a high energy process ($\approx$420 KJ/mole(aq.))$^{10}$. A transition-metal can have filled d-orbitals of suitable symmetry to interact with the $\sigma^*$ orbital (or possibly unfilled ones to accept electron-density from the H$_2$ $\sigma$ orbital) (fig. 1.2). Transfer of electron-density from d- to $\sigma^*$ orbitals destabilizes the H-H bond leading to formation of a dihydrido-metal complex (via I) or a monohydrido-metal complex if polarization of the H-H bond (i.e. $M\cdots$H$_2^-$=H$^+$, via II) occurs during cleavage. Heterolytic cleavage in the absence of metal is more favourable ($\approx$155 KJ/mole (aq.)) than homolytic cleavage, and base catalysed hydrogenation of aromatic ketones via hydride attack and subsequent protonation has been reported$^{11}$ but not similar reduction of C=C.

Although a dihydride is of the correct symmetry, direct cis-addition has not been proven$^3$. Superficially similar cis-additions to olefins are known for cis dioxo- and dinitrosyl-complexes$^{12}$ which are considered to be

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.2.png}
\caption{Possible orbital interactions between H$_2$ and a transition-metal centre.}
\end{figure}
analogous to 1,3 dipolar additions.

\[
[CpCo(NO)]_2 + 2\text{NO} \rightarrow 2[CpCo(NO)_2] \tag{1.7}
\]

\[
[CpCo(NO)_2] + \begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
R_4
\end{array} \rightarrow \begin{array}{c}
\text{CpCo}
\end{array} \begin{array}{c}
N \\
O \\
R_1 \\
R_2 \\
R_3 \\
R_4
\end{array} \tag{1.8}
\]

The metal centre also appears to be essential for activation during the H transfer step. Ordinary isolated double bonds are unreactive to nucleophilic attack \(^{13-15}\) (i.e. H\(^-\) or M-H), but coordinated olefins often are reactive \(^{16}\). The reasons are not obvious but for d\(^8\) Pt complexes coordination of H and olefin in a cis-coplanar arrangement (1), optimal for insertion,

\[
\begin{array}{c}
H \\
\text{M}
\end{array} \begin{array}{c}
- \\
- \\
\cdots
\end{array} \begin{array}{c}
\text{C}
\end{array}
\]

removes unfavourable repulsion between filled olefin and hydride orbitals by mixing these with olefin \(\pi^*\) and metal d-orbitals \(^{15}\). The repulsion then occurs with an empty d orbital. The results do not necessarily bear extension to other metals, but do indicate another expected role of a transition metal in hydrogenation.

The following sections present a brief overview of experimentally derived observations regarding catalytic hydrogenation. The examples used principally involve mononuclear Rh-based systems with monoene substrates. More complete discussions, including polynuclear complexes and polyene substrates, are found in recent reviews and books \(^{1-6,36}\).
1.1.1 Activation of hydrogen

Both heterolytic and homolytic cleavage of H₂ have been found to occur. Homolytic cleavage is favoured for low oxidation state, electron-rich metal-centres that are coordinatively unsaturated; heterolysis is favoured for higher oxidation state, labile metal centres in the presence of a proton sink (usually added base). Polar media stabilize the polarized transition-state of the latter and possibly the released proton as well, if basic or hydrogen-bonding. Formation of a hydridic species is not synonymous with catalysis since for kinetic or thermodynamic reasons some are catalytically inactive.¹⁷

(i) Heterolytic cleavage

The process involves ligand replacement with no change in formal oxidation state (eq'n. 1.9, 1.10). A vacant site or prior ligand dissociation

\[ M^{II}X + H₂ \leftrightarrow M^{II}H + H^+ + Cl^- \] (1.9)

\[ [\text{RhCl}_6]^{3-} + H₂ \rightarrow [\text{RhHCl}_5]^{3-} + H^+ + Cl^- \] (1.10)

may be required. The proton produced is stabilized by added base (often NEt₃), solvent or by interaction with the ligand 'X', possibly via a four-centre transition-state (2).¹⁸ The same net heterolytic splitting of H₂ could result from an initial oxidative addition followed by reductive elimination of HCl, possibly base assisted (1.11-1.13)¹⁹,²⁰. The initial oxidative addition is less likely for Rh(III) but is possible for Ru(II) (e.g. RuH₄(PPh₃)₃ formation)²¹.
\[ \text{M}^\circ \text{X} + \text{H}_2 \rightleftharpoons \text{XM}^{\text{II}} \text{H}_2 \rightarrow \text{M}^\circ \text{H} + \text{HX} \quad (1.11) \]

\[ \text{RhCl}_3 + \text{H}_2 \rightleftharpoons \text{RhH}_2\text{ClL}_3 \xrightarrow{\text{base}} \text{RhHL}_3 + \text{base-HCl} \quad (1.12) \]

\[ \text{RhL}_2^2\text{S}^+ + \text{H}_2 \rightleftharpoons \text{RhH}_2\text{L}_2^2\text{S}^+ \xrightarrow{\text{base}} \text{RhHL}_2\text{S}^2 + \text{base-H}^+ \quad (1.13) \]

(L= tertiary phosphine, S= solvent)

Hydrogenolysis of coordinated hydrocarbon ligands is formally similar (eq'n. 1.14)\(^ {22} \), probably via oxidative addition of \text{H}_2 followed by reductive elimination:

\[ \text{R-Rh(PPH}_3)_3 \xrightarrow{\text{H}_2} \text{HRh(PPH}_3)_3 + \text{R-H} \quad (1.14) \]

The reversibility of equation 1.9 can be a useful characteristic.

Kinetic evidence in conjunction with \text{H}_2-\text{D}_2\text{O} (or \text{D}_2\text{-solvent}) exchange provided evidence of non-detectable mono-hydrides in a number of systems\(^ {23} \).

Proton elimination from a mono-hydride sometimes leads to an active hydrogenation system. This is exemplified by Rh(III) systems where two-equivalent reduction to Rh(I) occurs (eq'n. 1.15). The Rh(I) formed usually enters the catalytic cycle via substrate activation prior to \text{H}_2 activation.

\[ \text{Rh}^{\text{III}} \text{H} \rightleftharpoons \text{Rh}^{\text{I}} + \text{H}^+ \quad (1.15) \]

Initial steps such as these have been proposed for a number of systems\(^ {24} \) including chlororhodolate(III)/DMA\(^ {25} \), cis-\text{RhCl}_3(\text{Et}_2\text{S})_3/DMA\(^ {26} \) and \text{RhCl}_3(DMSO)_3/DMSO\(^ {27} \). Chlororhodolate(III) in 3M HCl was also reduced in the presence of olefin to form a Rh(I)-olefin complex, which unlike the analogous DMA system, was not catalytically active\(^ {28} \).

(ii) Homolytic cleavage

Oxidative addition of \text{H}_2 to mono-nuclear metal centres is commonly observed\(^ {29} \). Coordination number and formal oxidation state increase by two
(eqn 1.16, 1.17)\textsuperscript{30} Addition is cis, trans dihydrides usually resulting in
\[
\begin{align*}
\text{M}^I + \text{H}_2 & \iff \text{MIIIH}_2 \\
\text{trans-IrX(CO)(PR}_3)_2 + \text{H}_2 & \iff \text{IrH}_2\text{X(CO)(PR}_3)_2
\end{align*}
\] (1.16) (1.17)
from subsequent reactions such as cis-trans rearrangements (e.g. \(\text{MH}_2\text{L}_4\) (\(\text{M} = \text{Fe}, \text{Ru}\))\textsuperscript{31}). Low oxidation state, high metal basicity and coordinative unsaturation promote oxidative addition\textsuperscript{32}, although addition of \(\text{H}_2\) to a saturated metal centre with concomitant loss of ligand is well known (eqn 1.18)\textsuperscript{33}. Note that addition of hydrogen has been considered reductive for
\[
[\text{Ir(CO)}_2(\text{PPh}_2\text{Me})_3]^{\text{+}} + \text{H}_2 \longrightarrow [\text{IrH}_2(\text{CO})(\text{PPh}_2\text{Me})_3] + \text{CO}
\] (1.18)
[\text{Ir(COD)L}_2]\textsuperscript{\text{+}} and [\text{Ir(COD)}]\textsuperscript{\text{34}}. This illustrates the sometimes equivocal nature of oxidation state formalism in relation to metal hydrides which are perceived as becoming less hydridic and more covalent or acidic in nature on passing from the early to late transition metal hydrides\textsuperscript{35,36}.

Addition across two metal centres usually results in an increase of formal oxidation state and coordination number of one (eqn 1.19-1.21)\textsuperscript{37}:
\[
\begin{align*}
(\text{ML}_n)_2 + \text{H}_2 & \iff 2\text{MHL}_n \\
2\text{ML}_n + \text{H}_2 & \iff 2\text{MHL}_n
\end{align*}
\] (1.19) (1.20)
\[2\text{CoII(CN)}_5^{3\text{-}}\text{ (or Co}_2(\text{CN})_{10}^{6\text{-}}) + \text{H}_2 \iff 2\text{CoIIIH(CN)}_5^{3\text{-}}\] (1.21)
Dinuclear complexes are known to form hydrides with one H bound to each metal ([IrH(\(\mu\text{-SBu}^\text{+}\))(CO)(PPh)_3]_2)\textsuperscript{38} or add \(\text{H}_2\) to only one metal ([(Ph_3P)_2Rh(\(\mu\text{-Cl}\))_2RhH_2(PPh_3)_2])\textsuperscript{39}.
1.1.2 Activation of substrate and hydrogen transfer

Catalytic cycles where the metal hydride has been preformed and olefin subsequently coordinated have been termed the 'hydride' route. On the other hand olefin binding followed by hydrogen activation has been called the 'unsaturate' route.

Coordinative unsaturation is essential to catalysis. As a coordinating ligand, solvent can act as a weakly coordinating (labile) ligand facilitating unsaturation. Solvent can also compete with substrate for vacant metal sites, especially with weakly binding simple terminal olefins (e.g. solvent = aromatic hydrocarbon). Other complications include side-reactions such as between alcohols and added base (a common combination) to form alkoxides. As a result, elucidation of a complete mechanism can be a complex problem. In the following discussion these factors should be borne in mind, although the topic will not be expanded further.

(i) Monohydride catalysts

Proposed non-free-radical mechanistic pathways involving mono-hydride catalysts are outlined in scheme 1.1. The unsaturate route goes via step(a), exemplified by the chloro-ruthenate(II) catalysed hydrogenation of \( \alpha,\beta \) unsaturated carboxylic acids. On the basis of kinetic, deuterium tracer and exchange studies the mechanism is proposed to go via the 'acd' pathway. The hydride route is suggested for \([\text{RuHCl(PPh}_3)_3]\) and \([\text{RhH(CO)(PPh}_3)_3]\) via 'bcef', and for trichlorostannate(II) complexes of Pt(II) via 'bcd'. The insertion of olefin into the metal hydride bond (or hydride migration to olefin) is believed to be facile and stereospecifically cis, the 4-centre transition-state (1) requiring coplanar arrangement. The reversibility
Scheme 1.1 Mechanistic pathways for mono-hydride catalysts

of the steps 'bc' and 'ac' provide an explanation for olefin isomerization in the absence of H₂, and isotope exchange between metal hydride and alkene hydrogens, and also with solvent and/or H₂. These are commonly observed reactions of mono-hydride catalysts. The metal-alkyl (3) intermediate has not been directly observed under catalytic conditions.

The product release step (d,g or e-f) must occur with retention of configuration when overall cis addition of H₂ to substrate is observed. For example, hydrogenation of fumaric and maleic acids catalysed by chlororuthenate(II)/D₂ yielded (±)-dideuterosuccinic acid with the former, while meso-2,3-dideutero succinic acid was obtained with the latter (via step d, protonolysis). Observation of non-stereospecific addition of D₂ to (Z)- and (E)-cinnamic acid catalysed by Pt(II)/SnCl₃⁻ complexes has been ascribed to isomerization via equilibration of rotamers of (3) and the reversibility
of step c. Hydrogenolysis via steps e and f represents net heterolytic splitting of $H_2$. The hydrogen transfer step f is considered to be fast and the dihydridoalkyl complex (4) has not been directly observed.

Binuclear reductive elimination (step g) has been proposed for $[\text{CoH(CN)}_5]^{3-}$, $[\text{RuHCl(PPh}_3)_2]^2$ and $[\text{CoH(CO)}_4]^{49}$ systems, among others. It offers an alternate pathway when oxidative addition of $H_2$ to (3) is unfavourable.

Free-radical pathways have been proposed for hydrogenation of polycyclic aromatic hydrocarbons catalysed by $[\text{CoH(CO)}_4]^{51}$. Hydrogenation of some $\alpha,\beta$-unsaturated acids, esters and nitriles catalysed by $[\text{CoH(CN)}_5]^{3-}$ may also involve H-atom transfer. The hydride was formulated as $[\text{Co}^{II}(\text{CN})_5(\cdot H)]^{3-}$. Net cis addition of $H_2$ was usually observed, indicating that recombination of organic radical with Co within a solvent cage is faster than rotation about the $\alpha,\beta$ C-C bond.

Two-electron reduction of substrate and addition of two protons to form the saturated product has been noted in the absence of $H_2$. The mechanisms proposed are basically two: (i) protonation at metal followed by oxidative hydride transfer and protonolysis to release the product, and (ii) coordination of substrate followed by electron transfer and protonation of the resultant carbanion and then protonolysis. Stoichiometric reductions probably via (ii) are well known for Cr(II) and V(II) salts among others. Pathway (i) is available to the more acidic metal hydrides (cf. reverse of eq'n. 1.15), such as $[\text{Rh(dipy)}_2]^+$ for catalysis a sacrificial reducing agent such as Zn/HCl, borohydride, CO or an electrochemical process would be required. Strangely enough $H_2$ has not been firmly established as a reductant in any
(ii) Dihydride catalysts

Essential mechanistic pathways proposed for dihydride catalysts are summarized in scheme 1.2. The hydride route goes via step 'a' and the unsaturate route via step 'b'. Dihydride formation and olefin binding are usually rapidly established equilibria. Like the monohydride systems overall cis-addition of H₂ to olefin results from the coplanar migratory insertion (step 'c') followed by reductive elimination with retention of configuration at the metal bonded carbon (step 'd'). The alkyl-hydride (6) and hydrido-alkene (5) species have rarely been observed. The cis,cis-complex [IrH₂(COD)(PMePh₂)₂]⁺ forms cyclooctane and dihydride via cycle 'cdfb' on warming from -40°C under H₂. In the absence of H₂, the release of H₂ to form [Ir(COD)(PMePh₂)]⁺ occurs. An alkyl-hydride complex has been observed at low temperature (see below).

Unlike monohydride systems, little hydrogen isotopic scrambling or
olefin isomerization is observed for easily reduced substrates. Step d in this case must be faster than alkyl-hydride formation which is consistent with the difficulty of observing (6).

Two "dihydride" catalytic systems are well understood in the sense that kinetic and equilibrium parameters for each step in the proposed mechanisms have been measured. Hydrogenation of cyclohexene with RhCl(PPh₃)₃ (Wilkinson's catalyst) is principally via the hydride path 'acde' \(^{60}\). In contrast hydrogenation of mono-olefins with Rh(diphos)S\(^2\)+ appears to operate via the unsaturate route 'bcdf' \(^{61,63}\). Preference for unsaturate vs. hydride route for these catalyst precursors appears to be in part due to avoidance of less thermodynamically stable configurations where the hydride ligand is trans to phosphine \(^{62,63}\). For example, [Rh(diphos)(nbd)]\(^+\) reacts with 2 moles of H\(_2\) to form norbornane and solvated Rh(diphos)\(^+\), whereas the PPh\(_3\) analogue reacts with 3 moles of H\(_2\) forming a cis-hydride and saturated product \(^{63}\). However, related Rh(Ph\(_2\)P(CH\(_2\)\(_n\))PPh\(_2\))\(^2\)+ species do form dihydrides with the trans configuration \(^{64}\). Preference can be affected, of course, by the relative binding strength of the olefin to species (7) and (8). In general, species that form metal under H\(_2\) in the absence of olefin must go via the unsaturate route. That route is usually proposed if the dihydride (7) is undetectable. If one is detectable or isolable, the hydride route is generally proposed, or both routes if olefin and H\(_2\) are found to coordinate separately (e.g. RhCl(PPh₃)₃, see below).

Scheme 1.3 illustrates the mechanism proposed for the RhCl(PPh₃)₃ catalysed hydrogenation of cyclohexene. The boxed part corresponds to the hydride route of scheme 1.2. None of the species within the box are observable
Scheme 1.3 Mechanism of RhCl(PPh₃)₃-catalysed hydrogenation of cyclohexene.

under catalytic conditions. The 14-electron bisphosphine complex (9) was proposed on kinetic grounds and is $10^4$ times more reactive towards $\text{H}_2$ than the trisphosphine complex (10). Thus the solvated dihydride (11) is more readily formed via (9) than via the isolable species (10) and (12). Less
efficient catalytic cycles based on the observed species (13) and (14) have been reported. In addition, evidence indicates that with styrene a further pathway involving species with two coordinated styrenes exists.

Scheme 1.4 illustrates the proposed mechanism for Rh(diphos)S$_2^+$ (S= MeOH)-catalysed hydrogenation of methyl (Z)-acetamidocinnamate. From 0-50°C the reaction with H$_2$ was rate-determining, however, at -78°C the reductive elimination step stopped and species (15) was detectable by $^1$H, $^{31}$P, $^{13}$C and $^{15}$N NMR. The molecular structure of the olefin complex (16) and

Scheme 1.4 Mechanism of Rh(diphos)S$_2^+$ (S= MeOH)-catalysed hydrogenation.
Rh(diphos)S₂⁺ have been crystallographically determined⁶⁶. A dihydro-olefin complex (i.e. (5)) has not been detected because the insertion step is very fast, probably due to the migrating hydrides position trans to phosphine.

The Rh(diphos)S₂⁺ catalyst system is of special interest because related catalysts containing chiral derivatives of diphos (e.g. (R,R)-bappe (formerly dipamp) (17) or (S,S)-chiraphos (18)) are very effective for the asymmetric hydrogenation of prochiral alkenes to give optically active amino acids (eq'n. 1.22)⁶. The high enantioselectivity is usually ascribed to prefered binding of the prochiral alkenic substrate controlled by the orientation of the four phenyl groups of the chiral diphosphine. However, for bappe and chiraphos systems the product was found to result from reaction
of $H_2$ with the **minor** diastereomer of (16). Control of the asymmetric 
induction is subtle, small changes in ligand or substrate structure affecting 
the enantiomeric excess of the product. A small bias in regioselectivity 
of HD addition to (Z)-$\alpha$-acetamidocinnamic acid catalysed by Rh(dip)$S_2^+$ 
(dip= (19)) has also been noted.

1.2 Role of chlorostannate(II) in catalysis.

The SnCl$_3^-$ ligand has been usually regarded as an ancillary $\pi$-acceptor 
ligand. Commonly SnCl$_2\cdot$H$_2$O or SnCl$_2$(anhydr.) is added as cocatalyst to a 
catalyst precursor with a metal chloride bond (eq'n. 1.23), into which SnCl$_2$

\[
\text{PtCl}_2(\text{PR}_3)_2 + \text{SnCl}_2 \rightarrow \text{PtCl(SnCl}_3)(\text{PR}_3)_2
\]  

(1.23)

inserts. In the presence of Cl$^-$, SnCl$_3^-$ can be formed (eq'n. 1.24) and

\[
\text{SnCl}_2 + \text{Cl}^- \rightleftharpoons \text{SnCl}_3^-
\]  

(1.24)

and coordinate. Additionally, molten tetraalkylammonium salts of SnCl$_3^-$ 
have been used as the media for hydrogenation of monoenes and dienes by Pt 
salts.

The electronic nature of SnCl$_3^-$ has been considered to be important 
in a number of hydroformylation, carbonylation, hydrogenation, and isomerization 
systems using Pt(II) and Pd(II) catalysts. Little work 
has been reported on rhodium-based systems (see below). The systems tend to 
be much less active or selective without the addition of stannous chloride.

The SnCl$_3^-$ ligand has been generally considered as a weak $\sigma$-donor 
(<CO, PF$_3$) and strong $\pi$-acceptor (>CO, PF$_3$). Its strong trans effect 
was considered to activate Pt(II) and Pd(II) centres towards nucleophilic
substitution. It has also been suggested that coordination of \( H^- \) and olefin was enhanced by reduction of the charge at the metal centre due to \( \pi \)-acceptance by \( \text{SnCl}_3^- \). This factor also stabilizes against reduction to metal or low oxidation state \( \text{SnCl}_2 \). On the other hand, coordination of \( \text{SnCl}_3^- \) has been suggested to make M-H bonds more hydridic (i.e. \( \text{Sn-M-H} \)) in nature, which is in accord with the reducing power of tin(II).

Examination of the stoichiometric carboylation of phenylplatinum(II) complexes promoted by \( \text{SnCl}_2 \) indicated that \( \text{SnCl}_3^- \) was acting as a good leaving group of moderate nucleophilicity. The key step involved attack by \( \text{SnCl}_3^- \) to form a 5-coordinate intermediate from which insertion occurred (scheme 1.5).

![Scheme 1.5 Carbonylation of phenylplatinum(II)](image-url)

It was noted that \( I^- \), and to a lesser extent \( Br^- \), which are better nucleophiles and worse leaving groups promoted the reaction less effectively. A similar
promotion of insertion via a 5-coordinate intermediate was proposed for the SnCl$_3^-$ catalysed insertion of C$_2$H$_4$ into trans-PtHClL$_2$ (L = phosphine) to form trans-Pt(C$_2$H$_5$)ClL$_2$.

Recent investigation of the precatalytic and catalytic chemistry of cis- PtCl$_2$(L)(PR$_3$)/SnCl$_2$·2H$_2$O and Pt$_2$(μ-Cl)$_2$Cl$_2$(PR$_3$)$_2$/SnCl$_2$·2H$_2$O (L = PR$_3$, CO, thioether, amine; R = aryl, alkyl) olefin hydrogenation and hydroformylation systems reveals a rich solution chemistry involving stannous chloride. The stannous chloride acts both as an ancillary ligand as well as disproportionating to form SnCl$_3^-$ and cationic hydrates. Simple insertion was observed in CH$_2$Cl$_2$ solution, but disproportionation occurs in acetone leading to formation of a mixture of anionic and neutral Pt complexes, electroneutrality being maintained by the cationic tin hydrates. The role of stannous chloride was not limited to a specific intervention at a key step, but was proposed to be the promotion of the multicomponent system. Most components of the mixture were shown to be essential to the catalysis.

Examples of a redox role for Sn in catalytic systems are rare. In some cases where both Sn(II) and Sn(IV) cocatalysts are effective (e.g. 1,5-cyclooctadiene isomerization with PtCl$_2$(PPh$_3$)$_2$), the possibility should be considered. A water-gas-shift catalyst system composed of K$_2$PtCl$_4$/SnCl$_4$·5H$_2$O in HCl/HOAc/H$_2$O under CO and ethylene or propylene is believed to involve a Sn(II)/Sn(IV) couple. The olefin was hydrogenated but H$_2$ added to the system was not consumed. Thus a hydride formed in a water-gas-shift cycle was believed to react with the olefin, followed by protonation to release alkane (scheme 1.6). The water-gas-shift cycle had been previously reported to depend on the interaction of a Sn(II)/Sn(IV) couple with a cycle involving...
Scheme 1.6 Hydrogenation of C₂H₄ catalysed by K₂PtCl₄/SnCl₄·2H₂O/CO.

\[ \text{Pt}^0/\text{Pt}^{II}/\text{Pt}^{IV} \text{ (eq'ns. 1.25, 1.26)} \]

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} + \text{SnCl}_6^{2-} & \xrightarrow{\text{Pt species}} \text{CO}_2 + 2\text{H}^+ + \text{SnCl}_3^- + 3\text{Cl}^- \quad (1.25) \\
2\text{H}^+ + \text{SnCl}_3^- + 3\text{Cl}^- & \xrightarrow{\text{Pt species}} \text{H}_2 + \text{SnCl}_6^{2-} \quad (1.26)
\end{align*}
\]

1.3 Aim of this work

The aim was to prepare a Rh-SnCl₃ catalyst precursor complex and examine its olefin hydrogenation activity. Addition of stannous chloride to platinum(II) chloride systems in the early 1960s was found to give an active ethylene hydrogenation system. Shortly afterwards ethanol solutions of \([\text{RhCl(SnCl}_3]_2\) were reported to be active for the hydrogenation of hex-1-ene and n-heptaldehyde. Little further work has been reported, so further investigation was felt to be warranted. Additionally, the absence of tertiary group VA ligands is noteworthy in view of the abundance of studies involving Rh complexes containing these ligands.
CHAPTER II
EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Solvents

Spectral or analytical grade organic solvents were obtained from MCB, Mallinckrodt, Eastman or Fisher Chemical. Solvents were dried under Ar before use, as described below. The dried solvents were handled under flowing Ar and stored under Ar (slightly greater than 1 atmosphere).

Acetonitrile, diethyl ether and dichloromethane were distilled from CaH$_2$. Acetone was dried over molecular sieves (Fisher type 4 Å). Nitromethane was distilled from P$_2$O$_5$. Ethanol (95-100%) was predried over BaO before distillation from magnesium ethoxide. Aqueous HCl solutions were made up from reagent grade (A.C.S.) concentrated HCl from AMACHEM.

Deuterated solvents were used without further purification. D$_2$O (99.7 atom %) and CD$_3$CN (99 atom %) were obtained from Merck, Sharp and Dohme Canada Ltd. DCl (38% in D$_2$O; 99 atom %) and (CD$_3$)$_2$NO$_2$ (99 atom %) were from Stohler Isotope Chemicals. CDCI$_3$ and (CD$_3$)$_2$CO (99.8 atom %) were from Aldrich Chemical Co. The 38% DCl was diluted to 3M with D$_2$O before use.

2.1.2. Gases

Purified oxygen, argon, carbon dioxide and nitrogen were obtained from Canada Liquid Air Ltd., or from Union Carbide Canada Ltd., and were used without further purification. Hydrogen, carbon monoxide and lecture bottles
of methane were from Matheson Gas Co. ("research grade") or Union Carbide Canada Ltd. ("specialty gas"). Hydrogen was passed through an Engelhard Deoxo catalytic purifier to remove traces of oxygen, and then through a drying column containing calcium chloride and $P_2O_5$ to remove $H_2O$.

2.1.3 Olefinic Substrates

C.P. grade ethylene was obtained from Matheson Gas Co. and used without further purification. Maleic and fumaric acids were reagent grade from Mallinckrodt and were recrystallized from $H_2O$ before use.

2.1.4 Other materials

The tetraalkylammonium chlorides were obtained from Eastman. Tetraphenylarsenium chloride was from K & K Laboratories Inc. Stannous chloride, stannic chloride and lithium chloride were reagent grade from Fisher Chemical Co. The $[Et_4N][SnCl_3]$ was prepared by the literature method. All tin(II) compounds were stored under anhydrous conditions in an argon atmosphere.

2.1.5 Rhodium Complexes

The rhodium was obtained as $RhCl_3 \cdot 3H_2O$ (41.87% Rh) from Johnson, Matthey Ltd. The rhodium(I) complex $Rh_2Cl_2(COT)_4$ was a gift from Dr. D. Mahajan. Standard Schlenk techniques were employed for synthetic procedures under anaerobic conditions. Schlenkware wrapped in black electrical tape was used in procedures requiring absence of light. The isolated products of
reactions were stored under anhydrous conditions to prevent hydrolysis by atmospheric moisture.

2.1.5.1 Preparation of fac-[Me₄N]₃[RhCl₃(SnCl₃)₃]

The method of Kimura was used. Under aerobic and ambient light conditions 0.15 g RhCl₃·3H₂O (0.61 mmole) was dissolved in 35 mL 3M HCl. To this solution was added 0.386 g SnCl₂·2H₂O (1.7 mmole). The solution was stirred for 70 min at 90°C. The resultant dark red-orange solution was stored for 20 - 24 h at -5°C. Careful addition of Me₄NCl until no further precipitation occurred yielded a reddish orange powder that was washed successively with 5 mL 3M HCl (containing a few mg of Me₄NCl), 3M HCl and dry ethanol. The precipitate was then dried in vacuo. Yield was ~60%.

The product is insoluble in non-polar solvents but is slightly soluble in 3M HCl and ethanol, moderately soluble in CH₃CN, (CH₃)₂CO and CH₃NO₂, and very soluble in DMSO and DMA, where it probably decomposes as judged by the resultant weakly coloured solutions. Solutions of the complex are light sensitive.

Elemental analysis (% found (calc.)) for C₁₂H₃₆Cl₁₂N₃RhSn₃ was C 12.90 (13.02), H 3.30(3.28), Cl 38.60(38.43), N 3.72(3.80) and Rh 9.70(9.30).

Far-IR (Nujol mull, CsI plates) has bands (ν(M-Cl)) at 362, 336, 321, 303(sh), 275 cm⁻¹ (fig.2.1). Solution UV-VIS spectra has λ_max (ε, M⁻¹cm⁻¹) in 3M HCl at 424 nm (4360), 304 nm (29500) and 257 nm (15400) (fig. 2.2). In CH₃CN the spectrum (fig. 2.3) depends on whether there is excess Cl⁻ present or not, but the resultant spectrum stabilized within minutes in both cases (see also chapter IV).
Figure 2.1  Far-IR spectrum (Nujol, CsI plates) of fac-[Me₄N]₃[RhCl₃(SnCl₃)₃] (-----) compared to that reported in ref. 91(----) (ref. 91, fig. 1-(2A); resampled digitally and scaled to match the absissa ).
Figure 2.2  3M HCl solution UV-VIS spectrum of $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]$ (——) compared to that reported in ref. 91(-----) (ref.91, fig. 2-(2A); see note fig. 2.1).
Figure 2.3 CH₃CN solution UV-VIS spectra of [Me₄N]₃[RhCl₃(SnCl₃)₃] (6.04 x 10⁻⁴ M, 0.1 cm cell) (—) without added chloride and with a 10-fold excess of Et₄NCl·H₂O (—). 

2.1.5.2 Preparation of [Me₄N]₃[RhCl₂(SnCl₃)₄]·H₂O

The method of Kimura⁹¹ was used at half-scale. Under aerobic and ambient light conditions, 0.19 g RhCl₃·3H₂O (0.77 mmole) was dissolved in 12.5 mL of 3M HCl at 90°C. Addition of 0.33 g Me₄NCl (3.0 mmole) and 0.49 g
SnCl₂·2H₂O (2.1 mmole) instantly yielded an orange precipitate. The suspension was heated for two hours at 90°C with constant stirring. After filtering hot, the precipitate was washed successively with small amounts of 3M HCl containing Me₄NCl, 3M HCl and dry ethanol. The orange powder (50% yield) was dried in vacuo.

The solubilities and reactivities towards solvent are similar to those of [Me₄N]₃[RhCl₃(SnCl₃)₃]. Solutions of the complex are also light sensitive. Additionally, one tin ligand dissociates in solution (see Chapter IV); however, the rate is slow enough in CH₃CN (t₁/₂ ≈ 1450 s) to allow the use of initial spectra for characterization.

The complex is considered to be the trans isomer. A trans arrangement of chloride and SnCl₃ gives rise to ν(M-Cl) at 375 cm⁻¹ in fac-[RhCl₃(SnCl₃)₃]³⁻ and [RhCl₄(SnCl₃)₂]³⁻, which is absent in the tetrakis complex (see below).

Elemental analysis (% found (calc.)) for C₁₂H₃₈Cl₁₄N₃ORhSn₄ was C 10.58(10.96), H 2.90(2.74), Cl 38.00(37.82) N 3.04(3.20) and Rh 7.76(7.84). The far-IR (Nujol, CsI plates) has bands (ν(M-Cl)) at 363 (sh), 326 and 287 (sh) cm⁻¹ (fig. 2.4). The CH₃CN solution UV-VIS spectrum is shown in figure 2.5. In 3M HCl solution the spectrum was unstable in light and dark, but was similar to that reported in reference 91. The Mössbauer spectrum (77°K; fig. 2.6) gave I.S. (rel. to BaSnO₃) = 1.68 ± 0.06 mm/s and Q.S. = 1.80 ± 0.03 mm/s.

2.1.5.3 Preparation of [Et₄N]₃[Rh(SnCl₃)₄(SnCl₄)]·(Et₄NCl)₀.₅

This procedure was done under anaerobic conditions and in the dark, up to the stage at which the solids were drying in vacuo.
Figure 2.4  Far-IR spectrum (Nujol, CsI plates) of $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\cdot \text{H}_2\text{O}$ (-----) compared to that reported in ref. 91 (----) (ref. 91, fig. 1-(3); see note fig. 2.1).
A solution of 0.125 g RhCl$_3$·3H$_2$O (0.47 mmole) in 25 mL 3M HCl was heated to 60°C and 0.860 g [Et$_4$N][SnCl$_3$] (2.42 mmole) was carefully added, with stirring, in the dark; the temperature was then raised to 90°C for 1 h. After cooling to room temperature the solution was filtered and the yellow-orange precipitate washed with dry ethanol and dried in vacuo (75% yield).
The filtrate was colourless or very pale coloured.

Recrystallization from warm, dry deaerated CH$_3$CN in the absence of light yielded a darker orange microcrystalline product in less than 30% yield. Further recrystallization gave a very low yield of small needle-like crystals unsuitable for crystallographic determination.

The complex is less soluble than the Rh(III) complexes described in

Figure 2.6 Mössbauer spectrum of [Me$_4$N]$_3$[RhCl$_2$(SnCl$_3$)$_4$]·H$_2$O at 77°K.
the preceding two sections, but shows a similar pattern of solubilities and reactivities. It is stable in the solid state if stored in the absence of light under anhydrous conditions and can be handled in air for short periods without noticeable change. In solution the complex is very light sensitive while in the dark it decomposes to give free SnCl$_3^-$ and a mixture of Rh(III) and Rh(I) species (see Chapter 4). In CH$_3$CN the process has a $t_{1/2}$ of 6000 sec in the dark, so the initial spectrum is usable to characterize the complex, while in 3M HCl the decomposition reaction is quite fast.

Elemental analysis (% found (calc)) for C$_{28}$H$_{20}$Cl$_{16}$N$_3$5RhSn$_5$ was C 19.55(19.35), H 4.20(4.03), Cl 34.14(33.74), N 2.80(2.82) and Rh 5.96(5.93) for the unrecrystallized sample. For a recrystallized sample the analysis was C 20.45, H 4.60, Cl 34.91 and N 3.43. The far-IR (Nujol, CsI plates) for the unrecrystallized sample has bands at 348, 332(sh), 327, 315 and 307(sh) cm$^{-1}$ and for a recrystallized sample at 355, 332(sh), 327, 318(sh) and 306 (sh) (fig. 2.7). The UV-VIS spectrum for a CH$_3$CN solution of the recrystallized (or recrystallized) product is shown in figure 2.8. Pertinent data for this and for other solvents are summarized in table 2.1. The Mössbauer spectrum (77°K; fig. 2.9) was an asymmetric doublet I.S. (rel. to BaSnO$_3$) = 1.79 ($\pm$0.03) mm/s and Q.S. = 1.84 ($\pm$0.02) mm/s. Conductance in nitromethane (in absence of light and air) increased with time; the initial value of $\Lambda_m$ was 249 ohm$^{-1}$ mol$^{-1}$ cm$^2$ (1.2 x 10$^{-3}$ M, 25°C). After decomposition in acid solution in the presence of Fe$^{3+}$, under argon, the complex yielded 10.1 reducing equivalents (Fe$^{3+}$$\rightarrow$Fe$^{2+}$) per mole of rhodium as determined by titration with Ce$^{4+}$. 
Figure 2.7 Far-IR spectrum (Nujol, CsI plates) of unrecrystallized $[\text{Et}_4\text{N}]_3[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)] \cdot [\text{Et}_4\text{NCl}]_{0.5}$ (—) compared to that after recrystallization from $\text{CH}_3\text{CN}$ (—-).
Figure 2.8 Initial CH$_3$CN solution UV-VIS spectrum of [Et$_4$N]$_3$[Rh(SnCl$_3$)$_4$ - (SnCl$_4$)]$\cdot$[Et$_4$NCI]$_{0.5}$ (1.93 x 10$^{-5}$M, 0.5 cm cell).

2.1.6 Other synthetic experiments discussed in chapter III.

Several of the experiments were simple variations on the procedures described in the preceding sections and deserve no further comment here. The exceptions are described below.
2.1.6.1 Trapping experiments using $[\text{Et}_4\text{N}][\text{SnCl}_3]$

Method A: All manipulations were performed anaerobically under ambient lighting conditions. To a solution of 0.0618 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.24 mmole) in 15 mL 3M HCl, at 40°C, was added 0.152 g $[\text{Et}_4\text{N}][\text{SnCl}_3]$ (0.43 mmole) with stirring. A yellow-orange precipitate formed immediately. The precipitate was filtered off, washed twice with 5 mL 3M HCl then Et$_2$O and dried in vacuo. The CH$_3$CN solution UV-VIS and I.R. spectra were similar to those of $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4] \cdot \text{H}_2\text{O}$, corrected for replacement of Me$_4$N$^+$ by Et$_4$N$^+$. The partial elemental analysis for C$_{24}$H$_{62}$Cl$_4$N$_3$ORhSn$_4$ was (% found (calc)) C 19.38 (19.43), H 4.18 (4.18) and N 2.85 (2.83). Yield was 0.067 g (42%).

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Solution UV-VIS data for $[\text{Et}_4\text{N}]<em>3<a href="%5Ctext%7BEt%7D_4%5Ctext%7BNCl%7D">\text{Rh(\text{SnCl}_3)_4(\text{SnCl}_4)}</a></em>{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>$\lambda_{\text{max}}$(nm) ($\varepsilon_{\text{approx}}$ (M$^{-1}$ cm$^{-1}$))</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>379 (81500)</td>
</tr>
<tr>
<td></td>
<td>277 (57800)</td>
</tr>
<tr>
<td>3M HCl</td>
<td>373 (a)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>382 (a)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$SO</td>
<td>386 (a)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$NC(0)CH$_3$</td>
<td>385 (a)</td>
</tr>
</tbody>
</table>

a. not estimated due to decomposition
Method B: All manipulations were performed anaerobically under ambient lighting conditions at 40°C. To a solution of 0.189 g RhCl$_3$·3H$_2$O (0.72 mmole) in 30 mL of 3M HCl was added dropwise a solution of 0.809 g [Et$_4$N][SnCl$_3$] (2.28 mmole) dissolved ~1.5 mL of 3M HCl. A yellow-orange precipitate formed as the tin solution was added. The precipitate was filtered off, washed twice with 3M HCl then Et$_2$O, and then dried in vacuo.
Further precipitation was observed in the filtrate and after standing overnight (~12 h) an orange precipitate was isolated in the same manner as the first. Yield of the first precipitate was 0.176 g and of the second 0.256 g.

Method C: The procedure as described in method B was modified by excluding light and lowering the temperature to ambient. The \([\text{Et}_4\text{N}]\text{[SnCl}_3\text{]}\) reagent was added either as a solid or in concentrated solution. The effect of the modification is discussed in sec. 3.3.4.

2.1.6.2 Reaction between \([\text{Rh}_2\text{Cl}_2(\text{COT})_4]\) and \([\text{Et}_4\text{N}]\text{[SnCl}_3\text{]}\)

All manipulations were performed anaerobically.

Method A: To a solution of 0.10 g \([\text{Rh}_2\text{Cl}_2(\text{COT})_4]\) (0.14 mmole) in 5 mL \(\text{CH}_2\text{Cl}_2\) was added, in the dark with stirring, a solution of 0.248 g \([\text{Et}_4\text{N}]\text{[SnCl}_3\text{]}\) (0.56 mmole) in 10 mL acetone at room temperature. The resultant purple-black precipitate was filtered off, washed with \(\text{CH}_2\text{Cl}_2\) until the washings were colourless and dried in vacuo. The purple solid had a brittle glass-like texture and gave purple \(\text{CH}_3\text{CN}\) solutions that faded to pale yellow-brown with time. The solids also changed colour with time, under anaerobic or aerobic conditions, to orange-brown.

Method B: A solution of 0.10 g \([\text{Rh}_2\text{Cl}_2(\text{COT})_4]\) (0.14 mmole) in 10 mL \(\text{CH}_2\text{Cl}_2\) was cooled to \(-23^\circ \text{C}\) by a dry-ice/CCl\(_4\) bath. A solution of 0.198 g \([\text{Et}_4\text{N}]\text{[SnCl}_3\text{]}\) (0.56 mmole) was added slowly from a dropping-funnel. The addition took \(~40\) min. Initially, an olive coloured suspension formed which became dark purple after \(~15\) min of addition. The final purple suspension was
allowed to settle and the yellow supernatant solution siphoned off. The slurry was washed with fresh cold CH₂Cl₂ which was also siphoned off. The solids that were on the sides of the glassware, not in contact with solvent, were olive or greenish-yellow-brown in colour while the 'wet' solids were purple. A sample of the purple material was quickly transferred into CH₃CN, giving a purple solution that quickly faded to pale yellow-brown. The flask containing the product was transferred to a vacuum line. As the sample warmed to room temperature the purple colour faded to brown-purple (colour faded radially inward). The purple colour could be restored by cooling the flask briefly with liquid nitrogen.

The dry solids were very air sensitive, discolouring immediately upon exposure to the atmosphere and becoming orange within a few hours. The orange material was not thermochromic.

2.2 Techniques.

2.2.1 Infrared Spectroscopy

Infrared spectra were recorded over the range 4000 - 250 cm⁻¹ on a Perkin Elmer model 457 or 598 grating spectrophotometer. Solid samples were run as Nujol mulls between CsI plates held in a clamp type cell holder (WILKS 531Q). Mulling and cell assembly were done under a nitrogen atmosphere, in a glove bag. Solution samples were run in 0.1 cm pathlength cavity cells with CaF₂ windows. The cells were purged with argon or carbon monoxide (in a fumehood) where appropriate. Calibration of spectra was
against a polystyrene film reference.

2.2.2 Electronic Spectroscopy

Spectra were recorded over the range 700 - 200 nm on either a Cary Model 17 or a Perkin Elmer Model 552A spectrophotometer fitted with thermostatted cell holders.

Conventional cells were used under aerobic conditions while for anaerobic experiments special spectral cells of the type illustrated in figure 2.10 were used. Light-sensitive solutions were also handled in this type of cell but all exposed surfaces (except ground glass and quartz cell) were wrapped with black electrical tape. A slip-off cover, made of tape, was used to cover the quartz cell and was removed at the spectrophotometer under a black cloth draped over the cell compartment.

In a typical anaerobic experiment, a weighed amount of solid complex was placed in the quartz cell. Solvent was pipetted into the side arm flask and then degassed by three freeze-pump-thaw cycles. The solvent and solid were then mixed until a homogeneous solution was achieved. For experiments where the resultant solution was light-sensitive, the freeze-pump-thaw degassing cycles were done before completely wrapping the sidearm flask with tape to avoid shattering the plastic tape at low temperature.

Solid-state spectra were run by soaking a small piece of filter paper in a Nujol mull of the complex to be examined. The paper was mounted on the face of a conventional cell. To partially compensate for light scattering a Nujol blank was used as reference. Alternatively, a solution was evaporated (in vacuo) and the spectrum of the coating on the cell walls taken.
Figure 2.10 Anaerobic spectral cell.
2.2.3 NMR spectroscopy

$^1$H NMR spectra were run on a Bruker WP-80, Bruker WP-400 or Varian XL-100 spectrometers in the Fourier Transform Mode using tetramethylsilane (TMS) as standard.

$^{119}$Sn FTNMR spectra were recorded at 29.88 MHz using a Bruker WP-80 spectrometer equipped with a 10 mm variable temperature probe. Some spectra were recorded, courtesy of Dr. C. Lassigne, at 37.336 MHz on a modified XL-100 spectrometer located at Simon Fraser University. This machine used a home built 22 mm probe. All spectra were run at ambient temperature (≈27°C). Tetramethylstannane (TMT) was used as an external standard, with upfield shifts being taken as negative. Typically, a sweep width of 10 KHz to 20 KHz was employed. Depending on the concentration and time available 6K to 300K scans would be accumulated. To quantitatively observe tin(IV) species a delay between pulses of 4-5 sec was employed; for some tin(II) species, up to 2 sec delay was needed although usually no delay was employed. A persistent problem, when using the Bruker machine, was a severely rolling baseline caused by signal breakthrough at sweep-widths of more than a few thousand Hz. Reducing the sweep-width reduced the effect, but increased the time needed to scan a reasonable range of chemical shifts (typically +100-1000 ppm) which additionally led to complications with folded-in signals. A sometimes necessary but unsatisfactory 'fix' was to drop the first four data points from the F.I.D. However, this led to difficulties in phasing the spectrum after Fourier transformation of the F.I.D. Spectrum simulation was performed using UBC PANIC and UBC ADD programs, as modified by Dr. O. Chan (see also Appendices B and C).
2.2.4 Mössbauer Spectroscopy

Tin Mössbauer measurements and calculations were performed by L. Sallos and Dr. J. Sams of this department. The measurements were made at liquid-nitrogen temperatures on solid samples which had been sealed in polyethylene containers under an atmosphere of nitrogen in a glove-bag. Isomer shifts are quoted relative to BaSnO₃.

2.2.5 Conductivity measurements

Conductivity measurements of nitromethane solutions were done at room temperature under an argon atmosphere using a Thomas Serfass conductivity bridge and cell.

2.2.6 Gas Chromatography

A Carle Model 311 analytical gas chromatograph with thermistor detectors was used to analyse gas mixtures. A 12 foot long 1/8" diameter stainless steel column packed with Porapak Type Q (Waters Associates, Inc.) was used. Typical machine parameters used for a 0.5 mL sample were: 15 - 20 psi He carrier gas and a column temperature of 30°C with no inlet heating. The order of retention times for selected gases and vapours was found to be:

\[ H_2O >> C_2H_4 >> CO_2 > CH_4 > CO, N_2, Ar, O_2 > H_2 \]

for example, the retention time for \( H_2 \) was typically 3.2 min (30°C, 20 psi He) and 15.5 min for \( CO_2 \) (30°C, 20 psi He). The detector sensitivity towards \( H_2 \) was much lower than for the other gases, being 0.045 times that
of CO$_2$. The sensitivity towards other gases and vapours was not quantitatively determined but was comparable to CO$_2$. Methane was used as an internal standard.

Typically a 0.5 mL sample was withdrawn from the gas phase over the reaction, through a septum, using a Precision Sampling Corp. Pressure-Lok gas syringe. The syringe needle was purged with 0.05 mL of the sample just before injection onto the column.

2.2.7 Mass spectrometry

Analysis of gas samples by mass spectrometry was performed by J. Nip and Dr. G. Eigendorf of this department using a Varian Mat CH4-B instrument fitted with a gas sample inlet. It was noted that because of the large internal volume of the machine, this method was less sensitive than the gas chromatograph for low concentrations, especially for the detection of H$_2$.

2.2.8 Gas Uptake measurements

A constant pressure gas-uptake apparatus was used in kinetic and stoichiometric studies. The procedure and apparatus are extensively described elsewhere.

For experiments where light-sensitive compounds were used, the reaction flask was wrapped in black electrical tape except for areas that would be immersed in the thermostat oil (which removes the tape!). These areas were carefully wrapped in foil instead.

Sample preparation was similar to that in reference 28. Typically,
3-5 mL of 0.01M Rh(III) stock solution (see below) was pipetted into an uptake flask (fig. 2.11) containing an appropriate amount of maleic or fumaric acid. The flask atmosphere was purged with argon and a small glass bucket containing a weighed amount of SnCl$_2\cdot$2H$_2$O was carefully mounted in the flask on a rotatable hook. After attaching the flask to a vacuum line, the solution was degassed by 3 freeze-pump-thaw cycles. After warming the flask to room temperature the bucket of SnCl$_2\cdot$2H$_2$O was dropped into the solution by rotating the hook. The solution was thoroughly mixed and H$_2$ (at 90 mmHg pressure) introduced without agitation of the solution. The flask was then transferred to the thermostated bath of the uptake apparatus and connected to the uptake apparatus. The sample was thermally equilibrated for about 15 min without agitation (to minimize H$_2$ diffusion into the solution at this point). The H$_2$ pressure was then raised to 450 mmHg and agitation started. The uptake of H$_2$ by the catalyst solution was monitored manometrically as described elsewhere$^94$.

The concentration of H$_2$ in 3M HCl at 80°C and 450 mmHg partial pressure is $3.60 \times 10^{-4}$ M$^{28}$. No correction for differences in solubility between H$_2$ and D$_2$ was made. In H$_2$O the latter can be as much as 1.07 times more soluble than H$_2$.$^97$

After completion of an uptake the organic products were extracted from aqueous solution with ether (5 x ~5 mL portions). The extracts were dried over anhydrous MgSO$_4$ before solvent removal on a roto-vac and drying in vacuo. The efficiencies of extraction for the various dicarboxylic acids used were similar except for malic acid which was 1/5$^{th}$ of the others.
The precatalytic Rh(III) species in 3M HCl solution, in the absence of SnCl₂·2H₂O, was principally RhCl₅(H₂O)²⁻, with minor amounts of [RhCl₄(H₂O)₂]⁻ and RhCl₆³⁻. At 60°C the relative ratios of the tetrachloro-, pentachloro- and hexachloro-species at equilibrium have been estimated to be 5:84:12. In the present investigation the stock Rh(III) in 3M HCl or 3M DCl/D₂O stock solution was heated at 80°C for a week before use. The visible spectral data are summarized in table 2.2 along with comparative literature data. Addition of maleic or fumaric acid to the stock solution did not cause any change in the spectra, thus ruling out formation of Rh-olefin complexes. The effect of adding stannous chloride is discussed in chapter III.

Figure 2.11 Uptake flask (25 mL)
Table 2.2  Solution Vis data for the Rh(III) stock solution

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\lambda_{1\text{max}}$(nm)</th>
<th>$\lambda_{2\text{max}}$(nm)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>stock Rh(III) sol'n</td>
<td>400 (113)</td>
<td>506 (106)</td>
<td>this work</td>
</tr>
<tr>
<td>ditto</td>
<td>404 (67)</td>
<td>511 (74)</td>
<td>28</td>
</tr>
<tr>
<td>$\text{RhCl}_4(H_2O)_2^-$</td>
<td>385 (54)</td>
<td>488 (72)</td>
<td>95</td>
</tr>
<tr>
<td>(cis)</td>
<td>381 (102)</td>
<td>&quot; (68)</td>
<td>96</td>
</tr>
<tr>
<td>(trans)</td>
<td>&quot; (&quot;&quot;)</td>
<td>&quot; (&quot;&quot;)</td>
<td>96</td>
</tr>
<tr>
<td>$\text{RhCl}_5(H_2O)_2^{2-}$</td>
<td>402 (73)</td>
<td>507 (73)</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>404 (104)</td>
<td>507 (105)</td>
<td>96</td>
</tr>
<tr>
<td>$\text{RhCl}_6^{3-}$</td>
<td>411 (94)</td>
<td>518 (112)</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>413 (82)</td>
<td>517 (111)</td>
<td>96</td>
</tr>
</tbody>
</table>

2.2.9 Determination of Fe$^{3+}$ reduction equivalents

About 100 mg of the complex to be analysed was oxidized with a large (10-fold) excess of Fe(NH$_4$)$_2$(SO$_4$)$_2$·12H$_2$O in 3MHC1-1MH$_2$SO$_4$ solution at 90°C for 5½ h under an argon atmosphere. The amount of Fe$^{2+}$ formed was determined by potentiometric titration with a 0.1M cerium ammonium sulfate solution. A Fisher Accumet pH Meter Model 140 with a combination glass/platinum electrode was used.

2.2.10 Elemental analysis

Elemental analyses for C, H, N and Cl were performed by Mr. P. Borda of this department. Analysis for rhodium was done colorimetrically by
reaction with excess stannous chloride in aqueous HCl\textsuperscript{99}, which was also used as a qualitative test for rhodium. A cacotheline solution \textsuperscript{100}, which is a reversible redox indicator for most tin(II) reactions, was used as a qualitative test for free tin(II) chloride in solution. On reaction with tin(II) a colour change from yellow to violet was observed.

2.3 Computational Techniques

In several instances analysis was facilitated by use of the computing facilities of the UBC Computer Center.

Some UV-VIS spectra acquired on the Cary 17 spectrophotometer were digitized using the Talos CYBERGRAPH digitizing table under control of the program *DIGIT described in the UBC DIGITIZER manual. The digital data were then used to analyse the spectra of mixtures by simple curve subtraction (see experiments described in Chapters 3 and 4). Interpolation routines described in UBC TSPLINE were used in simple FORTRAN IV programs to generate the curves to be subtracted. The results were displayed on a Tektronix 4010 series Storage Scope and/or plotted on a Houston Complot plotter using plotting routines described in UBC PLOT. Additionally, figures 1 and 2 from reference 91 were digitized and replotted to correct the scale for direct comparison to spectra obtained on the Perkin Elmer 598 and Cary 17 spectrophotometers. No interpolation was performed in these cases.

For analysis of some kinetic data a program was written in FORTRAN IV (see Appendix A for listing and description of use). The program facilitates first-order analysis and manipulation of data obtained in absorbance units.
Three kinds of first-order analysis were included: \( \ln(A-A_\infty) \) vs. \( t \), Guggenhiem's method \(101\) and the Kezdy-Swinbourne method \(101, 102\). The latter was also used to calculate by extrapolation a value of \( A_\infty \) that could then be used in a \( \ln(A-A_\infty) \) vs. \( t \) calculation. An estimate of the overall order could be also obtained using an approximate differential method \(101\). Curve fitting was by the least-squares method; the 'goodness of fit' measure was Pearson's Moment. To check the fit a table of residuals \( (A_{\text{OBS}} - A_{\text{CALC}}) \) could be printed. The sizes and signs of the residuals would then be examined for systematic skewing or obviously incorrectly entered data points. The program has a limited capability to handle data not in absorbance units, in which case data scaling may be required.
CHAPTER III

RESULTS (PART I)

THE SYNTHESIS OF VARIOUS TIN CONTAINING RHODIUM COMPLEXES

3.1 Introduction.

The initial goal of this project was to prepare salts of the rhodium(I) dimer \([\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^4-\). Treatment of 3M HCl or ethanolic solutions of rhodium trichloride trihydrate with a 2\(\frac{1}{2}\) fold excess of \(\text{SnCl}_2\cdot2\text{H}_2\text{O}\) at room temperature was reported to yield the salt upon addition of a less than 2-fold excess of \(\text{M}^+\text{Cl}^-\) (\(\text{M}^+ = \text{Me}_4\text{N}^+, \text{Ph}_3\text{PH}^+\)). The orange product was said to be stable in air and recrystallizable from a 10:1 ethanol-3M HCl mixture, in 85% yield. Jobs' Method experiments showed that the complex was fully formed at a Sn(II)/Rh(III) ratio of 3. Consonant with this, the overall reaction was formulated as:

\[
2\text{RhCl}_3 + 6\text{SnCl}_3^- \rightarrow \left[\begin{array}{c}
\text{Cl}_3\text{Sn} \\
\text{Cl}
\end{array}\right] \begin{array}{c}
\text{Rh} \\
\text{Rh}
\end{array} \left[\begin{array}{c}
\text{Cl}_3\text{Sn} \\
\text{Cl}
\end{array}\right] \text{SnCl}_3^- + 2\text{SnCl}_5^- \quad (3-1)
\]

A far-IR study on this dimer and the bromo-analogue resulted in spectral assignments consistent with the proposed structure (Table 3-1). Several Mössbauer studies have also included the chloro-dimer in their scope. However, more recent workers dispute the isolation of this complex (see below).

Using higher Sn(II)/Rh(III) ratios rhodium(I) monomers with Sn:Rh stoichiometries of 4 and 5 have been obtained from 3M HCl solution using similar
Table 3.1  Far-IR absorption frequencies ($\text{cm}^{-1}$) reported for $[\text{R}_4\text{N}]_4[\text{Rh}_2\text{X}_2(\text{SnCl}_3)_4]$ (ref. 105)*

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>$\nu(\text{SnX}_3)^{**}$</th>
<th>$\nu(\text{Rh-}\mu\text{-X})$</th>
<th>$\nu(\text{Rh-Sn})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Cl</td>
<td>363.0</td>
<td>288.2</td>
<td>209.8</td>
</tr>
<tr>
<td>Et</td>
<td>Cl</td>
<td>360.8</td>
<td>288.4</td>
<td>208.6</td>
</tr>
<tr>
<td>Et</td>
<td>Br</td>
<td>271.1</td>
<td>197.5</td>
<td>217.1</td>
</tr>
</tbody>
</table>

* Nujol mull
** Broad, asymmetric and not always resolved

procedures. When Sn(II)/Rh(III) was equal to five, $[\text{Me}_4\text{N}]_4[\text{Rh(\text{SnCl}_3)_5}]$ was isolated. With a large excess of SnCl$_2$·2H$_2$O(Sn(II)/Rh(III)=200) the impure salt, $[\text{Me}_3(\text{PhCH}_2)\text{N}]_3[\text{Rh(\text{SnCl}_3)_4}]$·2[$\text{Me}_3(\text{PhCH}_2)\text{N}]\text{SnCl}_3$·SnCl$_2$ was obtained. The latter species is of interest since the UV-VIS spectrum of the initial solution is the same as that reported for the solution species in the spectrophotometric determination of rhodium using stannous chloride. A rhodium(I) species with five tin ligands was identified, in situ, by $^{119}\text{SnFTNMR}$, as being the principle rhodium-tin complex in 3MHC1 solution where the Sn(II)/Rh(III) ratio was between 5 and 7. From similar solutions, $^{91}\text{Rh(\text{SnCl}_3)_4(\text{SnCl}_4)_5}^-$ was isolated in high yield by precipitation with the highly charged cations $\text{M(NH}_3)_6^{3+}(\text{M}=$Ir, Rh) or $\text{Rh(en)}_3^{3+}$. The violet or brown-
red crystalline products were found to contain also one molecule of free SnCl$_6^{4-}$ per rhodium(I) complex. A crystal determination$^{111}$ of the Rh(NH$_3$)$_6^{3+}$ salt revealed the geometry of the rhodium(I) complex as tbp at rhodium and distorted tbp at the unique tin(II), with the equatorial planes perpendicular (figure 3-1). The complex is approximately spherical. The chlorine atoms are arranged as a symmetrically distorted, 16 vertex, tetracapped truncated tetrahedron. This arrangement is comparable to the carbonyl arrangement in Os$_5$(CO)$_{12}^{112}$, and probably represents the most favourable way of packing the chlorides in space constrained by the bonding requirements of the tbp RhSn$_5$ unit. Use of tetraalkyl-ammonium, -phosphonium or -arsonium chlorides as precipitant resulted in the nearly quantitative isolation$^9$ of a diamagnetic complex with the empirical formula (R$_4$E)$_3$[RhSn$_5$Cl$_{15}$] (E=N,P,As). The infrared spectrum of this complex contains bands at 1940 cm$^{-1}$ and 600 cm$^{-1}$

![Figure 3.1](image-url) The molecular structure of [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{5-}$ (after ref. 111).
(sometimes split), which were shown to be neither due to a hydrido- or N₂-containing complex. The complex was unstable at room temperature in the solid state. The Fe³⁺ reduction equivalent of the complex decreased over a few weeks, from 11.2 to 8.70 equivalents with no change in the ratio of Rh:Sn:Cl. Concurrently, the bands at 1940 cm⁻¹ and 600 cm⁻¹ disappeared.

Regarding salts of [Rh₂Cl₂(SnCl₃)₄]⁴⁻, the same author⁹¹ found that for Sn(II)/Rh(III) ratios of 3 or less, under aerobic conditions, in 3MHC1 solution only rhodium(III) species were obtained. The series of tetraalkyl-ammonium salts of [RhCl₆-n(SnCl₃)n]⁻³ (4>n>1) was synthesized and characterized by full elemental analysis, IR, UV-VIS, magnetic susceptibility and Fe³⁺ reduction equivalent weights. By monitoring the progress of reactions where Sn(II)/Rh(III) equals 3, for varying time periods and at selected temperatures from -13°C to +100°C, it was determined that [RhCl₂(SnCl₃)₄]⁻³ was the precursor to [RhCl₃(SnCl₃)₃]⁻³, the thermodynamically more stable complex. An analogous conclusion was reached by other workers⁹⁰ who independently prepared, under anaerobic conditions, the series where 5≥n≥3 for both the bromo- and chloro-analogues. Salts of [RhCl(SnCl₃)₅]⁻³ were always precipitatable from freshly prepared 3MHC1 solutions where the Sn(II)/Rh(III) ratio was between 2 and 4. Complexes where n<4 were believed to form by a slow coproportionation with unreacted rhodium(III) halides. This phenomenon had been previously proposed in a brief report⁹⁷, as being general for Rh(III), Ru(II), Os(II) and Pt(IV) reactions with stannous halides and Sn(acac)₂ in aqueous acid.

A ¹¹⁹Sn FT NMR study of species formed in situ, under aerobic conditions, in 3MHC1 solution confirmed the existence of predominantly rhodium(III)
tin-containing complexes for Sn(II)/Rh(III) ratios of 4 or less (figure 3-2). As mentioned above, only at higher ratios was a rhodium(I) species with five tin ligands predominant.

From the beginning of our experimental work, the rhodium(I) dimer proved elusive (probably non-existent). Our results are consistent with the findings of other workers\textsuperscript{90,91,110} (reviewed above), whose data first came to our attention in late 1980. Somewhat serendipitously, the range of experiments undertaken in the present work overlaps with both the aerobic

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_2.png}
\caption{Distribution of rhodium complexes in 3M HCl solution as a function of mole ratio of total coordinated tin to total rhodium. a: [RhCl\textsubscript{5}(SnCl\textsubscript{3})\textsuperscript{3-}, b: [RhCl\textsubscript{4}(SnCl\textsubscript{3})\textsubscript{2}\textsuperscript{3-}, c: [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}\textsuperscript{3-}, d: uncharacterized Rh(III) species, e: [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}\textsuperscript{2-}, f: [RhCl(SnCl\textsubscript{3})\textsubscript{5}\textsuperscript{3-} and g: [Rh(SnCl\textsubscript{3})\textsubscript{5}\textsuperscript{3-}. (after ref. 110).}
\end{figure}
and anaerobic work described in the literature. In addition to product variation with the Sn(II) to Rh(III) ratio and temperature, we find effects due to the size of the cation, use of aerobic vs. anaerobic conditions, and light. These are discussed in the following sections. The complexes isolated in this study, with one exception, have been previously described in the literature. The nature of this new complex is considered in the next section.

3.2 The nature of [Rh(SnCl\(_3\))\(_4\)(SnCl\(_4\))]\(^{3-}\)

Formally, this complex can be regarded as a rhodium(I) adduct of SnCl\(_4\). The structural assignment is tentative, being based in part upon spectral data and in part upon mechanistic grounds. It is a kinetic product probably arising from trapping of a rhodium(I) intermediate by tin(IV) chloride, both being formed in situ from the reduction of a rhodium(III) chloro species by SnCl\(_3\)\(^-\) (see following sections). It has the same constitution as the known \(^{90}\) rhodium(III) complex [RhCl(SnCl\(_3\))\(_5\)]\(^{3-}\). Although elemental analysis, conductance and Fe\(^{3+}\) reduction equivalents (sec. 2.1.5.3) are consistent of course with the Rh(III) complex formulation, the \(^{119}\)Sn Mössbauer, IR and UV-VIS spectral data are not.

Mössbauer data from this work and reference \(^{90}\) are summarized in Table 3.2. Although the data sets are discordant, the difference between the I.S. of the [RhCl(SnCl\(_3\))\(_5\)]\(^{3-}\) and [Rh(SnCl\(_3\))\(_4\)(SnCl\(_4\))]\(^{3-}\) salts is apparent when taken relative to that of [R\(_4\)N]\(_3\)[RhCl\(_2\)(SnCl\(_3\))\(_4\)]. The far-IR spectrum of [Me\(_3\)N]\(_3\)[RhCl(SnCl\(_3\))\(_5\)] contains \(^{90}\) a broad strong \(\nu(\text{SnCl})\) band at 330 cm\(^{-1}\) and a weak \(\nu(\text{RhCl})\) band at 275 cm\(^{-1}\). This latter band is missing from the
Table 3.2 Mössbauer data for various rhodium-tin chloride complexes

<table>
<thead>
<tr>
<th></th>
<th>I.S</th>
<th>Q.S.</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₄N]₃[RhCl₂(SnCl₃)₄]·H₂O</td>
<td>1.68(±.06)</td>
<td>1.80(±.03)</td>
<td>this work</td>
</tr>
<tr>
<td>[Me₄N]₃[RhCl₂(SnCl₃)₄]</td>
<td>1.85(±.05)</td>
<td>1.83(±.05)</td>
<td>90</td>
</tr>
<tr>
<td>[Et₄N]₃[Rh(SnCl₃)₄(SnCl₄)]·(Et₄NCl)₀.₅</td>
<td>1.79(±.04)</td>
<td>1.84(±.01)</td>
<td>this work</td>
</tr>
<tr>
<td>[Me₄N]₃[RhCl(SnCl₃)₅]</td>
<td>1.83(±.05)</td>
<td>1.83(±.05)</td>
<td>90</td>
</tr>
</tbody>
</table>

spectra of the unrecrystallized and recrystallized samples of the Et₄N⁺ salt of [Rh(SnCl₃)₄(SnCl₄)]³⁻ (figure 2.7), which is consistent with the absence of a chloride ligand trans to SnCl₃⁻ in this complex. The changes due to recrystallization are problematic and will be briefly addressed below.

The CH₃CN solution UV-VIS spectrum (fig. 2.8) is distinctive and quite unlike that for [RhCl₃(SnCl₃)]³⁻ and [RhCl₂(SnCl₃)₄]³⁻ in CH₃CN solution (figures 2.3 and 2.5) or in 3M HCl (figure 3.3). The band at ~380 nm is also seen in fresh DMSO, 3M HCl or (CH₃)₂CO solutions, although the complex is unstable in these solvents (see also Chapter IV). We believe the distinctive spectrum arises from the d⁸-d¹⁰ metal-metal interaction implicit in the complex's formulation as [Rh(SnCl₃)₄(SnCl₄)]³⁻ which is rhodium(I) with four SnCl₃⁻ ligands and one SnCl₄⁻ ligand. Qualitatively, the spectrum resembles that of a rhodium(I) complex such as [Rh(CNC₂H₅)₄]ClO₄¹¹³ (in CH₃CN solution: λmax nm (ε, M⁻¹cm⁻¹): 435(260), 380(8400), 333(3450, sh), 308(24350), 282 (2100, sh)¹¹³. The band at 380 nm for our complex obeyed Beers Law over
the concentration range $2.5 \times 10^{-4}$ M to $3.0 \times 10^{-5}$ M in CH$_3$CN (in the dark).

Upon recrystallization changes were observed in the far-IR spectrum, as noted above. Additionally, the elemental analysis for C, H and N changed (see section 2.1.5.3). The elemental formula changed from C$_8$H$_{20}$N (ie. Et$_4$N$^+$) to C$_7$H$_{19}$N which suggests partial replacement of Et$_4$NCl by CH$_3$CN. There was no change in the solution spectra upon recrystallization (within experimental uncertainties). It is probable that the changes seen by far-IR are associa-

![Figure 3.3](image)

*Figure 3.3* 3MHC1 solution UV-VIS spectra of [Me$_4$N]$_3$ [RhCl$_2$(SnCl$_3$)$_4$] (---) (10°C, [SnCl$_2$·2H$_2$O] = 0.2M) and [Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_4$] (10°C) (----) (ref. 91 (fig. 2-(1) and 2-(2A) respectively); see note (fig. 2.1).
ted with the replacement of lattice \( \text{Et}_4\text{NCl} \) by \( \text{CH}_3\text{CN} \). Almost all the reported far-IR spectra of Group VIII metal chloride - tin chloride complexes exhibit a weak band in the 345-365 cm\(^{-1}\) region (see tables 3.1 and 3.3). Only in the case of the reported \([\text{R}_4\text{N}]_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]\) complexes was the origin of this weak band directly considered\(^{105}\), the conclusion being that it was not a \( \nu(\text{SnCl}) \) or \( \nu(\text{Rh-\mu-Cl}) \) band.

3.3 Effect of variation of some parameters on the synthetic methods used in 3M HCl.

3.3.1 Precipitant size.

Only impure products were obtained when \( \text{Me}_4\text{NCl} \) was substituted by \( \text{Et}_4\text{NCl} \) as precipitant in the procedures for synthesising \([\text{R}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]\) (sec. 2.1.5.1) and \([\text{R}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\cdot\text{H}_2\text{O}\) (sec. 2.1.5.2). These literature methods are reported to give pure products for \( \text{Me}_4\text{N}^+ \), \( \text{Et}_3\text{NH}^+ \), and \( \text{Et}_4\text{N}^+ \) in the former case and for \( \text{Me}_4\text{N}^+ \) in the latter one.

Using \( \text{Et}_4\text{NCl} \) in the procedure described for \([\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]\) resulted in a solid that showed (in comparison to the \( \text{Me}_4\text{N}^+ \) species) small differences in the solution (figure 3.4) and solid state (figure 3.5) spectra. These differences are too small to indicate what the coprecipitated species might be, but the elemental analysis for C, H, N (Table 3.4) is lower than expected. This would indicate the presence of a species with a higher tin to rhodium stoichiometry (eg. \([\text{Et}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\)). Differences in the isolated products from the \([\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\) procedure when using \( \text{Me}_4\text{NCl} \) or \( \text{Et}_4\text{NCl} \) are very noticeable. In particular, the \( \text{CH}_3\text{CN} \) solution
<table>
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<th>$\nu$(M-Cl)</th>
<th>ref.</th>
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<tr>
<td>$[\text{RuCl}(\text{SnCl}_3)_5][\text{Me}_4\text{N}]_4$</td>
<td>354</td>
<td>327</td>
<td>312</td>
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<tr>
<td>$[\text{OsCl}(\text{SnCl}_3)_5][\text{Me}_4\text{N}]_4$</td>
<td>340</td>
<td>325(sh)</td>
<td>314</td>
</tr>
<tr>
<td>$[\text{RhCl}_5(\text{SnCl}_3)][\text{Me}_4\text{N}]_3$</td>
<td>367</td>
<td>327</td>
<td>310</td>
</tr>
<tr>
<td>$[\text{RhCl}_4(\text{SnCl}_3)_2]\text{Cs}_3$</td>
<td>364(w)</td>
<td>344(s)</td>
<td>323(s)</td>
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<tr>
<td>cis-$[\text{RhCl}_4(\text{SnCl}_3)_2][\text{Me}_4\text{N}]_3$</td>
<td>348(w)</td>
<td>332(s)</td>
<td>310(s)</td>
</tr>
<tr>
<td>trans-$[\text{RhCl}_4(\text{SnCl}_3)_2][\text{Me}_4\text{N}]_3$</td>
<td>348(w)</td>
<td>332(s)</td>
<td>310(s)</td>
</tr>
<tr>
<td>$[\text{RhCl}_3(\text{SnCl}_3)_3][\text{Me}_4\text{N}]_3$</td>
<td>358(w)</td>
<td>337(s)</td>
<td>322(s)</td>
</tr>
<tr>
<td>$[\text{RhCl}_3(\text{SnCl}_3)_3][\text{Me}_4\text{N}]_3$</td>
<td>358(w)</td>
<td>335(s)</td>
<td>318(bs)</td>
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<td>$[\text{RhCl}_2(\text{SnCl}_3)_4][\text{Me}_4\text{N}]_3$</td>
<td>360(sh)</td>
<td>326(s)</td>
<td>287(sh)</td>
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<tr>
<td>$[\text{RhCl}(\text{SnCl}_3)_5][\text{Me}_4\text{N}]_3$</td>
<td>345(sh)</td>
<td>325(s)</td>
<td>310(sh)</td>
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<td>$[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4][\text{Me}_4\text{N}]_4$</td>
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<tr>
<td>$[\text{IrCl}_3(\text{SnCl}_3)_3][\text{Et}_4\text{N}]_3$</td>
<td>368</td>
<td>332</td>
<td>312</td>
</tr>
<tr>
<td>$[\text{IrCl}_3(\text{SnCl}_3)_3][\text{Me}_4\text{N}]_3$</td>
<td>330</td>
<td></td>
<td></td>
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<tr>
<td>Complex</td>
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<td>ref.</td>
<td></td>
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<tr>
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<tr>
<td>$[\text{IrCl}(\text{SnCl}_3)_5][\text{Et}_4\text{N}]_3$</td>
<td>330 316 304 272</td>
<td>196 g</td>
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<td>$[\text{Pd}(\text{SnCl}_3)_5][\text{Et}_4\text{N}]_3$</td>
<td>328 308 300</td>
<td>198 g</td>
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<td>$[\text{PdCl}_2(\text{SnCl}_3)_2][\text{Et}_4\text{N}]_2$</td>
<td>328 300</td>
<td>192 g</td>
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<td>$[\text{Pt}(\text{SnCl}_3)_5][\text{Et}_4\text{N}]_3$</td>
<td>338 316</td>
<td>209 h</td>
<td></td>
</tr>
<tr>
<td>$[\text{PtCl}_2(\text{SnCl}_3)_2][\text{Et}_4\text{N}]_2$</td>
<td>337 337</td>
<td>e f</td>
<td></td>
</tr>
<tr>
<td>cis-$[\text{PtCl}_2(\text{SnCl}_3)_2][\text{Et}_4\text{N}]_2$</td>
<td>356 339 317 290 278</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>352 337 306 280</td>
<td>f</td>
<td></td>
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<tr>
<td>$[\text{Ph}_4\text{As}]_2$</td>
<td>337(s) 320(bs) 289(s)</td>
<td>202 h</td>
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<tr>
<td>trans-$[\text{PtCl}_2(\text{SnCl}_3)_2][\text{Et}_4\text{N}]_2$</td>
<td>336 314 294 275</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ph}_4\text{As}]_2$</td>
<td>340(s) 335(w) 325(s)</td>
<td>209 h</td>
<td></td>
</tr>
</tbody>
</table>

- a ref. 114: KBr and Polyethylene pellets
- b ref. 92: Nujol mull
- c ref. 91: Nujol mull
- d ref. 90: Polyethylene discs
- e ref. 115: Nujol mull
- f ref. 106b: not stated
- g ref. 80: Polyethylene and KBr pellets
- h ref. 116: Nujol mull on polystyrene
- i ref. 105: Nujol mull
Figure 3.4 Initial CH$_3$CN solution UV-VIS spectra of (a) [Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$] (---), $[$ ]$_0$ = 0.550 g/L (4.97 x 10$^{-4}$M) and (b) that obtained using Et$_4$N$^+$ (-----), $[$ ]$_0$ = 0.672 gm/L. (pathlength = 0.1 cm; dotted line = baseline).

The spectrum of the tetraethyl derivative (figure 3.6a) looks like the sum of those of [RhCl$_2$(SnCl$_3$)$_4$] and [Rh(SnCl$_3$)$_4$(SnCl$_4$)$_3$]. Proceeding on this assumption, the spectrum of the latter was subtracted (section 2.3) from that of the mixture in order to estimate the stoichiometry. The difference spectrum (figure 3.6b) reveals that other species are present also
Figure 3.5  Far-IR spectra (Nujol, CsI plates) of (a) $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]$ (---) and (b) of the product obtained using $\text{Et}_4\text{N}^+$ (-----).
Table 3.4  Partial elemental analyses for products obtained from 
[RhCl₃(SnCl₃)₃]⁻ synthesis using Et₄NCl·H₂O precipitant

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>W</th>
<th>%cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected:</td>
<td>[Et₄N]₃[RhCl₃(SnCl₃)₃]</td>
<td>22.60</td>
<td>4.71</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td>[Et₄N]₃[RhCl₂(SnCl₃)]</td>
<td>19.67</td>
<td>4.10</td>
<td>2.87</td>
</tr>
<tr>
<td>Found:</td>
<td>&quot;[Et₄N]₃[RhCl₃(SnCl₃)₃]&quot;</td>
<td>19.99</td>
<td>4.20</td>
<td>2.93</td>
</tr>
</tbody>
</table>

(viz. the band at ~370 nm). From the subtraction procedure the ratio of [RhCl₂(SnCl₃)₄]⁻ to [Rh(SnCl₃)₄(SnCl₄)]⁻ was estimated to be 1.2(±0.2).

The new species seen in the difference spectrum was not further characterized. The far-IR spectra (fig. 3.7) are also consistent with the presence of a mixture.

3.3.2 Anaerobic vs. aerobic conditions.

Performing all manipulations in an argon atmosphere had a noticeable effect on the products obtained when using the procedure for preparing [Me₄N]₃[RhCl₃(SnCl₃)₃]. In the far-IR spectrum (fig. 3.8) a broad band at 330 cm⁻¹ has replaced the three band structure seen in the pure Me₄N⁺ salt (fig. 2.1), although the shape of this band and the band at 275 cm⁻¹ indicate it is present. The solution spectrum (fig. 9) resembles that observed for [RhCl₂(SnCl₃)₄]⁻ (fig. 2.5). In fact, visual comparison of the resultant spectrum from the subtraction of that of [RhCl₃(SnCl₃)₃]⁻
indicates only ~ 40% of the latter species is present (fig. 3.10). Consistent with the coprecipitation of salts with higher Sn:Rh ratios was an observed decrease in % cation, by elemental analysis (Table 3.5), of 4.3% and 1.7%

Figure 3.6 Initial CH\textsubscript{3}CN solution UV-VIS spectra of (a) [Me\textsubscript{4}N\textsubscript{3}][RhCl\textsubscript{2}(Sn-Cl\textsubscript{3})\textsubscript{4}] (- - - - -), [\text{\textsubscript{}}]\textsubscript{0} = 0.665 gm/L (5.13 x 10\textsuperscript{-4} M) with (b) that of the product obtained using Et\textsubscript{4}N\textsuperscript{+} (-----) [\text{\textsubscript{}}]\textsubscript{0} = 0.658 gm/L and (c) the resultant spectrum after subtraction of that of [Rh(SnCl\textsubscript{3})\textsubscript{4}(SnCl\textsubscript{4})\textsubscript{3}\textsuperscript{-}(------). (pathlength = 0.1 cm; dotted line = baseline for (a) and (b).
Figure 3.7 Far-IR spectra (Nujol, CsI plates) of (a) $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]$ (---) and (b) of the product obtained using $\text{Et}_4\text{N}^+$ (--) compared with $[\text{Et}_4\text{N}]_3[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]\cdot(\text{Et}_4\text{NCl})_{0.5}$ spectrum (-----).
Figure 3.8  Far-IR spectra (Nujol, CsI plates) of (a) $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]$ (— — —) and the isolated products of the anaerobic synthesis using (b) $\text{Me}_4\text{N}^+$ (——) and (c) $\text{Et}_4\text{N}^+$ (— — —).
Figure 3.9 Initial CH$_3$CN solution UV-VIS spectrum of the product obtained using Et$_4$N$^+$ in the synthesis of [Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$] under anaerobic conditions, [$\text{C}$]$_0$ = 0.670 g/L (path length = 0.1 cm; dotted line = baseline).

for the tetraethyl- and tetramethyl-ammonium salts, respectively.

No analogous experiments were performed using the procedure used for synthesis of [Me$_4$N]$_3$[RhCl$_2$(SnCl$_3$)$_4$] (but see sec. 3.3.3).
3.3.3 Variation of Sn(II):Rh(III) ratio, and temperature.

The synthetic procedure for $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]$ was modified by using Et$_4$NCl in place of Me$_4$NCl, anaerobic conditions and increasing the Sn(II)/Rh(III) ratio to 5. Initially, it was expected that $[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$ would be the major product $^{90}$; however, a complex mixture was obtained instead.

![Figure 3.10 Comparison of (a) resultant spectrum after the subtraction of 0.38 x fig. 2.8 ($[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$) from fig. 3.9 (-----) with (b) $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]$ spectrum (fig. 2.5)(---).](image-url)
Table 3.5 Partial elemental analysis for $[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$ salts

<table>
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<tr>
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<th>H</th>
<th>N</th>
<th>%cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected: $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]_1$</td>
<td>13.02</td>
<td>3.28</td>
<td>3.80</td>
<td>20.10</td>
</tr>
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<td>$[\text{Et}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]_2$</td>
<td>22.60</td>
<td>4.71</td>
<td>3.30</td>
<td>30.61</td>
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<tr>
<td>Found: &quot;1&quot;</td>
<td>11.79</td>
<td>3.01</td>
<td>3.63</td>
<td>18.43</td>
</tr>
<tr>
<td>&quot;2&quot;</td>
<td>19.52</td>
<td>3.97</td>
<td>2.81</td>
<td>26.30</td>
</tr>
</tbody>
</table>

The elemental analysis for the cation (C,H,N) was ~25%. This is higher than the 23.59% cation expected for $[\text{Et}_4\text{N}]_3[\text{RhCl(SnCl}_3)_5]$ but 1.3% lower than the comparable experiment where Sn(II)/Rh(III) was 3 (table 3.5, sec.3.3.2). The solid state IR spectrum (fig. 3.11a) of the yellow product was similar to that of $[\text{Et}_4\text{N}]_3[\text{RhSn}_5\text{Cl}_{15}]$ (% cation = 24.09%) \(^91\). Also consistent with such a species was the observed disappearance of the bands at 1923 cm\(^{-1}\) and 600 cm\(^{-1}\) over a period of several months (fig. 3.11b), while the region below 400 cm\(^{-1}\) remained essentially unchanged. The lack of bands at 275 cm\(^{-1}\) or at 273 cm\(^{-1}\) and 254 cm\(^{-1}\) indicates the absence of $[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$ or $[\text{RhCl}_4(\text{SnCl}_3)_2]^{3-}$ as major products \(^91\). The 400-250 cm\(^{-1}\) region is similar to that of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ (fig. 3.12). The CH\(_3\)CN UV-VIS solution spectrum (fig. 3.13) is comparable to that of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ (viz. bands at 290 nm and 428 nm), however there clearly are features which differentiate the two. No solution spectra have been reported for either the $[\text{RhSn}_5\text{Cl}_{15}]^{3-}$ or $[\text{RhCl(SnCl}_3)_5]^{3-}$ species. Attempts to synthesize
Figure 3.11 IR spectra (Nujol, CsI plates) of (a) the product isolated, using $\text{Et}_4\text{N}^+$, of the synthesis for $[\text{Me}_4\text{N}]_3 [\text{RhCl}_3(\text{SnCl}_3)_3]$ under anaerobic conditions, using $\text{Sn(II)}/\text{Rh(III)} = 5$, and (b) the same product several months later.
Figure 3.12 Far-IR spectrum (Nujol, CsI plates) of (a) the isolated product of the synthesis for \([\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]\) under anaerobic conditions and using Sn(II)/Rh(III) = 5 (-----), compared to (b) \([\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\) spectrum (----).
Figure 3.13 Initial CH$_3$CN solution spectra of the products isolated using (a) the synthesis of [Me$_4$N]$_3$ [RhCl$_3$(SnCl$_3$)$_3$] with Et$_4$N$,^+$ anaerobic conditions and Sn(II)/Rh(III) = 5 (---) and (b) the product of the literature synthesis$^{90}$ of [Me$_4$N]$_3$ [RhCl(SnCl$_3$)$_5$] (-----).
[Me₄N]₃[RhCl(SnCl₃)₅] using the literature method failed to give a pure product. This method is similar to ours, the difference being that the Sn(II):Rh(III) ratio is 7.5 with only 30 minutes heating at ~90°C rather than 60 minutes. The Sn FT NMR spectrum of the yellow product obtained from this source (fig. 3.14) reveals this complex to be the major product (multiplet: δ = -113.7 ppm, J₁₀₃Rh=₁₁₉Sn = 556 Hz). Other products observed are [RhCl₂(SnCl₃)₄]⁻ (δ = -219.8 ppm (doublet), J₁₀₃Rh=₁₁₉Sn = 586 Hz) and [RhCl₃(SnCl₃)₃]⁻ (δ = 310.9 ppm (doublet) J = 722 Hz). These assignments are based on the data in ref. 110. The weak doublet at δ = -50 ppm (J₁₀₃Rh=₁₁₉Sn = 528 Hz) is believed to be due to [Rh(H₂O)(SnCl₃)₅]⁻ (see Sec. 3.5), while that at δ = -268.3 ppm (J₁₀₃Rh=₁₁₉Sn = 678 Hz) is unassigned. Some decomposition was evident over the duration of the NMR experiment (~48 h). The dark red-brown colour of the concentrated solution faded to a paler yellow-orange and [Me₄N]₂[SnCl₆] precipitated out. The decomposition pathway is not known, but [Et₄N][SnCl₃] was found to react with CH₃NO₂ producing partially soluble [Et₄N]₂[SnCl₆] plus a very soluble yellow complex. Since a main thermal pathway of decomposition (see Chap. 4) of Rh(III)-Sn(II) complexes is via dissociation of SnCl₃⁻, it is probable that the Sn(IV) precipitate originates from this dissociation and subsequent reaction with the solvent. This would rationalize the presence of [RhCl₃(SnCl₃)₃]⁻ in solution. The IR of the yellow rhodium salt was nearly identical to that isolated by us (i.e. fig. 3.11a). The only point of departure was the lack of splitting in the band at 600 cm⁻¹, which is consistent with the presence of [Me₄N]₃[RhSn₅Cl₁₅]⁺ (i.e. substitution of Me₄N⁺ cation for Et₄N⁺ cation in the synthesis). Comparison of the CH₃CN
Figure 3.14  The 37.336 MHz $^{119}$Sn FTNMR spectrum of the product isolated using the literature $^{90}$ synthesis of $[\text{Me}_4\text{N}]_3[\text{RhCl(SnCl}_3)_5]$. (ambient temperature in CD$_3$NO$_2$; run on XL-100 (12 mm OD tube): 25 KHz sweep width, 130K scans).
solution UV-VIS spectra (fig. 3.13a and b) indicates that there is a greater difference between the two products than does the IR spectra. In particular, the relative amount of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{-3}$ appears to be less in the product from the literature procedure (see sec. 3.6 for further discussion).

Despite of the uncertainty in the identification of all isolated products, it is evident that increasing the Sn(II):Rh(III) ratio from 3 to 5 or more, under similar conditions, results in an increase in the tin to rhodium ratio in the products isolated.

The effects on the kinetic products of the reaction between Rh(III) chlorides and Sn(II) chloride are different. These experiments are analogous to the synthesis of $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4] \cdot \text{H}_2\text{O}$ (sec. 2.1.5.2) in that the tin reagent and precipitant are introduced together as $[\text{Et}_4\text{N}][\text{SnCl}_3]$. The precipitates were isolated when precipitation appeared complete, usually within 5 or 10 minutes of mixing, under anaerobic conditions. In all cases discussed in this section, precipitation occurred while this reagent was being added as a solid (or in concentrated solution in 3M HCl). At room temperature using a Sn(II)/Rh(III) ratio of 1.8, and $[\text{Rh}(\text{III})] = 0.017\text{M}$, $[\text{Et}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]$ was isolated in 78% yield ($\%$ Cation (calc.) = 26.36 (26.44); IR given in fig. 2.4; UV-VIS in fig. 2.5). At 40°C using a Sn(II)/Rh(III) ratio of 3, and $[\text{Rh}(\text{III})] = 0.056\text{M}$, an impure yellow-orange product was obtained. The IR spectrum (fig. 3.15a) also resembles that of $[\text{Et}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]$; however, from the UV-VIS of the CH$_3$CN solution (fig. 3.16a) the product was determined to be a mixture of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{-3}$ and $[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{-3}$ salts in a ratio of 4.4 to 1. Interestingly, slow precipitation continued for ~12 h. The IR spectrum of
this orange solid (fig. 3.15b, 3.17b) differs from that of the yellow-orange one (fig. 3.15a, 3.17a). The CH$_3$CN solution UV-VIS spectrum (fig. 3.16b) is comparable to that of fig. 3.6b (fig. 3.16c), which is of the product obtained using the Et$_4$N$^+$ modification of the synthesis of [Me$_4$N]$_3$[RhCl$_2$(SnCl$_3$)$_4$] (see sec. 3.3.1). In addition, the far-IR of the orange product is similar to that of the same product (fig. 17b, c). The amount of product obtained in the first and second precipitates was 176 mg and 256 mg, respectively. Using the estimated compositions of the yellow-orange and orange precipitates discussed above, the composition of the material aggregated over ~12 h at 40°C is comparable to that aggregated

![Figure 3.15](image)

Figure 3.15  IR spectra (Nujol, CsI plates) of the (a) first precipitate and (b) second precipitate isolated using [Et$_4$N][SnCl$_3$].
Figure 3.16  Initial CH$_3$CN solution UV-VIS spectra of the (a) first (---) and (b) second (----) precipitates isolated using [Et$_4$N][SnCl$_3$] compared to (c) fig. 3.6a (--------).
Figure 3.17  Far-IR spectra (Nujol, CsI plates) of the (a) first (---) and (b) second (-----) precipitates isolated using [Et₄N][SnCl₃] compared to (c) fig. 3.7b (.........).
over 2 h at 90°C.

3.3.4 The effect of ambient light.

A few trial syntheses were performed in the dark using previous experiments with \([\text{Et}_4\text{N}][\text{SnCl}_3]\) (considered above) for temporal estimates. All glassware was completely wrapped in black plastic electrical tape and manipulations of solids were done with overhead lights off. This had a noticeable effect on the products obtained from these procedures.

When \([\text{Et}_4\text{N}][\text{SnCl}_3]\) (solid) was added at a Sn(II)/Rh(III) ratio of 3, at room temperature, mixtures were obtained whose IR and UV-VIS spectra were similar to those formed using the procedures at 40°C in the light. However, the UV-VIS spectra indicated that relative proportions of \([\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}\) to \([\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}\) in the first collected precipitate dropped from 4.4:1 (light) to 1.7:1 (dark). Also, in the second precipitate \([\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}\) was roughly twice as abundant as in the previous (light) case. Surprisingly, when a concentrated solution of \([\text{Et}_4\text{N}][\text{SnCl}_3]\) (in 3M HCl) was added instead, only a trivial amount of precipitate was obtained from the first filtration in contrast to the few hundred milligrams previously obtained. After 5 days, filtration yielded reasonably pure \([\text{Et}_4\text{N}]_3[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]\) as revealed by the far IR (fig. 3.18) and UV-VIS spectra (fig. 3.19). The shoulders seen in the latter at ~270 and 290 nm are probably due to \(\text{SnCl}_2(\text{CH}_3\text{CN})\) arising from solvolysis of the rhodium complex (see sec. 4.2). As observed in the previous section, the rate of formation of salts of \([\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}\) is increased at 90°C. At this temperature and with a Sn(II)/Rh(III) ratio of 5, excellent yields of \([\text{Et}_4\text{N}]_3[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)] \cdot [\text{Et}_4\text{NCl}]_{0.5}\) were obtained (see sec. 2.1.5.3).
Figure 3.18  Far-IR spectra (Nujol, CsI plates) of the product isolated from the trapping experiment in the dark.
Figure 3.19 Initial CH$_3$CN solution UV-VIS spectrum of the product isolated from the trapping experiment in the dark.
3.4 Attempts to prepare salts of $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$.

The preparative procedure is outlined in section 3.1. Most of the experiments were undertaken at a 1/6th reduced scale, although using concentrations reported in the literature$^{103,104}$. The literature reports were vague about the reaction time; in the present experiments the addition of precipitant occurred about 20 minutes after the addition of $\text{SnCl}_2\cdot2\text{H}_2\text{O}$. Mixtures were obtained only. None of the spectral data could be correlated specifically with reported data$^{103}$ for the rhodium(I) dimer. Some components of these mixtures were identifiable as salts of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{2-}$, $[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$, $[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}$ and $[\text{RhSn}_5\text{Cl}_{15}]^{3-}$ (see below). Other uncharacterized species were also present. In addition to studies under aerobic conditions, anaerobic experiments using 3MHC1 and ethanol as solvent were carried out. Since the desired product was not obtained, direct ligand exchange was tried, by addition of stoichiometric amounts of $[\text{Et}_4\text{N}][\text{SnCl}_3]$ in acetone to a $\text{CH}_2\text{Cl}_2$ solution of $[\text{Rh}_2\text{Cl}_2(\text{COT})_4]$. This yielded a complex mixture of compounds highly sensitive to air and moisture, which could only be incompletely characterized (see below).

Under aerobic conditions and using 3MHC1 as solvent, an orange or yellow-orange product was obtained. The initial $\text{CH}_3\text{CN}$ solution UV-VIS spectrum (fig. 3.20a) is similar to that of the product obtained with a Sn(II):Rh(III) ratio of 5 (fig. 3.13). Under anaerobic conditions the product was more yellow (sometimes with a greenish tinge). After exposure to air for about a day, it became orange. The yellow product is less stable in $\text{CH}_3\text{CN}$ solution than that isolated under aerobic conditions. Changes in the solution UV-VIS spectrum were observed during scanning (viz: fig. 3.20b, breaks in curve at
Figure 3.20 Initial CH$_3$CN solution UV-VIS spectra of products isolated using the reported synthesis of $^{103}$[Me$_4$N]$_4$[Rh$_2$Cl$_2$(SnCl$_3$)$_4$]: (a) isolated under aerobic conditions, (---), (b) under anaerobic conditions (---) and (c) the dotted line is figure 3.13a for comparison.
A = 2.0; \lambda = 350 \text{ nm when scales were changed). Nevertheless,} [\text{Rh(SnCl}_3)_4(\text{SnCl}_4)]^{3-} \text{ is clearly a component of the mixture. Following storage of the solid for a few weeks under dry aerobic or anaerobic conditions, its solution spectrum was more like that of the product isolated at a higher Sn(II)/Rh(III) ratio (fig. 3.20c). The IR and far-IR spectra (fig. 3.21 and fig. 3.22) were similar to those obtained from the products at the higher ratio.}

A yellow product was also obtained from ethanol solution, under anaerobic conditions. The amount of product increased three-fold in the absence of light ('dark' product). The CH$_3$CN solution UV-VIS spectra (fig. 3.23a,b) differ from those of the products isolated from 3MHCl (fig. 3.23c,d). The band at 380 nm, due to [\text{Rh(SnCl}_3)_4(\text{SnCl}_4)]^{3-}, is now less prominent and there is little evidence for [\text{RhCl(SnCl}_3)_4]^{3-} (especially in the 'dark' product). Instead, there is a new band at \sim 328 \text{ nm (also seen in 3MHCl (317 nm), and CH}_2\text{Cl}_2 (332 nm)), which is most prominent for the 'dark' product. This peak decreased in intensity at a much slower rate than
Figure 3.22  Far-IR spectra (Nujol, CsI plates) of (a) the product isolated using the reported synthesis\textsuperscript{103} of $[\text{Me}_4\text{N}]_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$ but under anaerobic conditions (---) and (b) figure 3.12a (----).
Figure 3.23 Initial CH$_3$CN solution UV-VIS spectra of the products isolated using the reported synthesis$^{103}$ of [Me$_4$N]$_4$[Rh$_2$Cl$_2$(SnCl$_3$)$_4$] but under anaerobic conditions in ethanol: (a) isolated in the light (— — —) (b) isolated in the dark (— — —). Figures 3.20a, c are overlaid as (c) (— — —) and (d) (———) respectively.
the 380 nm peak (see Chap. 4 and sec.2.1.5). The band is probably one of the absorbances of \([\text{RhCl(SnCl}_3\text{)}_5]\)\(^{3-}\), which was identified as one of the more stable major species in an in situ \(^{119}\text{Sn}\) FTNMR experiment (sec. 3.5). This assignment is consistent with the observations made with respect to the UV-VIS and NMR experiments where the \(\text{Sn(II)}/\text{Rh(III)}\) was 5 or greater (sec. 3.3.3).

The elemental analysis for the \(\text{Et}_4\text{N}^+\) cation (table 3.6; C,H,N analysis) was close to that expected for the pentakis-trichlorostannato(II) species, although low overall.

It is difficult to assess the differences arising from the presence or absence of light. The elemental analysis for the cation, the solution spectra, and the far-IR (fig. 3.24), are not very different for the 'light' and 'dark' products, which suggests similar compositions. Addition of a further two equivalents of precipitant to each filtrate, after isolation of the initial precipitates, yielded brown or orange-brown precipitates. The yield in the presence of light was 2-3 fold greater than the corresponding initial

Table 3.6 Partial elemental analysis of yellow precipitate from ethanol (\(\text{Et}_4\text{N}^+\) salt)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>%cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product isolated in dark:</td>
<td>16.75</td>
<td>3.62</td>
<td>2.51</td>
<td>22.88</td>
</tr>
<tr>
<td>&quot; in light:</td>
<td>16.94</td>
<td>3.62</td>
<td>2.56</td>
<td>23.12</td>
</tr>
<tr>
<td>Expected for ([\text{Et}_4\text{N}_3][\text{RhCl(SnCl}_3\text{)}_5])</td>
<td>17.42</td>
<td>3.63</td>
<td>2.54</td>
<td>23.58</td>
</tr>
</tbody>
</table>
Figure 3.24 Far-IR spectra (Nujol, CsI plates) of the products isolated using the reported synthesis of $[\text{Me}_4\text{N}]_4[Rh_2\text{Cl}_2(\text{SnCl}_3)_4]$ but under anaerobic conditions in ethanol: (a) isolated in the light (---), (b) isolated in the dark (-----).
precipitate but the elemental analysis for C, H and N (table 3.7) was considerably higher and the empirical formula derived was not that of Et$_4$N$^+$. In the absence of light the amount of precipitate was about 1/10 that of the corresponding initial precipitate. The elemental analysis was correct for Et$_4$N$^+$ but higher than previously. Probably ambient light levels are promoting solvolysis of the rhodium-tin complexes yielding compounds with lower Sn:Rh ratios and containing solvent. However, no new bands in the IR due to coordinated ethanol could be observed.

The experiments discussed above are, in a sense, intermediate between those in which the kinetic products were isolated (i.e. using [Et$_4$N][SnCl$_3$] or simultaneous addition of SnCl$_2$·2H$_2$O and precipitant), and those in which a longer period of equilibration was used (i.e. synthesis of [RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ salts). It should be noted that products isolated from 3MHC1 using the room temperature procedures based on the reported [Rh$_2$Cl$_2$(SnCl$_3$)$_4$]$^{4-}$ synthesis are similar to those isolated under the more rigorous condition based on the

<table>
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<tr>
<th>Product isolated in dark:</th>
<th>22.00</th>
<th>4.69</th>
<th>3.37</th>
<th>30.06</th>
<th>C$<em>8$H$</em>{20}$N</th>
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</thead>
<tbody>
<tr>
<td>&quot; &quot; in light:</td>
<td>32.85</td>
<td>5.80</td>
<td>2.98</td>
<td>-</td>
<td>C$<em>{13}$H$</em>{27}$N</td>
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</table>

Table 3.7 Partial elemental analysis of brown precipitate from ethanol (Et$_4$N$^+$ salt)
synthesis of $[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$. The substitution of ethanol as solvent resulted in a much higher proportion of $[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$ than seen in the products isolated from 3MHC1. This alternation in product mixture was at least partially, due to the change in chloride concentration. The following experiment was illustrative: a 1:3:15 mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and LiCl was stirred for a few minutes in dry ethanol under argon before a 3 fold excess of Et$_4$NCl was added. The far IR (fig. 3.25) and CH$_3$CN solution UV-VIS (fig. 3.26) spectra of the dull orange product are similar to those of products isolated from 3MHC1 under similar conditions using [Et$_4$N][SnCl$_3$] (sec. 3.3.3). The principle components of the product are $[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}$ and probably $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$.

Since the literature methods (or related ones) did not yield $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ salts, the reaction between $[\text{Rh}_2\text{Cl}_2(\text{COT})_4]$ and SnCl$_3$ was examined. A deep purple, air and moisture sensitive precipitate was obtained, upon addition of a deaerated acetone solution of [Et$_4$N][SnCl$_3$] to a deaerated CH$_2$Cl$_2$ solution of $[\text{Rh}_2\text{Cl}_2(\text{COT})$, under argon in the dark (Sn(II)/Rh(I) ratio was 2.5). The product decomposed in a few days to a brown material whose infrared contained bands due to water (3500 cm$^{-1}$ and 1600 cm$^{-1}$). The source of the water was uncertain, since the same results were obtained with a different batch of acetone dried over molecular sieves. It is possible that traces of H$_2$O remained in the solvent or were adsorbed on the solid reagents which had been weighed at in air. The purple product showed a strong asymmetric $\nu$(M-Cl) band at $\sim$285 cm$^{-1}$ in the far-IR (fig. 3.27a). Exposed to air, the salt turned brown within hours. In addition to bands in the IR indicative of coordinated and/or absorbed water, the $\nu$(MCl) of
Figure 3.25: Far-IR spectrum of the isolated product of the reaction between \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) and \( \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \) in the presence of excess \( \text{LiCl} \) in ethanol.
Figure 3.26 Initial CH$_3$CN solution spectrum of the isolated product of the reaction between RhCl$_3$·3H$_2$O and SnCl$_2$·2H$_2$O in the presence of excess LiCl in ethanol.
the brown compound (fig. 3.27b) is shifted by about 15 cm\(^{-1}\) to higher wavenumber than in the purple compound. This shift would be consistent with formal oxidation of Rh(I) to Rh(III), leading to a reduction of electron-density on the tin and thus to a higher \(\nu(SnCl)\)\(^{115}\). Complexes of the type Rh(diolefin)(L)\(_3\)SnCl\(_3\) (L = phosphine, arsine or stibine) have two or three overlapping \(\nu(SnCl)\) bands just below and around 300 cm\(^{-1}\)\(^{118}\). These shift

![Far-IR spectra](image)

**Figure 3.27** Far-IR spectra (Nujol, CsI plates) of (a) the purple product of the reaction of \([Rh_2Cl_2(COT)_4]\) with \([Et_4N][SnCl_3]\) (---) and (b) the same product after air oxidation(----).
Figure 3.28 Initial CH$_3$CN solution UV-VIS spectrum of the purple product of the reaction of [Rh$_2$Cl$_2$(COT)$_4$] with [Et$_4$N][SnCl$_3$] (lower line). Upper line is of a second sample at higher scale expansion.

to higher wavenumber as L becomes less basic. Only bands assignable to Et$_4$N$^+$ and M-Cl were observed, while no COT appears to be present in the purple product. The purple product was probably a rhodium(I) stannous chloride complex. Elemental analysis was not obtained prior to decomposition. The initial CH$_3$CN UV-VIS spectrum (fig. 3.28) is similar (in the visible region) to that of [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$_{5^-}$ in 3M HCl solution (sec. 3.1).

In the dark the purple colour fades, quickly becoming yellow. If this yellow solution is evaporated under vacuum and the residue taken back up in CH$_3$CN, a purple solution is obtained. This behaviour is consistent with
reversible solvolysis of a labile rhodium(I) center.

Although some rhodium(I) complex has been isolated in low yield, it was likely to have been the monomeric pentakis tin species. In an attempt to slow down the formation of complexes with a higher Sn:Rh ratio, the synthetic procedure was repeated at -23°C, when a mixed deep purple and greenish/yellow-brown precipitate however was obtained. When allowed to warm to room temperature the product lost its deep purple colouration. This material was highly air sensitive, discolouring rapidly on exposure to air and becoming bright orange within a few hours. The initial CH₃CN solution UV-VIS spectrum of the orange oxidation product is that of [RhCl₃(SnCl₃)₃]⁻ (fig. 2.3). Part of the unoxidized product may contain a Rh(SnCl₃)₃ structural unit. When the flask containing the unoxidized material under an argon atmosphere was briefly cooled by liquid nitrogen, the purple colouration was restored. This colour change was reversible; several cool/warm cycles were completed with no apparent decay. On oxidation, the thermochromic behaviour was not observed. While this system was interesting, it was not investigated further.

3.5 ¹¹⁹Sn FT NMR experiments.

Anaerobic 3MDCl/D₂O and ethanol/acetone-d₆ (7:1 V/v) solutions with a Sn:Rh ratio of 3 were examined. The ethanolic solution additionally contained 3 equivalents of LiCl relative to rhodium. The rhodium concentration was 0.5M, which is an order of magnitude greater than in the synthetic experiments. Comparable data in 3MHC1 under aerobic conditions (Table 3.8 and fig. 3.29) have been published ¹¹⁰ (see also sec. 3.3.3, fig. 3.14).

Tin-¹¹⁹ (I = ½, natural abundance 8.68%) FT NMR spectroscopy is po-
Table 3.8 $^{119}$Sn FT NMR characteristics of various rhodium-tin complexes (after ref. 110)

(in 3M HCl solution unless otherwise indicated)

<table>
<thead>
<tr>
<th>Structure assignment</th>
<th>oxidation number of rhodium</th>
<th>number of coordinated tin ligands</th>
<th>$\delta$/ppm</th>
<th>$^1J(103_{Rh}^{119}_{Sn})$/Hz</th>
<th>$^2J(^{119}<em>{Sn}^{117}</em>{Sn})$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $[\text{RhCl}_5(\text{SnCl}_3)]^3^-$</td>
<td>III</td>
<td>1</td>
<td>-991.6</td>
<td>864</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-932.4$^a$</td>
<td>860$^a$</td>
<td>none$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-914.1$^b$</td>
<td>850$^b$</td>
<td>none$^b$</td>
</tr>
<tr>
<td>2 $[\text{RhCl}_4(\text{SnCl}_3)_2]^3^-$</td>
<td>III</td>
<td>2</td>
<td>-654.4</td>
<td>796</td>
<td>N.R.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-637.0$^a$</td>
<td>791$^a$</td>
<td>3056$^a$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-626.0$^b$</td>
<td>780$^b$</td>
<td>3091$^b$</td>
</tr>
<tr>
<td>3 $[\text{RhCl}_3(\text{SnCl}_3)_3]^3^-$</td>
<td>III</td>
<td>3</td>
<td>-411.1</td>
<td>718</td>
<td>2804</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-395.4$^b$</td>
<td>708$^b$</td>
<td>2840$^b$</td>
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<tr>
<td>4 d</td>
<td>III</td>
<td>2</td>
<td>-281.4</td>
<td>664</td>
<td></td>
</tr>
<tr>
<td>5 $[\text{RhCl}_2(\text{SnCl}_3)_4]^3^-$</td>
<td>III</td>
<td>4</td>
<td>-204.3</td>
<td>590</td>
<td>2158</td>
</tr>
<tr>
<td>6 $[\text{RhCl}(\text{SnCl}_3)_5]^3^-$</td>
<td>III</td>
<td>5</td>
<td>-100.5</td>
<td>547</td>
<td>1952$^c$</td>
</tr>
<tr>
<td>7 $[\text{Rh(SnCl}_3)_5]^4^-$</td>
<td>I</td>
<td>5</td>
<td>8.5</td>
<td>806</td>
<td>3634</td>
</tr>
</tbody>
</table>

a: concentrated residue after separation of $[\text{Me}_4\text{N}]_3[\text{RhCl}_3(\text{SnCl}_3)_3]$, 
b: 12M HCl solution, 
c: HMPA solution, 
d: not assigned.
tentially useful in characterizing rhodium chloride-tin chloride complexes. Coordination to rhodium results in a doublet due to spin-spin coupling with $^{103}\text{Rh}$ ($I = \frac{3}{2}$, natural abundance 100%). Complexes containing more than one tin ligand show coupling to $^{117}\text{Sn}$ ($I = 1/2$, natural abundance 7.61%) and/or $^{119}\text{Sn}$ ($I = \frac{9}{2}$, natural abundance 0.35%) at sufficiently high S/N. Usually the latter is not observable.

With one exception, patterns observed in 3MDCl (fig. 3.30, table 3.9) and ethanolic solution (fig. 3.31, table 3.10) can be matched to those reported in the literature (see above), on the basis of the chemical shift and $^{1}J_{119\text{Sn}-103\text{Rh}}$ data. The new resonance pattern observed is that centered

![Figure 3.29](image)

**Figure 3.29** $^{119}\text{Sn}$ FTNMR spectra of 3NHCl solutions containing various ratios of Sn(II) and Rh(III) chlorides (after ref. 110). Accompanying data are in table 3.8.
Figure 3.30  The 29.88 MHz $^{119}$Sn FTNNMR spectrum of a 3M DCl/D$_2$O solution containing a Sn(II)/Rh(III) ratio of 3, under argon. (Ambient temperature, run on WP-80 (10 mm O.D. tube); upper segment: 20 KHz sweep width, 20.88 K scans (pulse delay 2.0s, pulse width 7.0, 6.0 Hz line broadening), lower segment: 20 KHz sweep width, 16.82 K scans (pulse delay 5.0 s, pulse width 7.0, 6.0 Hz line broadening)).
Figure 3.31: The 29.88 MHz $^{119}\text{Sn}$ FTNMR spectrum of an ethanolic solution (15% acetone-$d_6$) containing a 1:3:3 ratio of Rh(III), Sn(II) and LiCl under argon. (Ambient temperature, run on WP-80 (10 mm O.D. tube); 20 KHz sweep width, 13.240 K scans (pulse delay 4.5 s, pulse width 7.0, 6.0 Hz line broadening); additionally, first 4 data points were removed from the f.i.d. to smooth the baseline).

at $\delta = -50$ ppm ($^{119}_1 J_{\text{Sn}-\text{Sn}}^{103}\text{Rh} = 526\text{Hz}$) in ethanolic solution, which appears as a six line multiplet overlapping those due to $[\text{RhCl(SnCl}_5]\]^{3-}$ at $\delta = -112$ ppm. With reference to fig. 3.14 (CD$_3$NO$_2$ solution), the same central doublet can be noted at $\delta = -52$ ppm ($^{119}_1 J_{\text{Sn}-\text{Sn}}^{103}\text{Rh} = 526\text{Hz}$).

The number of tin atoms ($n$) coordinated to the rhodium center can be estimated from the ratio of the intensity of satellite peaks, due to $^{119}\text{Sn} - 117\text{Sn}$ coupling, to the intensity of doublets due to species containing only one $^{119}\text{Sn}$ nuclei. For the simplest case where all the tin atoms
Table 3.9 $^{119}$Sn FT NMR characteristics of rhodium-tin complexes observed in 3M DCl/D$_2$O solution with Sn/Rh = 3

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<tr>
<th>Structure assignment</th>
<th>oxidation number of rhodium</th>
<th>number of coordinated tin ligands</th>
<th>$\delta$/ppm</th>
<th>$^1J_{^{103}Rh-^{119}Sn}$/Hz</th>
<th>$^2J_{^{119}Sn-^{117}Sn}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$</td>
<td>III</td>
<td>3</td>
<td>-415.7</td>
<td>718</td>
<td>2838</td>
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<tr>
<td>as #4 table 3.8</td>
<td>III</td>
<td>2</td>
<td>-282.7</td>
<td>664</td>
<td>n.o.</td>
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<tr>
<td>$[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$</td>
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<td>4</td>
<td>-209.6</td>
<td>600</td>
<td>n.o.</td>
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<td>n.o.: not observed</td>
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</tr>
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</table>

Table 3.10 $^{119}$Sn NMR characteristics of rhodium-tin complexes observed in ethanol/aceton-d$_6$ solution containing Sn/Rh = 3

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<th>Structure assignment</th>
<th>oxidation number of rhodium</th>
<th>number of coordinated tin ligands</th>
<th>$\delta$/ppm</th>
<th>$^1J_{^{103}Rh-^{119}Sn}$/Hz</th>
<th>$^2J_{^{119}Sn-^{117}Sn}$/Hz</th>
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</thead>
<tbody>
<tr>
<td>$[\text{RhCl}_4(\text{SnCl}_3)_2]^{3-}$</td>
<td>III</td>
<td>2</td>
<td>-600$^a$</td>
<td>&gt; 740$^a$</td>
<td>n.o.</td>
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<tr>
<td>$[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$</td>
<td>III</td>
<td>3</td>
<td>-425</td>
<td>737</td>
<td>n.o.</td>
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<td>$[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$</td>
<td>III</td>
<td>5</td>
<td>-112</td>
<td>556</td>
<td>b.</td>
</tr>
<tr>
<td>$[\text{Rh(H}_2\text{O})(\text{SnCl}_3)_5]^{3-}$</td>
<td>III</td>
<td>5</td>
<td>-50</td>
<td>526</td>
<td>1689</td>
</tr>
</tbody>
</table>

$^a$: estimated from "folded-in" signal at -540 p.p.m. Note that similarity "folded-in" signals due to uncoordinated Sn(IV) species are at -460 p.p.m.

b: see text for assignments and discussion.

n.o.: not observed.
are magnetically equivalent (or are undergoing rapid exchange on the NMR time scale) combinatorial analysis can be used to calculate the $I_{\text{satellite}}/I_{\text{main}}$ peak ($I_s/I_m$) ratio in the expected sextuplet pattern (for $n > 2$) (see Appendix B). Figure 3.32 is a plot of $I_s/I_m$ as a function of $n$. In 3MHC1 solution at ambient temperature, the observation of only one kind of satellite pattern (i.e. a sextuplet) can be attributed to fast intramolecular scrambling of the tin ligands on the NMR time scale. Assuming this to be the case in ethanolic solution for the sextuplet at $\delta = -50$ ppm, the number

![Figure 3.32 Plot of $I_{\text{satellite}}/I_{\text{main}}$ vs. the number of coordinated $^{119}$Sn and $^{117}$Sn nuclei ($n$) (see Appendix B).]
of tin ligands per rhodium is 5 (I_s/I_m(obs) = 14.4%). The formal oxidation state of the rhodium is probably (III) and not (I), by analogy to the trend reported for δ and 1J_{103Rh-119Sn} as a function of n, for Rh(III) and Ru(II) complexes. As n increases, δ becomes more positive and 1J_{103Rh-119Sn} decreases. Alternatively the Sn(II): Sn(IV); Rh mass balance could be computed since only one species is unknown. Due to time limitations, the data were not accumulated, although a folded-in signal associated with Sn(IV) species is observed at about δ = -465 ppm. The new pentakis(trichlorostannato(II)) rhodium(III) complex may be [Rh(H_2O)(SnCl_3)_5]^2-. The constancy of δ and 1J_{103Rh-119Sn} in two different solvent systems and the downfield shift relative to [RhCl(SnCl_3)_5]^3- indicate replacement of Cl^- by a less electronegative ligand (e.g. [RuCl(SnCl_3)_5]^4- vs. [Ru(CH_3CN)(SnCl_3)_5]^3- in CD_3NO_2) that is not the solvent media. Since the concentration of H_2O in the ethanolic solution is comparable to the chloride concentration and is much greater than in dry CD_3NO_2, water is the probable candidate.

The resonance pattern for [RhCl(SnCl_3)_5]^3- deserves comment. In 3MHC1 a sextuplet was observed, but in CD_3NO_2 (fig. 3.14) and ethanol/acetone-d_6 (7:1 V/v; fig. 3.31) the more complicated pattern suggests non-fluxional behaviour. If the molecule is assumed to be rigid and, if coupling due to ^115Sn and to molecules containing 3 spin active tin atoms are assumed to be unobservable because of the S/N, then a 28 line pattern is expected. The pattern is the weighted sum of two AX, four AMX and the AB parts of one ABX pattern (see Appendix B for details). The trans-^{119}Sn-^{117}Sn couplings are expected to be an order of magnitude greater than the cis-couplings ^110,119,120,121 (ie. ~20,000 Hz vs. ~2,000 Hz), and not readily
observed in fig. 3.31, because of the relatively narrow sweep width of 20,000 Hz. The spectrum illustrated in fig. 3.14 is sufficiently wide but no trans couplings can be noted. A simulation of the central pattern of resonances was attempted. Fewer than the expected 24 lines were observed in CD$_3$NO$_2$ (fig. 3.14) and ethanol/acetone (fig. 3.31), although relative intensities and the number of lines were the same. A simulated spectrum was generated using UBC PANIC and UBC ADD under the assumption that the difference in chemical shifts for the axial and equatorial tins is small enough so that the AX patterns merge due to the magnitudes of the peak width and digital resolution. Additionally, the cis-coupling constants were selected so that the low-field satellites nearly merge. The parameters used are listed on Appendix C. Comparison of the calculated and observed spectrum in ethanol/acetone-d$_6$ reveals a mismatch on the high field side (fig. 3.33). In particular, there is no correspondence between the calculated pattern of couplings with axial $^{119}$Sn and the observed pattern. The implication is that some exchange process is still being observed. Variable temperature experiments were not undertaken to investigate this point further.

Of primary interest are comparisons that can be drawn between the in situ NMR experiments and corresponding synthetic studies of the complexes \([\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^3^-\) (sec. 3.4) and \([\text{RhCl}_3(\text{SnCl}_3)_3]^3^-\) (sec. 3.3.1,2). The isolated products have been shown to be rhodium(III) or rhodium(I) complexes with four or more tin ligands rather than the reported rhodium(I) dimer. The species observed in the NMR experiments were shown to be stable for at least 48 h by collecting a second spectrum in each case. Very little change was noted. However, over longer periods (1-2 weeks) considerable change was noted; only uncoordinated Sn(IV) chlorides ($\sim$δ = -640 ppm) were
observed.

The distribution of species in ethanol/acetone-\textit{d}_6 solution is in reasonable agreement with the synthetic results. The pentakis(trichlorostannato)rhodium(III) complexes appear to be fairly stable in solution, although the presence of a minor amount of \([\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}\) possibly resulted from partial decomposition (see sec. 3.3.3). The addition of three equivalents of LiCl in the NMR experiment represents the chloride introduced with the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.33.png}
\caption{Comparison of observed (29.88 MHz) and synthesized resonances for \([\text{RhCl(SnCl}_3)_5]^{3-}\) as observed in ethanol/acetone-\textit{d}_6 solution (note: trans couplings not shown due to scale).}
\end{figure}
precipitant in the synthetic procedure. The correspondence between the two experiments suggests that the chloride ion concentration is important to the outcome of the synthesis (see also sec. 3.4).

In contrast both the anaerobic experiment in 3M DCl/D2O (fig. 3.31), and the reported aerobic experiment in 3M HCl/H2O\textsuperscript{110} (fig. 3.30; Sn/Rh = 3), indicate that [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}]\textsuperscript{3-} is the major species in solution. This is consistent with the [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}]\textsuperscript{3-} synthesis under aerobic conditions using Me\textsubscript{4}N\textsuperscript{+} as the precipitating cation. It is, however, inconsistent with the results using Et\textsubscript{4}N\textsuperscript{+} and/or anaerobic conditions where [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}]\textsuperscript{3-} was the major or significant product. This complex has been shown to decompose to [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}]\textsuperscript{3-} in 3M HCl\textsuperscript{91} (see also chap. 4), which could account for the present situation. On the other hand, weak resonances due to [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}]\textsuperscript{3-} are observable at -209.6 ppm (fig. 3.31) and the synthetic product distribution may arise from preferential precipitation of the less soluble [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}]\textsuperscript{3-} salt which could be in equilibrium with [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}]\textsuperscript{3-} in solution. There is, however, an interesting difference in composition between the aerobic and anaerobic NMR experiments. In the latter no multiplet is seen at +8.5 ppm due to a rhodium(I) complex\textsuperscript{110}, but there is a relatively greater amount of free Sn(IV) in relation to [RhCl\textsubscript{3}(SnCl\textsubscript{3})\textsubscript{3}]\textsuperscript{3-} (~20 - 25%) than in the aerobic case (~8%). Presumably, either more oxidation of Sn(II) to Sn(IV) (ie: reduction of Rh(III) to Rh(I)) occurs under anaerobic conditions than under aerobic conditions, or less coordinated tin is 'visible' as a result of exchange processes. The latter is more likely since the [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}]\textsuperscript{3-} resonances are reported to be temperature dependent\textsuperscript{110}. 
3.6 Discussion

Anionic rhodium(III) products were isolated under most conditions using RhCl₃·3H₂O as starting material. The complexes were not the result of air oxidation of rhodium(I) complexes since both anaerobic and aerobic conditions were involved. Trapping experiments in 3M HCl at or near ambient temperature revealed that [RhCl₂(SnCl₃)₄]⁻ was formed principally during the initial stages of reaction, whereas the new complex [Rh(SnCl₃)₄(SnCl₄)]⁻ was formed gradually. Additionally, the previously reported observation that [RhCl₃(SnCl₃)₃]⁻ is not a precursor to [RhCl₂(SnCl₃)₄]⁻ is corroborated. This, and the latter's rapid formation would tend to rule out uncatalysed 'classical' stepwise formation of [RhCl₂(SnCl₃)₄]⁻ by substitution or insertion processes. Based on the pattern of results presented in the preceding sections, preliminary concepts about the reaction mechanism can be formulated. It should be recognized that information is limited, since only the SnCl₃⁻ containing complexes were isolated (in moderate to good yields with respect to tin). The yield based on rhodium was often small when the isolated complexes contained Sn:Rh ratios in excess of the experimentally used ratio were obtained.

The probable mechanism involved competition between the expected 'straight-forward' reduction of Rh(III) by Sn(II)¹, and substitution of Rh(III) complexes catalysed by Rh(I). Similar catalysis by a lower valence species is implicated in the CO reduction of Rh(III) halides in aqueous halo-acid, and in the formation of [Rh(py)₄Cl₂]⁺ from [Rh(H₂O)Cl₅]₂⁻ and pyridine in ethanolic solution. The mechanisms are believed to be
analogous to the classic example of substitution at Pt(IV) catalysed by Pt(II) complexes, where the presence of four-coordinate Pt(II), or reducing agents capable of reducing Pt(IV) to Pt(II), produced a marked increase in rates.

3.6.1 Kinetic products

To the best of our knowledge, details of the reduction:

\[ \text{Rh(III)} + \text{Sn(II)} = \text{Rh(I)} + \text{Sn(IV)} \]  

have not been investigated but it is probably analogous to the known rapid reduction of Pt(IV) to Pt(II) by Sn(II). In 3MHC1 the principle reductant was \( \text{SnCl}_3^- \), and the reduction was more rapid than formation of 1:1 complexes between Pt(II) and Sn(II). At low \([\text{Cl}^-]\), the rate was slower due to formation of less active di- and mono-chloro Sn(II) species:

\[ [\text{SnCl}]^+ + \text{Cl}^- \leftrightarrow \text{SnCl}_2 \]  

\[ \text{SnCl}_2 + \text{Cl}^- \leftrightarrow [\text{SnCl}_3]^- \]  

The electron transfer was believed to be innersphere via the transition state \( ([\text{Cl}_5\text{Pt}...\text{Cl}...\text{SnCl}_3]^{3-})^+ \). In order to accommodate our synthetic observations, the subsequent reaction of Rh(I) with \( \text{SnCl}_3^- \) must occur at a rate comparable to or greater than the reduction step (see below). A second
premise is that \([\text{RhCl}_6-n(\text{SnCl}_3)_n]^{3-}\) complexes are not as readily reduced by \(\text{SnCl}_3^-\) as \(n\) increases. This is reasonable since the description of these complexes as formally Rh(III), in the same sense perhaps as \(\text{RhCl}_5(\text{H}_2\text{O})^{2-}\), may be inappropriate given the reducing nature of the \(\text{SnCl}_3^-\) ligand. The Rh(III)/Rh(I) formalism is used here, bearing this in mind.

The data on the kinetic products are consistent with the following mechanism. (It should be noted that the composition of the "\(\text{RhCl}_3\cdot3\text{H}_2\text{O}\)" solution is indefinite, although its exact composition is not crucial to the discussion). \(L\) is \(\text{Cl}^-\) or \(\text{H}_2\text{O}\).

\[
[\text{L}_5\text{Rh}^{\text{III}}\text{Cl}]^{n^-} + [\text{SnCl}_3]^- \rightarrow [\text{Rh}^\text{III}L_4]^{m^-} + \text{SnCl}_4 + L \quad (3.5)
\]

\[
[\text{RhL}_4]^{m^-} + 4[\text{SnCl}_3]^- \xrightarrow{\text{fast}} [\text{Rh}^\text{III}(\text{SnCl}_3)_4]^{3^-} + 4L^{P^-} \quad (3.6)
\]

\[
[\text{Rh}^\text{III}(\text{SnCl}_3)_4]^{3^-} + \text{SnCl}_4 \rightarrow [\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3^-} \quad (3.7)
\]

\[
\gamma^{m^-} + [\text{Rh}(\text{SnCl}_3)_4]^{3^-} + [\text{L}_5\text{RhCl}]^{n^-} \rightarrow 
\]

\[
[Y\cdot\text{Rh}(\text{SnCl}_3)_4\cdots\text{Cl}\cdots\text{RhL}_5]^{(3+m+n)^-} 
\]

\[
[Y\cdot\text{Rh}(\text{SnCl}_3)_4\text{Cl}]^{(2+n)^-} \quad [\text{RhL}_4]^{m^-} + L \quad (3.8)
\]

If \(Y = \text{H}_2\text{O}\) then a subsequent step could be 3.9, although this could be a slow step if unassisted.

\[
\text{RhCl}(\text{H}_2\text{O})(\text{SnCl}_3)_4^{2^-} + \text{Cl}^- \rightleftharpoons \text{RhCl}_2(\text{SnCl}_3)_4^{3^-} \quad (3.9)
\]
Intermediates similar to the chloride bridged Rh\textsuperscript{III}/Rh\textsuperscript{I} species in step 3.8 are commonly involved in inner-sphere redox processes\textsuperscript{129}, although high charge makes their chemical lifetime short. After a two-electron transfer (Rh(I)\textrightarrow Rh(III)) within the intermediate, decomposition occurs via cleavage of the newly labile Rh(I)-\(\mu\)Cl bond. Direct observation of analogous halide bridged d\textsuperscript{6}-d\textsuperscript{8} complexes is limited to an Ir(I)/Ir(III) dimer\textsuperscript{130}, formed by association of ((CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})NH\textsubscript{2})Ir(CO)\textsubscript{2}Cl and ((CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})NH\textsubscript{2})Ir(CO)\textsubscript{2}Cl\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}, having one of two possible structures:

The newly formed Rh(I) species (equation 3.8) can react with free SnCl\textsubscript{3} (equation 3.6) to complete a catalytic cycle. The selectivity towards high coordination numbers of SnCl\textsubscript{3} results in a scavenging effect with respect to the reductant. The kinetic products, [RhCl\textsubscript{2}(SnCl\textsubscript{3})\textsubscript{4}]\textsuperscript{3-}
and \([\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}\), are not stable in solution, and the products isolated at longer reaction times reflect this.

The observed photo-enhancement of the formation of \([\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}\) is not inconsistent with the postulated mechanism, and indeed, it might be construed as indirect support. Such photo-induced electron transfer reactions are known. For example

\[
[(\text{NH}_3)_5\text{Co}^{III}\text{NCRu}^{II}(\text{CN})_5]^- \xrightarrow{h\nu} 5\text{NH}_3 + \text{Co}^{II}\text{aq.} + [\text{Ru}^{III}(\text{CN})_6]^{3-} \quad (3.10)
\]

is effected by irradiation at 375 nm. Alternately, photo-induced substitution of the aquo-ligand in \([\text{RhCl}(\text{H}_2\text{O})(\text{SnCl}_3)_4]^{2-}\) by \(\text{Cl}^-\) could be important, although in 3MHC1 exposure of this complex to daylight appears to cause a net replacement of \(\text{SnCl}_3^-\) by \(\text{Cl}^-\) (see Chapter 4).

### 3.6.2 Subsequent reaction products

The net effect of competition (reduction vs. substitution) on the products isolated is intricately dependent upon starting conditions and reaction time. Initially the free \(\text{SnCl}_3^-\) is rapidly consumed by the combined action of the catalysed substitution reaction forming rhodium(III) trichlorostannato complexes and the formation of rhodium(I) trichlorostannato complexes, having tin to rhodium stoichiometries of 4 or 5. If the total tin to rhodium ratio is low (= 3), then Rh(III) and Rh(I) complexes which do not contain tin will also exist in solution. At higher \(\text{Sn}(II)/\text{Rh}(III)\) ratios (> 5), fewer Rh(III) or non-tin containing Rh(III) complexes will be present by virtue of the greater amount of reductant/ligand.
The presence of unreacted Rh(III) will be important under anaerobic conditions. Attempts at synthesizing $[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$ under these conditions resulted in isolation of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ as major product. Under aerobic conditions, however, $[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-}$ was the major product. The tetrakis-stannato complex is unstable in solution $^{91}$ (sec. 4.3), yielding tris-stannato species and free $\text{SnCl}_3^{-}$ as major products.

$$[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-} \xrightarrow{\text{solvent}} [\text{RhCl}_2(\text{solvent})(\text{SnCl}_3)_3]^{2-} + \text{SnCl}_3^{-}$$  \hspace{1cm} (3.11b)

$$[\text{RhCl}_3(\text{SnCl}_3)_3]^{3-} + \text{SnCl}_3^{-}$$  \hspace{1cm} (3.11a)

These substitution processes are accelerated by light (see 4.1) and it is likely that under conditions of a low overall Sn/Rh ratio, the free $\text{SnCl}_3^{-}$ thus formed (eq'ns 3.11a, b) reenters the catalysed substitution cycle. In this way $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ is partially replenished. The fate of $[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}$, the other major kinetic product, must also be accounted for.

With application of heat prior to isolation of products (i.e. the non-trapping experiments) the complex was not evident, although it could be trapped out as the salt during formation. At Sn(II)/Rh(III) = 5, the complex was obtained in high yield in this way, but at longer reaction times $[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$ was the major product with $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ and $[\text{RhSn}_5\text{Cl}_{15}]^{3-}$ also isolated. Similar mixtures were obtained under milder conditions in the anaerobic "$[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$" syntheses. After \textasciitilde20 min
reaction the Rh(I) complex was still found with \([\text{RhCl}_3(SnCl_3)_5]^{3-}\), 
[\text{RhSn}_5Cl_{15}]^{3-}\) and the expected \([\text{RhCl}_2(SnCl_3)_4]^{3-}\) product. Probably a net 
rearrangement is occurring to yield a formally Rh(III) complex from 
[\text{Rh(SnCl}_3)_4(SnCl_4)]^{3-}\).

\[
[Rh(SnCl_3)_4(SnCl_4)]^{3-} \rightarrow [RhCl(SnCl_3)_5]^{3-} \quad (3.12)
\]

As in the case of \([\text{RhCl}_2(SnCl_3)_4]^{3-}\), the Rh(III) complex could decompose 
via

\[
[RhCl(SnCl_3)_5]^{3-} + Cl^- \rightarrow [RhCl_2(SnCl_3)_4]^{3-} + SnCl_3^- \quad (3.13)
\]

Interestingly, the limited data on the decomposition of \([\text{Rh(SnCl}_3)_4(SnCl_4)]^{3-}\) 
to Rh(III) complexes in CH$_3$CN indicate that the rate of decomposition is 
not affected by air (sec. 4.4). This suggests that the shift in product 
distribution under aerobic conditions noted above for the synthesis of 
[\text{RhCl}_3(SnCl_3)_3]^{3-}\) is due to oxidation of SnCl$_3^-$ and Rh(I) intermediates 
formed via reaction such as 3.6.

The isolation of \([\text{RhSn}_5Cl_{15}]^{3-}\) in some of the experiments was taken 
as indicative of the presence of \([\text{Rh(SnCl}_3)_4(SnCl_4)]^{5-}\) in solution. Several plausible routes to this complex can be proposed (note that 
"SnCl$_3^-$ + Cl$^-$" could be replaced by "SnCl$_4^{2-}\)."

\[
[RhCl(SnCl_3)_5]^{3-} + SnCl_3^- + Cl^- \rightarrow [Rh(SnCl_3)_4(SnCl_4)]^{5-} + SnCl_4 \quad (3.14a)
\]

\[
[Rh(SnCl_3)_4]^{3-} + SnCl_3^- + Cl^- \rightarrow [Rh(SnCl_3)_4(SnCl_4)]^{5-} \quad (3.14b)
\]
\[
[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-} + \text{SnCl}_3^- + \text{Cl}^- \rightarrow [\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{5-} + \text{SnCl}_4
\]  

(3.14c)

It is not possible to distinguish between these alternatives with any confidence. However, the observations at Sn:Rh ratios ≥ 5 (sec. 3.3.3) tend to rule out reaction 3.14a, at least at higher temperature when \([\text{RhCl}(\text{SnCl}_3)_5]^{3-}\) is favoured. On the other hand, both the Rh(I) complex and \([\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{3-}\) are slowly formed at ambient temperatures (ref. 91 and sec. 3.3.3). Also their composition differs by only two electrons; thus reaction 3.14c is most probable.

When the solvent system was changed from 3MHC1 to ethanol, a shift in product distribution was observed which apparently results from the decrease in \([\text{Cl}^-]\). This was reflected in the decrease in \([\text{Cl}^-]\) content of the Rh(III) product; i.e. proportionally more \([\text{RhCl}(\text{SnCl}_3)_5]^{3-}\) is formed. More specifically, if \(Y = \text{solvent}\) in the scheme shown in 3.8 and reaction 3.9 lies to the left at low \([\text{Cl}^-]\), then

\[
[\text{RhCl(solvent)}(\text{SnCl}_3)_4]^{2-} + \text{SnCl}_3^- \rightarrow [\text{RhCl}(\text{SnCl}_3)_5]^{3-}
\]  

(3.15)

would be more favourable. Alternative factors could be an increase in contribution from reaction 3.8 when \(Y = \text{SnCl}_3^-\), or from

\[
[\text{Rh}(\text{SnCl}_3)_4]^{3-} + \text{SnCl}_3^- \rightarrow [\text{Rh}(\text{SnCl}_3)_5]^{4-}
\]  

(3.16a)
The effect of reducing $[\text{Cl}^-]$ was observed also in the pronounced drop in the yield for the reaction not protected from light. This was consistent with photo-induced substitution of solvent for coordinated $\text{Cl}^-$ or $\text{SnCl}_3^-$, resulting in much more soluble solvated species (sec. 3.4). In 3M HCl the same process could result in a shift in the product distribution to species containing a lower Sn/Rh ratio.
CHAPTER IV
RESULTS (PART II)
REACTIONS OF THE COMPLEXES

4.1 Introduction

The UV-VIS solution spectra of trans-[RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ and [Rh(SnCl$_3$)$_4$-(SnCl$_4$)]$^{3-}$ were important in the elucidation of the synthetic "system". The stability of these complexes and [RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ in CH$_3$CN and 3M HCl will be examined briefly in this chapter. The stoichiometry of the solvolysis reaction in CH$_3$CN with respect to SnCl$_3^{-}$ loss has been determined. Additional effects due to addition of chloride salts and to light are noted.

In the context of the use of initial spectra, mentioned above, a key element is the time taken to obtain a spectrum relative to its rate of change. In the present systems the complexes undergo solvolysis and/or net loss of SnCl$_2$ upon dissolution in CH$_3$CN. The minimum time needed to acquire a spectrum, on the Cary 17 spectrophotometer, between 500 - 200 nm was ~200 s (45-60 s for dissolving the sample and mounting, plus ~150 s to scan 300 nm). Under conditions comparable to those described in the previous chapter (i.e. ~25°C, ~5x10$^{-4}$ M complex concentration) less than 10% change was observed in the spectra of [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ and [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{3-}$ on this 200 s time scale.

The UV-VIS spectra of the Rh(III) complexes are characterized by intense bands ($\varepsilon$>10$^3$ M$^{-1}$ cm$^{-1}$). Such high intensity is usually indicative of symmetry-allowed metal to ligand (MLCT) or ligand to metal (LMCT) charge transfer transitions. For a d$^6$ octahedral transition-metal complex with $\sigma,\pi$-donor chloride ligands, two strong LMCT bands are expected: a high
energy transition originating from the largely Cl localized σ type MO (σ-LMCT) and a lower energy one, also Cl localized, from a π type MO (π-LMCT), both terminating on a Rh-centered empty MO (e.g. σ*).

This simple picture is complicated by the presence of the σ-donor, π-acceptor SnCl₂⁻ ligands. Charge transfer from the occupied t₂g (π*) to the Sn 5d acceptor orbitals (π-MLCT) would be expected to lie at higher energy than is observable here (i.e. >200 nm)¹¹³, while the σ,π LMCT should occur at lower energies than in the absence of SnCl₃⁻ because of destabilization of the
ligand based \(\sigma, \pi\) MOs by the more reducible \(\text{SnCl}_3^-\) ligand. However, although both \(\text{SnCl}_3^-\) and Cl\(^-\) are weak \(\sigma\) donors, the \(\sigma\) energy levels may be sufficiently different to give rise to distinguishable LMCT bands. Nevertheless, the lower energy band at \(\sim 420\) nm for \([\text{RhCl}_3(\text{SnCl}_3)_3]^3^-\) (fig. 4.4 (b); see sec. 4.3) and \([\text{RhCl}_2(\text{SnCl}_3)_4]^3^-\) (fig. 4.5) is tentatively assigned as \(\pi\)-LMCT and the most intense band at \(\sim 300 - 290\) nm as \(\sigma\)-MLCT.

The exact structure of \([\text{Rh}((\text{SnCl}_3)_4(\text{SnCl}_4)]^3^-\) is not known but has been discussed previously in the context of its UV-VIS spectrum (sec. 3.2).

In the work described in the following sections, solutions containing Rh complexes were handled anaerobically, in the dark and at 25\(^\circ\)C, unless otherwise noted. The result of exposure to light was dependent on solvent and chloride concentration: the UV-VIS spectrum of a \(\sim 10^{-4}\)M solution of \([\text{RhCl}_3(\text{SnCl}_3)_3]^3^-\) in 3M HCl showed a decrease in intensity and a shift of the 305 nm band to \(\sim 315\) nm (fig. 4.2). The higher wavelength band (420 nm) did not shift but decreased in intensity. The overall impression was that the tin-containing complexes were losing \(\text{SnCl}_3^-\) in a stepwise fashion since the spectrum of \([\text{RhCl}_4(\text{SnCl}_3)_2]^3^-\) was noted during the decay process. In the absence of light no spectral changes were observed. In 0.5M HCl and CH\(_3\)CN, the 305 nm peak did not shift, but a general decrease in intensity occurred. The final spectrum in 0.5M HCl had weak peaks at \(\sim 500\) nm, 386 nm, and a more intense one at 203 nm. In CH\(_3\)CN a continuum resulted with higher energy bands obscured by SnCl\(_2\)(CH\(_3\)CN) absorbance (see sec. 4.2). The spectra of both \([\text{RhCl}_2(\text{SnCl}_3)_4]^3^-\) and \([\text{Rh}((\text{SnCl}_3)_4(\text{SnCl}_4)]^3^-\) in 3M HCl solution in the light rapidly became like that of \([\text{RhCl}_3(\text{SnCl}_3)_3]^3^-\) and then followed a similar decay. In CH\(_3\)CN solution a continuum, as noted above, was observed.
Figure 4.2  Solution UV-VIS spectra of [Me₄N]₃[RhCl₃(SnCl₃)₃] in 3M HCl, showing changes (0 → 3) due to exposure to room illumination (concentration ≈ 5 × 10⁻⁴M, time intervals 5 - 10 min).
4.2 SnCl$_2$(CH$_3$CN)

When SnCl$_2$.2H$_2$O or [SnCl$_3$][NEt$_4$] is dissolved in dry CH$_3$CN, several bands are observed in the UV spectrum below 300 nm (fig. 4.3a). Upon shaking the solution with air, the bands disappear leaving a shoulder at $\sim$225 nm of much weaker intensity (fig. 4.3b). The changes are consistent with formation of a SnCl$_2$ adduct with CH$_3$CN and its subsequent oxidation to Sn(IV)$^{139}$. The UV bands are probably red-shifted $\pi-\pi^*$ ($\sim$225 nm) and n-\(\pi^*\) (270 and 290 nm) transitions of CH$_3$CN$^{140}$, the auxochrome being SnCl$_2$.

The stoichiometry of the adduct was not determined but can be reasonably assumed to be 1:1 since many such adducts of the Lewis acid SnCl$_2$ with N- and O-donors are known$^{137,141}$. Beer's law was obeyed over the range 0.7 - 1.7x10$^{-3}$ M. The characteristic shape and intensity were useful since 'free' Sn(II) was then readily identifiable in the spectroscopic studies described below. Estimates of its concentration were made by trial and error curve subtraction, using computer routines mentioned in sec. 2.3, and these estimates are believed to be accurate to $\pm$10%.

4.3 Fac-[RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ and trans-[RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$

The spectrum of fac-[Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$] in dry CH$_3$CN exhibited rapid change for $\sim$5 min and then remained unchanged for up to 13 h after that (fig. 4.4a). The change in absorbance at 430 nm (fig. 4.4: inset) was zero-order for the most part with a $t_{1/2} = 130s$. In the presence of an 8.7-fold excess of Et$_4$NCl-H$_2$O no changes were observed. Bands due to SnCl$_2$(CH$_3$CN)
Figure 4.3  CH$_3$CN solution UV-VIS spectra of SnCl$_2$(CH$_3$CN) (a) and of (b) a similar solution during air oxidation (---) and after air oxidation (----)
Figure 4.4 CH$_3$CN solution UV-VIS spectra of [Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$]: (a) final spectrum in absence of added Et$_4$NCl·H$_2$O (——) and (b) with 8.7-fold excess of Et$_4$NCl·H$_2$O (----). unchanged with time, compared to initial spectrum in 3M HCl (-----). Inset is the change in absorbance at 430 nm vs. time for the CH$_3$CN solution spectra ([ ]$_0$ = 4.97 x 10$^{-4}$M) in the absence of added salt.
were not observed.

The spectrum of \([\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4]\cdot\text{H}_2\text{O}\) also exhibited change, although slower than for the tris(trichlorostannato)complex. Additionally, the spectrum of \(\text{SnCl}_2(\text{CH}_3\text{CN})\) grew in at \(\sim225\) nm indicating net dissociation of \(\text{SnCl}_2\), with an isosbestic being observed at 248 nm (fig. 4.5a). The resultant spectra were different when a 12- and 23-fold excess of \(\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}\) was added (fig. 4.5b,c), and only an 'approximate' isosbestic was observed between 252 - 255 nm.

The amount of \(\text{SnCl}_2(\text{CH}_3\text{CN})\) estimated by spectrum subtraction was \(\sim1\) equivalent; the estimates ranged from 0.9 to 1.3 as the added \([\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}]\) was increased from zero. Some irreproducibility was observed: in one run in the absence of \([\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}]\) only 0.6 equivalents were found and in another, with added \([\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}]\), a stable spectrum did not result after formation of 1 equivalent of \(\text{SnCl}_2(\text{CH}_3\text{CN})\), intensity gradually decreasing across the spectrum (200 - 500 nm). However, most experiments were well-behaved and the spectra remained relatively stable after formation of \(\sim1\) equivalent of \(\text{SnCl}_2(\text{CH}_3\text{CN})\).

Comparison of the resultant spectra of the complexes in the presence of comparable amounts of \(\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}\) indicates that the major products are similar (fig. 4.6). It is generally not prudent to characterize transition metal complexes by electronic spectra alone. However, attempts to isolate the products by precipitation failed to give complexes whose spectra matched those before precipitation. The overall indication on the basis of the similarity and the formation of \(\sim1\) equivalent of \(\text{SnCl}_2(\text{CH}_3\text{CN})\) is that the
Figure 4.5 CH$_3$CN solution UV-VIS spectra of [Me$_4$N]$_3$[RhCl$_2$(SnCl$_4$)$_4$]-H$_2$O (a) in absence of added Et$_4$NCl·H$_2$O (---), (b) with a 12-fold excess (----) and (c) a 23-fold excess (------) of the salt. The dotted line is the initial spectrum.
Figure 4.6  Comparison of CH$_3$CN solution UV-VIS spectra of (a) [Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$] (---) and (b) [Me$_4$N]$_3$[RhCl$_2$(SnCl$_3$)$_4$]$\cdot$H$_2$O (-----) in the absence of Et$_4$NCl$\cdot$H$_2$O; (c) (-----) and (d) (.....) with a 8.7-fold excess of Et$_4$NCl$\cdot$H$_2$O and with a 12-fold excess of Et$_4$NCl$\cdot$H$_2$O, respectively.
tetrakis(trichlorostannato)complex decomposes to give the tris(trichlorostannato)-complex. The dependence of the product spectra on [Et$_4$NCl-H$_2$O] is consistent with replacement of $\sigma$, $\pi$ donor Cl$^{-}$ by $\sigma$ donor, $\pi$ acceptor CH$_3$CN. This would lead to stabilization of the ligand-based $\pi$ type MOs and result in a blue-shift of the $\pi$-LMCT band, while the higher energy $\sigma$-LMCT band would be relatively insensitive to the substitution. Scheme 4.1 is consistent with the observations.

Scheme 4.1  Reaction of [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ with CH$_3$CN.

The tin could be lost from [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ by dissociation of SnCl$_3^{-}$ (path b) or by "de-insertion" (path c). The rapid reaction of [RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ with CH$_3$CN is consistent with the previous observation that the fac-complex rapidly and reversibly exchanges the three Cl$^{-}$ ligands for Br$^{-}$ in hydrobromic acid. This was believed to be due to the strong trans effect of SnCl$_3^{-}$. Not surprisingly, dissolution of fac-[Me$_4$N]$_3$[RhCl$_3$(SnCl$_3$)$_3$] in CH$_3$CN with
excess Et₄NCl·H₂O results in a spectrum very similar to that observed for a 3M HCl solution (fig. 4.4). Interestingly the same is not true for [Me₄N]-[RhCl₂(SnCl₃)₄]·H₂O; the spectrum reported in 3M HCl solution is close to that in CH₃CN after losing one equivalent of Sn (fig. 3.3 vs fig. 4.5), implying a rapid loss of ligand in 3M HCl.

The stereochemistry of the reaction

\[
\text{trans-[RhCl}_2(\text{SnCl}_3)_4]^{3-} + \text{CH}_3\text{CN} \rightarrow \text{fac-[RhCl}_3(\text{SnCl}_3)_3]^{3-} + \text{SnCl}_2(\text{CH}_3\text{CN}) \quad (4.1)
\]

is not expected on the basis of trans effect alone, an initially formed mer-[RhCl₃(SnCl₃)₃]⁻ complex, before losing one of the mutually trans SnCl₃⁻ ligands, could have isomerised rapidly to the more stable fac-isomer.

The rate of decrease at 420 nm of the CH₃CN solution UV-VIS spectrum of [RhCl₂(SnCl₃)₄]³⁻ increased with increasing [Et₄NCl·H₂O] (fig. 4.7). Examination of the absorbance vs. time plots revealed a small 's' shaped component at 6 - 7 t₁/₂ s. At the highest [Et₄NCl·H₂O] shown in fig. 4.6, this occurs after 5000s. Good ln(A-A₀) vs time plots (r > .9995 for initial 12 pts.) covering > .4t₁/₂s were obtained for the data before the s-shaped component (t. 4.1). The values of A₀ were estimated using the method of Kezdy-Swinbourne. Extrapolation to t₀ gave consistent A₀ values from which ε₄₂₀nm was found to be 16840 ±160 M⁻¹ cm⁻¹. However, at the higher [Et₄NCl·H₂O] the calculated fit between 3000 - 6000 s underestimates the observed data. A better fit to this region was obtained when the first two points were dropped from the analysis, but the extrapolated A₀ value was higher (solid line, fig. 4.7).
Figure 4.7 Plots of absorbance at 420 nm vs. time for the decomposition of trans-$\text{[Me}_4\text{N}]_3\text{[RhCl}_2\text{(SnCl}_3\text{)}_4\text{]}\cdot\text{H}_2\text{O}$ in $\text{CH}_3\text{CN}$: (⊙) = run 1, (□) = run 2, (▽) = run 3. Dashed lines are first-order fits to the first 12 data points. Solid line: see text. Run #s refer to table 4.1.

The second 'step', readily monitored at 420 nm, did not give marked spectral changes below 350 nm. Since this step did not appear to be important in the estimation of $\text{SnCl}_2(\text{CH}_3\text{CN})$ and the overall appearance of the spectrum after the first 'step', it was not investigated further.
Table 4.1 Pseudo-first order rates of decomposition of $[\text{Me}_4\text{N}]_3[\text{RhCl}_2(\text{SnCl}_3)_4] \cdot \text{H}_2\text{O}$ in CH$_3$CN

<table>
<thead>
<tr>
<th>run</th>
<th>$[\text{Rh(III)}]_0$ (x10$^4$), M</th>
<th>$[\text{Et}_4\text{NCl-H}_2\text{O}]_0$ (x10$^4$), M</th>
<th>$k_{\text{obs}}$ (x10$^4$ s$^{-1}$)</th>
<th>$t_\frac{1}{2}$ (s)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>0.00</td>
<td>4.79</td>
<td>1449</td>
<td>.9996</td>
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<tr>
<td>2</td>
<td>4.28</td>
<td>49.9</td>
<td>6.28</td>
<td>1104</td>
<td>.9998</td>
</tr>
<tr>
<td>3</td>
<td>4.27</td>
<td>99.9</td>
<td>10.6</td>
<td>654</td>
<td>.9996</td>
</tr>
</tbody>
</table>

Comparison of the $t_\frac{1}{2}$ of the initial 'step' with the estimate of the time required to acquire an initial spectrum indicates that only $\sim$7% reaction would have occurred in the absence of added $[\text{Et}_4\text{NCl-H}_2\text{O}]$. The dependence of the rate on the chloride concentration probably accounts for the lack of observation of $[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ in 3M HCl. The limited data for the dependence of the rate on $[\text{Et}_4\text{NCl-H}_2\text{O}]$ suggest reaction via a chloride independent pathway and a chloride dependent pathway, i.e. $k_{\text{obs}} = k_1 + k_2[\text{Cl}^-]$, which is indicative of substitution via associative type processes involving both solvent and Cl$^-$ as incoming nucleophiles.$^{142}$

4.4 $[\text{Rh(SnCl}_3)_4(\text{SnCl}_4)]^{3-}$

The material used in these experiments was $[\text{Et}_4\text{N}]_3[\text{Rh(SnCl}_3)_4(\text{SnCl}_4)] \cdot (\text{Et}_4\text{NCl})_{0.5}$ recrystallized from CH$_3$CN. The recrystallization results in replacement of an indeterminate amount of occluded Et$_4$NCl (sec. 2.1.5.3). It was assumed that the molecular weight was that of the unrecrystallized
material, which leads to a $<3\%$ error assuming that at most half the occluded salt was replaced and is considered negligible.

The complex decomposes in CH$_3$CN more slowly than [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$ and, like the latter complex, the product spectra vary with added Et$_4$NCl·H$_2$O (fig. 4.8). In the absence of added Et$_4$NCl·H$_2$O, ~2 equivalents of SnCl$_2$(CH$_3$CN) were found by subtraction of the latter's spectrum. The estimate increased to ~3 equivalents with added chloride salt. In both cases approximate isosbestic points were observed at ~252, 270 and 335-344 nm. Use of Ph$_4$AsCl·H$_2$O in place of Et$_4$NCl·H$_2$O did not appreciably change the spectrum; neither did a 200-fold excess of H$_2$O in the absence of added chloride salt.

The complex was slightly soluble in 3M HCl, but decomposed rapidly. The product spectrum had $\lambda_{\text{max}}$ values of 314 and 424 nm with an intensity ratio of 18.1 ($\varepsilon$ values could not be reliably estimated) which is close to that reported for [RhCl$_4$(SnCl$_3$)$_2$]$^{3-}$: 320 nm and 432 nm in a ratio of 18.8$^9$. The difference was consistent with the presence of some [RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$. In CH$_3$CN solution with ~9-fold excess of chloride salt, the principal $\lambda_{\text{max}}$ is at ~315 nm and 3 equivalents of SnCl$_2$(CH$_3$CN) were found, implying that reaction 4.2 occurs.

$$[\text{Rh(SnCl$_3$)$_4$(SnCl$_4$)}]^{3-} \rightarrow [\text{RhCl$_4$(SnCl$_3$)$_2$}]^{3-} + 3\text{SnCl$_2$(CH$_3$CN)} \quad (4.2)$$

However, the apparent extinction coefficient in CH$_3$CN at 315 nm is ~44% lower than expected for [RhCl$_4$(SnCl$_3$)$_2$]$^{3-}$ (based on $\varepsilon = 37000$ M$^{-1}$ cm$^{-1}$ in 3M HCl)$^9$, which means that the estimate of SnCl$_2$(CH$_3$CN) includes contributions from sources other than reaction 4.2. The results for no added chloride salt can be considered a similar case. The spectrum resembles those seen in the case of
Figure 4.8 CH₃CN solution UV-VIS spectra of [Et₄N]₃[Rh(SnCl₃)₄(SnCl₄)]·(Et₄NCl)₀.₅ after decomposition in presence of various amounts of added chloride salts: (a) no added Et₄NCl·H₂O (---), (b) 8.8-fold excess of Et₄NCl·H₂O (----), (c) 8.8-fold excess of Ph₄AsCl·H₂O (-----) and (d) 12-fold excess of Et₄NCl·H₂O (-----). The dotted line is the initial spectrum (*indicates peaks due to Ph₄As⁺; note that (c) and (d) are coincident at higher λ).
[RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ and [RhCl$_2$(SnCl$_3$)$_4$]$^{3-}$, and the 2 equivalents observed matches the stoichiometry of reaction 4.3.

$$[\text{Rh(SnCl}_3)_4]^{4-} \rightarrow [\text{RhCl}_3(\text{SnCl}_3)_3]^{3-} + 2\text{SnCl}_2(\text{CH}_3\text{CN}) \quad (4.3)$$

Again, the apparent extinction coefficients above 260 nm are low.

The observations can be rationalized by noting that [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{3-}$ could decompose in at least two ways. As noted in sec. 3.6, rearrangement to [RhCl(SnCl$_3$)$_5$]$^{3-}$ followed by stepwise loss of SnCl$_3^-$ or SnCl$_2$ could occur (the "Rh(III) route"). The proposed rearrangement would involve a net Cl$^+$ transfer from SnCl$_4$ to Rh(I) via a halide bridged intermediate such as:

Such bridges are known or have be proposed as intermediates in halide exchange studies. Alternatively, the backward step of reaction 3.7 could occur (the "Rh(I) route"): 

$$[\text{Rh(SnCl}_3)_4(\text{SnCl}_4)]^{3-} \rightarrow [\text{Rh(SnCl}_3)_4]^{3-} + \text{SnCl}_4 \quad (4.4)$$

followed by,

$$[\text{Rh(SnCl}_3)_4]^{3-} + n\text{CH}_3\text{CN} \rightleftharpoons [\text{Rh(CH}_3\text{CN})_n(\text{SnCl}_3)_4-n]^{(3-n)^-} + n\text{SnCl}_3^- \quad (4.5)$$
or

\[
[Rh(SnCl_3)_4]^{3-} + nCl^- \rightleftharpoons [RhCl_n(SnCl_{4-n})]^{3-} + nSnCl_3^- \tag{4.6}
\]

or

\[
[Rh(SnCl_3)_4]^{3-} + nCH_3CN \rightleftharpoons [RhCl_n(SnCl_3)]^{3-} + nSnCl_2(CH_3CN) \tag{4.7}
\]

In CH\(_3CN\) these equilibria would tend to favour formation of SnCl\(_2(CH_3CN)\). Empirically, assuming that the overall intensity of bands due to rhodium(I) (and (III)) complexes with SnCl\(_3^-\) was proportionate to the number of SnCl\(_3^-\) ligands, formation of labile Rh(I) species would account for the decrease in apparent extinction coefficients above \(\approx 260\) nm without apparent decrease in SnCl\(_2(CH_3CN)\).

The change in absorbance at 378 nm was found to follow first or pseudo-first order kinetics (table 4.2). Plots of ln(\(A-A_{\infty}\)) vs. \(t\) gave good fits with \(r \geq 0.9993\) for 20 points covering at least 70% reaction, using estimates of \(A_{\infty}\) calculated by the Kezdy-Swinbourne method. By extrapolation to \(t_0\) an estimate of \(\epsilon_{378}\) was calculated to be 74210 \(\pm\) 5745 M\(^{-1}\) cm\(^{-1}\) which agrees well with a previous estimate (sec. 2.1.5.3). The agreement in estimated \(\epsilon\) values between runs 1 and 2 indicates that \([Rh(SnCl_3)_4(SnCl_4)]^{3-}\) obeys Beers Law over the range 0.39\(\times\)10\(^{-4}\) to 2.80\(\times\)10\(^{-4}\)M. There was little effect due to air on the rate but the rates increased with added chloride salt (table 4.2). As noted in the previous section, the form of the dependence, i.e. \(k_{obs} = k_1 + k_2[Cl^-]\), suggests an associative type mechanism with solvent and Cl\(^-\) as incoming
Table 4.2  Pseudo-first order rates of decomposition of $[\text{Et}_4\text{N}]_3\text{[Rh(SnCl}_3\text{)}_4\text{(SnCl}_4\text{)}] \cdot (\text{Et}_4\text{NCl})_{0.5}$ in CH$_3$CN.

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<th>$k_{\text{obs}}$ (x$10^4$s$^{-1}$)</th>
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<td>7149</td>
<td>.9999</td>
</tr>
</tbody>
</table>

† Ph$_4$AsCl-H$_2$O; ‡ H$_2$O; * air.

nucleophiles. The data are limited and some additional small effect of varying the cation is indicated (run 3 vs. 5).

4.5 Conclusion

The principle reaction of trans-$[\text{RhCl}_2(\text{SnCl}_3)_4]^{3-}$ or $[\text{Rh(SnCl}_3)_4-\text{(SnCl}_4\text{)}]^{3-}$ in freshly prepared CH$_3$CN solutions in the dark was found to involve a net loss of SnCl$_2$. The rates, under conditions similar to those used in the preceding chapter, were slow enough for the use of initial UV-VIS solution spectra in characterization. Less than 7% decomposition is expected during acquisition of a 300 nm wide spectrum on the Cary 17.
Also, although the reactions were followed only by UV-VIS, some interesting observations arise concerning the formation of the Rh(III) products and their stereochemistry.

It is well known that SnCl$_3^-$ has a strong trans influence and effect $^{76,109}$. The stability of the fac-complex and rapid exchange of ligands trans to SnCl$_3^-$ attests to this. In CH$_3$CN, trans-[RhCl$_2$-(SnCl$_3$)$_4$]$^{3-}$ loses SnCl$_2$ to give fac-[RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ presumably with a concomittant isomerization step. The interesting point arises in comparison to the presumed "Rh(III) rate" for decomposition of [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{3-}$. In the presence of added Cl$^-$ some [RhCl$_4$(SnCl$_3$)$_2$]$^{3-}$ is formed, which is difficult to rationalize unless regiospecific reactions bypass trans-[RhCl$_2$-(SnCl$_3$)$_4$]$^{3-}$ and fac-[RhCl$_3$(SnCl$_3$)$_3$]$^{3-}$ products. A possible precedent is the reversible insertion of SnX$_2$ into fac-Fe(CO)$_3$(PPh$_3$)$_2$ $(X,Y =$ halides) $^{144,145}$ yielding mer-Fe(CO)$_3$(PPh$_3$)$_2$(SnX$_2$Y), although it has not been established if the phosphine ends up trans to halide or not.
Chapter V
RESULTS (PART III)
HYDROGENATION OF MALEIC AND FUMARIC ACIDS

5.1 Introduction

The ultimate aim of the present work was to study catalysis by Rh-Sn complexes. An in situ approach was taken in this part rather than the intended one using defined precatalysts, since an understanding of the synthetic problem was reached late in the investigation.

Red-orange solutions of RhCl$_3$·3H$_2$O and SnCl$_2$·2H$_2$O in 3M HCl, at 80°C, with an excess of fumaric (FA) or maleic acid (MA) were found to absorb H$_2$ (450 mmHg) at conveniently measurable rates. When a 10-fold excess of olefin and Sn(II)/Rh(III) ratio of 3 or 6 was used, total uptakes corresponded to conversion of MA or FA to succinic acid (SA) plus reduction of Rh(III) to Rh(I). Hydration of olefin to malic acid (MLA) was competitive with the metal-centered processes. In contrast, a similar system without the added SnCl$_2$·2H$_2$O was previously found to yield a stoichiometric uptake corresponding to the reduction of Rh(III) to Rh(I) only.

\[
\begin{align*}
\text{Rh(III)} + \text{H}_2 & \rightleftharpoons \text{Rh(III)H}^- + \text{H}^+ \quad (5.1) \\
\text{Rh(III)H}^- & \longrightarrow \text{Rh(I)} + \text{H}^+ \quad (5.2) \\
\text{Rh(I)} + \text{MA} & \text{fast} \rightarrow \text{Rh(I)(MA)} \quad (5.3)
\end{align*}
\]
Reduction to Rh° was precluded by stabilization of Rh(I) by MA (eqn. 5.3) as a yellow complex (353 nm ($\varepsilon = 420 \text{ M}^{-1} \text{ cm}^{-1}$), 425 nm ($\varepsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$) in 3MHC1) of unknown stoichiometry.

The aim of the work presented in this chapter was to gain a preliminary understanding of the stoichiometry and stereochemistry of the modified system and thus mechanistic details. The hydrogenation was found to be very sensitive to the olefin concentration relative to that of rhodium. In the following discussions high [olefin] refers to experiments where [olefin] = 0.33M; and low [olefin] = 0.1M. [Rh]_{total} was always 0.01M.

5.2 Stoichiometry and kinetics at low [MA].

In the presence of 6-and 3-fold excesses of SnCl₂·2H₂O, uptakes were linear at least to 6 H₂/Rh. Within experimental uncertainties no difference was observed in rate between experiments in the light and those with total exclusion of light (table 5.1; fig. 5.1). A total uptake of ~9.9 H₂/Rh was observed with a 3-fold excess of SnCl₂·2H₂O and ~10.5 H₂/Rh with a 6-fold excess. Precipitated metal was present only near the end of the uptake. The resultant solution was filtered and extracted with ether (see sec. 2.2.8). The IR of the white ether evaporate contained bands due to SA but none due to MA or FA.

The product mixture of a run with Sn/Rh = 3, stopped at 5.6 H₂/Rh uptake, was also studied. The organic products were worked up as above. The IR of the ether evaporate indicated a mixture of FA and SA; this was
Table 5.1 Kinetic data at 80°C for the Rh/Sn/H₂/MA system in 3M HCl:

\[
\text{H}_2 \text{ press. } = 450 \text{ mmHg; } [\text{Rh}]_{\text{total}} = 0.01 \text{M, } [\text{MA}] = 0.10 \text{M.}
\]

<table>
<thead>
<tr>
<th>[Sn] (M)</th>
<th>[H₂] (x10⁴M)</th>
<th>rate of uptake (x10⁶Ms⁻¹)</th>
</tr>
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</table>

† in the absence of light.

confirmed by 80 MHz \(^1\)H NMR of an acetone-d₆ solution which in addition revealed the presence of a small amount of MA (fig. 5.2). Assuming SA to be formed only by hydrogenation, then the relative amounts of FA, MA and SA can be estimated from NMR integrations. Accordingly, based on initially 10 equivalents of MA, there were 5.6 SA, 2.5 FA and 0.3 MA after an uptake of 5.6 H₂/Rh leaving a 'residual' of 1.6 equivalents.

The total uptake, with a 3-fold excess of SnCl₂·2H₂O, was \(~9.9\) H₂/Rh instead of an expected uptake of \(~11\) H₂/Rh corresponding to hydrogenation of 10 equivalents of MA plus reduction of Rh(III) to Rh(I). The discrepancy was smaller at higher [SnCl₂·H₂O]. Hydration of MA or FA to MLA (sec. 5.4) and reduction by Sn(II) + 2H⁺ (sec. 5.5) also occur under these conditions and could explain the short-fall in total uptake, which could partially account for a difference of 1.6 H₂/Rh at 5.6 H₂/Rh uptake. However, \(~1\) equivalent is still unaccounted for. This may be attributable to the formation of the yellow Rh(I)(MA) complex reported previously since it is not extract-
able under these conditions (sec. 5.4). The UV-VIS spectrum of the uptake solution (fig. 5.3) had a $\lambda_{\text{max}}$ at 428 nm ($\varepsilon = 1880 \text{ M}^{-1} \text{ cm}^{-1}$). Addition of Et$_4$NCl·H$_2$O to similarly prepared solutions gave orange precipitates whose IR contained bands attributable principally to [Et$_4$N]$_3$[RhCl$_2$(SnCl$_3$)$_4$]. Bands due to carboxylate or olefinic groups were not observed. The observations were

![Graph](image)

**Figure 5.1** $\text{H}_2$ uptakes for the Rh/Sn/H$_2$/MA system in the light (⊙) and dark (▽) in 3M HCl solution at 80°C. [Rh] = 0.01M, [MA] = 0.10M and [Sn] = 0.03M.
consistent with the presence of some Rh\(^{I}(MA)\) but in 3M DCl/D\(_{2}\)O only \(^1\)H resonances due to FA, MA, SA and HDO were observed after 10800 s of reaction. Resonances due to coordinated olefin could be obscured by HDO or exchange.

Hydrogenation of a solution containing a 3-fold excess of SnCl\(_2\)·H\(_2\)O or SnCl\(_4\)·5H\(_2\)O but no olefin resulted in rapid formation of metal. With a 6-fold excess no metal was observed, and total uptakes of between 0.6 and 0.8 H\(_2\)/Rh were then measured. Addition of Et\(_4\)NCl·H\(_2\)O to the resultant dark red-orange/purple solutions (\(\lambda_{\text{max}} = 470\) nm (\(c = 3800\) M\(^{-1}\) cm\(^{-1}\))) yielded a pale-yellow precipitate. Analysis for C, H and N, and the IR spectrum, revealed
that the precipitate was primarily \([\text{Et}_4\text{N}]_3[\text{RhSn}_5\text{Cl}_{15}]\). Additionally, the pale-yellow precipitate gave a transient purple \(\text{CH}_3\text{CN}\) solution. These observations were all consistent with the reduced solution species being \([\text{Rh(SnCl}_3)_4-(\text{SnCl}_4)]^5^-\). Presumably the less than stoichiometric uptake was indicative of the partial reduction of Rh(III) to Rh(I) by Sn(II) prior to reduction by \(\text{H}_2\), which is expected from the observations in Chapter 3. The reason for metal formation at the lower Sn/Rh ratio is probably due to the presence of non-tin-containing Rh complexes, also consistent with the previous observations.

Substitution of Sn(IV) for Sn(II) in the hydrogenation experiments

![Graph](image_url)

**Figure 5.3** UV-VIS spectra of uptake solutions. Solid line is MA/H\(_2\)/HCl system and the dashed line is the FA/D\(_2\)/DCl system (olefin] = 0.10M, \([\text{Rh}] = 0.01M\).
Table 5.2 Kinetic data at 80°C for the Rh/Sn/H$_2$(D$_2$)/olefin system in 3M DC1/D$_2$O:

H$_2$(D$_2$) press. = 450 mmHg; [Rh]$_{total}$ = 0.01M, [Sn] = 0.03M.

<table>
<thead>
<tr>
<th>[MA] (M)</th>
<th>[FA] (M)</th>
<th>[gas] (x10$^4$M)</th>
<th>rate of uptake (x10$^6$ Ms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>-</td>
<td>3.60</td>
<td>1.1</td>
</tr>
<tr>
<td>0.10</td>
<td>-</td>
<td>3.60*</td>
<td>1.1</td>
</tr>
<tr>
<td>-</td>
<td>0.10</td>
<td>3.60*</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* gas = D$_2$

with MA resulted in a stoichiometric uptake to form the yellow Rh$^I$(MA) complex.

5.3 Deuteration studies at low [olefin]

Hydrogenation of MA at [Sn] = 0.03M was repeated in 3M DC1/D$_2$O. Uptakes using D$_2$ with both MA and FA were also performed. The rates (R) were nearly identical in the deuterated solvent, the average $R_H/R_D$ value being 1.39 (tables 5.1, 5.2). The reactions were stopped at uptakes of 4.9 to 6.9 H$_2$(D$_2$)/Rh, and the products were analysed as described in sec. 5.2. The IRs of the ether evaporates contained bands due to FA and bands indicating a mixture of di- and tetra-deuterated isomers of SA$^{146}$. No single isomer appeared to be predominant whether using MA or FA substrates.

Incorporation of deuterium into SA was also confirmed by $^1$H NMR. At 80 MHz or 100 MHz an asymmetric peak was observed at $\sim$2.4 ppm in DMSO-d$_6$, the position expected for methylene resonances of SA. At 400 MHz this was
resolved into two parts, slightly upfield from undeuterated succinic acid (fig. 5.4). The upfield shift indicates that replacement of $^1$H by $^2$H was shielding. The upfield shift on replacement of $^1$H by $^2$H has been previously noted in deuterated styrenes and vicinal groups. Increasing deuteration was found to lead to increasing upfield shift, which is assumed true here also. The sharper low field peak was assigned as the central portion of the $\text{AB}_2$ (or $\text{ABB}'$) pattern expected for mono-deutero SA. This approximates a triplet at $J_{\text{AB}}/\Delta \nu = 1$ (1:10:1 at $J_{\text{AB}}/\Delta \nu = 148$), which is believed to be the case here. The more intense higher field peak was assigned to symmetrically disubstituted species, which were expected to be the principal isomers. The unsymmetrically disubstituted and the trisubstituted species resonances overlap these but are probably minor.

The relative amount of mono-deutero SA was smaller in the MA/D$_2$/DCl/D$_2$O system than in the MA/H$_2$/DCl/D$_2$O one. This indicated that at least some of the H in the product originated from the gas phase. Notably, some mono-deutero SA was present in the MA/D$_2$/DCl/D$_2$O system; for FA/D$_2$/DCl/D$_2$O the proportion was higher. The 'additional' H cannot solely result from traces in the DCl/D$_2$O or from H$_2$O introduced with the hydrated starting materials since these should be swamped by DCl/D$_2$O. Probably $\beta$-elimination from alkyl intermediates was the source. Some unsymmetrically disubstituted SA
Figure 5.4 400 MHz $^1$H NMR spectrum of the deuterated products from hydrogenation of MA (expanded SA methylene region). Solid line is of product from MA/H$_2$/DCl/D$_2$O system. The dashed line is that from the MA/D$_2$/DCl/D$_2$O system. The SA methylene peak (dotted) is for reference.
would be expected, as well as isomerization of and deuterium incorporation into

\[
\begin{align*}
&\text{Rh} - \text{D} - \text{C} - \text{H} \\
&\text{Rh} - \text{C} - \text{A} - \text{H} \\
&\text{Rh} - \text{C} - \text{A} - \text{H}
\end{align*}
\]

the substrate. Attempts to use the \(^1\text{H}\) NMR integration to estimate the product distribution for the MA/D\(_2\)/DC\(_1\)/D\(_2\)\(_0\) system resulted in high estimates of the 'missing' component compared with the HCl/H\(_2\)O system, even using corrections for the presence of mono-deutero SA. This would be expected if deutero-FA or deutero-MA were present. Similar errors were seen for the FA/D\(_2\)/DC\(_1\)/D\(_2\)\(_0\) system but the error was particularly high for the MA/H\(_2\)/DC\(_1\)/D\(_2\)\(_0\) one, consistent with the observed increase in mono-deutero SA in the latter. Although the former system showed more monodeuteroproduct than for the MA/D\(_2\)/DC\(_1\)/D\(_2\)\(_0\) system, the lower error could be due to the stronger complexing ability of the isomerization product (deutero-MA). Deuterium is only slowly incorporated into SA in 3MDC\(_1\)/D\(_2\)\(_0\) at 80°C in the absence of metal catalysts, so is not considered to affect the above observations.

5.4 Stoichiometry and kinetics at high [MA]

The H\(_2\) uptakes at [Sn(II)] = 0.0, 0.03 and 0.06M were characterized by an initial rapid uptake followed by a close to linear region of slower uptake (fig. 5.5). The initial uptakes were essentially non-linear, the rates
decreasing somewhat with time. The rates of \( \text{H}_2 \) uptake for the later linear region were ca. 20% of those at the lower [olefin] (table. 5.3). There was no marked dependence of rate on [Sn(II)]. The red-orange solutions became yellow approximately at the end of the initial region (indicated in fig. 5.5 by y=).

---

Figure 5.5 \( \text{H}_2 \) uptakes for the Rh/H\(_2\)/MA system and Rh/Sn/H\(_2\)/MA system at high [olefin] in 3M HCl at 80°C. [Rh] = 0.01M, [MA] = 0.33M. [Sn] = 0.0 (O), 0.03 (O), 0.06 (∇). ( 'y=': see text)
Table 5.3 Kinetic and spectroscopic data for the Rh/Sn/H₂/MA system in 3M HCl: 
H₂ press. = 450 mmHg, [Rh] = 0.01M, [MA] = 0.10M.

<table>
<thead>
<tr>
<th>[Sn] (M)</th>
<th>rate of uptake (x10⁷Ms⁻¹)</th>
<th>quench time (x10⁻³s)</th>
<th>λ_max (nm)</th>
<th>ε (M⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.8</td>
<td>136</td>
<td>354</td>
<td>436</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>422</td>
<td>182</td>
</tr>
<tr>
<td>0.03</td>
<td>3.1</td>
<td>156</td>
<td>355</td>
<td>423</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>424</td>
<td>180</td>
</tr>
<tr>
<td>0.06</td>
<td>2.8</td>
<td>93</td>
<td>355</td>
<td>436</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>428</td>
<td>186</td>
</tr>
</tbody>
</table>

This colour change occurred at later times as [Sn] increased. The spectra of the yellow solutions were very similar to that reported for the yellow Rh⁷(MA) complex²⁸ (table 5.3).

Shortly after the colour change, white precipitate formed, which was characterized by IR and ¹H NMR as FA with a trace of SA. The soluble organic products were extracted with ether as described above. Monitoring by UV-VIS revealed that the yellow complex was not extracted into the ether. The IR of the ether evaporates indicated a mixture of FA and SA, which was confirmed by ¹H NMR. Additionally, the resonances probably due to MLA were observed (see below) in acetone-d₆ solution at δ = 4.82 ppm (t) and δ = 2.93 (m). An alternative assignment could be chloro-SA however, its characteristic band at 674 cm⁻¹ was absent in the IR.

Based on the precipitate yield (33%) and the ¹H NMR integrations
(corrected for inefficient extraction of MLA - sec. 2.2.8), an attempt was made to determine the product distribution for the case where \([\text{Sn(II)}] = 0.03\text{M}\). The assumption that SA was formed only by hydrogenation led to a large proportion of "missing" substrate. An improved balance was obtained assuming the total SA was equal to the uptake\(6.8\) minus \(1\ \text{H}_2/\text{Rh}\) for reducing \(\text{Rh(III)}\) to \(\text{Rh(I)}\) plus 3 equivalents from direct reduction by \(\text{Sn(II)} + 2\text{H}^+\) (sec. 5.5). The product distribution from 33 equivalents of MA was: 13.3 FA, 5.3 MLA and 8.8 SA. This left 4.6 equivalents unaccounted for. Included in this quantity would be the MA in the unextracted \(\text{Rh}^+(\text{MA})\) complex. The actual amount of MLA was the least accurately known, so some of the 4.6 equivalents may be accountable as error in determining the MLA.

The high [MA] appeared to favour the formation of the stable \(\text{Rh}^+(\text{MA})\) complex. However, the effect is sensitive to the order of mixing reagents. Prehydrogenation of a solution containing a 6-fold excess of Sn(II) over Rh(III) before addition of MA, as described at the end of sec. 5.2, led to a markedly different uptake. Within \(\sim120\text{s}\) of addition of a 30-fold excess of MA, the red-purple solution became red-orange. A linear uptake at a rate of \(2.6 \times 10^{-6}\ \text{Ms}^{-1}\) was observed. However, after an uptake of only 6.5 \(\text{H}_2/\text{Rh}\) the rate increased slightly and the solution darkened to opaque red-brown. Metal was clearly visible at 9.9 \(\text{H}_2/\text{Rh}\) uptake, a surprising observation.

The timing of the metal precipitation is interesting. Metal was observed at \(\sim3000\text{s}\) in the experiment involving prehydrogenation without olefin; this time coincides approximately with the transition to a slow linear uptake and yellow solution observed in the other experiments at
high [MA]. In the latter experiments, 1.5 - 7.5 equivalents of olefin would have been consumed depending on the extent of reduction by Sn(II) + 2H⁺, and formation of Rh⁺(MA) and MLA. In the former, ~9 - 10 equivalents would have been consumed principally by hydrogenation. In the absence of Rh/Sn, the rate constant for the disappearance of MA due to isomerization to FA and hydration to MLA was estimated to be 5.1x10⁻⁵ s⁻¹, assuming pseudo-first order decay. The estimate was based on product analysis by ¹H NMR of the ether evaporate from ether extraction of a 0.33M MA solution in 3M HCl that was heated at 80°C for 86400s. At [MA]₀ of 0.33M approximately 9 equivalents are left at 2800s and 4.5 equivalents MA at ~39000s. The correspondence between the two sets of figures suggests that the behaviour of the Rh/Sn system at high [MA] is strongly affected by differences between MA and FA substrates. The most obvious difference would be the stronger binding of MA than FA to a rhodium complex.²⁵,²⁶,¹⁵⁰,¹⁵¹

The cis-isomer (MA) is less sterically demanding than the trans-isomer (FA) when coordinated as a single-faced π-acceptor ligand. Steric differences would also be reflected in relative reactivity towards Rh complexes, and in an opposite sense when the olefin is a leaving group. It is difficult to assess electronic differences. The olefinic ligand in Fe(CO)₃(PPh₃) (methylmaleate) has the carboxylate groups oriented perpendicular to each other such that only one group can conjugate to the double bond.¹⁵² Similar effects with MA clearly would be less, but its π-acceptor properties could be less than those of FA. The net effect of the differences is observed in the failure of FA to stabilize Rh(I) against hydrogenation to metal in DMA, while MA does so.²⁵,²⁶
Further discussion on mechanistic inferences from the data at high [MA] will be deferred until sec. 5.6.

5.5 Reduction in the absence of H₂.

Solutions of SnCl₂·2H₂O in 3MHCl at 80°C with, and without, added RhCl₃·3H₂O or SnCl₄·5H₂O were found to reduce FA or MA to SA under an argon atmosphere. The concentration of Sn(II) was typically 0.055M and [olefin] from 0.0099M to 0.0267M. When added, [Rh(III)] and [Sn(IV)] were 0.0091M. Organic products were extracted with ether as described in sec. 5.2, and examined by IR and ¹H NMR. There were no noticeable differences with exclusion of light from Rh-containing solutions.

The reduction of MA in the presence of Sn(II) alone was slower than when Rh(III) was present (table 5.4). The initial dark red-orange colour of the Rh-containing solutions changed to lighter orange over the first 2500s, remaining essentially constant thereafter. Addition of Et₄NCl·H₂O to the orange solutions before extraction with ether yielded an orange or yellow-orange precipitate. IR and CH₃CN solution UV-VIS spectra showed the solid to be predominantly [Et₄N]₃[RhCl₂(SnCl₃)₄]. Yield was ~65% assuming this species only. Carboxylate or olefinic functional group absorbances were absent in the IR.

The loss of solution colour in the early part of the reaction is suggestive of a decrease in the concentration of the Rh(I) species [Rh(SnCl₃)₄(SnCl₄)]⁵⁻ believed to be present initially in solution under these conditions (sec. 5.2). The finding of Rh(III) and no Rh(I) complexes after reaction was consistent with the net reduction of the olefin by Rh(I) with a concomitant oxidation to Rh(III). This point will be returned to later.
Table 5.4 Extent of reduction of MA to SA at various times with net oxidation of Sn(II) to Sn(IV) in 3M HCl.

<table>
<thead>
<tr>
<th>[Sn(II)] (x10^2 M)</th>
<th>[Rh(III)] (x10^2 M)</th>
<th>[MA] (x10^2 M)</th>
<th>[SA]^a (x10^2 M)</th>
<th>% conversion</th>
<th>time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.55</td>
<td>-</td>
<td>1.98</td>
<td>0.13</td>
<td>6.5</td>
<td>8100</td>
</tr>
<tr>
<td>5.33</td>
<td>0.91</td>
<td>1.98</td>
<td>0.29</td>
<td>14.6</td>
<td>7200</td>
</tr>
<tr>
<td>5.30</td>
<td>0.91</td>
<td>1.98</td>
<td>0.34</td>
<td>17.1</td>
<td>10800</td>
</tr>
<tr>
<td>5.72</td>
<td>0.91</td>
<td>1.98</td>
<td>0.32</td>
<td>16.2</td>
<td>12300</td>
</tr>
</tbody>
</table>

a. From ^1H NMR integration, uncorrected for MLA.

The reduction was also examined in 3M DCl/D_2O which offered an opportunity to follow the formation of SA directly. For example, in the absence of Rh the reduction of FA was followed (fig. 5.6). At 100 MHz a resonance ~4 ppm upfield from FA was observed. Broader than the methylene resonance of SA, it indicated deuteration at the methylene positions. At 400 MHz this resonance was resolved into two peaks identical in relative positions to those observed in the hydrogenation experiments described in sec. 5.3 (i.e. fig. 5.4). It was notable that the same pattern was observed in the absence of Rh (fig. 5.7).

Estimated conversions of MA/FA → SA in 3M DCl/D_2O are summarized in Table 5.5. Relative to the 3MHCl system, values are overestimated due to the simplistic assumption that only diddeutero SA is formed. Even so, com-
Figure 5.6 $^1$H NMR monitoring of the reduction of FA by Sn(II) in the presence of Sn(IV), in 3M DCl/D$_2$O. (run 2, table 5.5).
Figure 5.7 Expansion of SA methylene region of the $^1$H NMR spectrum (400 MHz) of the same sample referred to in fig. 5.6.
parisons within the table are qualitatively valid. Conversions are lower at comparable times in the absence of Rh, as noted previously. There also appears to be an early rapid reduction of the olefinic substrate when Rh is present (table 5.5). This seems to coincide with the initial colour change from red-purple to orange, in the FA case. Interestingly, after complete reduction of 1 equivalent of FA the solution colour became dark red-orange and when a second equivalent of FA was added a colour change to lighter orange was observed with concomitant changes in the $^1$H NMR intensities (fig. 5.8). There was no darkening after complete reduction of FA nor was there any change on addition of a further equivalent. Monitoring by $^1$H NMR revealed that the reduction still occurred but at a much slower rate.

The overall reaction appears to be a net reduction by Sn(II).

\[
\text{Sn(II) + 2H}^+ + \text{MA} \rightarrow \text{Sn(IV) + SA} \quad (5.5)
\]
\[
\text{Sn(II) + 2H}^+ + \text{FA} \rightarrow \text{Sn(IV) + SA} \quad (5.6)
\]

In the presence of Rh(III) and a sufficient excess of Sn(II), reduction to some RhI(SnCl$_3$)$_x$ species occurs, which is apparently a more active reductant for the olefins. At Sn(II)/Rh $\leq$ 4, such species are not important (see Chapter III). In the presence of sufficient excess of Sn(II), or another reductant and Sn(II), the reaction would be considered catalytic in Rh.

The slightly lower conversions for MA vs. FA (table 5.5) appear to be correlated with the initially less purple colour of solutions containing MA, which indicates the presence of less RhI(SnCl$_3$)$_x$. Possibly, MA is inhibiting the latter's formation by virtue of strong binding to some Rh(I) precursor, and
Table 5.5  Extent of reduction of MA or FA to SA at various times with net oxidation of Sn(II) to Sn(IV) in 3M DC1/D2O.

<table>
<thead>
<tr>
<th>[Rh(III)] (x10^2 M)</th>
<th>[Sn(II)] (x10^2 M)</th>
<th>[MA] (x10^2 M)</th>
<th>[FA] (x10^2 M)</th>
<th>[SA]<strong>a</strong> (x10^2 M)</th>
<th>% conversion</th>
<th>time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>5.33</td>
<td>1.98</td>
<td>-</td>
<td>0.44<strong>c</strong></td>
<td>22</td>
<td>7200</td>
</tr>
<tr>
<td>0.91</td>
<td>5.76</td>
<td>-</td>
<td>0.99</td>
<td>0.23<strong>c</strong></td>
<td>23</td>
<td>300</td>
</tr>
<tr>
<td>0.00<strong>b</strong></td>
<td>5.46</td>
<td>-</td>
<td>2.76</td>
<td>0.47<strong>c</strong></td>
<td>17</td>
<td>11100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.70<strong>c</strong></td>
<td>25</td>
<td>17040</td>
</tr>
</tbody>
</table>

a. uncorrected for MLA formation.
b. in presence of 0.90 M SnCl4·5H2O.
c. in situ.
d. ether evaporate.

thus, in spite of its greater reducibility than FA**153**, inhibiting its own reduction.

Another interesting facet of the reduction as judged by the isomerization and deuterium scrambling is the implied presence of hydride intermediates even in the absence of H2. Whether these are formed by direct protonation at the metal, or by protonation of reduced organic ligand**153** followed by β-elimination to form a Rh(III) hydrido-olefin complex, is unclear. Certainly the latter process is implied by the isotope scrambling. Similar scrambling was observed in the absence of Rh. The data are very limited, but the
Figure 5.8 Comparison of the changes in absorbance (λ = 500nm) and $^1$H NMR (100MHz) with time for the reduction of FA by the Rh/Sn/DC1/D$_2$O system. (Numbers above resonances are $X_{SA}$ (or $X_{FA}$) values; $t_0$ spectrum is in stick representation).
mechanism likely involves Sn(IV) and similar intermediates as presumed in the case of Rh. Complexes of the type Cl₂Sn[CH₂CH₂C(O)X]₂ and Cl₃Sn[CH₂CH₂C(O)X] (X = OR, NH₂) are known. Interestingly these are formed from the low temperature reaction of the appropriate α,β unsaturated olefin with Sn° and HCl in THF. These reactions were believed to go via Cl₂SnH₂ or Cl₃SnH intermediates that react with the olefins. In the present work if such complexes were formed, alkane release would result by protonolyses of the Sn-C bond. Observation of mono-deutero SA suggests in both the Rh and non-Rh systems that H⁺/D⁺ exchange between solvent and hydride intermediates was slower than β-elimination and olefin exchange. Alternatively, an intermediate containing two organic moieties could be involved in the scrambling process.

5.6 Discussion

Modification of the "inactive" Rh/MA/H₂/3MHCl system by addition of SnCl₂·2H₂O resulted in catalytic hydrogenation of MA and FA. The activity was comparable to other systems involving d⁶ Ru and Rh precursor catalysts under similar conditions (Table 5.6). The mechanisms are disparate. The Rh systems in DMA are believed to primarily involve Rh(III) dihydride intermediates formed by homolytic H₂ activation within an "unsaturate route", although with RhCl₃(Et₂S)₃ a "hydride route" via a Rh(III) mono-hydride formed heterolytically was also evident. The Ru(II) system involved an "unsaturate route" with heterolytic activation of H₂ by Ru(II) (olefin) species. The present case is more complicated. Besides reduction of olefin involving catalytic hydrogenation, stoichiometric reduction involving net oxidation of
Table 5.6 Comparison of rates of H\textsubscript{2} uptake for various catalytic systems for the hydrogenation of MA at 80°C. [H\textsubscript{2}] = 3.60\times10^{-4} M, [MA] = 0.1 M, [catalyst] = 0.01 M.

<table>
<thead>
<tr>
<th>system</th>
<th>solvent</th>
<th>rate of uptake (x10\textsuperscript{6} Ms\textsuperscript{-1})</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/6Sn</td>
<td>3M HCl</td>
<td>2.6</td>
<td>this work</td>
</tr>
<tr>
<td>RhCl\textsubscript{3} \cdot 3H\textsubscript{2}O</td>
<td>1.2M LiCl/DMA</td>
<td>~ 4.7\textsuperscript{*}</td>
<td>25</td>
</tr>
<tr>
<td>&quot;RuCl\textsubscript{2}&quot;</td>
<td>3M HCl</td>
<td>~ 8\textsuperscript{†}</td>
<td>43</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}</td>
<td>DMA</td>
<td>~ 1.3\textsuperscript{‡}</td>
<td>26</td>
</tr>
</tbody>
</table>

\* Estimated from data at [H\textsubscript{2}] = 2.32\times10^{-3} M and [Rh] = 0.01 M; rate was 3.0\times10^{-5} Ms\textsuperscript{-1} with the rate-law of \( \frac{d[H_2]}{dt} = k[Rh][H_2] \).

\† Estimated from rate at [Ru] = 0.0122 M; corresponding rate-law as above.

\‡ Estimated from data at [H\textsubscript{2}] = 2.32\times10^{-3} M and [Rh] = 0.005 M; same rate-law, rate = 4.25\times10^{-6} Ms\textsuperscript{-1}.

Sn(II) to Sn(IV) has been observed.

The principle mode of hydrogen activation in the present case is believed to be heterolytic. Compared to the tin-free system reported earlier\textsuperscript{28}, hydrogenation activity increased upon addition of SnCl\textsubscript{2} \cdot 2H\textsubscript{2}O (i.e. SnCl\textsubscript{3} in 3M HCl) and olefin. The \( \pi \)-acceptor nature of both these ligands should promote nucleophilic attack (i.e. Rh + H\textsuperscript{6−} \ldots H\textsuperscript{6+}) and decrease activity towards oxidative addition of H\textsubscript{2}\textsuperscript{156}. Also the observed isotope scrambling and isomerization is more consistent with a mono-hydride intermediate (sec. 1.1.2).
Isomerization and isotope scrambling was observed for the "hydride route" via Rh(III)H for the RhCl$_3$(Et$_2$S)$_3$ system but not for the "unsaturate route" via Rh(III)H$_2$. Less conclusive in the present case is the fact that activity was greater for solutions with a higher fraction of total Rh present as Rh(III), which is not as susceptible to oxidative addition of H$_2$ as Rh(I).

Although the last item is less important as evidence towards heterolytic activation, it does reflect one of the probable roles of SnCl$_3^-$ in the catalysis. The reaction between Rh(III) and SnCl$_3^-$ has already been shown (Chap. 3) to give mixtures of Rh(I) and Rh(III) tin-chloride complexes, highly coordinated with SnCl$_3^-$, and Rh complexes not containing SnCl$_3^-$.

The relative amount of the latter was greater at lower Sn/Rh ratio. The initial solution composition in all hydrogenation experiments, except that involving prehydrogenation in the absence of olefin, was determined by modifications induced by the presence of FA or MA. The composition would be impossible to determine in any great detail, but some points are evident. Reduction to SA will occur by reaction with Rh(I) species of high Sn/Rh ratio, and with free Sn(II), presumably SnCl$_3^-$. Additionally, MA and FA should compete with SnCl$_3^-$ at labile Rh(I) centers to form Rh(I)(olefin) type complexes. During hydrogenation the distribution of Rh complexes should change with time due to the changes in Sn(II) and olefin concentrations. At low [Sn], metal precipitated in the absence of MA. In the presence of MA no metal formed until full consumption of MA, indicating probable formation of Rh(I)(MA). However, with FA metal was not formed
either, which is consistent with isotope scrambling and concomitant isomerization to MA. Solution composition during hydrogenation as indicated by UV/VIS (fig. 5.3) was different for the two substrates, although no effect on the rate of uptake was found.

Possible elements of the mechanism (mechanism A) which can qualitatively explain the observations are listed below

\[
(Sn)_n Rh^{III} + H_2 \rightarrow (Sn)_n Rh^{III}H^- + H^+ \quad (5.5)
\]

\[
(Sn)_n Rh^{III}H^- + FA \rightleftharpoons (Sn)_n Rh^{III}(alkyl) \rightleftharpoons (Sn)_n Rh^{III}H^- + MA \\
\downarrow H^+ \\
(Sn)_n Rh^{III} + SA \quad (5.6)
\]

\[
(Sn)_n Rh^{III}H^- \rightleftharpoons (Sn)_n Rh^I + H^+ \quad (5.7)
\]

\[
(Sn)_n Rh^I \rightleftharpoons Rh^I + nSn(II) \quad (5.8)
\]

\[
(Sn)_n Rh^I + MA \underset{K_m}{\overset{K_m^-}{\rightleftharpoons}} (Sn)_{n-1} Rh^I(MA) + Sn(II) \quad (5.9)
\]

\[
(Sn)_{n-1} Rh^I(MA) \rightleftharpoons Rh^I(MA) + (n-1)Sn(II) \quad (5.10)
\]

\[
(Sn)_n Rh^I + FA \underset{K_f}{\overset{K_f^-}{\rightleftharpoons}} (Sn)_{n-1} Rh^I(FA) + Sn(II) \quad (5.11)
\]

\[
(Sn)_{n-1} Rh^I(FA) \rightleftharpoons Rh^I(FA) + (n-1)Sn(II)(II) \quad (5.12)
\]
\[ \text{Rh}^I + \text{MA} \xleftrightarrow{K^1_m} \text{Rh}^I(\text{MA}) \]  
\[ \text{Rh}^I + \text{FA} \xleftrightarrow{K^1_f} \text{Rh}^I(\text{FA}) \]  
\[ (\text{Sn})_n\text{Rh}^I + \text{MA} \xrightarrow{k_m} (\text{Sn})_n\text{Rh}^{III}(\text{alkyl}) \]  
\[ (\text{Sn})_n\text{Rh}^I + \text{FA} \xrightarrow{k_f} (\text{Sn})_n\text{Rh}^{III}(\text{alkyl}) \]  
\[ \text{Sn}(\text{II}) + \text{MA} \xrightarrow{2\text{H}^+} \text{SA} \]  
\[ \text{Sn}(\text{II}) + \text{FA} \xrightarrow{2\text{H}^+} \text{SA} \]

The rate determining step is likely to be 5.5, since no dependence of rate on substrate was seen at low [olefin]. Constants such as \( K^m_m \), \( k_m \) and \( K^1_m \) are expected to be greater than \( K^m_f \), \( k_f \) and \( K^1_f \), respectively. At high [MA] the relatively inactive yellow solution, probably containing \( \text{Rh}^I(\text{MA}) \), is ultimately favoured as \( \text{Sn}(\text{II}) \) is 'burnt off' by direct reduction of olefin, thus a declining rate of uptake would be expected, and was observed. At high [Sn] formation of \( \text{Rh}^I(\text{MA}) \) would be retarded.

In the absence of Sn, catalytic hydrogenation was observed at high [MA]. Excluding the direct reductions, a similar mechanism (mechanism B) can be operative with olefin substituted for \( \text{SnCl}_3^- \) as the strong \( \pi \)-acceptor. The necessary formation of \( \text{Rh}(\text{III})(\text{olefin}) \) complexes could occur via \( \text{Rh}(\text{I}) \) catalyzed-substitution at \( \text{Rh}(\text{III}) \), as observed for \( \text{SnCl}_3^- \) and also proposed
in the RhCl$_3$(Et$_2$S)$_3$/olefin/H$_2$/DMA system$^{26}$. The increase in initial rate of uptake with increased [MA] relative to the reported rate of the reported stoichiometric uptake is consistent with this idea. However, the independent isomerization of MA to FA becomes important in the present work.

The effect of the independent isomerization of MA was strongest when the solution with Sn/Rh ratio of 6 was prehydrogenated before addition of MA (high [MA]). Unlike the alternate procedure, little Rh(III) was present initially. The surprising premature precipitation of metal during hydrogenation under these conditions could be ascribed to preferential reduction of MA via the 'short cut' reaction 5.15. This has two effects. First, MA is rapidly consumed, including that produced by isomerization of FA in reaction 5.6, but more importantly Rh(I) is apparently reoxidized back to Rh(III) before formation of other Rh(I) complexes that could lead to stable Rh(I)(MA). Thus, when the more reactive substrate is consumed, the rate of reoxidation will fall off and allow more Rh(I) to form, but the [MA] would be too low to stabilize against metal formation. A similar rate of uptake was observed at low initial [MA] and at a Sn/Rh ratio of 6. It appears that the choice of 10 equivalents of olefin for the low [olefin] was a coincidence in view of the observed metal formation.

Since metal was not observed using FA as substrate at low [olefin], it must be assumed that the rate of isomerization to MA is competitive with the formation of Rh(I) complexes susceptible to reduction to metal. However, the uptake in this case was not taken to the point of metal formation, so premature metal formation cannot be completely excluded.

In conclusion, it must be noted that although a catalytic hydrogenation
system for olefinic acids was generated by addition of SnCl$_2$·2H$_2$O to Rh(III) at 80°C in 3M HCl, the system is a constrained one due to competing isomerization (e.g. MA to FA). Clearly a broader range of conditions needs to be examined with an aim to reduce the effect of isomerization. Furthermore, the examination of the effect of light on the system was cursory. From the experiences in Chapters 3 and 4 and elsewhere$^{157}$, the lack of influence by light is surprising. Consideration of product and isotope distributions, as well as uptake rate, is necessary for a fuller statement on the effect of light.
CHAPTER VI
GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The most striking feature of the chemistry examined in this thesis was the complexity engendered by the addition of stannous chloride to the rhodium systems. However, while interesting and potentially important in catalysis, this feature made characterization difficult.

Treatment of solutions of "RhCl\(_3\cdot3H_2O"\) with stannous chloride followed by precipitation with tetraalkylammonium chlorides resulted in the isolation of various anionic rhodium-tin chloride complexes. The variation of the mixture of synthetic products under various conditions indicated Rh(I) catalysis of substitution at Rh(III) centres was occurring. In particular the very rapid formation of [RhCl\(_2\)(SnCl\(_3\))\(_4\)]\(^{3-}\) (probably the trans-isomer) was supportative of this. Formation of a new Rh(I) complex, tentatively characterized as [Rh(SnCl\(_3\))\(_4\)(SnCl\(_4\))]\(^{3-}\), formed via Sn(II) reduction of Rh(III), competed with the formation of Rh(III) products. The kinetic products were not stable, and decomposed ultimately to thermodynamic products (e.g. [RhCl\(_3\)(SnCl\(_3\))\(_3\)]\(^{3-}\)). The nature of products not precipitable by tetraalkylammonium chlorides was not determined.

[Rh(SnCl\(_3\))\(_4\)(SnCl\(_4\))]\(^{3-}\) may be similar in structure to [Rh(SnCl\(_3\))\(_4\)-(SnCl\(_4\))]\(^{5-}\) (see fig. 3.1); however, a molecular structure determination is required. Clearly the redox chemistry, and potential relationship with light activation, of these 'electron rich' (10 and 12 Fe\(^{3+}\) reduction equivalents, respectively) present a worthwhile avenue to pursue. For
example, it might be possible to generate the trianion electrochemically from the pentaanion.

It is curious that so few 'simple' rhodium-chloride/tin-chloride complexes were isolable. Reaction between \([\text{Rh}_2\text{Cl}_2(\text{COT})_4]\) and \([\text{Et}_4\text{N}][\text{SnCl}_3]\) did appear to yield unstable and thermochromic Rh(I) complexes that were not fully characterizable. Although \(\text{SnCl}_3^-\), as a \(\pi\)-acceptor ligand, would be expected to form stable Rh(I) complexes (sec. 1.2), these complexes must be readily oxidized (e.g. by Rh(III) in 3M HCl). Perhaps the relative stability of \([\text{Rh(SnCl}_3)_4(\text{SnCl}_4)]^{5-}\) is due to its nearly spherical outer arrangement of chlorides blocking oxidizing attack at Sn or Rh.

Under hydrogenation conditions, 3M HCl solutions of \(\text{RhCl}_3\cdot3\text{H}_2\text{O}\) and \(\text{SnCl}_2\cdot2\text{H}_2\text{O}\) catalysed the reduction of fumaric and maleic acids to succinic acid. Once again a complex system was observed. Stoichiometric reduction of olefin by Sn(II) and Rh(I) complexes was observed, protonation yielding the reduced product. These reactions competed with catalytic hydrogenation involving Rh and \(\text{H}_2\). Isotopic scrambling was found to have occurred in the product suggesting a mono-hydride catalyst. On the basis of the limited data, a "hydride-route" mechanism was proposed, with generation of hydride via heterolytic splitting of \(\text{H}_2\) at Rh(III). UV-Vis data indicate that the catalytic solutions at lower \([\text{Sn}]\) contain a high concentration of Rh(III) complexes which presumably favours a Rh(III)-based catalytic system. The role of stannous chloride may be non-specific, acting to promote formation of a complex 'soup' similar to that observed in the synthetic experiments. Additionally, some evidence points to coupling between stoichiometric reduction of olefin by a Rh(I)-tin chloride complex and \(\text{H}_2\) reduction of
the resultant Rh(III) product to complete the catalytic cycle. Confirmed examples of such a process are not known (sec. 1.1.2), so elucidation of this point would be useful. An overall understanding of the catalytic system may be elusive given the complexity indicated here. It is not at all obvious how to approach the kinetic problem.
REFERENCES


7. This section is based mainly on ref. 3 and references therein.


10. ref. 3c, p. 1.

11. ref. 3c, Chapter XVI, sec. G.


16. see ref. 3, 14 and 15.
17. ref. 3a, Table 2.
20. ref. 3b, p. 328.
23. ref. 3a., p. 296
24. ref. 3a., p. 299
29. ref. 3a., sec. 1.3.1(i).
37. ref. 3c., Chapter X.
39. ref. 3b., p. 321ff.
44. ref. 3b., sec. IIb.
45. ref. 3c., Chapter X, sec. F.
47. ref. 3c., Chapter X, sec. E.
48. ref. 3a., p. 309.
49. ref. 3c, Chapter X, sec. E.
50. ref. 3c., Chapter X, sec. B.
52. ref. 3c., Chapter X, sec. B.


55a. ref. 3a., sec. 1.3.2(i).


56. ref. 3c., Chapter XI, sec. A.

57. ref. 3a., sec. 1.3.2(i).

58. ref. 36, Chapter 4.


62. ref. 36, p. 338.

63. ref. 42.


65. ref. 3c., Chapter XI, sec. B.


b. ref. 3c., Chapter XIII, sec. B, C.


100. P. Szarvas, J. Lantos, Talanta (1963), 10, 477.


117. L.J. Farrugia; personnal communication.


122. see sec. 2.2.3 (note that these programs are no longer supported).
   b. B.R. James, G. Rosenberg, ibid (1976), 54, 313.
129. ref. 55b, Chapter 5.
131. ref. 129, Chapter 8.
132. ref. 129, p. 297.
136. ref. 1 p. 667ff.
137. J.D. Donaldson, Prog. Inorg. Chem. (1968), 8, 287.
149. ref. 13, Chapter 5; see also ref. 151.
156. ref. 3c., Chapter XII, section A.
Appendix A

Two programs were written to facilitate kinetic analysis. The first is a data storage program called DSTORE.F, which is used to interactively store data in a format usable by the actual kinetic analysis program called ALLKIN.F.

ALLKIN.F has a rudimentary command language by which the user can control program flow. The program listings follow (sec. A1 and A2), with imbedded comments that explain their operation; such statements are prefixed by 'C'. Note that there are 3 input streams to ALLKIN.F: (1) from a data file filled using DSTORE.F, (2) from a terminal, in the same format as (1), and (3) from a terminal as 'X,Y' pairs. Routes (1) and (2) are for data that can be described as a list of 'Y' values with the 'X' values specified by an initial 'X' and an interval 'ΔX' (e.g. absorbance sampled at constant time intervals). Output defaults to a terminal but 'hardcopy' can be generated on command via a temporary file which can then be listed on an appropriate device.
Section A.1
PROGRAM DSTORE.F: STATEMENTS IN DSTORE.F
OBJECTCODE IN DSTORE.O

PURPOSE: STORAGE OF ABSORBANCE DATA IN FILE ATTACHED TO UNIT 9 IN A FORMAT SUCH THAT 'ALLKIN' CAN RETRIEVE IT USING THE RUN-NUMBER CODE ('RNUM') VIA THE OPTION=1 DATA INPUT ROUTE OF 'ALLKIN'.

DIMENSION A(30)
INTEGER RNUM, LINE

READ IN NUMBER OF STORED RUNS ALREADY IN FILE ATTACHED TO UNIT 9 (9=[FILENAME]), THIS VALUE ('LINE') IS FOUND IN THE FIRST 2 BYTES OF THE FILE (FORMAT 12).

READ (9,50,END=30) LINE
LINE = LINE * 1000

INPUT 'RNUM', NUMBER OF DATA POINTS ('NUM'; <31 VALUES), INITIAL TIME 'TO', TIME INCREMENT 'TI'.

WRITE (6,60)
CALL FREAD('SCARDS', '2I:', RNUM, NUM, '2R:', TO, TI)

INPUT ABSORBANCE DATA AS A LIST (SEPARATED BY COMMAS).

WRITE (6,70)
CALL FREAD('SCARDS', 'R V:', A, 30, &20)

INPUT A-INFINITY 'A8'

WRITE (6,80)
CALL FREAD('SCARDS', 'R:', A8)

EXECUTE STORAGE
FIND (9'LINE)
WRITE (9,90) RNUM, NUM, TO, TI, (A(I),I=1,NUM), A8

INPUT REQUEST TO RECYCLE TO ENTER ANOTHER RUN (YES=1,NO=0)

WRITE (6,100)
CALL FREAD('SCARDS', 'I:', L)
IF (L .EQ. 0) GO TO 30
LINE = LINE + 1000
GO TO 10

WRITE (6,110)
LINE = (LINE + 1000) / 1000
FIND (9'1000)
WRITE (9,50) LINE
STOP
50 FORMAT (I2)
60 FORMAT ('&ENTER RUN ID#, NUMBER OF POINTS, TO, T1')
70 FORMAT ('&ENTER DATA POINTS')
80 FORMAT ('&ENTER A-INFINITY')
90 FORMAT (I5, I2, 2F11.4, 3F5.3)
100 FORMAT ('&ENTER MORE DATA')
110 FORMAT ('FINISHED')
END
INTERACTIVE PROGRAM TO FACILITATE FIRST-ORDER ANALYSIS
OF UV-VIS SPECTRAL DATA. ADDITIONALLY ROUTINES FOR SIMPLE
REACTION ORDER DETERMINATION AND LINEAR LEAST-SQUARES FIT
ARE INCLUDED. THE BASIC FLOW OF THE PROGRAM IS CONTROLLED
INTERACTIVELY USING A TWO CHARACTER COMMAND 'LANGUAGE'.
INITIALLY THE DATA SET IS INPUT FROM A SPECIAL FILE,
WHICH IS SET UP USING THE PROGRAM DTHA:DSTORE.O, OR DIRECTLY
FROM A TERMINAL. THIS DATA IS MAINTAINED SEPARATELY FROM
THE 'ACTIVE' COPY WHICH MAY BE MODIFIED BY THE USER. THUS
BY ISSUING A RESTART COMMAND ('RS') THE PROGRAM CAN BE RE-
INITIALIZED WITH THE ORIGINAL DATA AT ANY TIME. THE FIRST-
ORDER ANALYSES AVAILABLE ARE GUGGENHIEM, KEZDY-SWINBOURNE
AND THE 'NORMAL' LEAST-SQUARES FIT TO THE INTEGRATED FORM
OF A FIRST-ORDER RATE EQUATION FOR DATA WITH CONSTANT TIME
INTERVALS. ONLY THE FIT TO THE INTEGRATED FORM IS AVAILABLE
IF VARIABLE TIME INTERVALS ARE INPUT. OUTPUT IS TO TERMINAL
OR TO A TEMPORARY FILE '-PIT' FOR SUBSEQUENT PRINT-OUT.

NOTE: NO PROTECTION IS PROVIDED AGAINST FATAL INTERRUPTS
TERMINATING THE PROGRAM RESULTING IN LOSS OF INPUT
DATA WHEN THE DATA IS INPUT FROM A TERMINAL.

DIMENSION X(30), Y(30)
INTEGER RNUM, OPT
INTEGER*2 CMDL(10) /2HST, 2HRS, 2HOR, 2HDM, 2HFN, 2HFS, 2HFA,
1 2HNS, 2HDD, 2HLL/
INTEGER*2 CMD
COMMON /MAIN1/  RNUM, NUM, A(30), A81, T(30) /MAIN2/  LTAG
CALL FTNCMD('ASSIGN 3=--PIT;')

*ENTRY POINT FOR NS COMMAND
10 CALL FREAD(-1, 'PREFIX')

INDICATE TYPE OF DATA TO BE INPUTED: 1: ABS. DATA FROM UNIT 9
AT CONSTANT TI
2: DITTO FROM TERMINAL
3: X,Y DATA PAIRS FROM TERMINAL

(NOTE: NO MORE THAN 30 DATA PAIRS CAN BE USED.)
WRITE (6,290)
CALL FREAD('SCARDS', 'I:', OPT)
IF (OPT - 2) 20, 50, 90

C INPUT DATA FROM UNIT 9 (OPT=1)

20 WRITE (6,300)
   IP = 0
   CALL FREAD('SCARDS', 'I:', RNUM)
   FIND (9'1000)
   READ (9,310) LINE
   LT = LINE - 2
   DO 30 L = 1, LT
       READ (9,320) IDN
       IF (IDN .EQ. RNUM) GO TO 40
   30 CONTINUE
   WRITE (6,340)
   GO TO 270
   40 IT = (L + 1) * 1000
       READ (9*IT,330) NUM1, TO, TI, (Y(I),I=1,N1), A8
       GO TO 70

C INPUT DATA: CONSTANT TIME INTERVALS (T0=INITIAL TIME; TI=INCREMENT)
ALSO NEED A-INFINITY(OBS) (OPT=2)

50 WRITE (6,350)
   CALL FREAD('SCARDS', '2I:', RNUM, NUM1, '2R:', T0, TI)
   WRITE (6,360)
   CALL FREAD('SCARDS', 'R V:', Y, 30, 60)
   60 WRITE (6,370)
   CALL FREAD('SCARDS', 'R:', A8)

C INITIALIZATION: 1: FILL A&T MATRICES
   2: FILL A81 (I.E. A-INFINITY)

   *ENTRY POINT FOR RS COMMAND (DATA OPT .NE. 3)

70 DO 80 IT = 1, NUM1
   A(IT) = Y(IT)
   T(IT) = T0 + TI * (IT - 1)
   80 CONTINUE

   A81 = A8
   A8C = A8
   NUM = NUM1
   GO TO 130

C INPUT DATA: FROM TERMINAL AS X,Y PAIRS (5<N<31) FOLLOWED BY
      A-INFINITY (OPT=3)

90 WRITE (6,380)
   CALL FREAD('SCARDS', '2I:', RNUM, NUM1)
WRITE (6, 280)

DO 100 IV = 1, NUM1
   CALL FREAD('SCARDS', '2R:', X(IV), Y(IV))
100 CONTINUE

*ENTRY POINT FOR RS COMMAND (DATA OPT .EQ. 3)

110 DO 120 IU = 1, NUM1
   A(IU) = Y(IU)
   T(IU) = X(IU)
120 CONTINUE

NUM = NUM1

CHOOSE INITIAL OPTIONS IN PROGRAM FLOW

ON PROMPTING (I.E. ":" ) THE FOLLOWING COMMANDS ARE VALID:

DD : DISPLAY ACTIVE DATA TABLE
DM : DATA MANIPULATOR/MODIFIER
FA : GUGGENHIEM, KEZDY-SWINBOURNE & NORMAL
   FIRST-ORDER ANALYSIS USING "SWIN A-INFINITY"
   (DISABLED IF OPT=3)
FN : NORMAL FIRST-ORDER ANALYSIS USING
   A-INFINITY(OBS)
FS : FN USING "SWIN A-INFINITY" (DISABLED IF
   OPT=3)
LL : LINEAR LEAST-SQUARES ANALYSIS OF (X,Y)
NS : RESTART WITH NEW DATA SET
OR : DIFFERENTIAL ANALYSIS FOR REACTION ORDER
RS : RESTART WITH CURRENT DATA SET RE-INITIALIZED
ST : STOP

130 CALL FREAD(-2, 'PREFIX', ':')

*SET LTAG=0

140 CALL FREAD('SCARDS', 'S:', CMD, 2)

DO 150 L = 1, 10
   IF (CMD .EQ. CMDL(L)) GO TO 160
150 CONTINUE

GO TO 140

160 GO TO (260, 250, 170, 180, 190, 210, 220, 10, 230, 240), L
170 CALL ORDER(&140)
180 CALL DAMASS(&140)
A8C = A81
CALL NORMAL(A8C, &140)
CALL SWIN(A8C, &200, OPT, &140)
CALL GUGGE(&210, OPT, &140)
CALL DATA(A8C, &140)
CALL LSQ(&140)
IF (OPT .EQ. 3) GO TO 110
GO TO 70

***TERMINATION***
WRITE (6, 390)
STOP

FORMAT (' ENTER DATA PAIRS(X,Y);NOTE: X->T,Y->A', /
FORMAT ('&ENTER DATA TYPE:(1,2 OR 3)')
FORMAT ('&IDENTIFY RUN FOR ANALYSIS')
FORMAT (I2)
FORMAT (I5)
FORMAT (5X, I2, 2F11.4, 31F5.3)
FORMAT (I2, 'RUN SPECIFIED NOT FOUND. RUN TERMINATED', /
FORMAT ('&ENTER RUN ID#,NUMBER OF POINTS,T0,TI')
FORMAT ('&ENTER DATA POINTS')
FORMAT ('&ENTER A-INFINITY')
FORMAT ('& ENTER RUN ID#, NUMBER OF DATA PAIRS (5<NUM1<31)')
FORMAT ('FINISHED')
END
SUBROUTINE ORDER: Calculates the reaction order using simple differential approximation.

SUBROUTINE ORDER(*)

DIMENSION X(30), Y(30)
INTEGER RNUM
INTEGER*2 LT /1HY/, LL
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT, 1 SESLP, SEYNT, CLS90, CLI90, R, N /MAIN2/ LTAG
N = NUM - 1

DO 10 I = 1, N
  D = A(I) - A(I + 1)
  AV=A81-(A(I)+A(I+1))/2.0
  X(I) = ALOG(ABS(AV))
  Y(I) = ALOG(ABS(D/(T(I + 1) - T(I)))))
10 CONTINUE

CALL LLSQ(X, Y)

OUTPUT TO TERMINAL

WRITE (6,20) RNUM, SLP, SESLP, R
WRITE (6,30)

HARDCOPY OPTION (UNIT 3)

CALL FREAD('SCARDS', 'S:', LL, 2)
IF (LL .EQ. LT) WRITE (3,20) RNUM, SLP, SESLP, R

*SET LTAG=3

LTAG = 3
RETURN 1

20 FORMAT (' RUN ID=', I5, '/', ' ------', '/', ' ORDER(S.E.)=', 1 F6.3, '( ', F8.5, ') R=', F9.5)
30 FORMAT ('&HARDCOPY(Y,N)')
END
SUBROUTINE LLSQ: CALCULATES LINEAR LEAST-SQUARES FIT TO X,Y PAIRS PASSED FROM CALLING ROUTINES AS AN ARRAY.

SUBROUTINE LLSQ(X, Y)

REAL X(30), P90(30), Y(30)

DATA P90 /6.31, 2.92, 2.35, 2.13, 2.02, 1.94, 1.90, 1.86, 1.83, 1.81, 1.80, 1.78, 1.77, 1.76, 1.75, 1.75, 1.74, 1.73, 1.73, 1.73, 1.73, 1.73, 1.73, 1.73, 1.73, 1.71, 1.71, 1.71, 1.71, 1.71, 1.70/

COMMON /MAIN4/ SLP, YINT, SESLP, SEYNT, CLS90, CLI90, R, N

C INITIALIZATION

SY2 = 0.0
SX2 = 0.0
SXY = 0.0
SY = 0.0
SX = 0.0

DO 10 L = 1, N
   SY2 = SY2 + Y(L)**2
   SX2 = SX2 + X(L)**2
   SXY = SXY + X(L) * Y(L)
   SY = SY + Y(L)
   SX = SX + X(L)
10 CONTINUE

YM = SY / N
XM = SX / N
SYS = SY2 - N * (YM**2)
SX2 = SX2 - N * (XM**2)
SSXY = SXY - N * XM * YM

SLP = SSXY / SX2
YINT = YM - SLP * XM

C STANDARD ERROR (SESLP: FOR SLOPE; SEYNT: FOR Y-INTERCEPT)
DN = (N - 2) * SX2
W = SYS - SLP * SSXY
SESLP = SQRT(ABS(W/DN))
SEYNT = SQRT(ABS(W*((1/N + XM**2)/DN)))

C CONFIDENCE LIMITS '90% LEVEL' (CLS90: FOR SLOPE; CLI90: INTERCEPT)
SI = N - 2
CLS90 = P90(SI) * SESLP
CLI90 = P90(SI) * SEYNT

C PEARSONS MOMENT CORRELATION COEFFICIENT
R1 = SQRT(ABS(N*SX2 - SX**2))
R2 = SQRT(ABS(N*SY2 - SY**2))
R = (N*SXY - SX*SY) / (R1*R2)
RETURN
END
SUBROUTINE GUGGE: FIRST-ORDER ANALYSIS BY GUGGENHIEM'S METHOD (CALLED BY 'FA')

REAL KOBS
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT, 1 SESLP, SEYNT, CLS90, CLI90, R, N /MAIN5/ M(2), RATE(2), 2 RC(2)
DIMENSION X(30), Y(30)
IF( OPT. EQ. 3 ) RETURN 2
N = NUM / 2

DO 10 I = 1, N
   Y(I) = ALOG(ABS(A(I + N) - A(I)))
   X(I) = T(I)
10 CONTINUE

CALL LLSQ(X, Y)
KOBS = SLP
RATE(1) = KOBS
RC(1) = R
M(1) = 1
RETURN 1
END
SUBROUTINE SWIN: FIRST-ORDER ANALYSIS BY KEDDY-SWINBOURNE METHOD. ALSO CALCULATES A-INFINITY FOR USE BY 'NORMAL'. (CALLED BY 'FA' AND 'FS')

SUBROUTINE SWIN(A8C,*,OPT,*):

REAL K_OBS
DIMENSION X(30), Y(30)
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT, SESLP, SEYNT, CLS90, CLI90, R, N /MAIN5/ M(2), RATE(2), RC(2)

IF( OPT. EQ. 3) RETURN 2

N = NUM / 2

DO 10 I = 1, N
    X(I) = A(I + N)
    Y(I) = A(I)
10 CONTINUE

CALL LLSQ(X, Y)
K_OBS = ALOG(ABS(SLP)) / (T(N + 1) - T(1))
A8C = YINT / (1 - SLP)
RATE(2) = K_OBS
RC(2) = R
M(2) = 1
RETURN 1
END
SUBROUTINE NORMAL: FIRST-ORDER ANALYSIS BY INTEGRATED FORM USING A-INFINITY(OBS) IF CALLED BY 'FN' OR A-INFINITY CALCULATED BY 'SWIN' IF CALLED BY 'FA' OR 'FS'. (CALLED BY 'FA', 'FS' AND 'FN')

SUBROUTINE NORMAL(A8C, *)

INTEGER RNUM
INTEGER*2 LT /1HY/, LL
DIMENSION X(30), Y(30)
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT, SESLP, SEYNT, CLS90, CLI90, R, N /MAIN5/ M(2), RATE(2), RC(2) /MAIN2/ LTAG
A8 = A8C
N = NUM

DO 10 I = 1, N
   X(I) = T(I)
   Y(I) = ALOG(ABS(A8 - A(I)))
10 CONTINUE

CALL LLSQ(X, Y)
AO = A8 + EXP(YINT)
DEL = A(N) - A(1)
IF (DEL.GT.0.0) AO = A8 - EXP(YINT)
TH = ALOG(2.0) / ABS(SLP)

OUTPUT ON TERMINAL
WRITE (6, 40) RNUM
IF (M(1) .EQ. 1) WRITE (6, 50) RATE(1), RC(1)
IF (M(2) .EQ. 1) WRITE (6, 60) RATE(2), RC(2), A8
WRITE (6, 70) SLP, R, A8, AO, TH
WRITE (6, 80) NUM
WRITE (6, 30)

HARDCOPY OPTION (UNIT 3)
CALL FREAD('SCARDS', 'S:', LL, 2)
IF (LL .NE. LT) GO TO 20
WRITE (3, 40) RNUM
IF (M(1) .EQ. 1) WRITE (3, 50) RATE(1), RC(1)
IF (M(2) .EQ. 1) WRITE (3, 60) RATE(2), RC(2), A8
AO = A8 + EXP(YINT)
DEL = A(N) - A(1)
IF (DEL.GT.0.0) AO = A8 - EXP(YINT)
TH = ALOG(2.0) / ABS(SLP)
WRITE (3, 70) SLP, R, A8, AO, TH
WRITE (3,80) NUM
20   M(1) = 0
     M(2) = 0

C
C *SET LTAG=1
C
    LTAG = 1
    RETURN 1

C
30   FORMAT ('&HARDCOPY(Y,N)')
40   FORMAT (' RUN ID=', I5, '/', ' ------', '/)
50   FORMAT (' GUGGE: K(OBS)=', E10.4, ' R=', F9.5, '/)
60   FORMAT (' SWIN : K(OBS)=', E10.4, ' R=', F9.5, '/,
1        A-INF (CALC)=', F6.3, '/)
70   FORMAT (' NORM : K(OBS)=', E10.4, ' R=', F9.5, '/,
1        A-INF =', F6.3, '
2        T-1/2=', F11.4)
80   FORMAT (3X, 'NUMBER OF DATA PAIRS=', 12, '/)
END
SUBROUTINE DAMASS: DATA MANIPULATION ROUTINE. ALLOWS CORRECTION OF INPUT ERRORS OR MODIFICATION OF 'ACTIVE' VALUES FOR A-INFINITY, NUMBER OF DATA PAIRS OR DELETION OF OUTLIERS. THE ROUTINE USES IT'S OWN COMMAND LANGUAGE AND INPUT PROMPT ('>'). THE ORIGINAL DATA SET IS NOT MODIFIED BY THIS ROUTINE. (CALLED BY 'DM')

SUBROUTINE*2 DAMASS(*)

INTEGER*2 CMDL(5) /2HNS, 2HDE, 2HA8, 2HST, 2HCP/
INTEGER*2 CMD
REAL P(30)
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN2/ LTAG
N = NUM
CALL FREAD(-2, 'PREFIX', '>

10 ' CALL FREAD('SCARDS', 'S:', CMD, 2, 'R V:', P, 30, &20)
20 CONTINUE

DO 30 L = 1, 5
 IF (CMD .EQ. CMDL(L)) GO TO 40
30 CONTINUE
GO TO 10

EXECUTE 'NS'

40 IF (L .EQ. 1) NUM = P(1)
EXECUTE 'A8'
IF (L .EQ. 3) A81 = P(1)
IF (L .EQ. 4) GO TO 90
IF (L .EQ. 5) GO TO 80
IF (L .NE. 2) GO TO 10

C EXECUTE 'DE'

CALL FREAD(-2, 18, IVAL)
KT = 0
IVAL = IVAL - 1
IF (IVAL .LE. 0) GO TO 70

DO 60 K = 1, IVAL
   IPT = P(K) - KT

   DO 50 J = IPT, N
      T(J) = T(J + 1)
      A(J) = A(J + 1)
   50 CONTINUE

   KT = KT + 1
60 CONTINUE

NUM = NUM - KT
70 WRITE (6,100) IVAL, NUM
GO TO 10

C EXECUTE 'CP'

80 LP = P(1)
T(LP) = P(2)
A(LP) = P(3)
GO TO 10

C *SET LTAG=0

90 LTAG = 0

C EXECUTE 'ST'

CALL FREAD(-2, 'PREFIX', ':')
RETURN 1

100 FORMAT (3X, I2, ' POINTS DELETED; TOTAL NOW =', I2)
END
SUBROUTINE DATA: DATA TABULATION AND DISPLAY ROUTINE. LISTS 'ACTIVE' T, A AND A81 VALUES AS WELL AS A(CALC.) AND (A-A(CALC.)) WHEN APPROPRIATE. (CALLED BY 'DD')

SUBROUTINE DATA(A8C,*)

INTEGER RNUM
INTEGER*2 LT /1HY/, LL, L0 /1HN/
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT, SESLP, SEYNT, CLS90, CLI90, R, N /MAIN2/ LTAG

LL = L0
10 IF (LL .EQ. LT) CALL FTNCMD('EQUATE 6=3;') WRITE (6,90) RNUM

CLTAG INDICATES LAST ACTIVE PROGRAM SEGMENT.
0= DAMASS OR INITIALIZATION
1= NORMAL
2= LLSQ
3= ZERO

IF (LTAG .EQ. 3) GO TO 50
WRITE (6,110)
IF (LTAG .EQ. 0) WRITE (6,140)
IF (LTAG .NE. 0) WRITE (6,120)

DO 40 I = 1, NUM
IF (LTAG .EQ. 0) GO TO 30

YC = SLP * T(I) + YINT
DEL = A8C - A(1)
IF (LTAG .EQ. 1 .AND. DEL .LT. 0.0) YC = A8C + EXP(YC)
IF (LTAG .EQ. 1 .AND. DEL .GT. 0.0) YC = A8C - EXP(YC)
20 D = A(I) - YC
WRITE (6,130) I, T(I), A(I), YC, D
GO TO 40

LTAG=1 OR 2

YC = SLP * T(I) + YINT
DEL = A8C - A(1)
IF (LTAG .EQ. 1 .AND. DEL .LT. 0.0) YC = A8C + EXP(YC)
IF (LTAG .EQ. 1 .AND. DEL .GT. 0.0) YC = A8C - EXP(YC)
20 D = A(I) - YC
WRITE (6,130) I, T(I), A(I), YC, D
GO TO 40

LTAG=0

30 WRITE (6,180) I, T(I), A(I)
40 CONTINUE

WRITE (6,150) A8C
WRITE (6,160) NUM
GO TO 70
50 WRITE (6,170)
C
DO 60 K = 1, N
   D = A(K) - A(K+1)
   AV = 0.5*(A(K)+A(K+1))/2.0
   X = ALOG(ABS(AV))
   Y = ALOG(ABS(D/(T(K + 1) - T(K))))
   YC = SLP * X + YINT
   DF = Y - YC
   WRITE (6,130) K, X, Y, YC, DF
60 CONTINUE
C
C HARDCOPY OPTION (UNIT 3)
C
70 IF (LL .EQ. LT) GO TO 80
   WRITE (6,100)
   CALL FREAD('SCARDS', 'S:', LL, 2)
   IF (LL .EQ. LT) GO TO 10
80 CALL FTNCMD('EQUATE 6=SPRINT;')
   RETURN
90 FORMAT (3X, 'RUN ID=', 15, /)
100 FORMAT ('&HARDCOPY(Y,N)')
110 FORMAT ('&', 2X, '#', T5, 'TIME(SEC)', T21, 'A(OBS)')
120 FORMAT (T7, 'A(CALC)', T20, 'DIFF', /)
130 FORMAT (1X, I2, 1X, F11.4, 3X, F9.4, 3X, F9.4, 3X, E9.2)
140 FORMAT (' ', /)
150 FORMAT (' ', 3X, 'A-INFINITY=', F9.4)
160 FORMAT (3X, 'NUMBER OF DATA PAIRS=', I2, /)
170 FORMAT (2X, '#', T7, 'X(OBS)', T21, 'Y(OBS)', T33, 'Y(CALC)',
   T46, 'DIFF', /)
180 FORMAT (1X, I2, 1X, F11.4, 3X, F9.4)
SUBROUTINE LSQ: SIMPLE LINEAR LEAST-SQUARES ANALYSIS
ON ANY X,Y DATA PAIR SET. USUALLY DATA IS ENTERED VIA OPTION 3.
(CALLED BY 'LL')

SUBROUTINE LSQ(*)

INTEGER RNUM
INTEGER*2 LT /1HY/, LL
COMMON /MAIN1/ RNUM, NUM, A(30), A81, T(30) /MAIN4/ SLP, YINT,
1 SESLP, SEYNT, CLS90, CLI90, R, N /MAIN2/ LTAG

N = NUM

*SET LTAG=2

LTAG = 2
CALL LLSQ(T, A)

OUTPUT ON TERMINAL

WRITE (6,20) RNUM, SLP, SESLP, CLS90
WRITE (6,30) YINT, SEYNT, CLI90
WRITE (6,40) R
WRITE (6,50)

HARDCOPY OPTION (UNIT 3)

CALL FREAD('SCARDS', 'S:', LL, 2)
IF (LL .NE. LT) RETURN 1
WRITE (3,20) RNUM, SLP, SESLP, CLS90
WRITE (3,30) YINT, SEYNT, CLI90
WRITE (3,40) R
RETURN 1

10 FORMAT (3X, 'NUMBER OF DATA PAIRS=', I2, //)
20 FORMAT (' RUN ID=', I5, //, ' ------', //, ' SLOPE(S.E.)=',
1 E10.4, '(', E10.5, ') CL90=', E10.5, //)
30 FORMAT (' Y-INT(S.E.)=', F6.3, '(', F6.4, ') CL90=', F6.4, //)
40 FORMAT (' CORRELATION COEFF.(R)=', F9.5, //)
50 FORMAT ('&HARDCOPY(Y,N)')
END
Appendix B

Estimation of intensities of $^{119}$Sn FT NMR resonance intensities for $[\text{RhCl}_6\text{SnCl}_3]^{3-}$ complexes.

B.1 As noted in section 3.5, the splitting patterns and the intensities of $^{119}$Sn FT NMR resonances in the spectra of $[\text{RhCl}_6\text{SnCl}_3]^{3-}$ complexes are useful for determining the number of coordinated SnCl$_3$ ligands. The octahedral Rh complexes are considered to be fluxional in 3M HCl, making the SnCl$_3$ ligands magnetically equivalent. For complexes with more than one tin nuclei ($n \geq 2$), a sextuplet pattern is expected due to coupling to $^{117}$Sn, assuming intensities of signals due to complexes with 3 or more spin active nuclei, or $^{115}$Sn, to be negligible (see sec. 3.5). The problem of determining the coordination number from intensities has been addressed in ref. 110 where the measure used was the ratio of a satellite peak intensity to that of a main peak ($I_s/I_m$; see fig. B.1). The method used was "simple statistics", which were not described and we have not been able to exactly duplicate. In this work the ratios were calculated using combinatorial probabilities, as described below. The results are summarized in fig. 3.32; the values reported in ref. 110 lie slightly higher and follow a linear relation.

The first section (B.2) concerns complexes with equivalent tin ligands, while the second deals with the special case of a rigid $[\text{RhCl(SnCl}_3)_5]^{3-}$ complex, which was the subject of a simulation (sec. 3.5 and Appendix C). Table B.1 summarizes the natural abundance values used in the calculations.
B.2

B.2.1 For $n = 2$:

Case (i). $1 \times ^{119}\text{Sn}$

$\Pr[(A \cap D) \cup (D \cap A)] = 0.1438$; intensity $(I) = 0.1438$

Case (ii). $2 \times ^{119}\text{Sn}$

$\Pr[(A \cap A)] = 0.0074$; $I = 0.147$

Case (iii). $1 \times ^{119}\text{Sn}, 1 \times ^{117}\text{Sn}$

$\Pr[(A \cap B) \cup (B \cap A)] = 0.0131$; $I = 0.0131$

$I_s / I_m = 4.13%$

---

Table B.1 The natural abundances of various isotopes of tin and rhodium.$^{159}$

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{103}\text{Rh}$</td>
<td>$1/2$</td>
<td>$1.0000$</td>
</tr>
<tr>
<td>$^{119}\text{Sn}$ (A)</td>
<td>$1/2$</td>
<td>$0.0858$</td>
</tr>
<tr>
<td>$^{117}\text{Sn}$ (B)</td>
<td>$1/2$</td>
<td>$0.0761$</td>
</tr>
<tr>
<td>$^{115}\text{Sn}$ (D)</td>
<td>$1/2$</td>
<td>$0.0035$</td>
</tr>
<tr>
<td>Other Sn</td>
<td>0</td>
<td>$0.8345$</td>
</tr>
</tbody>
</table>

$^{159}$

The natural abundances of various isotopes of tin and rhodium are listed in Table B.1. The concentrations are represented as percentages of the total abundance for each isotope.
B.2.2 For \( n = 3 \):

Case (i) \( 1 \times ^{119}\text{Sn} \)
\[ P \left[ (\text{A} \land \text{D} \land \text{D}) \lor (\text{D} \land \text{A} \land \text{A}) \lor (\text{D} \land \text{D} \land \text{A}) \right] = 0.1808; \quad I = 0.1808 \]

Case (ii) \( 2 \times ^{119}\text{Sn} \)
\[ P \left[ (\text{A} \land \text{A} \land \text{D}) \lor (\text{A} \land \text{D} \land \text{A}) \lor (\text{D} \land \text{A} \land \text{A}) \right] = 0.0186; \quad I = 0.0370 \]

Case (iii) \( 1 \times ^{119}\text{Sn}, 1 \times ^{117}\text{Sn} \)
\[ P \left[ (\text{A} \land \text{B} \land \text{D}) \lor (\text{A} \land \text{D} \land \text{B}) \lor (\text{D} \land \text{A} \land \text{B}) \lor (\text{D} \land \text{B} \land \text{A}) \lor (\text{B} \land \text{D} \land \text{A}) \lor (\text{B} \land \text{A} \land \text{D}) \right] = 0.0328; \quad I = 0.0328 \]

\( I_s/I_m = 7.54\% \)

B.2.2 For \( n = 4 \) the values are similarly calculated:

Case (i) \( 1 \times ^{119}\text{Sn} \)
\[ P = 0.202; \quad I = 0.2020 \]

Case (ii) \( 2 \times ^{119}\text{Sn} \)
\[ P = 0.0312; \quad I = 0.0624 \]

Case (iii) \( 1 \times ^{119}\text{Sn}, 1 \times ^{117}\text{Sn} \)
\[ P = 0.0552; \quad I = 0.0552 \]

\( I_s/I_m = 10.41\% \)

B.2.4 For \( n = 5 \):

Case (i) \( 1 \times ^{119}\text{Sn} \)
\[ P = 0.2115; \quad I = 0.2116 \]

Case (ii) \( 2 \times ^{119}\text{Sn} \)
\[ P = 0.0430; \quad I = 0.0866 \]
Case (iii) 1 x $^{119}\text{Sn}$, 1 x $^{117}\text{Sn}$

\[ P = 0.0760; I = 0.0768 \]

\[ \frac{I_s}{I_m} = 12.88\% \]

B.3 In the case of a rigid octahedral \( n = 5 \) complex the distribution of the isotopes was accounted for by apportioning the probabilities (or 'weights') according to the number of possible arrangements of each combination. There are 1 axial and 4 equivalent equatorial sites:

![Octahedral diagram]

Case (i) 1 x $^{119}\text{Sn}$

There are 5 arrangements, one of which has an axial $^{119}\text{Sn}$. Thus there would be 2 doublets in a 1:4 ratio.

Case (ii) 2 x $^{119}\text{Sn}$

10 arrangements are possible:
- 4 with $^{119}\text{Sn}$ axial
- 4 with both $^{119}\text{Sn}$ equatorial and cis
- 2 with both $^{119}\text{Sn}$ equatorial and trans

The two latter arrangements give rise to a doublet at \( \nu_e \) of intensity = 6 and an ABX pattern of intensity = 4.
Case (iii) Both $^{119}\text{Sn}$ and $^{117}\text{Sn}$ present

20 arrangements are possible: - 4 where $^{119}\text{Sn}$ is axial
- 4 where $^{117}\text{Sn}$ is axial
- 8 where both are equatorial and cis
- 4 where both are equatorial and trans

The patterns are all AMX with the first one centered at $\nu_a$ and the rest at $\nu_e$. The $^2J_{\text{trans}}$ coupling will be an order of magnitude greater than the cis coupling $^{119-121}$.

Table B.2 summarizes the patterns and weights used in calculating a simulated spectrum for $[\text{RhCl(SnCl}_3)_5]^{3-}$. The simulated spectrum was assembled by sequentially simulating the pattern expected for a particular arrangement (using UBC PANIC) and then forming a linear combination of weighted amounts of these spectra (using UBC ADD).

$$a = \frac{1}{103} J_{\text{Rh-}^{119}\text{Sn}}$$

$$b = 2^J_{^{119}\text{Sn-}^{117}\text{Sn}}$$

Figure B.1 Expected sextuplet pattern
Table B.2 Weights used for various arrangements of isotopes in simulating the $^{119}$Sn FT NMR spectrum of $[\text{RhCl}(\text{SnCl}_3)_5]^{3-}$.

<table>
<thead>
<tr>
<th># of isotopes</th>
<th>arrangement</th>
<th>weight at $(\nu_e)$</th>
<th>weight at $(\nu_a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x $^{119}$Sn</td>
<td>e or a (AX)</td>
<td>0.1665</td>
<td>0.0416</td>
</tr>
<tr>
<td>2 x $^{119}$Sn</td>
<td>cis e,e (AX)</td>
<td>0.0510</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cis e,a (ABX)</td>
<td>0.0171 + 0.0171</td>
<td></td>
</tr>
<tr>
<td>1 x $^{119}$Sn</td>
<td>cis e,e (AMX)</td>
<td>0.0304</td>
<td></td>
</tr>
<tr>
<td>+ 1 x $^{117}$Sn</td>
<td>cis e,a (AMX)</td>
<td>0.0152</td>
<td>0.0152</td>
</tr>
<tr>
<td>1 x $^{117}$Sn</td>
<td>trans e,e (AMX)</td>
<td>0.0152</td>
<td></td>
</tr>
</tbody>
</table>
Appendix C

Values used in calculation of simulated spectrum of $[\text{RhCl(SnCl}_3]_5^{3-}$ at a digital resolution of 4.88 Hz/pt.

\[
\begin{align*}
\nu^{(103\text{Rh})} & = \text{arbitrarily large (1000000 Hz)} \\
\nu^{(119\text{Sn}_e)} & = -2988 \text{ Hz} \\
\nu^{(119\text{Sn}_a)} & = -2938 \text{ Hz} \\
1J_{119\text{Sn}_e-103\text{Rh}} & = 556 \text{ Hz} \quad 30 \text{ Hz FWHH} \\
1J_{119\text{Sn}_a-103\text{Rh}} & = -532 \text{ Hz} \quad 50 \text{ Hz} \\
2J_{\text{cis}119\text{Sn}_e-117\text{Sn}_e} & = 1918 \text{ Hz} \quad 30 \text{ Hz} \\
2J_{\text{cis}119\text{Sn}_e-117\text{Sn}_a} & = 1832 \text{ Hz} \\
2J_{\text{cis}119\text{Sn}_a-117\text{Sn}_e} & = 2013 \text{ Hz} \\
2J_{\text{cis}119\text{Sn}_e-119\text{Sn}_a} & = 20000 \text{ Hz} \\
2J_{\text{trans}119\text{Sn}_e-119\text{Sn}_e} & = 20000 \text{ Hz} \quad \dagger
\end{align*}
\]

\dagger \text{Not included in simulation.}