A STUDY OF CATALYTIC AUTOXIDATION OF ORGANIC SUBSTRATES USING
\( \text{H}_2\text{O}_2 \) MIXTURES IN THE PRESENCE OF RHODIUM COMPLEXES
CONTAINING DIMETHYLSULFOXIDE LIGANDS

BY

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ABSTRACT

Dimethylacetamide (DMA) solvent is oxidized catalytically to CH$_3$CON(CH$_3$)CH$_2$OOH and CH$_3$CON(CH$_3$)CHO under H$_2$/O$_2$ mixtures at 50°C in the presence of the dimethylsulfoxide complex RhCl$_3$(DMSO)$_3$ (I) at a rate which is much faster than peroxide-initiated autoxidation of DMA under O$_2$ alone. The hydroperoxide is thought to be the initial product, and the N-formyl derivative its decomposition product. An accompanying metal-catalyzed hydrogenolysis of O$_2$ leads to H$_2$O$_2$ and H$_2$O. Hydrogen peroxide and CH$_3$CON(CH$_3$)CH$_2$OOH are the only products formed in the early stages of the catalytic reaction. The maximum rate of gas uptake in this initial region is independent of the partial pressure of O$_2$, but shows linear dependences on Rh and H$_2$. Stoichiometry, rate and spectral data are consistent with an initiation reaction between complex I and H$_2$, and then O$_2$ to give a catalytically active Rh$^{III}$(O$_2^{-}$)(DMA) species (II) (eq. 1).

\[
\begin{align*}
\text{Rh}^{III}($DMSO$) + \text{DMA} & \xrightarrow{\text{DMSO}} \text{Rh}^{III}(\text{DMA}) \\
& \xrightarrow{\text{DMA}} \xrightarrow{\text{H}_2} [\text{Rh}^{I}(\text{DMA})] \\
& \xrightarrow{\text{O}_2} \xrightarrow{\text{II}} \text{Rh}^{III}($O_2^{-}$)(DMA)
\end{align*}
\]

The autoxidation of DMA and the hydrogenolysis of O$_2$ are postulated to occur via independent pathways involving II (eqs. 2 and 3).
In the absence of H₂, II degenerates to catalytically inactive species. The role of H₂ in the DMA autoxidation is thought to be the regeneration of Rhᴵ species and hence II, from deactivated forms of II. Eventual slow, irreversible deactivation of the catalyst and the probable participation of the H₂O₂ product in peroxide-initiated free-radical autoxidations complicate the interpretation of later stages of reaction.

Diphenylsulfide (DPS) is catalytically oxidized to the sulfoxide by complex I under H₂/O₂ in DMA at 50°C, but accompanying oxidation of the solvent persists even in the presence of a 100-fold excess of DPS over Rh. Oxidation of the sulfide is thought to involve H₂O₂ liberated in the catalytic hydrogenolysis of O₂.

Complex I in CH₂Cl₂ or C₂H₄Cl₂ reacts with CO to give the dimethylsulfide complex RhCl₃(DMS)₃ via a facile reduction of DMSO ligands. Dimethylsulfoxide is reduced also by Rhᴵ species in CH₂Cl₂ in the presence of two equivalents of acid to yield DMS, RhᴵІΙ and H₂O. However, Rhᴵ/2H⁺/DMSO systems are relatively stable in DMA, because of the proton affinity of the solvent.
Complex I reacts also with the strongly basic tertiary amine NEt$_3$ via a redox process in which the Rh$^{	ext{III}}$ is reduced to Rh$^{	ext{I}}$ with an accompanying dehydrogenation of the amine (eq. 4).

\[
\text{RhCl}_3 + 3\text{NEt}_3 \rightarrow \text{RhCl} + 2\text{NEt}_3\cdot\text{HCl} + \text{CH}_2=\text{CHNEt}_2 \quad (4)
\]

The resulting ethenamine then reacts with I to give the $\eta^1$-ylidic complex, RhCl$_3$(DMSO)$_2$(¬CH$_2$CH=NEt$_2$). Data from an earlier thesis, on a reaction between complex I and 1,8-bis(dimethylamino)naphthalene (or Proton Sponge), are reinterpreted in terms of a similar redox reaction that gives an N-carbene fragment (eq. 5), which is stabilized within the Rh$^{	ext{III}}$ complex, RhCl$_3$(DMSO)$_2$(¬CH=N(Me)−C$_{10}$H$_6$NMe$_2$•HCl).

\[
\text{RhCl}_3 + 2\text{P.S.} \rightarrow \text{RhCl} + \text{P.S.}\cdot\text{HCl} + \text{:CHN} \quad (5)
\]
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ABBREVIATIONS AND SYMBOLS

The following list of abbreviations and symbols will be employed in this thesis.

A

angstrom(s)

A

absorbance

atm

atmosphere; 1 atm = 760 mm Hg

COE

cyclooctene

d

day(s); doublet

DES

diethylsulfide

DESO

diethylsulfoxide

DMA

N,N-dimethylacetamide, CH₃CON(CH₃)₂

DMA·HCl

N,N-dimethylacetamidehydrochloride

DMA·HBF₄

N,N-dimethylacetamidehydrofluoroboride

DMF

dimethylformamide

DMS

dimethylsulfide

DMSO

dimethylsulfoxide

DMSO₂

dimethylsulfone

DPS

diphenylsulfide

DPSO

diphenylsulfoxide

DPSO₂

diphenylsulfone

g

gram(s)

h

hour(s)

Hz

hertz, cycles per second

ir

infrared

J

coupling constant, in Hz
k  rate constant
K  equilibrium constant
log  logarithm
m  medium
M  molar, moles per liter
mL  milliliter
nm  nanometers
nmr  nuclear magnetic resonance
Ph  phenyl
PPh₃  triphenylphosphine
ppm  parts per million
P.S.  Proton Sponge, 1,8-bis(dimethylamino)-naphthalene
P.S. HCl  Proton Sponge hydrochloride
py  pyridine
r  correlation coefficient
r.t.  room temperature
s  second(s); singlet; strong
t  time; triplet
TMS  tetramethylsilane
TMSO₂  tetramethylene sulfone
w  weak
δ  chemical shift in ppm downfield from TMS
ε  molar extinction coefficient, M⁻¹ cm⁻¹
λ  wavelength, nm
λ_max  wavelength of maximum absorbance
ρ  rocking modes in ir vibrations
ν  stretching modes in ir vibrations
[ ] concentration

[x/y/z] uncharacterized species possibly made from components x, y, and z.

(\textsuperscript{1}H) proton decoupled
Acknowledgements

I am grateful to Professor B.R. James for his guidance, support and encouragement through the course of this work. Discussions with him on the content and form of this thesis were particularly rewarding. I thank him for his patience and time. I also thank members of the group, both past and present, for their support, particularly during some lean times.

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Finally, I dedicate this thesis to Rohan and Jit for giving me the strength to keep my head above the murky waters of autoxidation catalysis.
CHAPTER I

INTRODUCTION
I  INTRODUCTION

I.1 Metal-catalysis in the autoxidation of organic substrates

The slow deterioration of organic materials such as rubber, natural oil and fats has long been understood to be caused by aerial oxidation. The oxidative decay processes have historically been known as autoxidations, probably because of their apparent spontaneous nature. Now the term autoxidation is generally applied to distinguish oxidations by O₂, from other types of oxidations.¹,² The control of autoxidation is desirable not only from the standpoint of inhibiting the oxidative deterioration of industrially important raw materials and products, but also for promoting selective autoxidations of industrial importance.³

Catalysis by metals and/or metal derivatives plays an important role in the control of selective, partial oxidation of alkanes, olefins and aromatic hydrocarbons to useful products.³-⁵ The use of metals or metal-derivatives for the heterogeneous catalysis of the autoxidation of organic substrates has been, and is of, widespread use in the petrochemical industry.⁶ Homogeneous catalysis in the liquid phase offers some advantages over heterogeneous catalysis because of the lower energy requirements and better level of process control attainable in the liquid phase; not only can temperature and mixing be better controlled than in the heterogeneous phase, but also the nature of the active catalytic species is regulated more effectively. Homogeneous processes are also more amenable to studies by spectroscopic and kinetic methods, and therefore offer more potential for the fine tuning of known catalysts, or the design of new catalysts.⁴
Homogeneous catalysis of autoxidations by soluble metal salts or complexes can be complicated, because of the variety of mechanistic pathways available. A major pathway is via the interaction between metal catalyst and trace hydroperoxide impurities in a system, while direct interactions between metal and substrate, or metal and dioxygen, can also lead to autoxidations.

Metal-hydroperoxide interactions

Transition-metal ions can catalytically decompose hydroperoxides to give the free radicals RO• and RO2• (eqs. I.1-I.3).

\[
\begin{align*}
\text{M}^{n+} + \text{ROOH} & \rightarrow \text{M}^{n+1} + \text{RO}• + \text{HO}^+ & \text{I.1} \\
\text{M}^{n+1} + \text{ROOH} & \rightarrow \text{M}^{n+} + \text{RO}_2• + \text{H}^+ & \text{I.2} \\
2 \text{ROOH} & \rightarrow \text{RO}• + \text{RO}_2• + \text{H}_2\text{O} & \text{I.3}
\end{align*}
\]

Trace free-radicals may initiate free-radical chain autoxidations of organic substrates. Mechanisms of such autoxidations are well characterized, a simple form of such an oxidation is given in Scheme I.1. Since the immediate products of hydrocarbon autoxidations are themselves hydroperoxides, the rate of production of free-radicals (eq. I.3) and therefore the rate of initiation (eq. I.4) increase continually, to give an autoacceleration of the oxidation at the beginning. After some time the hydroperoxide concentration reaches a
steady state, and a maximum rate of reaction is attained. In the maximum rate region the rate is independent of the rate of initiation (eq. I.4) and is dependent only on the rate of propagation (eq. I.6). In such cases, the catalysis of free-radical chain oxidations by transition metal ions is only a catalysis of initiation.

Scheme I.1

Initiation:

\[
\text{RH} \rightarrow \text{R}^\cdot + \text{InH} \quad \text{(I.4)}
\]

(In.; initiating free-radicals, usually RO\cdot or RO_2\cdot)

Propagation:

\[
\text{R}^\cdot \xrightarrow{\text{fast}} \text{RO}_2^\cdot \quad \text{(I.5)}
\]

Termination:

\[
2 \text{RO}_2^\cdot \rightarrow \text{non free-radical products} \quad \text{(I.7)}
\]
Metal-substrate interactions

In some situations the metal ions or complexes may catalyze autoxidations via direct interactions with the substrate. The industrially important oxidation of alkyl benzenes to carboxylic acids with a cobalt catalyst is a relevant example (eq. I.8).

\[
\text{ArCH}_3 + \text{Co}^{III} \rightarrow [\text{ArCH}_3]^+ + \text{Co}^{II}
\]

The mechanism suggested involves an initial interaction between \text{Co}^{III} and the substrate, to give a benzyl radical (eqs. I.9 and I.10). Under autoxidation conditions the benzyl radical is trapped by \text{O}_2 (eq. I.11). The peroxy radicals formed are good oxidizing agents which catalyze the regeneration of \text{Co}^{III} species from \text{Co}^{II} (eq. I.12).

\[
[\text{ArCH}_3]^+ \rightarrow \text{ArCH}_2^- + \text{H}^+
\]

\[
\text{ArCH}_2^- + \text{O}_2 \rightarrow \text{ArCH}_2\text{O}_2^-
\]

\[
\text{ArCH}_2\text{O}_2^- + \text{Co}^{II} \rightarrow \text{ArCH}_2\text{O}_2^- + \text{Co}^{III}
\]

The effective total reaction is a metal-catalyzed free-radical autoxidation (Scheme 1.2).
A net "autoxidation" reaction results also from Wacker-type oxidations which are widely used in industry to functionalize olefins, for example, to produce acetaldehyde and vinylacetates from ethylene; these involve the activation of the olefin by coordination to the metal centre (reaction A, Scheme I.3). The oxygen atom(s) incorporated in the oxidation are derived from $H_2O$. A metal-$O_2$ interaction may or may not occur with the Cu cocatalyst, whose role is essentially the regeneration of the active $Pd^{2+}$ species from the inactive $Pd^0$ produced in the oxidation of the olefin (reactions B and C, Scheme I.3).

**Metal-dioxygen interactions**

In the presence of suitable ligands, transition-metal ions react with $O_2$ to give metal-dioxygen complexes. A large number of such complexes, particularly those of $Pt^0$, $Pd^0$, $Co^{II}$, $Rh^I$ and $Ir^I$, have been isolated and characterized. Metal-dioxygen complexes are widely used in nature not only for binding and reversibly carrying $O_2$ (e.g. myoglobin,
hemoglobin), but also for the oxidation of organic substrates. The oxidation processes occur either via enzymic oxygenases, which incorporate one or two atoms of O$_2$ to a substrate, or via oxidases that convert both atoms of O$_2$ to water or hydrogen peroxide. The heme unit which contains an Fe-porphyrin active centre, is particularly prevalent, and, for example, is found in myoglobin and hemoglobin, the monoxygenase cytochrome P-450, tryptophan dioxygenases, and in cytochrome C oxidase- the terminal enzyme in the respiratory redox chain that reduces O$_2$ to water. The monoxygenase enzyme, cytochrome P-450, is of particular interest because of its ability to hydroxylate hydrocarbons with regio- and stereoselectivity (eq. I.13).

\[ \text{RH} + O_2 + \text{NADH} + H^+ \rightarrow \text{ROH} + H_2O + \text{NAD}^+ \]  

I.13
The suggested mechanism for the hydroxylation reaction *(Scheme I.4)*\(^{11a}\) involves a selective oxygen atom transfer within the constraints of an enzyme-\(O_2\) substrate complex, where the dioxygen is activated by coordination to the iron centre.

Achieving selective autoxidations in vitro, via a similar activation of \(O_2\) by a direct interaction between the metal catalysts and \(O_2\), has received much attention in the last two decades.\(^{12}\) Although, a catalyst system of any industrial significance has not yet emerged from such studies,\(^{13}\) there is a continuing interest in this area of study.\(^ {14}\)

---

**Scheme I.4**
Some background information on metal-dioxygen complexes and a brief summary of the literature in the area are given in the next two sections.

I.2 Metal-dioxygen complexes

Dioxygen in its ground state contains two unpaired electrons in the $\pi^*$ orbitals (Fig. I.1.a). The bonding in metal-dioxygen complexes arises essentially from the interaction of the dioxygen $\pi^*$ orbitals (Fig. I.1) with the d-orbitals of the metal (Fig. I.1.b), the $O_2$ ligand acting essentially as an electron acceptor.  

![Diagram of molecular orbitals and molecular orbital diagram for an MO$_2$ complex](Image)

Fig. I.1  (a) The molecular orbitals of $O_2$

(b) Molecular orbital diagram for an MO$_2$ complex
Table I.1

Structural classification and nomenclature of dioxygen complexes

<table>
<thead>
<tr>
<th>Structure</th>
<th>II Nomenclature (Vaska)</th>
<th>III Nomenclature (Gubelmann and Williams)</th>
<th>IV Example</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>0</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type Ia (superoxo)</td>
<td>(\eta^1) dioxygen</td>
<td>([\text{Co(CN)}_5\text{O}_2]^3-)</td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Type IIa (peroxo)</td>
<td>(\eta^2) dioxygen</td>
<td>(\text{Pt(O}_2)(\text{PPh}_3)_2)</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{M-O})</td>
<td></td>
<td></td>
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<td>/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-M</td>
<td>Type Ib (superoxo)</td>
<td>(\eta^1:\eta^1) dioxygen</td>
<td>([(\text{NH}_3)_5\text{CoO}_2\text{Co(NH}_3)_5]^5^+)</td>
</tr>
<tr>
<td>(\text{O-M})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type IIb (peroxo)</td>
<td>(\eta^1:\eta^1) dioxygen</td>
<td>([(\text{NH}_3)_5\text{CoO}_2\text{Co(NH}_3)_5]^4^+)</td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{O})</td>
<td></td>
<td></td>
<td>(\eta^2:\eta^2) dioxygen</td>
</tr>
<tr>
<td>/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
<td>(\eta^2:\eta^1) dioxygen</td>
</tr>
<tr>
<td>(\text{O—M})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref 10
**Table I.2**

**Properties of some dioxygen species**

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Order</th>
<th>Compound</th>
<th>0-0, Å</th>
<th>(v_{0-0}, \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_2^+)</td>
<td>2.5</td>
<td>(O_2\text{AsF}_6)</td>
<td>1.123</td>
<td>1858</td>
</tr>
<tr>
<td>(O_2)</td>
<td>2</td>
<td>(O_2)</td>
<td>1.207</td>
<td>1555</td>
</tr>
<tr>
<td>(O_2^-)</td>
<td>1.5</td>
<td>(KO_2)</td>
<td>1.32-1.35</td>
<td>1146</td>
</tr>
<tr>
<td>(O_2^{2-})</td>
<td>1</td>
<td>(Na_2O_2)</td>
<td>1.45-1.50</td>
<td>738-880</td>
</tr>
</tbody>
</table>

In his review on metal-dioxygen complexes, Vaska\(^{15}\) identified four structural types (column II, Table I.1); superoxo compounds (types Ia and Ib) where the 0-0 distance is roughly constant (~1.3 Å) and close to the value reported for the superoxide anion \(O_2^-\) (Table I.2), and peroxo compounds (type IIa and IIb) where the 0-0 distance (~1.5 Å) is close to the values reported for \(H_2O_2\) and \(O_2^{2-}\) (Table I.2). The notations a or b distinguish complexes where the \(O_2\) is bound to one metal atom (type a) or bridges two metal atoms (type b). Gubelmann and Williams\(^{10}\) have recently introduced an alternate nomenclature using "hapto" notations (column III, Table I.1). They argue that the metal-dioxygen bond, although polarized with the dioxygen carrying at least a partial
partial negative charge, generally has an appreciable covalent character, and therefore, the assignment of formal oxidation states may not be too accurate.\textsuperscript{10} In this thesis most of the discussion is based on Vaska's classifications since it is a convenient nomenclature which is still widely used in the literature,\textsuperscript{12} though the exact electronic distribution in the cited cases may or may not correspond to the meanings implied by the terms superoxo and peroxo.

Superperoxo- or $\mu$-peroxo- metal complexes are generally found for transition metal ions such as Fe\textsuperscript{II}, Co\textsuperscript{II}, Mn\textsuperscript{II} and Cu\textsuperscript{I}, which show one electron oxidations, while a majority of peroxo complexes are found for Rh\textsuperscript{I}, Ir\textsuperscript{I}, Pd\textsuperscript{0} and Pt\textsuperscript{0} metals; some examples are found in Table I.1. Measurement of the dioxygen stretching frequency is the most useful method available for distinguishing between superoxo- and peroxo-metal complexes. In his review, Vaska showed how the $v_{0-0}$ values then known corresponded to the two principal types of complexes, Type I (or superoxo) and Type II (or peroxo), in his classification. For superoxo complexes the frequencies lay in the range 1075-1195 cm\textsuperscript{-1} and for peroxo complexes in the range 790-932 cm\textsuperscript{-1}. The frequencies of ionic superoxides and peroxides, respectively, are close to the middle of these ranges (Table I.2). Although some dioxygen stretching frequencies outside these limits are noted in some recent studies,\textsuperscript{10} Vaska's observations still remain valid for most metal-dioxygen complexes. The electronic spectra of metal-dioxygen complexes are not well characterized. Systematic studies in the area have been limited by the instability of many of these complexes in solution.\textsuperscript{10} Some chemical properties of metal-dioxygen complexes are discussed in the next section, in the context of their catalytic activity.
I.3 Metal-catalyzed activation and transfer of $O_2$ to organic substrates

The reactions are classified broadly in the literature\textsuperscript{12a} as those involving superoxo and/or $\mu$-peroxo, and peroxo metal complexes (see column II, Table I.1).

**Catalysis via superoxo or $\mu$-peroxo complexes**

Oxidation of organic substrates catalyzed by superoxo or $\mu$-peroxo complexes are often interpreted in terms of initial production of radicals via H-atom abstraction by the complexes (eq. I.14) perhaps by analogy with the R-O-O· radical.\textsuperscript{12b}

\[
M-O-O\cdot + RH \longrightarrow M-O-O-H + R\cdot \quad \text{I.14}
\]

Such mechanisms were earlier thought to be central to the observed catalytic effect of superoxo-metal complexes in the autoxidation of hydrocarbons, but it was later shown that the effect arose from the metal-catalyzed decomposition of hydroperoxide impurities,\textsuperscript{12a} as in eq I.3. The catalytic autoxidation of phenolic substrates is interpreted also in terms of initial production of radicals by H-atom abstraction by Co$^{III}$($O_2\cdot\cdot$) or Co$^{III}$($O_2^-\cdot$)Co$^{III}$ moieties (eq. I.15) and subsequent metal-catalyzed steps to produce quinones (eq. I.16).\textsuperscript{12b}
Sheldon and Kochi suggest that perhaps the superoxo-metal complexes react first as bases or nucleophiles to abstract protons from phenols (e.g. eq I.17\(^{12a}\)); because of the net electron transfer involved in a metal-dioxygen bond, the \(\text{O}_2\) ligand may act as a base or a nucleophile.\(^{10}\) Subsequent metal-catalyzed steps involve alkylperoxocobalt species similar to eq. I.16 above (e.g. eq. I.17.1).
The dioxygen ligands of peroxo-metal complexes also exhibit basic or nucleophilic behaviour. The reactivity of the Pt(O₂)(PPh₃)₂ complex towards electrophiles is an illustration of this property (eq I.18- I.21).

Simple olefins do not react with peroxo complexes but they may be rendered electrophilic by coordination to metal. The isolation of the
complex IrCl(PPh₃)₂(C₂H₄)(O₂), perhaps, resulted from such an attempt at oxidation of ethylene.¹² Since from about 1967 many efforts have been made to use metal-dioxygen complexes or their precursor complexes such as RhCl(PPh₃)₃, RhCl(CO)(PPh₃)₃ and Pd(PPh₃)₄, for the catalytic autoxidation of organic substrates. The majority of the reports involve the oxidation of cyclic olefins, typically at temperatures >60°C. Some initial results on these systems were thought to be due to metal-centred transfer of O₂, but more detailed studies have invariably revealed that the role of the metal in such reactions is to catalyze the initiation of free radical reactions as in eq. I.3.¹²ᵃ,ᵇ

The first authentic example of a non free-radical catalytic reaction was the co-oxidation of terminal olefins and triphenylphosphine to methyl ketones and triphenylphosphine oxide, respectively, by the RhCl(PPh₃)₃ complex in benzene, at r.t., reported by Read and Walker¹⁷ (eq. I.22). Radical chain processes were not detected and triphenylphosphine was found to be essential for the catalytic activity.

\[
\text{RCH=CH}_2 + \text{PPh}_3 + \text{O}_2 \rightarrow \text{RCOCH}_3 + \text{PPh}_3\text{O} \quad \text{I.22}
\]

Later, Mimoun and coworkers demonstrated a catalyst system for the oxidation of terminal olefins without the need for a coreducing agent such as PPh₃.¹⁸ Using mixtures of Rh and Cu salts in alcoholic solvents, sometimes with added acid, two molecules of terminal olefins were converted to two molecules of methyl ketone (eq. I.23).

\[
2 \text{RCH=CH}_2 + \text{O}_2 \rightarrow 2\text{RCOCH}_3 \quad \text{I.23}
\]
In both of the above systems, the suggested mechanism involved the initial formation of a peroxometallacycle by reaction of a Rh$^\text{I}$ catalytic species with the olefin and O$_2$ (eq I.24).

\[
\text{Rh}^\text{I} + \text{RCH} = \text{CH}_2 + \text{O}_2 \rightarrow \text{Rh}_\text{C}(\text{RCH} = \text{CH}_2) + \text{O}^\text{O} \quad \text{I.24}
\]

In the detailed mechanistic scheme suggested by Mimoun and coworkers, the peroxometallocycle is thought to break down into the ketone and a Rh$^\text{III}$-O intermediate (path A, Scheme I.5); such oxo intermediates are invoked in P-450 catalyzed systems. The second oxygen atom transfer and the regeneration of the catalyst occurs via a Wacker process (path B; cf. reaction A in Scheme I.3). In the presence of excess PPh$_3$ the Rh$^\text{I}$ species may be regenerated by the reaction between Rh$^\text{III}$-O and PPh$_3$ (path B').

Scheme I.5
Autoxidation of non-olefinic substrates such as PPh₃ and thioethers by peroxometal complexes has received some attention also. Initially, there had been high expectations for the facile transfer of coordinated dioxygen to coordinated substrates (eq I.24.1).¹⁹

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{O} \\
\downarrow & \quad \downarrow \\
\text{M} & \quad \text{M} \\
\text{Ph}_3\text{P} & \quad \text{O} \\
\end{align*}
\rightarrow

\begin{align*}
\text{P} & \quad \text{O} \\
\downarrow & \\
\text{M} & \quad \text{O} \\
\downarrow & \\
\text{P} & \\
\end{align*}
\rightarrow M + 2\text{PPh}_3\text{O} \quad \text{I.24.1}
\]

Later, detailed studies on the catalytic oxidation of PPh₃ by the Pt(O₂)(PPh₃)₂ complex²⁰ showed that the phosphine is oxidized by free H₂O₂⁻, which is catalytically generated in the presence of protic impurities; a second PPh₃ molecule regenerates the active oxidant (Scheme I.6).

Free peroxide is thought to be the active oxidant also in the Ru⁺⁺⁺ catalyst-catalyzed autoxidation of thioethers in primary or secondary alcohol solvents (eq I.25-I.27).²¹

\[
\begin{align*}
\text{Ru}^{II} + \text{O}_2 & \rightleftharpoons \text{Ru}^{IV} + \text{O}_2^{2-} \quad \text{I.25} \\
\text{Ru}^{IV} + \text{R}_1\text{R}_2\text{CHOH} & \rightarrow \text{Ru}^{II} + \text{R}_1\text{R}_2\text{CO} + 2\text{H}^+ \quad \text{I.26} \\
\text{R}_2\text{S} + \text{H}_2\text{O}_2 & \rightarrow \text{R}_2\text{SO} + \text{H}_2\text{O} \quad \text{I.27}
\end{align*}
\]
I.4 Catalytic autoxidations in the presence of H₂ cosubstrate

Studies on metal-catalyzed autoxidations in this laboratory in the past few years have concerned some oxidations in the presence of H₂, where the O₂ appears to be activated as a MOOH species which forms via an effective insertion of O₂ to an M-H bond (eq. I.28).

\[
M-H + O_2 \rightarrow M-O_2H
\]  

I.28

The work initiated from an accidental finding about 15 years ago: while solvent effects on catalytic hydrogenation were being studied, a
Rh\textsuperscript{III}\textsuperscript{--}catalyzed H\textsubscript{2} reduction of (CH\textsubscript{3})\textsubscript{2}SO to the sulfide and H\textsubscript{2}O was discovered.\textsuperscript{23} The suggested mechanism involved a hydridorhodium(III) intermediate containing S-bonded sulfoxides. (Reactions of Rh\textsuperscript{III} complexes with H\textsubscript{2} generally lead to Rh\textsuperscript{I} species, most likely via heterolytic activation of H\textsubscript{2} to give initial Rh\textsuperscript{III}(H) species which then dissociate to Rh\textsuperscript{I} and H\textsuperscript{+} (eq I.29).\textsuperscript{22}).

\[
\text{Rh}^{\text{III}} + \text{H}_2 \xrightleftharpoons{+\text{H}^+} \text{Rh}^{\text{III}H} \xrightarrow{-\text{H}^+} \text{Rh}^{\text{I}} + \text{H}_2 \text{O}
\]

The reaction rates of the DMSO reduction decreased eventually and this was attributed to the build-up of inactive Rh\textsuperscript{I} species. In an attempt to maintain catalytic activity by reoxidation of the Rh\textsuperscript{I}, a H\textsubscript{2}/O\textsubscript{2} mixture was used. This led to a surprising catalytic oxidation of the sulfoxide to the sulfone and H\textsubscript{2}O (reaction I.30)\textsuperscript{23} which is stoichiometrically similar to the oxidations carried out by the P-450 enzyme systems (eq. I.13).

\[
(\text{CH}_3)_2\text{SO} + \text{H}_2 + \text{O}_2 \rightarrow (\text{CH}_3)_2\text{SO}_2 + \text{H}_2\text{O}
\]

Neither Rh\textsuperscript{III} nor Rh\textsuperscript{I} species under O\textsubscript{2} alone performed this catalysis, which was interpreted as a strong indication that a hydridorhodium(III) species was the effective O\textsubscript{2}-carrier. Trocha-Grimshaw and Henbest also had found that isopropanol solutions of Rh\textsuperscript{III} and Ir\textsuperscript{III} salts carried out the same oxidations using just O\textsubscript{2},\textsuperscript{24} and such a medium is very effective for forming hydride species.\textsuperscript{25}

The suggested catalytic cycle (Scheme I.7)\textsuperscript{26} included an M(OOH)
intermediate \((M=\text{Rh}^{III})\), which is formed by a reaction between MH and \(O_2\). The oxidation of the substrate \((S=DMSO)\) was postulated to occur via the metal hydroperoxide.

The effective insertion of \(O_2\) to \(\text{Rh}^{III}(H)\) to give \(\text{Rh}^{III}(\text{OOH})\) species is well documented for \(\text{RhH}(\text{NH}_3)_5\) and \(\text{RhH}(\text{CN})_4(\text{H}_2\text{O})_2^-\),\(^{27}\) while oxygen atom-transfer from a \(\text{Pd-OOH}\) species is reported in the catalytic oxidation of terminal olefins by \(\text{H}_2\text{O}_2\) in the presence of \(\text{Pd}^{II}\)-carboxylate catalysts \((\text{Scheme I.8}).^{29}\)

In other studies attempting to detect the role of \(M-\text{OOH}\) intermediates, a \(\text{CH}_2\text{Cl}_2\) solution of the dimer \([\text{IrCl}_2(H)(\text{C}_8\text{H}_{12})]_2\) was reported
to yield with \( \text{O}_2 \), a single cyclooctene-one product and an Ir species, the infrared spectrum of which indicated the conversion of coordinated -OOH to -OH; the data were interpreted in terms of eq I.31 (written for a monomer).\(^{26,28}\)

\[
\text{IrCl}_2(\text{H}(\text{C}_8\text{H}_{12})) + \text{O}_2 \rightarrow \text{IrCl}_2(\text{OOH})(\text{C}_8\text{H}_{12}) \rightarrow '\text{Ir(OH)}\text{Cl}_2' + \text{C}_8\text{H}_{12}\text{O}
\]

I.31

The suggested mechanism for oxygen atom transfer is similar to that suggested by Roussel and Mimoun for the oxidation of terminal olefins by \( \text{H}_2\text{O}_2 \) via a Pd-OOH intermediate (Scheme I.8).\(^{29}\)

**Scheme I.8**

\[
\text{(RCO}_2\text{)}_2\text{Pd} \begin{array}{c}
\text{H}_2\text{O}_2 \rightarrow \text{RCO}_2\text{Pd-OOH} \end{array} \rightarrow \text{RCO}_2\text{Pd-OOH} \]

Addition of excess \( \text{C}_8\text{H}_{14} \) to the \([\text{IrCl}_2(\text{H})(\text{C}_8\text{H}_{12})]_2\) system and the use of a \( \text{H}_2/\text{O}_2 \) mixture to regenerate the \( \text{Ir}^{\text{III}}(\text{H}) \) from the \( \text{Ir}^{\text{III}}(\text{OH}) \), as in
Scheme I.7, gave low but catalytic yields of the ketone and a large excess of $\text{H}_2\text{O}$ from an independent, metal-catalyzed hydrogenolysis of $\text{O}_2$. The low catalytic activity towards the olefin oxidation was attributed to the low activity of the 'Ir(OH)' intermediate towards $\text{H}_2$ (Scheme I.7).\textsuperscript{26}

A catalytic cycle analogous to that in Scheme I.7 was proposed by Tabushi and Yazaki\textsuperscript{30} for the epoxidation of olefins using a Mn\textsuperscript{III} porphyrin under $\text{O}_2$ with $\text{H}_2$/colloidal platinum as the coreductant. The suggested mechanism (Scheme I.9) is analogous to that postulated for the Ir system in Scheme I.7 in that both involve $\text{M-OOH}$ intermediates, formed by the protonation of coordinated dioxygen species and the insertion of $\text{O}_2$ into a Ir\textsuperscript{III}-H bond, respectively. The subsequent oxygen transfer in the Mn system is thought to occur via a Mn\textsuperscript{IV}-$\text{O}$ species, similar to the Fe\textsuperscript{III}=O species implicated in the P-450 systems (Scheme I.4).

**Scheme I.9**

\[
\begin{array}{c}
\text{Mn}^{\text{II}} \quad \text{O}_2 \quad \text{Mn}^{\text{IV}}(\text{O}_2^{=}) \quad \text{H}^+ \\
\text{e} \quad \text{Mn}^{\text{III}} \quad \text{Mn}^{\text{IV}}
\end{array}
\]

$\text{Mn}^{\text{IV}}(\text{OOH}) \xrightarrow{\text{H}^+} \text{Mn}^{\text{IV}}$-$\ddot{\text{O}}$
I.5 Contents of this thesis

The general aim behind the work described in this thesis was to use \( \text{H}_2/\text{O}_2 \) mixtures in the presence of rhodium catalysts for selective autoxidation of organic substrates as in Scheme I.7. As a prelude to such a study it was attempted to generate \( \text{Rh}^{\text{III}}(\text{OOH}) \) species by reaction of suitable \( \text{Rh}^{\text{III}} \) complexes with \( \text{H}_2 \) followed by \( \text{O}_2 \). Sulfoxide complexes were selected as suitable precursors for the hydride complexes, since such chemistry had already been studied with some success for these complexes.\(^{23}\)

Attempts at generating \( \text{Rh}^{\text{III}}(\text{H}) \) species containing DMSO ligands are summarized in Chapter III. An interesting redox reaction between \( \text{RhCl}_3(\text{DMSO})_3 \) and \( \text{NEt}_3 \), which was observed in the course of the work given in Chapter III, is detailed in Chapter IV. A rhodium- and \( \text{H}_2 \)-dependent oxidation of DMA, which was discovered accidentally in some preliminary studies on the use of \( \text{Rh}^{\text{III}} \) catalyst for autoxidations under \( \text{H}_2/\text{O}_2 \) mixtures, is described in Chapter V.
CHAPTER II

EXPERIMENTAL
II EXPERIMENTAL

II.1 General instrumentation

Visible spectra were recorded on a Perkin-Elmer 552A spectrophotometer, fitted with thermostatted cell compartments. Near infra-red spectra were obtained using a Cary 17D spectrophotometer. Spectral cells used were anaerobic type with quartz cells of 1 cm or 0.1 cm pathlength (Fig II.1 and Fig II.2).

Infra-red spectra were recorded on a Perkin-Elmer 457 or 598 grating spectrometer calibrated with the 1601.4 cm\(^{-1}\) or 906.7 peaks of polystyrene, or a Nicolet 5DX FT-IR instrument. Solid samples were run as Nujol mulls between CsI plates or as KBr discs. Solution samples were run in 0.1 cm pathlength cavity cells with KBr windows.

Proton and carbon-13 nuclear magnetic resonance (\(^1\)H nmr) spectra were recorded on Bruker WP80 (80 MHz), Varian XL100 (100 MHz) or Bruker WH400 (400 MHz) spectrometers operating in the Fourier transform mode, generally with tetramethylsilane (TMS) at \(\delta 0.0\) as an internal standard.

For gas chromatographic analysis a Carle Analytical Gas Chromatograph (Model 311), or a temperature programmable Hewlett-Packard 5750, both in the thermal conductivity detector mode, was used. The columns used were of stainless-steel with 1/8" internal diameter. A hand-packed 6' foot column containing PPQ (Water Associates, Inc., 80-100 mesh) was used for H\(_2\)O determination while a 12' foot column was used to determine H\(_2\), O\(_2\) and C\(_2\)O. Carbowax 20 M on Chromosorb WHP (80-100 mesh) was the packing material used for estimating organic oxidation products. A 6'
Fig. II.1 Schematic representation of an anaerobic spectral cell
Fig. II.2  Schematic representation of a combination anaerobic spectral cell and gas uptake flask
column containing 5% Carbowax purchased from Chromatographic Specialities Ltd., and a hand-packed 6' column containing home-made packing material with ~1% Carbowax 20 M, were both used.

Conductivity measurements were made at 25°C using a Thomas Serfass conductivity bridge and cell.

II.2 Gas-uptake apparatus and measurement

II.2.1 The apparatus

The constant pressure gas-uptake apparatus used for determining gas stoichiometrics and kinetic studies is shown schematically in Fig. II.3.

The pyrex two-neck reaction flask (A), equipped with a dropping side-arm bucket, was attached to a flexible glass spiral tube, which connected flask A to a capillary manometer (D) at tap C. The reaction flask was clipped to a Welch variable speed electric motor so that the flask could be shaken whilst held in the thermostatted oil-bath (B). The oil-bath consisted of a four liter glass beaker with silicone oil and was held in a polystyrene-foam lined wooden box for insulation. The capillary manometer contained n-butyl phthalate, a liquid of negligible vapor pressure, and was connected to the gas measuring burette which had a precision bored tube (N) of known diameter and a mercury reservoir (E). The capillary manometer and gas measuring burette were thermostatted at 25°C in a perspex water bath. By means of an Edwards high vacuum needle valve (M), the burette was connected to the gas-handling
Fig. II.3  Schematic representation of a constant pressure gas uptake apparatus
part of the apparatus. The latter consisted of a mercury manometer (F), the gas inlet (Y), and connections to a Welch Duo-Seal rotary vacuum pump (G). The thermostatting of the two baths was controlled by Jumo thermo-regulators and Merc-to-Merc relay control circuits, with 40 Watt elongated light bulbs used for heating. This, with mechanical stirring, meant that the temperature could be maintained within ± 0.5°C. The gas-uptake was measured with a vertically mounted cathetometer.

In each experiment 5.0 mL of solvent was pipetted into the 25 mL reaction flask and any other cocatalysts or substrates required were weighed or pipetted in. The weighed complex was suspended on the hook of the side arm of the reaction flask. The flask with the connected spiral arm was attached to the gas-handling part of the apparatus at joint O. The substrate solution was degassed by a freeze and thaw static vacuum technique which was carried out three times. The reaction flask was then filled with gas to a pressure slightly less than that required, and taps C and P were closed. The flask and spiral arm could then be removed and connected to the capillary manometer at H. The flask was placed in the oil-bath, and attached to the motor driven shaker (I) which was then started. The whole system up to tap C was evacuated with taps, H, K, L, J, and M open. After a 10 minute shaking to attain thermal equilibration of the reaction flask and to saturate the solution with gas, the shaking was stopped, and the required gas was admitted to the rest of the apparatus at pressure slightly less than required. Tap C was opened and the pressure increased to that desired. The needle valve and taps K and L were closed; shaking was continued for another 5 min to complete thermal equilibration and the initial reading of the mercury level in N taken.
II.2.2 A general experiment

An experimental run was started by dropping a bucket containing the complex, and starting the shaker and timer. The gas-uptake was indicated by the difference in the oil levels of the manometer (D). The manometer was balanced by allowing gas to the burette through the needle valve and thereby maintaining a constant pressure in the reaction flask. The corresponding rise in the mercury level in N was measured at appropriate intervals of time. Since the diameter of the manometer (N) was known, the volume of gas consumed could be calculated and expressed as mmols of uptake per mg (mmol) of complex.

II.2.3 Solubility of gases

The solubility of H₂ and O₂ in DMA at specific temperatures and pressures was determined using the gas-uptake apparatus discussed previously. The DMA was degassed but was left under vacuum when taps C and P were closed, and the flask with the spiral arm transferred to the capillary manometer. The system was then evacuated to tap C and filled with the required gas to the approximate pressure required. Tap C was opened, and the pressure immediately adjusted to that required. With taps K and L, and the needle closed, the timer and shaker could be started, and the immediate uptake of gas could be measured.

The solubility of H₂ in DMA at 50°C was measured to be \((1.90 \pm 0.05) \times 10^{-3}\) M and \((1.36 \pm 0.05) \times 10^{-3}\) M at 700 and 500 torr, respectively. At 60°C the solubility of H₂ in DMA obeys Henry's Law to give a K value of
2.82 \times 10^{-6} \text{M torr}^{-1} \text{ where } K = \frac{[H_2]}{\text{partial pressure of } H_2}. A K \text{ value of } (2.70 \times 0.05) \times 10^{-6} \text{M torr}^{-1} \text{ was deduced for the solubility at } 50^\circ C. \text{ The solubility of } O_2 \text{ at } 50^\circ C \text{ at 760 torr was deduced to be } 4.0 \times 10^{-3} \text{ M.}

II.2.4 Gas-stoichiometries

The procedure described in Section II.2.3 was used to determine gas stoichiometries for reaction solutions. For accurate measurements it was necessary to keep the contact time between the reaction solution and the gas phase to a minimum to avoid reaction between the gas phase and the solution surface, between the time the gas is introduced and the initial monitoring of the uptake. The total gas-uptake observed was corrected for gas solubility under the same conditions.

II.2.5 Gas evolution

The same uptake apparatus was used to measure gas evolutions corresponding to about $4 \times 10^{-2}$ mmol of gas at S.T.P. The upper limit given was determined by the height of the mercury column in the gas buret (N,E; Fig II.3) of the particular apparatus used. The procedure was the same as that for an uptake experiment except that the manometer was balanced in the present case by releasing gas into the part right of the needle-valve which was under a pressure less than that used in the reaction conditions.
II.2.6 Introduction of gas mixtures

General procedure

A pre-mixed gas mixture, contained in a mixing flask T (Fig II.4) at a pressure \( P' \), was allowed to diffuse instantly into the evacuated reaction flask and the rest of the apparatus to the desired pressure \( P \). For ease of explanation the part of the apparatus from the reaction flask A to the needle valve M will be designated \( V_3 \), that enclosed by M, P, Y and E taps designated \( V_2 \), and the YTQ + QX + QZ part, \( V_1 \) (Fig II.4).

To pre-mix the gases, for example in a 1:1 ratio in \( \text{H}_2 \) and \( \text{O}_2 \), the two gases were introduced separately and consecutively to the evacuated \( V_1 + V_2 \) at a pressure of \( P/2 \) each, via gas lines (1) and (2), respectively, and \( V_1 \) was isolated by closing taps Y, X and Z. The rest of the system upto the greaseless tap A' was evacuated and tap R was closed. The greaseless tap A' was opened to connect the already evacuated reaction system to the rest of the apparatus. On opening Y slowly, the gas at a pressure of \( P' \) in \( V_1 \), flowed instantly into \( V_2 + V_3 \) to give the final desired pressure of \( P \) in \( V_1 + V_2 + V_3 \). The system was allowed to equilibrate for 1/2 h before closing Y to proceed as required for a general uptake experiment (Section II.2.2). The final total pressure \( P \) was estimated using the relation \( P = P' V_1 / (V_1 + V_2 + V_3) \). The ratio \( V_1/V_1 + V_2 + V_3 \) was experimentally derived for the apparatus used. In the particular apparatus a \( P' \) of 920 torr in \( V_1 \) was required to obtain a final pressure of 760 torr in \( V_1 + V_2 + V_3 \).
Fig. II.4 A simplified version of a gas uptake apparatus with details of the modified gas inlet
The part $V_2$ consists of several narrow tubes making up the manometer and the connections to it. To ensure that the problem of incomplete mixing of gases did not significantly affect the ratio of gases in $V_1$, a volume of $V_1 > 10V_2$ was used.

Hydrogen diffuses 3.6 times faster than $O_2$ in air under comparable conditions. It is not too clear what rate differentials are operative when a mixture of $H_2$ and $O_2$ at, for example, 920 torr, is opened to a vacuum composed of several interconnected narrow tubes. If the rates are significantly different, the gas mixtures in $V_3$, particularly in the reaction flask A and the immediate surroundings, will be richer in $H_2$ than calculated.

To check the homogeneity of the gas mixture in $V_1+V_2+V_3$, 0.5 mL aliquots of a 1:1 gas mixture in $V_1+V_2+V_3$ equilibrated for 30 min were sampled at A and near T in Fig II.4 by gas chromatography using 12’ PPQ packed column at 30°C with the carrier gas He delivered at 30 psi; retention times: $H_2$ 2 min, $O_2$ 2.5 min; thermal conductivity detector sensitivity: $O_2/H_2$, 27. The aliquots from A gave a ratio of $28 \pm 2$ for the peak area of $O_2/H_2$ while those from T gave $30 \pm 2$. Therefore the gas mixture in $V_1+V_2+V_3$ can be considered homogeneous within the limits of the analytical method used.

II.3 Spectral measurements

Anaerobic cells as shown in Figs II.1 and II.2 were used to monitor reactions spectrophotometrically.
In a typical experiment, a weighed amount of the complex was placed in the cell (Fig II.1) and 1.0-5.0 mL of solvent pipetted into the 25 mL flask. The solvent was degassed three times by employing a freeze and thaw static vacuum technique and the gas(es) of choice was introduced via attachments to the B7 socket. The solid and solvent were then mixed and shaken to obtain a homogeneous solution. For reactions at temperatures close to ambient, the cell was placed in the thermostatted cell compartment and the spectral changes recorded immediately. For reactions at higher temperatures the solvent in the flask was brought to that temperatures before mixing with the solid and placing in the thermostatted cell.

To obtain the visible spectrum of a solution used in an uptake experiment a reaction flask with a quartz cell attachment was used (Fig II.2). After the uptake was monitored for the desired time period, the greaseless tap was closed and the flask detached from the apparatus. The solution was transferred into the cell by tilting the flask in order to record the visible spectrum. Further experiments were carried out, if necessary, by reconnecting the flask to the uptake apparatus. This method was particularly useful for obtaining the visible spectra of extremely air-sensitive species.

The same reaction flask was used to obtain the nmr spectra of highly air-sensitive reaction solutions by attaching a sealing nmr tube via the B7 socket (2) (Fig II.2).
II.4 Materials

II.4.1 Solvents

Spectral or reagent grade solvents were obtained from Aldrich, Eastman, Fisher, Mallinckrodt or MCB Chemical Co. Dimethylacetamide (DMA) was stirred over CaH$_2$ under a N$_2$ atmosphere over 24 h and vacuum distilled. When specified as dry, other solvents were distilled from the following drying agents under N$_2$: CH$_2$Cl$_2$ from P$_2$O$_5$; acetone from anhydrous K$_2$CO$_3$; alcohols with the corresponding magnesium alkoxide. All dried solvents were stored under N$_2$ or Ar and dispensed under the same.

II.4.2 Gases

Purified oxygen, argon, nitrogen and carbon monoxide were obtained from Canada Liquid Air Ltd., Union Carbide of Canada Ltd., or Matheson Gas Co., and were used without further purification. Purified hydrogen for hydrogenation reactions was obtained from Union Carbide and was passed through an Engelhard Deoxo catalytic purifier to remove traces of O$_2$. The gases were dried where necessary by passing them through CaCl$_2$ drying tubes.
II.4.3 Rhodium Complexes

II.4.3.1 General

Rhodium(III) trichloride was obtained as the trihydrate from Johnson Matthey Ltd. and was kept in a desiccator. Literature methods were used to prepare \( \text{RhCl}_3(\text{DMSO})_3 \)\(^{33} \), \([\text{NEt}_4][\text{RhCl}_4(\text{DMSO})_2]^{33} \), \([\text{RhCl}(\text{DMSO})_5][\text{BF}_4]_2^{34} \), \( \text{RhCl}_3(\text{Et}_2\text{S})_3^{35} \), \( \text{RhCl}_3(\text{Me}_2\text{S})_3^{35} \) and \([\text{RhCl}(\text{COE})_2]_2^{36} \). The complex \([\text{RhCl}(\text{CO})_2]_2\) was a gift from Dr. D. Mahajan. Some experiments are described in Chapter III in cases where departures from the literature reports were observed or modifications of the reported methods were used.

II.4.3.2 Mer-cis-trichloroaquobis(S-dimethylsulfoxide)rhodium(III), mer-cis-RhCl\(_3\)(H\(_2\)O)(DMSO)\(_2\)

To \( \text{RhCl}_3\cdot3\text{H}_2\text{O} \) (0.2 g, 0.8 mmol) dissolved in 2-propanol solvent (3 mL) containing 20% \( \text{H}_2\text{O} \) (0.6 mL), about 3 equivalents of DMSO (0.16 mL, 2.3 mmol) were added. The yellow suspension which formed after stirring the solution for approximately 1 h, was filtered, washed with 2-propanol and ether, and dried at r.t. under vacuum. Anal. calcd. for \( \text{C}_4\text{H}_{14}\text{Cl}_3\text{O}_3\text{S}_2\text{Rh} \): C 12.86, H 3.72; found: C 12.81, H 3.74. \(^1\text{H}\) nmr (TMS) \((\text{CD}_3)_2\text{CO}\): 3.67 (s, 6H, S-CH\(_3\)), 3.50 (s, 6H, -SCH\(_3\)). \( ^{13}\text{C}\) nmr (\(\nu_{\text{CO}}\)) 1140 cm\(^{-1}\) (s, \(\nu_{\text{SO}}\)); 1060 cm\(^{-1}\) s and 980 cm\(^{-1}\) w (\(\rho_{\text{CH}_3}\)); 3200 cm\(^{-1}\) (br \(\nu_{\text{O-H}, \text{H}_2\text{O}}\)); 1600 cm\(^{-1}\) (w, br, \(\delta_{\text{H}_2\text{O}}\), \(\text{H}_2\text{O}\)). The complex was soluble in \( \text{H}_2\text{O}, \) acetone and \( \text{CH}_3\text{NO}_2 \) and insoluble in \( \text{CH}_2\text{Cl}_2 \).
II.4.3.3 Trichloro(diethylethenamine)bis(S-dimethylsulfoxide)-rhodium(III), RhCl$_3$(CH$_2$CH=NEt$_2$)(DMSO)$_2$

To a suspension of RhCl$_3$(DMSO)$_3$ (1.0 g, 2.25 mmol) in acetone (25 mL), NEt$_3$ (0.63 mL, 4.5 mmol) was added with stirring, all under Ar. Most of the suspension dissolved immediately to give a red-brown solution and a turbidity appeared after 10-20 min. The mixture was stirred overnight to yield an off-white precipitate and a red-brown solution. The off-white solid mixture was filtered off under Ar, recrystallized from EtOH and identified as NEt$_3$·HCl (156 mg, 1.1 mmol). Anal. calcd. for C$_6$H$_{16}$C1N: C 52.13, H 11.70, N 10.17; found: C 51.13, H 11.54, N 9.68. $^1$H nmr $\delta$TMS(CDC$_3$): 1.40 (t, 9H, N-CH$_2$CH$_3$), 3.10 (dq, 6H, NCH$_2$CH$_3$) and 12.2 (br, -1H, N$^+$-H). Ir (Nujol): 2400-2600 cm$^{-1}$, br, s ($\nu_{N-H}$). Ir(CH$_2$Cl$_2$): 2400 cm$^{-1}$, br, s and 2560 cm$^{-1}$, s ($\nu_{N-H}$).

The red-brown solution was concentrated by pumping to about 5 mL and warmed to dissolve any precipitates formed. The resulting solution was allowed to cool slowly when a crystalline yellow precipitate deposited. The solution was filtered under Ar to yield an air-stable yellow solid and an air-sensitive mother liquor. Repeating the sequence of concentrating, warming and slow cooling gave two other crops of the yellow product. All three crops were combined and recrystallized from warm acetone to yield 250 mg (0.5 mmol) of product in 22% yield based on rhodium. Further precipitation yielded material contaminated by an air-sensitive species. Anal. calcd. for C$_{10}$H$_{25}$NO$_2$S$_2$Cl$_3$Rh: C 25.85, H 5.42, N 3.02; found: C 25.86, H 5.34, N 2.99. $^1$H nmr data (Fig IV.2 and Table IV.1). $^{13}$C ($^1$H) nmr data (Table IV.2). Ir(KBr): 1645 cm$^{-1}$, s ($\nu_{C=N^+}$); 1110 cm$^{-1}$, s and 1125 cm$^{-1}$, sh ($\nu_{SO}$); other details in Fig.
IV.8). The complex dissolves readily in CHCl₃, CH₂Cl₂, acetone, CH₃OH and H₂O and slightly in EtOH, and is non-conducting in CH₃NO₂. The compound exists in CDCl₃ solution as two isomers --60% mer-trans and 40% mer-cis after equilibration for <4 h (see Fig. IV.1.b and Section IV.2.3), and essentially as the mer-trans in acetone (see Fig. IV.10a and Section IV.2) or immediately after dissolution in CDCl₃ (Fig. IV.1.a). Slow diffusion of ether into an acetone solution or a CDCl₃ solution yields a compound containing about 70% of the mer-cis isomer as judged by a ¹H nmr of the sample.

II.4.3.4 Mer-cis-trichloro(dimethylsulfide)bis(S-dimethylsulfoxide)-rhodium(III), mer-cis-RhCl₃(DMS)(DMSO)₂

Approximately one equivalent of DMS (20 μL, 0.25 mmol) was added to a solution of RhCl₃(DMSO)₃ (110 mg, 0.25 mmol) in dry CH₂Cl₂ (10 mL). The solution was stirred overnight and ether was added slowly to obtain a yellow precipitate. Anal. calcd for C₆H₁₈Cl₃O₂S₃Rh:  C 16.85, H 4.24; found:  C 17.00, H 4.25. ¹H nmr δTMS (CDCl₃): 2.44 (d, J = 2 Hz, 6H); 3.64 (s, 6H); 3.56 (s, 6H). Ir (Nujol): 1130 cm⁻¹, s (νSO, DMSO); 1030 and 985 cm⁻¹, m (νCH₃ asymm. and symm., respectively); also see Section III.3.2.
II.4.3.5 Mer-trichlorotris(dimethylsulfide)rhodium(III), mer-RhCl$_3$(DMS)$_3$

A degassed solution of RhCl$_3$(DMSO)$_3$ (50 mg, 0.11 mmol) in C$_2$H$_4$Cl$_2$ (15 mL) was stirred at 50°C under a CO atmosphere for 3 d. A yellow precipitate was obtained from the concentrated solution by adding ether. Recrystallization from CH$_2$Cl$_2$/ether gave a deep orange crystalline product in 65% yield. Anal. calcd. for C$_6$H$_{18}$Cl$_3$O$_3$S$_3$Rh: C 18.21, H 4.59; found: C 18.31, H 4.59. $^1$H nmr $^\delta_{TMS}$ (CDCl$_3$): 2.50 (d, J = 2 Hz, 12H) and 2.30 (d, J = 2 Hz, 6H).

This complex was prepared also by a literature procedure using RhCl$_3$·3H$_2$O and DMS.$^{35}$

II.4.3.6 Product from the reaction between RhCl$_3$(DMSO)$_3$ and CO in DMA in the presence of an equivalent of added H$_2$O

A degassed solution of RhCl$_3$(DMSO)$_3$ (0.2 g, 0.45 mmol) in DMA (15 mL) containing added H$_2$O (9 µL, 0.5 mmol) was stirred under 1 atm CO for 24 h. A solution color change from deep to light orange indicated the completion of the reaction. The solvent was distilled off at 50°C under vacuum to yield a yellow residue. Further pumping turned the precipitate into a yellow-orange oil, while white crystals were collected on the walls of the tall Schlenk tube used. The highly hygroscopic crystals were carefully scraped off under Ar and were shown to be DMA·HCl by comparing the $^1$H nmr and ir (Nujol) data with those of the authentic compound (Section II.4.5). The amount of DMA·HCl recovered
was approximately 20 mg (-0.2 mmol). The oily residue was dissolved in CO-saturated CH₂Cl₂ and CO-saturated ether was added slowly to make the solution just turbid. Leaving the mixture in an ice/salt bath at ~-10°C for a few hours yielded pale-yellow, needle-like crystals. These were filtered under Ar, washed with ether and dried by leaving under a dynamic vacuum. Filtering under CO changed the color of the filtered crystals from pale-yellow to light-green; this color change was reversed on resubjecting the crystals to Ar. Yield 60 mg. found: C 29.46, H 4.74, N 6.92. \( \text{Ir (KBr)}: 2025 \text{ m and 1985, s (} \nu_{\text{CO}} \text{)}; 1850, \text{ m (} \nu_{\text{CO}} \text{)}; 600-1700, \text{ br (absorptions due to the (DMA)}₂\text{H}^+ \text{ cation); see also Fig III.14.a.} \)

\[ ^1H \text{ nmr } \delta_{\text{TMS}} \ (\text{CDCl₃}): 2.38 \ (s, 6H, CH₃CO-), 3.14 \ (s, 12H, CH₃CON(CH₃)), 6.56 \ (br, 1H, D₂O sensitive, (DMA)₂H^+). \] In some other trials oily products were obtained. A discussion on the crystalline product is given later in Section III.4, p. 97.

II.4.4 Derivatives of dimethylacetamide

The N-methyl-N-methylolacetamide compound CH₃CON(CH₃)CH₂OH, was prepared by a literature method³⁷ as an in situ mixture containing about 30% starting materials N-methylacetamide, CH₃CON(CH₃)H (Eastman), and paraformaldehyde, H(CHOH)ₙOH. The preparation and some properties of CH₃CON(CH₃)CH₂OOH and CH₃CON(CH₃)CHO are described below. Proton nmr data for all of the derivatives are summarized also in Table V.1.
N-Methyl-N-formylacetamide; CH\textsubscript{3}CON(CH\textsubscript{3})CHO

Dimethylacetamide (2.0 mL) was heated at 100°C under \textsubscript{O}\textsubscript{2} (1 atm) for 2.5 d. After pumping off most of the DMA, the residual liquid (~0.5 mL) contained about 10% CH\textsubscript{3}CON(CH\textsubscript{3})CHO in DMA, as judged by \textsuperscript{1}H nmr. Further enrichment was not possible because of the loss of the compound with DMA on prolonged pumping. A small quantity of CH\textsubscript{3}CON(CH\textsubscript{3})CHO containing <10% DMA was isolated using 4 x 50 µl portions of the enriched reaction mixture on an OV-17 column in a Varian Aerograph model 90-P preparative gas chromatograph at 95°C. \textsuperscript{1}H nmr \(\delta\text{TMS (CDCl}_3\): 2.40 (s, 3H, CH\textsubscript{3}CO-), 3.11 (s, 3H, N-CH\textsubscript{3}), 9.21 (s, 1H, N-CHO), see also Table V.1. Mass spec: m/e 101 (0.1), CH\textsubscript{3}CON(CH\textsubscript{3})CHO\textsuperscript{+}; 73 (36), CH\textsubscript{3}CON(CH\textsubscript{3})\textsuperscript{+}; 58 (21), CH\textsubscript{3}CONH\textsuperscript{+}; 43 (100), CH\textsubscript{3}CO\textsuperscript{+}. The percentage intensities for all fragments except the parent ion were obtained from a gc/ms of the 90% pure sample, in order to minimize interference from impurities. The parent ion was not discernible in a gc/ms on a column containing 1% carbowax on Chromasorb WHP at 90°C.

N-Methylacetamido-methylhydroperoxide, CH\textsubscript{3}CON(CH\textsubscript{3})CH\textsubscript{2}OOH

Dimethylacetamide (5.0 mL, 60 mmol) containing a trace of \textsuperscript{t}BuOOH (10 µl of 70% aqueous solution, 0.08 mmol) at 80°C was shaken under 1 atm of \textsubscript{O}\textsubscript{2} for 24 h. Most of the unreacted DMA was then vacuum transferred in about 45 min to leave a syrupy liquid (~0.5 mL). Further pumping for about 2 days at room temperature yielded a small amount of CH\textsubscript{3}CON(CH\textsubscript{3})CH\textsubscript{2}OOH (~60 µl, 80 mg, 0.8 mmol) containing <5% of DMA as
impurity, as judged by $^1$H nmr data in CDCl$_3$ (Fig V.1.a). Anal. calcd. for C$_4$H$_9$NO$_3$: C 40.33, H 7.62, N 11.75; found: C 40.05, H 7.60, N 11.47. Ir: 3399, 3231 cm$^{-1}$ (s, $\nu_{O-OH}$), 1634 cm$^{-1}$ (s, $\nu_{CO}$), 775 and 822 (m, $\nu_{O-0H}$). Ir(CDCl$_3$): 3526 (m, $\nu_{O-OH}$). $^1$H nmr $\delta_{TMS}$(CDCl$_3$): Fig V.2, Table V.1). Longer reaction times gave lower yields of the hydroperoxide and increasing amounts of CH$_3$CON(CH$_3$)CHO, as judged by $^1$H nmr.

Attempts at purifying an approximately 70% mixture of CH$_3$CON(CH$_3$)-CH$_2$OOH in DMA by separatory gas chromatography gave a decomposition product identified as CH$_3$CON(CH$_3$)CHO by $^1$H nmr: $\delta_{TMS}$(CDCl$_3$): 2.4 (s, 3H, CH$_3$CO), 3.1 (s, 3H, N-CH$_3$) and 9.2 (s, 1H, N-CHO). Almost quantitative decomposition of the hydroperoxide to the formyl derivative is observed under analytical gas-chromatographic conditions (Section II.5.4).

II.4.5 Other materials

Proton sponge, (1,8-bis(dimethylamino)naphthalene), supplied by Aldrich, was sublimed before use. Triethylamine, 2,6-di-t-butylpyridine and dimethylaniline (MCB Chemical Co.) were used as supplied.

Dimethyl-, diethyl- and diphenylsulfides (Aldrich), spectral grade dimethylsulfoxide (Section II.4.1), diphenylsulfoxide (Eastman), diphenylsulfone and dimethylsulfone (Aldrich), were used without further purification. Care should be taken in handling dimethylsulfoxide since the compound is readily absorbed by the skin.

Cyclooctanone (Aldrich), catalase from bovine liver (Sigma Chemicals), chromotropic acid (Fisher Scientific Co.), 2-thiobarbituric acid (Aldrich), and 53% HBF$_4$ in ether (Alfa Chemicals) were used as
supplied.

Dimethylacetamide hydrochloride (DMA·HCl) was prepared by passing gaseous HCl through neat DMA and recrystallized from EtOH. $^1$H nmr $\delta_{\text{TMS}}$ (CDCl$_3$): 2.32, 3H, CH$_3$CO; 3.10, 6H, N(CH$_3$)$_2$; ~8 br, ~1H (DMA)$_2$H. Ir (Nujol): 1900-2700 cm$^{-1}$, br, $\nu_{\text{OH}}$: 1770 cm$^{-1}$, br $\delta_{\text{OH}}$: 1660 cm$^{-1}$, s, $\nu_{\text{C=H}}$. The $^1$H nmr and ir data gave good correspondence with literature data. $^{38}$ Dimethylacetamide hydrofluoroborate (DMA·HBF$_4$) was prepared by adding 53% HBF$_4$ in ether to neat DMA. The precipitate formed was recrystallized from EtOH. Anal. calcd. for C$_4$H$_{10}$NOBF$_4$: C 27.47, H 5.76, N 8.00; found: C 27.36, H 5.50, N 7.89.

II.5 Analysis of oxidation products in DMA solvent

This section describes the analytical methods used to estimate oxidation products of DMA and diphenylsulfide in DMA solvent.

II.5.1 H$_2$O

Major literature methods used for analysis of water include the Karl Fischer method,$^{39,40}$ gas chromatography,$^{41}$ and near-infrared spectroscopic analysis.$^{40,42}$ The near infrared method was found to be a very convenient, non-destructive method requiring no internal standards and was convenient for the purposes of the present work. Water shows an absorption maximum at around 1900 nm which has been used previously$^{42}$ for analysis of H$_2$O in a variety of solvents, including
polar hygroscopic solvents such as methanol or isopropanol. In the present work the same method was used successfully for H₂O in DMA solvent. Though not emphasized in the literature reports, handling of the sample under anaerobic conditions was found to be essential for the success of the method for hygroscopic solvents like DMA.

Dimethylacetamide (5.0 mL) was transferred under Ar to a reaction flask equipped with a quartz cell of 1 cm pathlength. The absorbance of the solvent A₀ (eq. II.1) was measured at 1930 nm against a 1 cm reference cell containing DMA under Ar. Quartz glass and DMA solvent (€₁₉₃₀, 0.2 mol⁻¹Lcm⁻¹) absorb in the near-IR region. Since the two cells used were not perfectly matched a net absorbance, positive or negative, can be expected for A₀. For the particular two cells used, a net positive absorbance was noted (Fig II.5.). Known amounts of H₂O were syringed into the sealed reaction flask via the septum cap to obtain the absorbance A (eq II.2) for different amounts of added H₂O (Curves 2-6, Fig II.5.a). The difference (A-A₀) obeyed Beer's law for concentrations up to 0.10 M H₂O in DMA (Fig II.6). For concentrations less than ~0.01M the method is not too useful because of low sensitivity. The extinction coefficient of H₂O was determined to be 2 mol⁻¹Lcm⁻¹.

\[ A_0 = A_s - A_r \quad \text{II.1} \]

(Aₘ and Aᵣ are the absorbances of the sample and reference cells, respectively).

\[ A = (A_{\text{added H}_2\text{O}} + A_s) - A_r \quad \text{II.2} \]
Fig. II.5 Absorbance (A) of DMA in a 1 cm cell against a reference containing the same: $A_0$, no added $H_2O$; $A_1$, 0.057 M; $A_2$, 0.117 M; $A_3$, 0.170 M; $A_4$, 0.222 M; $A_5$, 0.281 M $H_2O$
Fig. II.6  Plot of A-A₀ at 1930 nm vs. the concentration of added H₂O in DMA in 1 cm cell (see Fig. II.5 for details and some spectra)
In an experimental run, the initial absorbance of the solvent, with or without added substrate \( A_0 \), was obtained as described above. The reaction flask was opened under Ar to introduce the bucket containing the catalyst into the side arm (Fig II.2), and the flask was re-stoppered. After a gas-uptake experiment (see Section II.2.2), the new absorbance \( A_T \) of the reaction solution was obtained. The amount of \( \text{H}_2\text{O} \) formed in the reaction was estimated by using the calibration data (eq II.3) for the same set of sample and reference cells.

II.5.2 Peroxides

Organic peroxides (ROOR), hydroperoxides (ROOH) and \( \text{H}_2\text{O}_2 \) were analyzed together as 'total peroxides' by a slightly modified literature method. An approximately 2 mM solution of \( \text{Na}_2\text{S}_2\text{O}_3 \) was standardized using analytical grade \( \text{KBrO}_3 \) just prior to the peroxide determination. To 1.0 mL of the reaction solution diluted with \( \text{H}_2\text{O} \) (20 mL), \( \text{KI} \) (1.0 g) 4 M \( \text{H}_2\text{SO}_4 \) (6 mL) and 10% aqueous ammonium molybdate (2-3 drops) were added in quick succession and the solution left in the dark, for 20 minutes. Blank solutions of DMA (1.0 mL) containing catalytic amounts of \( \text{RhCl}_3(\text{DMSO})_3 \) were used to make appropriate corrections for aerial oxidation, and usually accounted for less than 0.5 mL of 2 mM \( \text{Na}_2\text{S}_2\text{O}_3 \) in a typical titration requiring 10-20 mL.

A literature method with slight modifications was used for determining organic peroxides in the presence of \( \text{H}_2\text{O}_2 \). An aliquot of

\[
A - A_0 = A_{\text{added H}_2\text{O}} = k [\text{H}_2\text{O}]_{\text{added}}
\]
the reaction mixture (1.0 mL) was diluted with H₂O (20 mL). A saturated NaHCO₃ solution (3 mL) was then added, followed by 0.1% aq. catalase (~5 drops) and the solution was allowed to stand for about 10 min to remove any H₂O₂ (eq. II.4). Peroxidic analysis on the resulting solution was then carried out as described above.

The difference between the above two peroxide analyses was taken to be the concentration of H₂O₂ in a sample.

II.5.3 Formaldehyde, formic acid and carbon dioxide

A colorimetric method was used for determining HCHO. The method employed the development of a chromophore (λ_max, 580 nm) by the reaction between HCHO or (HCHO)_n with chromotropic acid under acidic conditions. As a minor modification for analysis in DMA solvent, a 0.10 mL aliquot of the reaction solution was diluted to 4.0 mL with H₂O and the suggested procedure for 4.0 mL aliquot of an aqueous solution was followed. A reference solution of RhCl₃(DMSO)_3 catalyst in DMA was used as a blank.

For the analysis of HCO₂H an aliquot of the reaction solution (2.0 mL) was diluted with H₂O (20 mL) and titrated with approximately 0.01M NaOH using phenolphthalein indicator. A DMA solution containing RhCl₃(DMSO)_3 catalyst was used as a blank. The NaOH solution was standardized using potassium hydrogen phthalate.

Other more sensitive methods given in the literature for HCO₂H were not suitable for the conditions used in the present work. For example, it was not possible to employ a literature colorimetric method
using thiobarbituric acid reagent\textsuperscript{45c} because of strong interference from the CH\textsubscript{3}CON(CH\textsubscript{3})CHO product formed in oxidation reactions of interest. A gas chromatographic method using a glass column containing a porapak Q support coated with 3\% phosphoric acid\textsuperscript{45d} was thought to be unsuitable for analysis of basic DMA solutions.

Carbon dioxide was detected qualitatively by taking 0.5 mL aliquots from the gas phase of a reaction mixture and analyzing by gas chromatography using a 12' column packed with Porapak Q support at 30°C with the He carrier gas delivered at 30 psi (Retention time, 10.5 min).

II.5.4 Other organic products

(a) Diphenylsulfide, diphenylsulfoxide and diphenylsulfone

The reaction solvent DMA was pumped off under vacuum and the residue, with added DMSO\textsubscript{2} as the internal standard, was dissolved in CDCl\textsubscript{3}, and the products were identified and quantified by their characteristic chemical shifts and integrations of the para protons in a 270 MHz or 400 MHz \textsuperscript{1}H nmr spectrum. \(\delta\text{\textsubscript{TMS(CDCl_{3})}}\) for DPS: 7.33, m, 10 H; \(\delta\text{\textsubscript{TMS(CDCl_{3})}}\) for DPS\textsubscript{O}: 7.45, m, 6H, ortho and meta to -SO; 7.66, m, 2H, para to -SO. \(\delta\text{\textsubscript{TMS(CDCl_{3})}}\) for DPS\textsubscript{2}: 7.50, m, 4H, ortho; 7.56, m, 4H, meta; 7.90, m, 2H, para.
(b) **N-methyl-N-formylacetamide and N-methyl-acetamido-methyl-hydroperoxide**

A known amount of mesitylene was added as the internal standard to a reaction solution to obtain a gas chromatogram (1% carbowax on chromosorb WHP at 80°C for 1 min, increased to 200°C at 10°C/min). Flow rate of He, 25 mL min⁻¹; retention times, min: mesitylene 1.4, DMA 3.2, CH₃CON(CH₃)CHO and CH₃CON(CH₃)CH₂OOH 4.8, CH₃CON(CH₃)H 5.1). The quantitative decomposition of the hydroperoxide to the formyl under the above gas chromatographic conditions was determined independently using an authentic sample of the former.

(c) **N-methylacetamide, N-methyl-N-methylolacetamide, dimethylsulfoxone and other organics**

A column containing 5% carbowax on chromosorb WHP at 100°C with He carrier gas delivered at 20 psi was used for detection by gas chromatography. Retention times: H₂O; ~2 min, DMA, ~4 min; cyclooctanone, ~8 min; DMSO, 10 min; CH₃CON(CH₃)CHO, 11 min; CH₃CON(CH₃)H and CH₃CON(CH₃)CH₂OH: 15 min; DMSO₂, 45 min. Cyclooctanone was used as an internal standard. Dimethylsulfoxone can be also detected by ¹H nmr; δTMS(CDCl₃): 3.0.
CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF DMSO COMPLEXES OF Rh$^{\text{III}}$

AND THEIR REACTIONS WITH H$_2$ AND CO
III Synthesis and characterization of DMSO complexes of Rh$^{III}$ and their reactions with $H_2$ and CO.

III.1 Some general properties of metal sulfoxides

The chemistry of sulfoxides$^{46}$ and their metal-complexes$^{47,48}$ is well reviewed. A free sulfoxide, for example, DMSO, has a pseudo-pyramidal structure with the sulfur atom at the apex, in the gas phase or in the solid state. The molecular structure of DMSO is represented by two canonical forms I and II, based on basicity, dipole-moment, and the evidence for a net positive charge on the sulfur atom.$^{46,48}$ The bonding between the sulfur and the oxygen is represented as involving a $\sigma$ interaction and a $d\pi$-$p\pi$ interaction.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\downarrow \quad \rightarrow & \quad \uparrow \\
S=O & \quad + \quad S=O
\end{align*}
\]

Because of the polarity of the bond in the direction of sulfur to oxygen, coordination to metal is expected to occur via the oxygen atom, and this mode of bonding is in fact the most commonly observed. Coordination through the sulfur atom, generally found in Pt metal sulfoxides, is harder to envisage. Some workers have included a third canonical form, III, to explain bonding through the sulfur atom.$^{49,50}$
In his detailed review on metal sulfoxides, Davies argues against such a formulation, based largely on evidence for an increase in the net positive charge on the sulfur atom on S-coordination. Instead, a general explanation based on 'soft' centres preferring 'soft' donor atoms is offered. The occurrence of both modes of bonding in Pt metal complexes is explained on the basis of the usual balance of steric and electronic effects.

Coordination through the sulfur atom (DMSO) or the oxygen atom (DMSO) can be readily distinguished by ir and nmr spectroscopy. Coordination through sulfur is expected to increase the oxygen to sulfur bond order. For example, in the ir spectra of rhodium complexes of DMSO, this is reflected by an increase in $\nu_{SO}$ by about 30-100 cm$^{-1}$ from the 1055 cm$^{-1}$ value found for free DMSO. The $\rho_{CH_3}$ modes of free DMSO, found at 918(w), 945 (m), and 1008 (s) cm$^{-1}$; also shift to higher frequency on coordination and may overlap with the $\nu_{SO}$ region. Because of this problem, the assignments for $\nu_{SO}$ are often checked by comparison of their ir with those of the DMSO-d$_6$ analogues of the complexes. The $\rho_{CH_3}$ modes show isotopic shifts on coordination, while the $\nu_{SO}$ peaks remain unchanged. Coordination through oxygen decreases the $p\pi$-$d\pi$ bonding and results in a decrease in $\nu_{SO}$ from the free value; for example, the $\nu_{SO}$ peaks of rhodium complexes of DMSO generally occur in the range 920-1000 cm$^{-1}$. 
Proton nmr spectra of metal sulfoxides are especially useful in structural studies of these complexes. The methyl protons of both DMSO and DMSO are found at a lower field than the free molecule chemical shift at $\delta 2.6$. Because of their proximity to the metal centre, the methyls on S-bonded sulfoxides are more deshielded than their O-bonded analogues; for example the methyl protons of DMSO and DMSO on Rh$^{III}$ generally appear at $\delta 3.1-3.7$ and $\delta 2.7-3.0$, respectively.\textsuperscript{33,34}

III.2 Synthesis and characterization of some Rh$^{III}$(DMSO) complexes

The synthesis of a variety of neutral, cationic or anionic Rh$^{III}$(DMSO) is documented.\textsuperscript{33,34} A major part of the work in this thesis involved the RhCl$_3$(DMSO)$_3$ (1) complex. Some relevant details of its synthesis and characterization and the preparation of two related complexes, mer-cis-RhCl$_3$(DMSO)$_2$(H$_2$O) and mer-cis-RhCl$_3$(DMSO)$_2$(DMS) are described in this section. Two other complexes RhCl$_3$(DMSO)$_2$(CH$_2$CH$^+$NEt$_2$) and [NEt$_2$H$_2$][RhCl$_4$(DMSO)$_2$] are described in Sections IV.2 and IV.6, respectively.

III.2.1 RhCl$_3$(DMSO)$_3$ (1)

The title complex was isolated in about 70% yield by reacting RhCl$_3$·3H$_2$O (1.0 g, 3.8 mmol) in DMSO (5 mL) at 70°C for ~4 h. The product was precipitated by adding dry EtOH, and recrystallized from CH$_2$Cl$_2$/ether as a yellow-range crystalline product. The ir data in
Nujol (1145 cm$^{-1}$, s, $\nu$$_{SO}$; 935, s, $\nu$$_{SO}$; 1032 and 980, s, $\rho$$_{CH}$) and the $^1$H nmr data in CDCl$_3$ (δ 3.625, 6H, DMSO; 3.443, 6H, DMSO; 2.871, 6H, DMSO) correspond well with literature values for the mer-cis-RhCl$_3$(DMSO)$_2$-(DMSO) isomer (1A).$^{33,34}$ The $^1$H nmr spectrum (Fig. III.1) shows several other DMSO and DMSO peaks corresponding to ~20% of the total DMSO and DMSO. Attempts to obtain a purer sample of the mer-cis isomer by repeated recrystallizations with CH$_2$Cl$_2$/ether gave a highest purity of ~90% for a total yield of <50%. Barnes et al. had obtained the mer-cis isomer in about 95% purity for an overall yield of 35%, using different reaction conditions.$^{34}$ For the purposes of the present work where RhCl$_3$(DMSO)$_3$ was expected to be used mainly as a synthetic precursor, a higher overall yield was considered more important than a relatively smaller increase in present purity, and the product containing ~80% of the mer-cis isomer was employed.

Identification of the minor isomers was carried out by solution $^1$H nmr spectroscopy. Barnes et al. have done a detailed study on the isomeric distribution of a series of [RhCl$_n$(DMSO)$_{6-n}$]$^{3-n}$ complexes.$^{34}$ The chemical shifts of overlapping peaks due to minor isomers of RhCl$_3$(DMSO)$_3$ were deduced indirectly by $^1$H-{$^{103}$Rh} INDOR measurements and were assigned to various geometrical and valence isomers. The higher resolution of the 400 MHz $^1$H nmr spectrometer used in the present work enabled us to obtain the proton features directly. Of the extremely small peaks in a $^1$H nmr spectrum of 1 in CDCl$_3$ (Fig. III.1), the apparent doublet at δ 2.439 and two other peaks at δ 3.645 and 3.560 (marked with asterisks in the Figure) are assigned to mer-cis-RhCl$_3$-(DMSO)$_2$(DMS) by comparison with data for the authentic compound (Section III.2.3). Four readily discernible minor peaks are found at δ 3.525,
Fig. III.1  400 MHz $^1$H nmr spectrum of RhCl$_3$(DMSO)$_3$ in CDCl$_3$
3.501, 3.496 and 2.780. In the presence of excess DMSO the peaks at δ 3.525 and 2.780 disappear, while the other two appear unchanged in intensity. The two peaks at δ 3.501 and 3.491 which occur in an approximate 2:1 ratio, are assigned to mer-RhCl₃(DMSO₃) (1B) to account for three DMSO ligands and the inequivalence of two of them. The two peaks at δ 3.525 and 2.780, which occur also in an approximately 2:1 ratio are assigned to mer-trans-RhCl₃(DMSO)₂(DMSO) (1C) to account for two equivalent DMSO ligands and a single DMSO. The alternate fac geometry is discounted on the grounds that the particular geometry is not found with RhCl₃L₃ complexes (L = DMS₃ and DMSO₃) reported in the literature. The assignments are summarized in Table III.1 along with those deduced by Barnes et al.³⁴ using a sample of RhCl₃(DMSO)₃ in CH₂Cl₂. Discrepancies in the relative chemical shifts of the DMSO ligands of the minor isomers could be due to the differences in the solvent effects of the two systems.

III.2.2 Mer-cis-RhCl₃(DMSO)₂(H₂O)

The title complex was isolated in an attempt to repeat another literature method for the synthesis of RhCl₃(DMSO)₂(DMSO) under ambient conditions.³³ According to the literature, a solution containing RhCl₃·3H₂O and three equivalents of DMSO in isopropanol solvent containing 20% H₂O changed color from red to yellow within an hour of reaction, and deposited orange crystals on leaving overnight. Some departures from these general observations were noted in that initial brown or yellow suspensions were sometimes obtained. In the present work, a
Table III.1

400 MHz $^1$H nmr data for RhCl$_3$(DMSO)$_3$ (1) in CDCl$_3$

<table>
<thead>
<tr>
<th>RhCl$_3$(DMSO)$_3$ in CDCl$_3$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.625</td>
<td></td>
</tr>
<tr>
<td>3.443 (~80%)(b)</td>
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<td>2.871</td>
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</table>

<table>
<thead>
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<th>RhCl$_3$(DMSO)$_3$ in CH$_2$Cl$_2$</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>3.551</td>
<td></td>
</tr>
<tr>
<td>3.363 (~95%)(b)</td>
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</tr>
<tr>
<td>2.811</td>
<td></td>
</tr>
</tbody>
</table>

1A, mer-cis-RhCl$_3$(DMSO)$_2$(DMSO)

<table>
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<tr>
<th>RhCl$_3$(DMSO)$_3$ in CDCl$_3$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.501 (~13%)(b)</td>
<td></td>
</tr>
<tr>
<td>3.496 (~6%)(b)</td>
<td></td>
</tr>
<tr>
<td>2.780</td>
<td></td>
</tr>
</tbody>
</table>

1B, mer-RhCl$_3$(DMSO)$_3$

<table>
<thead>
<tr>
<th>Other (-1%)</th>
<th>RhCl$_3$(DMSO)$_2$(DMS) and other species</th>
</tr>
</thead>
</table>

(a) Literature values for a sample prepared by a different method$^{34}$

(b) As a percent of total coordinated DMSO.
yellow suspension resulted from the initially clear solution, within one to six hours of reaction, in all three experiments attempted. However, in two of these, the final product obtained after stirring the initial yellow suspension overnight, was contaminated with metal. In the third experiment the initial yellow product was filtered, washed with isopropanol and cold acetone, and dried. A $^1$H nmr spectrum of the sample in acetone-d$_6$ showed two peaks of equal intensity for sulfur-coordinated DMSO (Section II.4.3), while the ir spectrum showed a characteristic $\nu_{SO}$ peak at 1140 cm$^{-1}$. The ir peaks at 1060 cm$^{-1}$, s, and 980 cm$^{-1}$, w, were assigned to $\rho_{CH_3}$ asymmetric and symmetric modes, respectively, by comparison with the data for the RhCl$_3$(DMSO)$_2$(DMSO) complex (Section III.2.1) which have been confirmed by deuteration studies.$^{33}$ Evidence for the coordinated H$_2$O was seen in the ir spectrum (Section II.4.3).

Isopropanol or ethanol is widely used as a solvent for substitution reactions of Rh$^{III}$ complexes,$^{53}$ which are generally rather slow (particularly those of cationic and neutral complexes), because of their d$^6$ electronic configuration.$^{54}$ The ability of reducing alcohols to catalyze these reactions has been known for a long time.$^{55}$ The role of the solvent is to generate a catalytic amount of Rh(I) (eq. III.1), which then catalyzes the substitution process.$^{56}$ The formation of metal by-product is almost certainly due to the decomposition of the intermediate Rh(I) species (eq. III.2).$^{57a}$

$$\begin{align*}
\text{Rh}^{III} + R_1R_2CHOH & \longrightarrow \text{Rh}^I + 2H^+ + R_1R_2CO \quad \text{III.1} \\
2\text{Rh}^I & \longrightarrow \text{Rh}^{II} + \text{Rh}^0 \quad \text{III.2}
\end{align*}$$
III.2.3 Mer-cis-RhCl₃(DMSO)₂(DMS)

Mer-cis-RhCl₃(DMSO)₂(DMS) was isolated in ~70% yield by adding an equivalent of DMS to a CH₂Cl₂ solution of RhCl₃(DMSO)₂(DMSO) (Section II.4.3). The doublet at δ 2.44 (J = 1 Hz) is assigned to DMS coordinated to RhIII; the occurrence of doublets in the same region, with ¹⁰³Rh(I = 1/2) coupling constants of ~1 Hz, are reported for the mer-RhCl₃(DMS)₃ complex. An IR spectrum of the mixed DMSO/DMS complex shows two symmetric peaks of medium intensity at 980 and 1035 cm⁻¹, assigned to ρ(CH₃) modes of coordinated DMS. Dimethylsulfoxide ligands also show two characteristic peaks centred at ~1000 cm⁻¹ assigned to ρ(CH₃) modes, but these appear as two non-equivalent peaks for complexes containing only sulfur coordinated DMSO (e.g. IR spectrum of RhCl₃-(DMSO)₂(CH₂CH=N⁺Et₂) in Fig. IV.7). In the presence of oxygen-coordinated DMSO, e.g. in RhCl₃(DMSO)₂(DMSO), the ρ(CH₃) modes appear as two approximately equivalent peaks centred at ~1000 cm⁻¹. Therefore in mixed DMSO/DMS complexes of RhIII, two approximately symmetric modes centred ~1000 cm⁻¹ may be taken as evidence for the presence of DMS ligands, provided that no DMSO is present in the complex.

III.3 Reactions of RhIII(DMSO) complexes with H₂

The reactions of RhIII(DMSO) complexes with H₂ were studied for the purpose of generating RhIII(H) species (Section I.4). The addition of strong bases is usually required for the activation of H₂ by Rh(III) complexes, but the discovery of a reaction between RhCl₃(DMSO)₃ and
strongly basic tertiary amines like P.S. and NEt\textsubscript{3} (Section IV), precluded the use of such bases. Weaker bases such as 2,6-di-t-butylpyridine or 2,6-dimethylpyridine did not facilitate a reaction between RhCl\textsubscript{3}(DMSO\textsubscript{3}) and H\textsubscript{2} in C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}. Dimethylacetamide (DMA) has been used previously with success, as a basic medium for the catalytic hydrogenation of olefins by RhCl\textsubscript{3}(DES\textsubscript{3}), where the catalytic Rh\textsuperscript{I} species was derived from the initial H\textsubscript{2} reaction of the Rh\textsuperscript{III} precursor (eq. III.3).\textsuperscript{57b}

\[
\text{Rh}^{\text{III}} + \text{H}_2 \xrightleftharpoons{-\text{H}^+} \text{Rh}^{\text{III}}(\text{H}) \xrightleftharpoons{-\text{H}^+} \text{Rh}^{\text{I}} \quad \text{III.3}
\]

Hydridoruthenium (II) complexes have been isolated by reactions of Ru(II)/PPh\textsubscript{3} complexes with H\textsubscript{2} in DMA.\textsuperscript{58} The reaction between Rh\textsuperscript{III}(DMSO) complexes and H\textsubscript{2} in DMA was thus investigated in the present work to see if Rh\textsuperscript{III}(H) species were formed. Although it was not possible to isolate or detect Rh\textsuperscript{III}(H) species using Rh\textsuperscript{III}(DMSO) precursors, the reaction between RhCl\textsubscript{3}(DMSO\textsubscript{3}) (1) and H\textsubscript{2} in DMA was investigated in detail, because of the discovery of an interesting catalytic autoxidation of DMA by that complex in the presence of H\textsubscript{2} (Chapter V). This section summarizes mainly the work on complex (1).

III.3.1 RhCl\textsubscript{3}(DMSO\textsubscript{3}) (1) in DMA

James and Morris reported the facile substitution of the DMSO
ligand in the major mer-cis isomer in CDCl₃ by various ligands (eq. III.4);³³

\[
\text{mer-cis-RhCl}_3(\text{DMSO})_2(\text{DMSO}) + \text{L} \rightleftharpoons \text{RhCl}_3(\text{DMSO})_2\text{L} + \text{DMSO} \quad \text{III.4}
\]

(e.g., L = DMF, OPPMe₂, pyridine-N-oxide, DMA)

The substitution reactions were monitored by ¹H nmr. Dimethylacetamide was found to be a weaker donor (Kₑq = 0.01±0.005) than, for example, DMF (Kₑq = 0.8±0.4). In the present work, because of the unavailability of DMA-d₉, it was not possible to observe the equilibrium in neat DMA by ¹H nmr. A multiple solvent suppression ¹H nmr of a ~0.02 M solution of (1) in DMA/toluene-d₈ (~1:1) shows two sets of major peaks at δ 3.42 and 3.62, and δ 3.46 and 3.67 and other smaller peaks (Fig. III.2). The positions of the major peaks correspond with those assigned for unreacted IA and RhCl₃(DMSO)₂(DMA) in CDCl₃ (δ 3.44 and 3.62, and 3.49 and 3.67, respectively) by James and Morris.³³ However, the absence or the presence of peaks due to coordinated DMA or free DMSO could not be ascertained because of the total suppression of peaks lying near or between the irradiated solvent peaks (δ 2.1, CH₃CO; 2.9 and 3.1, N(CH₃)₂; for example, a multiple solvent suppression ¹H nmr spectrum of a 0.06 M solution of DMSO in DMA/toluene-d₈ (~1:1) did not show the expected peak at δ ~2.6 for DMSO.

A solution of complex 1 in DMA does not show any conductance. The visible spectrum of 1 in DMA is invariant with time for at least 1 h and gives an extinction coefficient of 360 mol L⁻¹ cm⁻¹ at λ_max 435 nm. Species containing coordinated DMA could not be isolated from the
Fig. III.2  400 MHz multiple solvent suppression $^1$H nmr of RhCl$_3$(DMSO)$_3$ in DMA/toluene-d$_8$ (1:1)
solution. Addition of ether to a solution of 1 in DMA or pumping off the solvent yielded RhCl$_3$(DMSO)$_3$ species with or without adsorbed DMA ($\text{Ir: } 1630 \text{ cm}^{-1}, \nu_{\text{CO}}$; $^1\text{H nmr } \delta(\text{CDCl}_3): 2.1, \text{ s, } 3\text{H, and } 3.0, \text{ d, } 6\text{H}$). The amount of the mer-cis isomer in the isolated product was ~50%, compared to the 80% in the starting complex.

By using the data in the literature$^{33}$ for $K_{\text{eq}}$ in CDCl$_3$ (eq. III.4), and the assumption that the solvent effects on $K_{\text{eq}}$ are minimal, a $1 \times 10^{-2}$ M solution of mer-cis-RhCl$_3$(DMSO)$_2$(DMSO) in DMA is calculated to contain about 90% of mer-cis-RhCl$_3$(DMSO)$_2$(DMA). The inability to isolate any DMA-substituted Rh$^{III}$(DMSO) from solutions of complex 1 in DMA presumably results from a shift of eq. III.4 ($L = \text{DMA}$) to the left on removing or diluting the DMA solvent. The absence of any detectable visible spectral changes suggests that the ligand substitution is a rapid reaction.

### III.3.2 Reaction of RhCl$_3$(DMSO)$_3$ (1) in DMA with H$_2$

A $1.0 \times 10^{-2}$ M solution of 1 in DMA takes up H$_2$ under ambient conditions. Increasing the temperature to $50^\circ\text{C}$ gave conveniently measurable rates, and at $50^\circ\text{C}$ about 0.8 equivalents of H$_2$ per rhodium were taken up in the first 25 min (Fig. III.3). The uptake data beyond this point were not reproducible; a sudden increase in the rate was observed in some trials. Leaving the solution under H$_2$ for longer periods of time led to the formation of Rh metal. The irreproducibility of uptake data in the latter part of the reaction results from metal precipitation. Visible spectral changes for the reaction under similar
Fig. III.3  $H_2$ uptake plot for $1.0 \times 10^{-2}$ M solution of $\text{RhCl}_3(\text{DMSO})_3$ in DMA at 50°C under 1 atm $H_2$
conditions gave non-isosbestic behaviour (Fig. III.4, inset I). A sudden increase in the intensity of the visible absorption was a definite indicator of metal formation in these reactions. Because of problems of metal precipitation on prolonged exposure of the solution to H₂, the final reaction stoichiometry could not be ascertained directly. However, metal precipitation was avoided by removing H₂ from the system after 25 min of reaction, or after about 0.8 equivalents of uptake, by freeze-thaw degassing the solution three times. The visible absorption spectrum after degassing (Curve C, Fig. III.4) was essentially unchanged from that under H₂ (Curve B, Fig. III.4). The irreversibility of the H₂ reaction was shown by the absence of any further H₂ uptake by the degassed product solution in about the first 500 seconds of exposure (cf. Fig. III.3); leaving the solution under H₂ any longer led to metal precipitation. (In further discussion, the various reaction solutions will be referred to as A or B ... or E, depending on the designation given to the visible spectrum of each in Fig. III.4).

Solution C was stable under Ar for at least 1-2 h, but decomposed slowly over a period of several days to give small amounts of precipitated metal and an air-stable solution F (spectrum F, Fig. III.4). A ¹H nmr spectrum of the residue from F, dissolved in CDCl₃, showed some RhIII(DMS) (δ2.2-2.5, Section III.2.3) which accounted for about 15-20% of all the DMSO and DMS in the residue.

Attempts to isolate pure Rh species from solution C gave air-stable products containing RhIII(DMS). In a typical workup procedure, the DMA solvent was pumped off to yield a red oily reaction residue which was recrystallized from CH₂Cl₂/ether or acetone/ether, all under Ar. The resulting yellow-orange product appeared air-stable, and showed
Fig. III.4 Visible spectra of in situ Rh(I) in DMA obtained from the reaction between 3.0x10^{-3} M RhCl₃(DMSO)₃ in DMA and 0.8 equivalents of H₂ at 50°C under various conditions (A gives the spectrum of RhCl₃(DMSO)₃ in DMA): B, under H₂ (inset I, changes from A to B taken at intervals of 100 s); C, under Ar or vacuum (remains unchanged for at least 1 h)

(cont’d. on next page)
Fig. III.4 (cont'd) D, within 50-100 s after introducing O₂ to C at 1 atm; E, after leaving D at 50°C under O₂ for ~25 min (inset II, changes from D to E at r.t.); F, solution C after several days
peaks characteristic of Rh\textsuperscript{III}/DMSO (δ 3.4-3.6), Rh\textsuperscript{III}/DMSO (δ 2.8), Rh\textsuperscript{III}/DMS (δ 2.2-2.4), and free DMA (δ 2.1, 2.95, 3.05) in CDCl\textsubscript{3} (Fig. III.5a); the Rh\textsuperscript{III}/DMS accounted for ~15% of the total DMSO and DMS. An ir spectrum of the yellow precipitate in Nujol showed bands due to DMSO (1130 cm\textsuperscript{-1}) and DMSO (930 cm\textsuperscript{-1}); the ir data were not useful for characterizing coordinated DMS because of interference from the oxygen-coordinated DMSO (Section III.2.3).

(a) In situ characterization of products

The product solutions did not show any high field signals in the δ 0 to -50 region in a \textsuperscript{1}H nmr analysis, using either a 60 MHz CW or a 80 MHz FT spectrometer. For the latter, the reactions with H\textsubscript{2} were carried out in a 4:1 mixture of DMA and toluene-d\textsubscript{8} mixture, and a multiple solvent suppression technique was used to reduce the intensity of DMA peaks; a similar technique was used by Dekleva\textsuperscript{59} to observe Ru\textsuperscript{II}H(Cl) species in DMA solvent. No information about the fate of the DMSO ligands after the H\textsubscript{2} reaction could be obtained from the \textsuperscript{1}H nmr, because of the intensity of solvent peaks in the 60 MHz CW experiment, and the suppression of the peaks neighbouring the DMA peaks in the multiple solvent suppression experiment (Section III.3.1). The DMA solvent avails two windows in the regions ~1800-2900 cm\textsuperscript{-1} and ~750-900 cm\textsuperscript{-1} for ir analysis. No significant peaks were found in either region.

The visible spectrum of the H\textsubscript{2}-product solution under vacuum (curve C, Fig. III.4) changed rapidly on exposure to 1 atm of O\textsubscript{2} at r.t. or 50°C (curve D). To obtain more quantitative data, the amount of O\textsubscript{2}
Fig. III.5 80 MHz $^1$H nmr spectrum of: (a) the product isolated from solution B in Fig. III.4, in CDCl$_3$ under Ar; (b) residue from solution E in Fig. III.4, in CDCl$_3$ (x, solvent impurity)
taken up by degassed product solutions was measured as described in Section II.2.4; in all the experiments, the initial $H_2$ reaction was stopped after a $H_2$/Rh uptake ratio of $-0.8$ in order to avoid complications due to metal precipitation on prolonged exposure to $H_2$. The amount of $O_2$ taken up per equivalent of $H_2$ used gave values of $0.70$, $0.75$, $0.75$ for three different experiments. All $O_2$ uptakes were complete within 100-200 s of exposure, and there was no further uptake for at least another hour at $50^\circ C$. The absorbance of the initial oxygenated species $D$ decreased continuously under Ar or under $O_2$ to give a stable spectrum (curve E, Fig. III.4) within $\sim 20$ min. At room temperature, the change from $D$ to $E$ took a few hours but there was a rapid decrease in about the first 0.5 h. The ir spectrum of solution $D$, taken within a few minutes after the exposure to $O_2$, showed a weak, broad hump $\sim 850$ cm$^{-1}$, which was partly masked by another broad band at $\sim 930$ cm$^{-1}$ (Fig. III.5.1). Stripping off solvent DMA from solution $E$ yielded a yellow, oily residue. A gas chromatogram of the stripped solvent (Section II.5.4.c) showed the presence of $\sim 0.2$ equivalents of $CH_3CON(CH_3)CHO$ per rhodium and some unquantified amount of $H_2O$. A $^1H$ nmr of a $CDCl_3$ solution of the reaction residue (Fig. III.5.b) shows free DMA ($\delta$ 2.1, 2.95 and 3.03), DMSO ($\delta$ 3.4-3.6), DMSO ($\delta$ 2.85 and 2.75) and DMS ($\delta$ 2.2-2.5). The $D_2O$-sensitive broad peak around $\delta$ 6.7 roughly accounts for $\sim 0.5$-1.0 equivalents of protons for 3 equivalents of total DMSO, DMSO and DMS in solution. The broad peak was not observable in some other trials. An ir spectrum of the residue showed peaks due to free DMA (1630 cm$^{-1}$, s, $\nu_{CO}$), DMSO (1140 cm$^{-1}$, s, $\nu_{SO}$) and DMSO (930 cm$^{-1}$, s, $\nu_{SO}$).

Rhodium(III) complexes generally take up one equivalent of $H_2$ to give Rh$^I$ species, most likely via Rh$^{III}$(H) intermediates (eq. III.3).
Fig. III.5.1 F.T. ir spectra of: (a) 4x10^{-2} M RhCl_3(DMSO)_3 in DMA, (b) species D (see Fig. III.4) within a few minutes after its formation (solution in (a) was used to generate D; path length of KBr windows used, 0.5 mm)
Both RhI and RhIII(H) species may be O2-sensitive; the sensitivity of Rh(I) complexes to O2 is a noted feature in their chemistry (see later), while the reactions of RhIII(H) with O2 to given RhIII(OOH) are documented also. The O2-sensitivity of the product solution and the absence of any evidence for RhIII(H) species -- i.e., high-field ¹H nmr signals, or ir bands at ~2000 cm⁻¹ -- indicate the product to be a RhI species. Rhodium(I) complexes are known to form a variety of RhI•O2 adducts mostly of the peroxo type (Section I.2). The ir band due to the O-O stretch, occurring at 750-900 cm⁻¹, is the most useful method available for in situ analysis of these adducts. Reaction of the [RhCl(COE)₂]₂ dimer in DMA, containing an excess of LiCl, with O2 at 25°C is reported to form a RhI•O2 adduct in situ, which shows a band at 895 cm⁻¹ assignable to an O-O stretch. The broad band at ~850 cm⁻¹ observed in the present case likely arises also from an O-O stretch of a RhI•O2 adduct. The ir spectrum of the starting material 1 in DMA shows a band at 930 cm⁻¹ (a, Fig. III.5.1) assigned to νSO of DMSO (Section III.2.1). In the spectrum of solution D (b, Fig. III.5.1) the 930 cm⁻¹ band is broader. The peak at 698 cm⁻¹ in spectrum (a), attributable to νC-S, is reduced in intensity and is accompanied by the appearance of two new bands at 678 and 668 cm⁻¹ (spectrum b). The reasons for these changes are not clear; further discussion on the postulated RhI•O2 species is given in Section V.3.2.

The amount of O2 taken up by the H2 product solution of complex 1 (solution B, Fig. III.4) is less than that expected for a prior total reduction of 1 to a RhI species. If all of complex 1 reduces to a Rh(I) species, and the RhI reacts with O2 in a 1:1 ratio (eq. III.5), the
O₂/H₂ ratio should be equal to 1; but however, the observed O₂/H₂ ratio averages only ~0.75.

\[
\text{RhCl₃(DMSO)}_3 + H_2 \rightarrow [\text{Rh}^{I}/2H^{+}/3\text{Cl}^{-}/3 \text{DMSO}] \stackrel{O_2}{\rightarrow} [\text{Rh}^{I}·O_2/2H^{+}/3\text{Cl}^{-}/3 \text{DMSO}]
\]

The low value very likely results from a side-reaction where H₂ is consumed in a reduction of DMSO to DMS. A Rh³⁻-catalyzed reduction of DMSO to DMS by H₂ is documented (eq. III.6).²³

\[
\text{DMSO} + H_2 \rightarrow \text{DMS} + H_2O
\]

A ¹H nmr of the residue from solution E (Fig. III.5b) indeed shows some Rh³⁻(DMS) (δ(CDCl₃): 2.2-2.5), accounting for about 5-10% of the total DMSO and DMS in the residue. The Rh³⁻(DMS) observed almost certainly results from the H₂ reaction of A to B, because the O₂ reaction of B to give D and then E cannot possibly lead to a reduction of DMSO.

A total reaction stoichiometry as in eq. III.7 accommodates both the O₂/H₂ ratio of 0.75, and the reduction of some DMSO to DMS.

\[
\text{RhCl₃(DMSO)}_3 + 0.8 \text{H}_2 \rightarrow 0.6 [\text{Rh}^{I}/2H^{+}/3\text{Cl}^{-}/3 \text{DMSO}] + 0.2 [\text{Rh}^{III}/3\text{Cl}^{-}/2\text{DMSO/DMS}] + 0.2 \text{[unreacted RhCl₃(DMSO)}_3] + 0.2 \text{H}_2O
\]
According to eq. III.7, 0.6 equivalents of total H$_2$ used is spent on the reduction of Rh$^{III}$ to Rh$^I$ (eq. III.5), and 0.2 equivalents on the reduction of DMSO (eq. III.6). In the O$_2$ reaction only the Rh$^I$ will form a Rh$^I$·O$_2$ adduct. Therefore, the corresponding O$_2$/H$_2$ ratio will be only 0.75. Similarly, the expected yield of Rh$^{III}$(DMS) is calculated as ~7\% of the total DMSO/DMS (eq. III.7). These assumptions allow for good correspondence with the experimental data.

Further evidence for an in situ Rh$^I$ product that reacts with O$_2$ in a 1:1 stoichiometry is provided by some comparative studies with a model system using the labile [RhCl(CO$_2$)$_2$ dimer$^{62}$ as the Rh$^I$ precursor. Addition of the dimer to DMA solutions containing 2 equivalents of DMA·HCl and 3 equivalents of DMSO per equivalent of Rh gives a system stoichiometrically equivalent to (Rh$^I$/2H$^+$/3Cl$^-$/3DMSO) (cf. eq. III.5). Under O$_2$, the model system rapidly absorbs one equivalent of gas per rhodium at 50°C (Fig. III.6); the longer reaction time of ~2000-3000s taken by the more concentrated solution corresponds with the time taken by the complex to dissolve. Both reaction solutions show a slower catalytic uptake, following the initial rapid reaction; the catalytic uptake was not monitored for solution (a). Essentially the same reactivity pattern was observed when 2 equivalents of LiCl were used in place of DMA·HCl (see Section V.3.2 for further discussion).

The visible spectrum of the model system under Ar (curve C$_0$, Fig. III.7) changes slowly with time over 24 h to give a stable spectrum (curve C). The equilibrated solution rapidly absorbs approximately one equivalent of O$_2$ per Rh to give a spectral change (C $\rightarrow$ D in Fig. III.7) similar to that of the H$_2$ product solution of 1 (C $\rightarrow$ D in Fig. III.4). The spectrum of the oxygenated model system changes at r.t.,
Fig. III.6  O$_2$ uptake plots for [RhCl(CO$_2$)$_2$]$_2$ dimer in DMA containing 2 equivalents of HCl and 3 equivalents of DMSO per rhodium at 50°C at Rh concentration of: (a) $0.60 \times 10^{-2}$, (b) $2.1 \times 10^{-2}$ M
Visible spectra of 4.5x10^{-3} M solutions of [RhCl(COE)]_2 dimer in DMA containing 2 equivalents of HCl and 3 equivalents of DMSO per rhodium at r.t. under various conditions: C_0, immediately after dissolving under Ar; C, after leaving C_0 under Ar over a few hours; D, 50-100 s after flushing C with O_2; E, several hours after leaving C under O_2 at 1 atm.
rapidly in approximately the first 0.5 h and then more slowly to give a final stable solution (curve E, Fig. III.7).

Attempts to isolate characterizable products from either O₂ reaction of the in situ Rhᴵ species generated from complex 1 in DMA, or the Rhᴵ model system, were not successful. Further discussions of the oxygen reaction of in situ Rhᴵ are found on p. 178 and p. 179.

(b) Redox decomposition of in situ [Rhᴵ/2H⁺/3Cl⁻/3DMSO] species

The relative stability of the in situ Rhᴵ product in DMA solvent, and its decomposition to Rhᴵᴵ(III) species in the workup procedure, suggest that a redox reaction as in eq. III.8 is facilitated in the absence of DMA.

\[
\text{Rhᴵ/2H⁺/3Cl⁻/3DMSO} \rightarrow \text{Rhᴵᴵ/3Cl⁻/2DMSO/DMS + H₂O} \quad \text{III.8}
\]

Similar redox reactions are documented for several other transition-metal complexes. Reduction of sulfoxides is an important reaction in organic synthesis where intermediate sulfoxides need to be reduced selectively to the respective thioethers.⁴⁶,⁴⁸ Salts or complexes of Tiᴵᴵ, VII or Mo⁴V which act as oxygen acceptors are used for such reductions (e.g. eq. III.9).⁶³

\[
\text{MoO(S₂CNEt₂) + DMSO} \rightarrow \text{Mo(O)₂(S₂CNEt₂) + DMS} \quad \text{III.9}
\]

For Pt group metal complexes, the presence of 2 equivalents of strong acid is generally required for the deoxygenation of the sulfoxide; the
concomitant oxidation of the metal centre is noted in some cases.\textsuperscript{64}

The suggested decomposition reaction in eq. III.8 may be accomplished by using the dimer \([\text{RhCl(COE)}]_2\) as the Rh\textsuperscript{I} precursor. The dimer (110 mg, 0.025 mmol in Rh) was added to a degassed solution of \(\text{CH}_2\text{Cl}_2\) (10 mL) containing 2 equivalents of DMSO·HCl (55 mg, 0.05 mmol) and 3 equivalents of DMSO (50 \(\mu\)L, 0.09 mmol) under Ar, and the solution was stirred overnight. The final solution remained qualitatively unchanged from the original yellow-orange, and was air-stable. Ether was added slowly to obtain, a yellow precipitate which was recrystallized as \([\text{Rh·3Cl·2DMSO·DMS}]\) in \(-60\%\) Yield. Anal. calcd. for \(\text{C}_6\text{H}_{18}\text{Cl}_3\text{O}_2\text{S}_3\text{Rh}\): C 16.85, H 4.24; found: C 17.09, H 4.26. The \(^1\text{H} \) nmr spectrum of the product in CDCl\(_3\) (Fig. III.8) shows an approximate DMSO, DMSO/DMS ratio of 2:1. A solution of the product in DMA is non-conducting, showing the product to be non-ionic.

The multitude of peaks observed for Rh\textsuperscript{III}/DMS in the \(^1\text{H} \) nmr spectrum suggests the presence of several Rh\textsuperscript{III} species. Dimethylsulfide ligands are known to form dimeric Rh\textsuperscript{III} complexes containing bridging DMS ligands.\textsuperscript{65} Since the compound is non-conducting, only monomeric structures with a 6:1 ligand to metal ratio are possible; a dimeric formulation would require an ionic nature with at least one non-associated Cl\textsuperscript{-} ion. Further characterization was not possible because of the difficulty of analyzing the \(^1\text{H} \) nmr spectrum. The complexity of \(^1\text{H} \) nmr spectrum suggests the product to be composed of several isomeric forms.

The redox reaction between the Rh\textsuperscript{I} precursor dimer and DMSO in the presence of added HCl was essentially complete within 15 min of reaction as judged by \(^1\text{H} \) nmr. The spectrum of a reaction solution, after about
Fig. III.8  80 MHz $^1$H nmr spectrum of RhCl$_3$ 2DMSO·DMS in CDCl$_3$
15 min of mixing Rh\textsuperscript{I} precursor with 2 equivalents of HCl and 3 equivalents of DMSO in CDCl\textsubscript{3} under Ar, did not show peaks of DMA·HCl (δ 3.1, s, 3H; 2.3, s, 6H; -9, br, 1H), but only of DMA (δ 3.0, d, 6H; 2.1, s, 3H). Peaks due to coordinated DMS and DMSO were in an approximate ratio of 1:2, as for the isolated complex.

The rapidity of the redox decomposition of the [Rh\textsuperscript{I}/2H\textsuperscript{+}/3Cl\textsuperscript{-}/3DMSO] model system in CH\textsubscript{2}Cl\textsubscript{2} contrasts with the relative stability of the same system in DMA; the solution changes under Ar over 24 h (C\textsubscript{0} → C in Fig. III.7) but the equilibrated solution remains sensitive to O\textsubscript{2}, according to spectral (C → D, Fig - III.7) data. The observations on the model system parallel those on the H\textsubscript{2}-product solution of I in DMA.

The relative stability of the Rh\textsuperscript{I}/2H\textsuperscript{+}/3Cl\textsuperscript{-}/3DMSO systems in DMA results perhaps from the unavailability of protons in this medium compared to CH\textsubscript{2}Cl\textsubscript{2}. James et al.\textsuperscript{23} suggested that the initial step in the Rh\textsuperscript{III}-catalyzed reduction of DMSO by H\textsubscript{2} was the protonation of a coordinated DMSO; the catalytically active rhodium species was postulated to be Rh\textsuperscript{III}(H) (eq. III.10).

\[
\begin{array}{c}
\text{H} \\
\text{Rh}^{\text{III}}\text{S—CH}_3
\end{array}
\xrightarrow{H^+} 
\begin{array}{c}
\text{H} \\
\text{Rh}^{\text{III}}\text{S—CH}_3
\end{array}
\xrightarrow{OH^+} 
\begin{array}{c}
\text{Rh}^{\text{III}} \\
\text{S(CH}_3)_2 \\
\text{H}_2\text{O}
\end{array}
\]

III.10

The mechanism proposed for the Rh\textsuperscript{I} system in the present work involves a similar initial protonation step given as an equilibrium reaction (eq. III.11), and an electron transfer from the Rh\textsuperscript{I} to the electron deficient sulfur atom (eq. III.12).
The reactivity difference in DMA and CH₂Cl₂ solvent may be attributed to the proton scavenging action of the DMA solvent. Dimethylacetamide reacts instantaneously with gaseous HCl to give solid DMA·HCl. In DMA solvent, competition between complex and solvent for protons will shift eq. III.11 to the left and thereby slow the redox reaction III.12.

The suggested presence of about 0.2 equivalents of Rh₃(DMS) in the H₂ product of complex I (eq. III.7) requires comment. Since the RhI/DMSO product is stable in DMA solution for a few hours, the Rh₃(DMS) most likely results from a Rh₃-catalyzed reduction of DMSO by H₂ (eq. III.10) which occurs via a Rh₃(H)(DMSO) intermediate formed in the H₂ reaction of RhCl₃(DMSO)₃ (eq. III.13). In keeping with the arguments developed in this section, a protonation of the DMSO, within the coordination sphere (eq. III.14) is preferred over protonation by a 'free' H⁺ as suggested in eq. III.10.

\[
\text{Rh}^{\text{III}}(\text{DMSO}) + \text{H}_2 \rightarrow [\text{Rh}^{\text{III}}(\text{H})(\text{DMSO})] + \text{H}^+ \rightarrow \text{Rh}^\text{I}(\text{DMSO}) + 2\text{H}^+ \quad \text{III.13}
\]
III.3.3 Hydrogen reactions of other complexes

The cationic species [RhCl(DMSO)₅](BF₄)₂ in DMA under H₂ at 50°C gave metal instantly, while [NEt₄][RhCl₄(DMSO)₂] took up H₂ essentially at the same rate as complex 1. The Rh⁺/DMSO complex containing an ethenamine ligand, RhCl₃(DMSO)₂(⁻CH₂CH⁺NEt₂), was inactive towards H₂ in C₂H₄Cl₂.

Thioether complexes of Rh⁺, e.g. RhCl₃(DES)₃ and RhCl₃(DMS)₃, in DMA were less stable under H₂ than the analogous DMSO complex, 1, and gave metal within 200-500 s at 50°C.

III.4 Reactions of RhCl₃(DMSO)₃ (1) with CO

The reactions with CO were studied with the aim of using CO as an alternative reagent to H₂. In the presence of stoichiometric amounts of H₂O, CO can act as a two equivalent reducing agent to generate Rh⁺ species (eq. III.15), or perhaps, as a H⁺ donor reagent to generate Rh⁺(H) species (eq. III.16). The former reaction is well documented for Rh⁺ complexes, 66-68 while the latter is based on the success with
Pt$^{2+}$ systems (eq. III.17).$^{69}$

$$\text{Pt}^{II} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Pt}^{II(\text{H})} + \text{CO}_2 + \text{H}^+ \quad \text{III.17}$$

$$\text{Rh}^{III} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Rh}^{III(H)} + \text{CO}_2 + \text{H}^+ \quad \text{III.16}$$

$$\text{Rh}^{III} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Rh}^{III} + \text{CO}_2 + 2\text{H}^+ \quad \text{III.15}$$

In a detailed mechanistic study of the reaction of RhCl$_3$·3H$_2$O with CO in DMA, James and Rempel found the initial step to be the formation of a Rh$^{III(\text{CO})}$ species (eq. III.18). Hydrolysis of the Rh$^{III(\text{CO})}$ to yield a Rh$^{I(\text{CO})}_2$ species (eq. III.19) was a much slower reaction.$^{68}$

$$\text{Rh}^{III} + \text{CO} \rightarrow \text{Rh}^{III(\text{CO})} \quad \text{III.18}$$

$$\text{Rh}^{III(\text{CO})} + \text{H}_2\text{O} \rightarrow [\text{Rh}^{I}] + 2\text{CO} \rightarrow \text{Rh}^{I(\text{CO})}_2 \quad \text{III.19}$$

In the present work it was of interest to try and isolate a Rh$^{III(\text{CO})}$ intermediate from a reaction between RhCl$_3$(DMSO)$_3$ and CO under anhydrous conditions, in order to be able to control the hydrolysis step to obtain Rh$^{III(\text{H})}$ species (eq. III.16). The RhCl$_5$(CO)$_2^-$ complex has been made via the carbonylation of chlororhodate(III) species,$^{70}$ while several other Rh$^{III(\text{CO})}$ species have been made by the oxidative addition of, for example, a halogen X$_2$ to Rh$^{I(\text{CO})}$ complexes.$^{71}$

Some reactions were done with the deliberate addition of 1-2 equivalents of H$_2$O per rhodium, in order to check whether this could be a convenient route to a Rh$^{I}$ complex containing CO and DMSO ligands. Such a
complex, $\text{RhCl(CO)(DMSO)₂}$, has been made by the reaction between $[\text{Rh(CO)₂Cl}]₂$ and DMSO.\(^{72}\)

The reactions requiring anhydrous conditions were conducted in CH₂Cl₂ or C₂H₄Cl₂, and those requiring H₂O conducted in DMA.

(a) In CH₂Cl₂ or C₂H₄Cl₂

The reactions with CO were monitored using the rate of net gas uptake with time in C₂H₄Cl₂ solvent. A $2.4 \times 10^{-2}$ M C₂H₄Cl₂ solution of RhCl₃(DMSO)₃ (1) takes up approximately one net equivalent of gas per equivalent of rhodium in less than 2 h (Fig. III.9). A slow gas evolution was noticeable after about 5500 s, and the presence of CO₂ in the gaseous phase at this stage was verified by gas chromatography (Section II.5.3).

Visible spectral changes for a 2.25 mM CH₂Cl₂ solution of RhCl₃(DMSO)₃ under CO are given in Fig. III.10. Within the first 30 min of reaction, the absorbance at 435 nm ($ε = 350$ M⁻¹ cm⁻¹) decreases steadily. After 30 min, an increase in the overall absorbance at 435 nm is noted and this continues for about 24 h to give a final spectrum with a shoulder at 405 nm ($ε = 520$ M⁻¹ cm⁻¹). The final visible spectrum corresponds well with the absorption spectrum of RhCl₃(DMS)₃ in CH₂Cl₂ ($ε = 542$ M⁻¹ cm⁻¹ at 405 nm). The initial visible spectral changes correspond with the time scale for the uptake of one equivalent of gas (Fig. III.9), suggesting the initial formation of a RhIII(CO) intermediate. An air-sensitive oily-residue isolated from a reaction mixture after a net uptake of one equivalent of CO per Rh shows two peaks at
Fig. III.9 An uptake plot for the reaction of $2.4 \times 10^{-2}$ M $\text{RhCl}_3(\text{DMSO})_3$ in $\text{C}_2\text{H}_4\text{Cl}_2$, with CO (1 atm) at 30°C

Fig. III.10 Visible spectral changes for a solution of $2.25 \times 10^{-2}$ M $\text{RhCl}_3(\text{DMSO})_3$ in $\text{CH}_2\text{Cl}_2$, under CO (1 atm) at ambient conditions (between 10-70 min of reaction time, the spectra were recorded every 5 min); A, initial spectrum
1980 and 2100 cm\(^{-1}\). Attempts to isolate a characterizable product from the residue were not successful. The \([\text{Rh}^{I}(\text{CO})_{2}\text{Cl}_{2}]^-\) anion shows two absorptions at 1975 cm\(^{-1}\) and 2060 cm\(^{-1}\),\(^{71}\) but the formation of a dicarbonylrhodium(I) product is not consistent with the approximately 1:1 uptake of CO by Rh\(^{III}\), and a Rh\(^{III}(\text{CO})\) intermediate seems likely. James et al. noted similar \(\nu_{\text{CO}}\) absorptions (1970 and 2070 cm\(^{-1}\), respectively) in an impure compound isolated after an initial, relatively rapid uptake of one equivalent of CO by Rh\(^{III}\) in DMA;\(^{68}\) attempts to isolate an analytically pure compound from the reaction residue were also unsuccessful.

A complex analyzing as mer-RhCl\(_3\)(DMS)\(_3\) was isolated in \(-65\%\) yield as the final product from a reaction of an approximately 0.01 M solution of RhCl\(_3\)(DMSO)\(_3\) in C\(_2\)H\(_4\)Cl\(_2\) with 1 atm of CO at 50°C, after a reaction time of over 24 h (Section II.4.3.5). The \(^1\text{H} nmr\) spectrum of a sample in CDCl\(_3\) showed two doublets (\(J = 1\) Hz) in a 2:1 ratio at \(\delta\) 2.50 and 2.30, respectively; the data correspond with those for an authentic sample of mer-RhCl\(_3\)(DMS)\(_3\) prepared by a literature method\(^{35}\) (\(\delta\) (CDCl\(_3\)): 2.53, d, \(J = 1\) Hz, 12H and 2.30, d, \(J = 1\) Hz, 6H). An ir spectrum of the complex shows two almost equivalent peaks at 980 and 1035 cm\(^{-1}\) which are assigned to the \(\alpha_{\text{CH}_3}\) modes of the DMS ligands.\(^{35}\)

Larger scale preparations using concentrations of RhCl\(_3\)(DMSO)\(_3\) greater than 0.05 M in CH\(_2\)Cl\(_2\) or C\(_2\)H\(_4\)Cl\(_2\) yielded mixtures of products, the main components of which were identified as mer-RhCl\(_3\)(DMS)\(_3\) and mer-cis-RhCl\(_3\)(DMS)\(_2\)(DMSO), respectively, by a \(^1\text{H} nmr\) spectrum of the product in CDCl\(_3\). Identification of the former was by reference to the peak positions of the authentic compound given above. The remaining peaks occurring at an \(-1:1:1\) ratio at \(\delta 3.55\) (s, 6H, \((\text{CH}_3)_2\text{SO}\)), 2.48 (d, \(J = 1\)
Hz, 6H, (CH$_3$)$_2$S), 2.38 (d, J = 1 Hz, 6H, (CH$_3$)$_2$S) were assigned to mer-cis-RhCl$_3$(DMS)$_2$(DMSO) to account for two non-equivalent DMS ligands and an S-coordinated DMSO ligand. Longer reaction times or refluxing conditions improved the yield of mer-RhCl$_3$(DMS)$_3$, but still gave at least 20% of the bis(dimethylsulfide) product. Attempts to obtain pure RhCl$_3$(DMS)$_2$(DMSO) by a different route using RhCl$_3$(DMSO)$_3$ and 2 equivalents of DMS in CDCl$_3$ gave an approximately 1:1 mixture of mer-cis-RhCl$_3$(DMS)$_2$(DMS) (Section II.4.3.4) and mer-cis-RhCl$_3$(DMSO)-(DMS)$_2$, as judged by solution $^1$H nmr. Longer reaction times showed additional peaks due to some mer-RhCl$_3$(DMS)$_3$.

In the CO reduction of complex 1 to RhCl$_3$(DMS)$_3$ in CH$_2$Cl$_2$ or C$_2$H$_4$Cl$_2$ under ambient conditions (eq. III.20) the observed spectral data are consistent with an initial 1:1 reaction between 1 and CO to give a Rh$^{III}$(CO) species (eq. III.21).

$$\text{RhCl}_3(\text{DMSO})_3 + 3\text{CO} \rightarrow \text{RhCl}_3(\text{DMS})_3 + \text{CO}_2$$ III.20

$$\text{RhCl}_3(\text{DMSO})_3 + \text{CO} \rightarrow \text{RhCl}_3(\text{DMSO})_2(\text{CO}) + \text{DMSO}$$ III.21

The reduction of DMSO then can occur via a nucleophilic attack on the coordinated CO by DMSO to yield a Rh$^{III}$(DMS) species and CO$_2$ (eq. III.22); for electronic book-keeping purposes the Rh$^{III}$(CO) moiety is represented as Rh$^{II}$-C≡O$^+$. 
A closely analogous reaction is the reduction of tertiary amines oxides to tertiary amines by metal-bound carbon monoxide (e.g. eq. III.23).\textsuperscript{73a}

\[
\begin{align*}
\text{(CO)}_4\text{Fe}=\text{C}=\text{O} + (\text{CH}_3)_3\text{N}^+\text{O}^- & \quad \rightarrow \quad (\text{CO})_4\text{Fe}^+=\text{C}=\text{O}^+\text{N}^+(\text{CH}_3)_3 \\
& \quad \rightarrow \quad (\text{CO})_4\text{Fe}(\text{N}(\text{CH}_3)_3) + \text{CO}_2
\end{align*}
\]

III.23

In the present case, the resulting $\text{RhCl}_3(\text{DMSO})_2(\text{DMS})$ complex can react further, in a similar manner, to give $\text{RhCl}_3(\text{DMSO})(\text{DMS})_2$ and then $\text{RhCl}_3(\text{DMS})_3$.

(b) With added $\text{H}_2\text{O}$ in DMA

A gas uptake plot for the CO reaction of a 0.020 M solution of complex 1 in DMA in the presence of an added equivalent of $\text{H}_2\text{O}$ at 30°C
(Fig. III.11) shows a net uptake of approximately 2 equivalents of CO per equivalent of Rh within the first 6000-7000 s. Uptake data for the RhCl₃·3H₂O complex in DMA, reproduced from a literature report,⁶ are given in the same figure; a brief discussion on these data is given later in this Section. With 1, the solution color changes from a deep orange to a light orange during the uptake. There is no significant increase in the total uptake over the next 20 h. Carbon dioxide is detected in the gas phase of the reaction mixture within 2 h of reaction time.

Visible spectral changes for an analogous system under ambient conditions are given in Fig. III.12. The changes are non-isosbestic in behaviour. After some relatively rapid changes in about the first 1.75 h (or ~6000 s), slower changes continue to occur over the next few hours to give a final stable spectrum E in < 24 h (Fig. III.12). The relatively rapid changes in the first 6000 s, correspond well with the net uptake region of the uptake plot (Fig. III.11). An ir spectrum of a solution after 24 h of reaction shows two strong bands at 1982 and 2060 cm⁻¹, and two other much weaker bands at 1950 and 2087 cm⁻¹ (Fig. III.13). The two strong bands correspond to the two characteristic bands at 1975 and 2060 cm⁻¹ reported for the cis-[Rh(CO)₂Cl₂]⁻ anion; the literature data are for the salts of either (C₄H₉)₄N⁺ or (C₆H₅)₄As⁺, in Nujol.⁷¹ The source of the two smaller bands is not clear. A 60 MHz cw¹H nmr spectrum of the reaction solution in the δ0 to -40 region does not show any peaks due to rhodium-hydride protons.
Fig. III.11 Uptake plots for reactions of Rh complexes in DMA (2.0x10^{-2} M) with CO (1 atm): (a) RhCl_3(DMSO)_3 with one equivalent of added H_2O per Rh at 30°C; (b) RhCl_3·3H_2O at 40°C

Fig. III.12 Visible spectral changes under CO (1 atm) at 30°C for a solution of 2.0x10^{-2} M RhCl_3(DMSO)_3 in DMA containing added H_2O (2x10^{-2} M); A, initial spectrum (between B and C, the spectra were recorded every 60 s)
In the workup procedure to isolate the reaction products, DMA-HCl was isolated in about 50% yield based on rhodium (Section II.4.3.6). A rhodium species, postulated to contain the novel [(DMA)₂H]⁺ cation, was also obtained from the reaction residue. A discussion on the isolated rhodium product is given later in this section.

The experimental data are consistent with a net stoichiometry involving a reduction of RhIII to RhI:

\[
\text{Rh}^\text{III} + 3\text{CO} + \text{H}_2\text{O} \rightarrow \text{Rh}^\text{I}(\text{CO})_2 + \text{CO}_2 + 2\text{H}^+ \tag{III.24}
\]

Whether or not a CO reduction of DMSO to DMS and CO₂ occurs, similar to
the CH₂Cl₂ system discussed previously (eq. III.20), cannot be ascertained from the uptake data, since such a side-reaction will release an equivalent of CO₂ for each equivalent of CO taken up. The net uptake of 2 equivalents of gas, the detection of the [Rh(CO)₂Cl₂]⁻ anion in the reaction solution and CO₂ in the gas phase, and isolation of DMA·HCl as by-product, support the proposed stoichiometry. The major reaction product detected and the reaction stoichiometry are identical to those reported for the reaction between RhCl₃·3H₂O and CO in DMA;⁶⁸ thus, the DMSO ligands have no effect on the CO/H₂O reaction of Rh³⁺ in terms of the final product. However, the overall rate of reaction in the RhCl₃(DMSO)₃ system at 30°C is faster than that reported⁶⁸ for the RhCl₃·3H₂O system at 40°C (Fig. III.11). In the latter case, an initial faster gas uptake was attributed to formation of a Rh³⁺(CO) species (eq. III.18). The additional net uptake of one equivalent of gas in a slower second phase of the reaction was assigned to the combination of a slow hydrolysis step (that releases an equivalent of CO₂) and a rapid uptake of 2 equivalents of CO by the Rh¹ species subsequently formed (eq. III.19). In the present case a similar mechanism is probable, but the absence of a distinct initial phase corresponding to a CO/Rh ratio of 1 shows the hydrolysis step is faster than in RhCl₃·3H₂O system even at 30°C. Presumably, the DMSO ligands exert an effect on the rate of the hydrolysis reaction.

Isolation of a rhodium product

James et al. isolated the cis[RhCl₂(CO)₂]⁻ anion as the [Ph₄As]-
[RhCl₂(CO)₂] salt, by adding a methanol solution of the Ph₄AsCl salt to the RhCl₃·3H₂O and CO reaction product in DMA. In the present work, a product was isolated by working up the reaction mixture without an added cation (Section II.4.3.6). The proton nmr spectrum of the isolated complex in CDCl₃ (Fig. III.14.a) showed three peaks at δ 2.38, 3.14 and 6.6 (br) in the ratio 3:6:0.5, attributed to CH₃CO-, -N(CH₃)₂ and the acidic proton, respectively, of the [(DMA)₂H]⁺ cation. The peak positions assigned to the methyl protons of the (DMA)₂H⁺ cation are close to those of the DMA·HCl adduct (Section II.4.5), but the ir spectrum of the complex (Fig. III.14.b) is quite distinct from that of the DMA·HCl salt (Section II.4.5). In fact, the broad band in the ir spectrum which extends from ~600 cm⁻¹ to ~1700 cm⁻¹ confirms the presence of a (DMA)₂H⁺ cation. Salts containing symmetrically H-bonded cations are known to cause such broad bands in this region. A closely related literature example is (DMF)₂H⁺ cation in the [(DMF)₂H][Pd₂Cl₆] salt. In the case of (DMSO)₂H⁺ cation in [(DMSO)₂H][RhCl₄(DMSO)₂], the symmetric nature of the H-bond has been confirmed by a crystal structure (2, Ortep diagram of (DMSO)₂H⁺ cation).
Fig. III.14  (a) A 80MHz $^1$H nmr spectrum in CDCl$_3$ and (b) an ir spectrum in KBr of the product isolated from the reaction between RhCl$_3$(DMSO)$_3$ and CO in DMA in the presence of an equivalent of added H$_2$O
By analogy with the \((\text{DMF})_2\text{H}^+\) and \((\text{DMSO})_2\text{H}^+\) cations a similar symmetrically H-bonded structure (3) is proposed for the \((\text{DMA})_2\text{H}^+\) cation. A similar protonation at the carbonyl oxygen is observed with the \(\text{DMAH}^+\) cation in the \(\text{DMA-HCl}\) adduct.\(^{75}\)

\[
\begin{array}{c}
\text{CH}_3\text{N}^+\text{C} = \text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{N(CH}_3\text{)}_2
\end{array}
\]

(3)

The product analyzes well for a complex salt of the molecular formula \([\text{DMA})_2\text{H}[\text{RhCl}_2(\text{CO})_2]\) (Anal. calcd. for \(\text{C}_{10}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}_4\text{Rh}\): C 29.65, H 4.73, N 6.91; found: C 29.46, H 4.74, N 6.92), but the \(\nu_{\text{CO}}\) region of its ir spectrum (Fig. III.14b) shows three well-defined absorptions (1875 m, 1985 s and 2025 m, cm\(^{-1}\)) in the solid state. The pattern is quite different from that of the in situ product in DMA solvent (Fig. III.13) assigned to cis-\(\text{RhCl}_2(\text{CO})_2\), but resembles that of the \([\text{RhCl}(\text{CO})_2]_2\) dimer (2035 s, 2090 s and 2105 m, cm\(^{-1}\)) in terms of the number of bands. The appearance of three bands in the ir spectrum of \([\text{RhCl}(\text{CO})_2]_2\) is explained in terms of a bent molecule (4).\(^{73b}\)

(4)
In the solid state the DMA$^2$H$^+$ cation may well interact with the RhCl$_2$(CO)$_2^-$ anion via the halide ligands, e.g. as in structure 5; an interaction between the cation and Cl$^-$ ligands in the counter anion is observed also with the [EtNH$_2$][RhCl$_4$(DMSO)$_2$] salt (Fig. IV.14). However, such an interaction does not explain the occurrence of 3 bands assignable to $\nu_{CO}$ and further studies (solution IR experiments) are needed to resolve this problem.

III.5 Summary

Reaction between RhCl$_3$(DMSO)$_3$ and H$_2$ in DMA leads to a Rh$^I$ species as the major product. Slow decomposition of the Rh$^I$ product is postulated to occur via a redox decomposition reaction between Rh$^I$ and DMSO in the presence of 2 equivalents of acid; the proton affinity of the DMA solvent is thought to slow down the decomposition in this solvent at least for 1-2 h at r.t.

The clean reduction of RhCl$_3$(DMSO)$_3$ to Rh$^{III}$(DMS) species by CO in CH$_2$Cl$_2$ or C$_2$H$_4$Cl$_2$ is a novel reaction. In a literature report on the carbonylation of Pd$^{II}$(DMSO) complexes, formation of a mixed CO/DMSO complex was observed. No other reports on carbonylation of metal-DMSO
complexes or any other reports on the reduction of DMSO by CO has come to our attention.

The reaction between $\text{RhCl}_3(\text{DMSO})_3$ and CO in the presence of $\text{H}_2\text{O}$, in DMA gave the $[\text{RhCl}_2(\text{CO})_2]^{-}$ anion which was isolated in low yield as the $[(\text{DMA})_2\text{H}][\text{RhCl}_2(\text{CO})_2]$ complex. The rhodium anion product is the same as that generated by the corresponding reaction with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. 
CHAPTER IV

REACTION OF RhCl$_3$(DMSO)$_3$ WITH TERTIARY AMINES
IV Reaction of RhCl₃(DMSO)₃ with Tertiary Amines

IV.1 Introduction

The addition of strong bases is sometimes required for activation of H₂ by higher-valent metal complexes.⁵⁷ The strong base, 1,8-bis-(dimethylamino)naphthalene, commercially known as Proton Sponge (P.S.), has been successfully used, for example, to facilitate the reaction between Ru(III) and H₂.⁷⁶ During attempts to bring about a base-promoted reaction between RhCl₃(DMSO)₃ (1) and H₂ in C₂H₄Cl₂, Morris⁵⁰ discovered a reaction between 1 and P.S. A protonated P.S. (P.S.H⁺) species was detected by ¹H nmr and ir spectroscopy, and a complex containing a P.S. derivative was isolated but not characterized.

As part of the work in this thesis, several other bases were tested as possible proton scavengers. The same reactivity of 1 was found towards Et₃N (pKₐ 3.4), which is comparable in base strength to P.S. (pKₐ 2.7), but no reactions occurred with weaker bases such as dimethylaniline (pKₐ 8.8) and 2,6-di-t-butyl pyridine (pKₐ 8.2). The reaction between RhCl₃(DMSO)₃ and NEt₃ appeared particularly interesting because of the widespread use of the base as a cocatalyst in reactions catalyzed by Rh complexes.⁷⁷-⁸¹ A Rh-ethenamine complex was isolated as a product of the reaction between RhCl₃(DMSO)₃ and NEt₃.

This chapter summarizes the characterization of the species and details of the overall reaction.
IV.2 Characterization of RhCl₃(DMSO)₂(−CH₂CH=⁺NEt₂), 6

Complex 6 (see Section II.4.3.2 for details on isolation) exists in CDCl₃ in two isomeric forms. The ¹H nmr spectrum of 6 within ~5 min of dissolution in CDCl₃ shows mainly the peaks due to one isomer, designated A (Fig. IV.1.a). The relative intensity of peaks due to another isomer (B) increased over 3 h to give an equilibrium mixture estimated to be 60% in A and 40% in B (Fig. IV.1.b); the triplet and quartet at δ 1.42 and 3.10, respectively, are due to NEt₃·HCl impurity in the sample of 6 used.

A purer sample of 6 was equilibrated in CDCl₃ solution for ~4 h to obtain a ¹H nmr spectrum suitable for more detailed analysis (Fig. IV.2). The multitude of peaks was first divided into two sets A and B by reference to Figs. IV.1.a and IV.1.b; assignments within each isomer, summarized in Table IV.1, were made by selective decoupling experiments.

The two overlapping triplets (δ ~8.3) are assigned to the −CH₂−CH=⁺NEt₂ protons of each isomer. There are several reports in the literature on metal-ethenamine complexes.⁸²-⁸⁶ A definite assignment of an η¹-ylidic coordination mode is made in two of the reports,⁸²,⁸³ where highly deshielded −CH⁺NEt₂ protons with chemical shifts in the range δ 7-8 have been noted. The doublet of doublets at δ 4.049 and another at 3.626 are assigned to the −CH₂−CH=⁺NEt₂ protons of isomers B and A, respectively. Irradiation of each doublet of doublets collapsed the corresponding triplets (Fig. IV.3). The simultaneous irradiation of the overlapping triplets at δ ~8.3 showed the collapse of each doublet of doublets into a doublet with a coupling constant of 2.5 Hz (Fig. IV.4). The smaller coupling is assigned to the expected interaction between the
Fig. IV.1 400 MHz $^1$H nmr spectrum of $\text{RhCl}_3(\text{DMSO})_2(\text{CH}_2\text{CH}^+\text{NEt}_2)$ in CCl$_3$: (a) ~5 min after dissolution, shows peaks mainly due to isomer A; (b) 3 h after (a) (x, $\text{NEt}_3\cdot\text{HCl}$ impurity; *, isomer B; other unlabelled peaks due to the ethenamine ligand)
Fig. IV.2 400 MHz $^1$H nmr spectrum of $\text{RhCl}_3(\text{DMSO})_2(\text{CH}_2=\text{CH}^+\text{NET}_2)$ ~4 h after dissolution in $\text{CDCl}_3$ (a, b ... h refer to centres of quartets or triplets; see also Table IV.1)
IV.3 (a) Details of the multiplet at $\delta 8.3$ of Fig. IV.2 relevant to $-\text{CH}=\text{CH}$ assignments; (b) and (c), after irradiation at 4.049 and 3.626, respectively.

IV.4 (a) Details of the $\delta 3.5-4.5$ region of Fig. IV.2 relevant to $-\text{CH}_2-$ assignments; (b), after irradiation at $\delta 8.3$. 
Rh(III) (I = 1/2) and the methylene protons of the \( ^{1}\text{CH}_2\text{-CH}=^{+}\text{NEt}_2 \), and corresponds to literature values; e.g. the Rh(III)\(^{1}\text{-CH}_3 \) couplings in Rh(C\(_5\text{H}_5\))(CH\(_3\))\(_2\)(S(CH\(_3\))\(_2\)) and a related complex have been found to be 2.7 and 2.6 Hz, respectively.\(^{87}\) There is no apparent coupling between the Rh nucleus and the \( ^{1}\text{CH}_2\text{-CH}=^{+}\text{NEt}_2 \) protons. The relative magnitudes of coupling between the metal centre and the olefinic protons of the ethenol ligand, \( \text{CH}_2\text{-CH-CH}=^{+}\text{OH} \), have been used successfully to distinguish between the \( \eta^1\)-ylidic and \( \eta^2\)-olefinic modes of this ligand. For example, in Pt(acac)Cl(\( \eta^2\text{-CH}_2\text{-CH}=^{+}\text{OH} \)) the Pt-H\(^{\beta\text{-}}\) coupling (J=76 Hz) is of the same order of magnitude as the Pt-H\(^{\alpha\text{-}}\) coupling (J=71 Hz),\(^{88}\) while in Pt(acac)Cl(\( \eta^1\text{-CH}_2\text{CHO} \)) the Pt-H\(^{\beta\text{-}}\) coupling (J = 113 Hz) is much greater than the Pt-H\(^{\alpha\text{-}}\) coupling (J=20 Hz).\(^{89}\)

Further evidence for an \( \eta^1\)-ylidic coordination mode for 6 in solution is the observed non-equivalence of N-Et groups in the ethenamine ligand in both isomeric forms 6A and 6B. The detailed assignments for the N-Et protons were made by irradiation experiments. Each of the letters a, b, .. g,h in Fig. IV.2 refers to a centre of a multiplet. The circles round a, c, e and g denote that they all belong to the ethenamine ligand on isomer 6B. The triplets e, f, g and h, due to \(-\text{NCH}_2\text{CH}_3 \) protons of both isomers, are well separated from the other peaks, but, because of overlap or the proximity of the peaks, clean irradiation of each was not possible. Simultaneous irradiation of the two overlapping triplets e and f caused the collapse of the c, d quartet pair (Fig. IV.5). Since e and c are already known to belong to isomer B, they are assigned to an -NEt group on the B isomer, and d and f multiplets to an -NEt group on the A isomer. The remaining multiplets are assigned similarly and all assignments are summarized in Table IV.1.
Fig. IV.5  (a) Details of the $\delta 3.5-4.5$ region of Fig. IV.2 relevant to $-\text{NCH}_2-$ assignments; (b) and (c), after irradiation at e and f, and g and h, triplets in Fig. IV.2, respectively.
Summary of 400 MHz $^1$H nmr data for an equilibrated solution of RhCl$_3$(DMSO)$_2$($^\text{CH}_2$CH=$^+$NEt$_2$) (6) in CDCl$_3$ (Fig. IV.2)(a)

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer A</td>
<td></td>
</tr>
<tr>
<td>3.626 (dd, $J = 8.5$ 2.5 Hz, 2H)</td>
<td>$^\text{CH}_2$CH=$^+$NEt$_2$</td>
</tr>
<tr>
<td>8.258 (t, $J = 8.5$ Hz, 1H)</td>
<td>$^\text{CH}_2$CH=$^+$NEt$_2$</td>
</tr>
<tr>
<td>b: 3.768 (q); h: 1.367 (t)(b)</td>
<td>$^+$N$/^\text{CH}_2^b$/CH$_3^h$</td>
</tr>
<tr>
<td>d: 3.587 (q); f: 1.478 (t)</td>
<td>$^\text{CH}_2^d$/CH$_3^f$</td>
</tr>
<tr>
<td>3.517 (s), 12H</td>
<td>(CH$_3$)$_2$SO (S-coordinated)</td>
</tr>
<tr>
<td>Isomer B</td>
<td></td>
</tr>
<tr>
<td>4.049 (dd, $J = 9$, 2.5 Hz, 2H)</td>
<td>$^\text{CH}_2$CH=$^+$NEt$_2$</td>
</tr>
<tr>
<td>8.299 (t, $J = 8.5$ Hz, 1H)</td>
<td>$^\text{CH}_2$CH=$^+$NEt$_2$</td>
</tr>
<tr>
<td>a: 3.845 (q); g: 1.396 (t)(b)</td>
<td>$^+$N$/^\text{CH}_2^a$/CH$_3^g$</td>
</tr>
<tr>
<td>c: 3.653 (q); e: 1.497 (t)</td>
<td>$^\text{CH}_2^c$/CH$_3^e$</td>
</tr>
<tr>
<td>3.466 (s), 6H</td>
<td>(CH$_3$)$_2$SO (S-coordinated)</td>
</tr>
<tr>
<td>3.263 (s), 6H</td>
<td>(CH$_3$)$_2$SO (S-coordinated)</td>
</tr>
</tbody>
</table>

(a) Consists of two isomers A and B in an approximately 60:40 ratio. Integrations for the N-Et protons are not given. Chemical shift given in $\delta$.

(b) a, b, ...... g and h refer also to the centres of the corresponding peaks in Fig. IV.2. Coupling constants for the quartets and triplets average to $-7$ Hz.
The summarized assignments show that the ethenamine ligand, whether in isomer A or B, contains non-equivalent -NEt groups (see below for additional features).

Coordination of the ethenamine as an olefin, as in 7, would lead to equivalent -NEt groups because of free rotation about the C-N bond; the non-equivalence definitively eliminates the possibility of \( \eta^2 \)-olefinic coordination.

![Image of molecular structure](image1)

IV.1

The non-equivalence of the -NEt groups further shows that there is no solution equilibrium such as eq. IV.1 for complex 6, since this will lead to scrambling of -NEt groups on a ligand.

![Image of molecular structure](image2)

Other possible coordination modes such as bonding through the N atom, 8, or an \( \eta^3 \)-coordination, 9, have not been reported in the
literature. In addition, the experimental data in the present case exclude such possibilities; for example, an $\eta^1$-N-ethenamine complex such as 8 is expected to give an ABX pattern for the $H^\alpha$, $H_1^\beta$, and $H_2^\beta$ olefinic protons, while an allylic form such as 9 will require the complex to be in an ionic form, e.g. \([\text{RhCl}_2(\text{DMSO})_2(\eta^3-\text{CH}_2=\text{CHNEt}_2)]\text{Cl}\), to maintain an 18 electron configuration in the valence shell (the evidence for the coordination of both DMSO molecules to Rh(III) is given below). The experimental data show an A$_2$X pattern for the olefinic protons (Table IV.1) and the complex is non-conducting in solution (Section II.4.3.1).

Sulfur-bonded DMSO ligands of Rh$^{\text{III}}$ are readily assigned by nmr spectroscopy (see Section III.1). The singlets at $\delta$ 3.517, 3.466 and 3.263 (Fig. IV.2 and Table IV.1) are in the range expected for DMSO. Changes in the nmr spectrum of 6 with time (Fig. IV.1) show that the peak at $\delta$ 3.517 belongs to isomer A and the other two peaks to B. The small peak due to free DMSO at $\delta$ 2.635 most likely results from some ligand dissociation in solution.

An nmr spectrum of 6 in acetone shows only the one DMSO peak attributable to isomer A in significant amounts (Fig. IV.6); smaller peaks due to isomer B may or may not be concealed by other peaks. Since the compound was isolated on a preparative scale from acetone, it is highly likely that it exists, mostly or totally, as the A isomer in the solid state. On redissolution of 6 in CDCl$_3$, the A isomer is found in about 85% abundance, as judged from a spectrum taken after about 5 min (Fig. IV.1.a). The decrease in A with time again suggests that 6 probably existed solely as isomer A at zero time.

The presence of two DMSO peaks of equal intensity for the isomer B (Fig. IV.2) indicates the non-equivalence of the two DMSO ligands.
Fig. IV.6 A $^1$H nmr spectrum of RhCl$_3$(DMSO)$_2$($^\Delta$CH$_2$CH=NEt$_2$) in acetone-$d_6$ (x, NEt$_3$·HCl impurity)
Therefore a mer-cis geometry, 10, is assigned to B. For isomer 6A either a mer-trans, 11, or a fac-cis, 12, geometry would account for the observed equivalence of DMSO ligands (Fig. IV.2). Generally DMSO ligands trans to one another occur at a lower field in their $^1$H nmr than those to trans to Cl$^\text{-}$. The DMSO in isomer A is more deshielded than either DMSO in isomer B. Therefore isomer A is most likely to show the mer-trans geometry, 11. In fact, a mer-trans geometry should be the more favorable steric arrangement for the three larger ligands.

$\text{Cl}$

$\text{OS}$

$\text{Cl}$

$\text{Cl}$

$\text{OS}$

$\text{Cl}$

$\text{Cl}$

$\text{-CH}_2-$

$\text{Cl}$

$\text{Cl}$

$\text{SO}$

$\text{Cl}$

$\text{Cl}$

$\text{OS}$

$\text{Cl}$

$\text{Cl}$

$\text{-CH}_2-$

$\text{Cl}$

$10$, mer-cis

$11$, mer-trans

$12$, fac-cis

$^{13}\text{C}[^1\text{H}]-\text{nmr}$ data obtained for an equilibrated solution of 6 in CDCl$_3$ (Table IV.2) are also consistent with the given formulation for 6. For example, the assignments for the $\text{C=N}^+$ and the $\text{-CH}_2-$ carbons, and other N-Et carbons correspond well with those reported$^8$ for the Pd$^{\text{II}}[\text{-CH}_2\text{CH=N}^+(\text{CH(CH}_3)_2)_2]$ complex ($\delta$(CDCl$_3$): 17.45, $\text{CH}_2$; 164.92, C=N; 50.74, C-N; 52.45, C-N; 19.16, 2 x CH$_3$; 23.04, 2 x CH$_3$); the assignments for A and B isomers in the present case were made on the assumption that the trend in $^{13}\text{C}$ chemical shifts parallels that of $^1\text{H}$ chemical shifts in Table IV.1. The observed $^{103}\text{Rh-^{13}C}$ coupling constant is 10 Hz. The $^{195}\text{Pt-^{13}C}$ coupling in the Pt$^{\text{II}}(\text{-CH}_2\text{-C}^+(\text{NMe}_2)_2)$ complex is reported to be 584 Hz.$^8$ The value of 10 Hz obtained for the Rh-ethenamine complex (6)
in the present case appears reasonable since the $^{195}\text{Pt-}^1\text{H}$ coupling constant for the $^{1}\text{CH}_2$- protons in the above Pt complex ($J = 104 \text{ Hz}$)\textsuperscript{85} is also about 50 times greater than the corresponding $^{103}\text{Rh-}^1\text{H}$ coupling constant in complex 6 (Table IV.2). The three peaks at $\delta$ 42.6, 42.8 and 43.3 (Table IV.2), which are deshielded from the free DMSO value at 39.4, are assigned to coordinated DMSO. No data are available in the literature for comparison.

A solid state ir spectrum of 6 is given in Fig. IV.7. The strong absorption at 1643 cm$^{-1}$ agrees well with the values of 1613 and 1615 cm$^{-1}$ reported for $\nu_{\text{C=N}}$ of $\eta^1$-ethenamine complexes of Pd(II)\textsuperscript{82} and Pt(II),\textsuperscript{83} respectively. The $\nu_{\text{C=N}}$ absorptions of cyclic imminium perchlorates, e.g. 12.1, were reported to lie in the range 1660-1700 cm$^{-1}$\textsuperscript{90}

The strong band at 1110 cm$^{-1}$ in Fig. IV.7 is assigned to $\nu_{\text{SO}}$ of equivalent DMSO ligands of 6A. The other strong band at 1020 cm$^{-1}$ and the weak band at 985 cm$^{-1}$ are assigned to $\rho_{\text{CH}_3}$ modes of sulfur-coordinated DMSO by reference to other Rh(III)/DMSO complexes (Section III.2), though a comparison with a DMSO-$d_6$ analogue of the complex is necessary for a definitive assignment (Section III.1). The small shoulder at 1125 cm$^{-1}$ is perhaps due to a small amount of isomer B in the solid state.
Summary of 400 MHz $^{13}$C ($^1$H) nmr data for an equilibrated solution of RhCl$_3$(DM$_2$O)$_2$(CH$_2$NEt)$_2$ (6) in CDCl$_3$ (a)

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer A</td>
<td></td>
</tr>
<tr>
<td>12.6 (d, J = 10 Hz)</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>187.5</td>
<td>$^1$C—$^2$NEt$_2$</td>
</tr>
<tr>
<td>45.8</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>53.3</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>19.2</td>
<td>$^1$CH$_2$—CH$_3$</td>
</tr>
<tr>
<td>23.2</td>
<td>$^1$CH$_2$—CH$_3$</td>
</tr>
<tr>
<td>42.8</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td>Isomer B</td>
<td></td>
</tr>
<tr>
<td>14.0 (d, J = 10 Hz)</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>188.3 (d, J = 10 Hz)</td>
<td>$^1$C—$^2$NEt$_2$</td>
</tr>
<tr>
<td>46.2</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>53.4</td>
<td>$^1$CH$_2$—</td>
</tr>
<tr>
<td>19.4</td>
<td>$^1$CH$_2$—CH$_3$</td>
</tr>
<tr>
<td>23.3</td>
<td>$^1$CH$_2$—CH$_3$</td>
</tr>
<tr>
<td>42.6</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td>42.4</td>
<td></td>
</tr>
</tbody>
</table>

(a) Shown by $^1$H nmr to contain ~60% 6A and ~40% 6B; chemical shifts given in $\delta$. 
Fig. IV.7  An ir spectrum of RhCl$_3$(DMSO)$_2$(CH$_2$CH$=^{+}$NEt$_2$) in KBr
Fig. IV.8  A stereo-view ORTEP diagram of mer-cis-RhCl₃(DMSO)₂(\textsuperscript{−}CH₂CH=⁺NEt₂) (Some structural parameters given in Appendix I)
An X-ray crystal structure of a single crystal isolated from a CDCl₃ solution of 6 by slow precipitation with ether confirms the structure assigned to 6 by spectroscopic data. The crystal isolated shows the mer-cis geometry assigned to the minor 6B isomer (Fig. IV.8). The sulfoxide ligands on 6B are both sulfur coordinated as predicted. The S=O bond lengths at 1.472(2) and 1.476(2) Å (Appendix I) correspond well with the S=O bond lengths in RhCl₃(py)₂(DMSO)₂ (1.47 Å)⁴⁸ or [(DMSO)₂H][RhCl₄(DMSO)₂] (1.48 Å)⁷⁴c. The ethenamine ligand shows an η¹-ylidic coordination mode as predicted.

The bond angles C(2)-N-C(5), C(2)-N-C(3) and N-C(2)-C(1) (see Fig. IV.9 for an illustration) at 120.3°(2), 122.9°(2) and 126.7°(2),
respectively (Appendix I), correspond well with the 120° angle expected if there is a double bond between N and C(2). The length of the N-C(2) bond (1.291(3) Å), as compared to the N-C(3) (1.475(3) Å) and N-C(5) (1.481(3) Å) bond lengths, further confirm a higher bond order between C(2) and N. McCrindle et al. 82 found the N-C(2)-C(1) bond angle for an analogous PdII(ethenamine) complex to be relatively large at a value of 136°(10), but the reported N-C(2) bond length at 1.249(12) Å compares well with the corresponding bond length in the present RhIII(ethenamine) complex 6B.

IV.3 Reaction Stoichiometry

The complex RhCl3(DMSO)2(=CH2-CH=NEt2), 6, and NEt3-HCl were isolated as pure products from the reaction between RhCl3(DMSO)3 and NEt3 (Section II.4.3.2). Addition of NEt3 to a solution of RhCl3(DMSO-d6)3 in CDCl3 under Ar showed peaks due to NEt3H+ (CDCl3): 1.38, t; 3.20, q, -11, br) consistent with the abstraction of protons from NEt3. Equation IV.2 shows the dehydrogenation of one NEt3 molecule by two others. If an accompanying reaction such as eq. IV.3 is invoked to maintain the redox equivalence of the system the total redox reaction would be as in eq. IV.4. However, the isolation of RhCl3(DMSO)2(=CH2-CH=NEt2) requires at least another equivalent of Rh(III) in an overall reaction such as eq. IV.5.

$$3\text{NEt}_3 \rightarrow 2\text{NEt}_3\text{H}^+ + \text{CH}_2=\text{CHNEt}_2 + 2e \quad \text{IV.2}$$
Rh(III) + 2e → Rh(I) \text{ IV.3}

Rh(III) + 3NEt₃ → Rh(I) + 2NEt₃H⁺ + CH₂=CHNET₂ \text{ IV.4}

2RhCl₃(DMSO)₃ + 3NEt₃ → RhCl₃(CH₂CH⁺NET₂)(DMSO)₂
+ 2NEt₃HCl + Rh(I)/Cl⁻/4DMSO \text{ IV.5}

Early in the investigation, reaction mixtures containing various ratios of NEt₃:Rh were tested to find the optimum conditions for isolation of pure products. It was first noted that the $^1$H nmr peak positions for N-CH₂-CH₃ and N-CH₂CH₃ protons of a reaction mixture were dependent on the amount of excess NEt₃ in the system. A $^1$H nmr study with several mixtures of pure NEt₃ and NEt₃·HCl gave a single triplet and a single quartet with averaged chemical shifts dependent on the composition of each mixture (Table IV.3). For the analysis of in-situ reaction mixtures by 100 MHz $^1$H nmr, the set of triplets due to -N-CH₂-CH₃ protons was selected as a suitable probe, since the interferences by other peaks were least in that region. Data for various mixtures are summarized in Table IV.4. Reaction mixtures containing NEt₃/Rh(III) in a ratio < 1.5 show a triplet at $\delta$1.38. The use of higher ratios of NEt₃/Rh(III) leads to an upfield shift of the averaged triplet which, according to the studies with NEt₃/NEt₃H⁺ mixtures, suggests the presence of excess NEt₃ in the system. The observations are reasonably consistent with the NEt₃/Rh ratio of 1.5 proposed in eq. IV.5.
Table IV.3

100 MHz $^1$H nmr data for NEt$_3$, NEt$_3$·HCl, and mixtures of both in CDCl$_3$

<table>
<thead>
<tr>
<th>Molar ratio of</th>
<th>t, -NCH$_2$CH$_3$</th>
<th>q, -NCH$_2$CH$_3$</th>
<th>-N$^+$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt$_3$/NEt$_3$·HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure NEt$_3$</td>
<td>0.95</td>
<td>2.42</td>
<td>(a)</td>
</tr>
<tr>
<td>10</td>
<td>0.94</td>
<td>2.48</td>
<td>8.92 (br)</td>
</tr>
<tr>
<td>3</td>
<td>1.09</td>
<td>2.65</td>
<td>(a)</td>
</tr>
<tr>
<td>1</td>
<td>1.25</td>
<td>2.85</td>
<td>7.7 (br)</td>
</tr>
<tr>
<td>0.5</td>
<td>1.32</td>
<td>2.97</td>
<td>11.7 (br)</td>
</tr>
<tr>
<td>0.1</td>
<td>1.38</td>
<td>3.10</td>
<td>(a)</td>
</tr>
<tr>
<td>Pure NEt$_3$·HCl</td>
<td>1.42</td>
<td>3.10</td>
<td>12.2 (br)</td>
</tr>
</tbody>
</table>

(a) Peaks not observed.
### Table IV.4

$100 \text{ MHz } ^1\text{H nmr data for the } -\text{NCH}_2\text{CH}_3 \text{ protons of NEt}_3, 1-2 \text{ h after adding the amine to RhCl}_3(\text{DMSO})_3 \text{ in CDCl}_3 \text{ under Ar}$

<table>
<thead>
<tr>
<th>Molar ratio of</th>
<th>$t, -\text{NCH}_2\text{CH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt$_3$:RhCl$_3$(DMSO)$_3$</td>
<td>t, -NCH$_2$CH$_3$</td>
</tr>
<tr>
<td>0.5</td>
<td>1.38</td>
</tr>
<tr>
<td>1</td>
<td>1.38</td>
</tr>
<tr>
<td>1.5</td>
<td>1.39</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
</tr>
<tr>
<td>3</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>1.10</td>
</tr>
<tr>
<td>8.5</td>
<td>1.05</td>
</tr>
<tr>
<td>50</td>
<td>0.90</td>
</tr>
</tbody>
</table>
By inspection of a $^1$H nmr spectrum (Fig. IV.10.c), a $\text{CH}_2\text{CH}^+\text{NEt}_2/(\text{total NEt}_3\text{ added})$ ratio of 1:3.5 was estimated for a final reaction mixture that initially contained NEt$_3$/Rh in a ratio of 1.5. In other words, about 30% of the initial NEt$_3$ had been converted to the dehydrogenated form. This value corresponds to the 33% conversion expected from the stoichiometry of eq. IV.5. Direct evidence for the presence of Rh(I) species was harder to obtain. Several unsuccessful attempts were made to isolate a Rh(I) species such as [NEt$_3$H][RhCl$_2$-(DMSO)$_2$]. Two highly air-sensitive Rh(I)/DMSO species, [RhCl(DMSO)$_2$]$_2$ and [PSH][RhCl$_2$(DMSO)$_2$], isolated by Morris, gave methyl proton nmr peaks at $\delta$(CDCl$_3$/(CD$_3$)$_2$CO), 3.32 (br), and $\delta$(CDCl$_3$), 2.8 (br), respectively. No such significant peaks were found in the reaction between RhCl$_3$(DMSO)$_3$ and NEt$_3$ (1:1.5) in CDCl$_3$ under Ar, and indeed free DMSO is present (Fig. IV.10.c). It may be that, in solution, Rh(I) exists in association with other ligands such as Cl$^-$ and/or unreacted NEt$_3$. Strong indirect evidence for the presence of Rh(I) in concentrations approximating the expected 50% of the total Rh (eq. IV.5) is given by data for the uptake of O$_2$ by the reaction solution. A solution of RhCl$_3$(DMSO)$_3$ and NEt$_3$ (1:2) in C$_2$H$_4$Cl$_2$ was contained in a reaction flask connected to an uptake apparatus (see Section II.2.1) and shaken under Ar for over 2 hours. The solution was then degassed and the subsequent rapid uptake of O$_2$ monitored as described in Section II.2.4. The instantaneous uptake of O$_2$ corresponded to 0.32 and 0.45 mol of O$_2$ per mol of RhCl$_3$(DMSO)$_3$ in two trials, suggesting the presence of about 0.3-0.5 equivalents of Rh(I) per initial RhCl$_3$(DMSO)$_3$ in the system. Further details on the reactions of such Rh(I) species with O$_2$ are given in Section III.3.2.a.
Fig. IV.10  (a) 400 MHz $^1$H nmr spectra of RhCl$_3$(DMSO)$_3$ in CDCl$_3$ under Ar, (b) ~5 min after adding 1.3-1.5 equivalents of NEt$_3$ to (a) under Ar, (c) 24 h after (b) (inset, expanded 2.3-2.5 region of (c)); o, DMSO of RhCl$_3$(DMSO)$_3$; x, impurity; o, DMSO of RhCl$_3$(DMSO)$_2$(CH$_2$CH=NEt$_2$); •, new DMSO and DMS peaks
The recent communication reporting the reaction between PdCl₂(PhCN)₂ and several tertiary amines described the isolation of several Pd(II)/ethenamine complexes. A metal-centred dehydrogenation of the amines was proposed to explain the isolation and the detection of, for example, Pd(II)/ethenamines (35%), Pd(0) (28%) and the amine-HCl (7%), using ethyl di-isopropylamine. The overall reaction, represented as eq. IV.6, parallels that established in the present work (eq. IV.5).

In a series of articles published in the early 1950's on the organic chemistry of cyclic amines, Leonard et al. used mercuric acetate

\[
2 \text{Pd(II)} + 3 \text{(iPr)}_2 \text{NCH}_2 \text{CH}_3 \rightarrow \text{Pd(0)} +
\]

\[
[(\text{iPr})_2 \text{N}^+ \text{-CH-CH}_2^-] \text{Pd(II)} + 2 \text{amine.HCl}
\]

as the dehydrogenating agent in a convenient synthesis of cyclic ethenamines. In a typical experiment, a fourfold excess of Hg(OAc)₂ over the amine was used to obtain near quantitative dehydrogenation. The acetate ligands were found to act as proton acceptors, and the metal centre as the electron acceptor (eq. IV.7), in a reaction analogous to those of eqs. IV.5 and IV.6.
A similar redox process (eq. IV.8), coupled with other reactions (eqs. IV.9 and IV.10), was suggested to be intermediate in a catalytic generation of H₂ from H₂O, where NEt₃ is the effective reductant (eq. IV.11 in Scheme IV.1).⁹²

Scheme IV.1

\[
2\text{RuL}_3^{2+} + 2\text{NEt}_3 \xrightarrow{h\nu} 2\text{RuL}_3^{+} + \text{Et}_3\text{NH}^+ + \text{CH}_3\text{CH}^=\text{NEt}_2 \quad \text{IV.8}
\]

\[
2\text{RuL}_3^{+} + 2\text{H}^+ \xrightarrow{\text{Pt/O}_2} 2\text{RuL}_3^{2+} + \text{H}_2 \quad \text{IV.9}
\]

\[
\text{CH}_3\text{CH}^=\text{NEt}_2 + \text{H}_2\text{O} \xrightarrow{} \text{CH}_3\text{CHO} + \text{Et}_2\text{NH}_2^+ \quad \text{IV.10}
\]

The total reaction:

\[
\text{Et}_3\text{N} + \text{H}_2\text{O} \xrightarrow{h\nu, \text{RuL}_3^{2+}} \text{Et}_2\text{NH} + \text{CH}_3\text{CHO} + \text{H}_2 \quad \text{IV.11}
\]

L = 2,2'-dipyridyl
IV.4 Mechanistic Aspects

The mechanism of the dehydrogenation reaction (eq. IV.5) could theoretically involve either an intermediate Rh(III)/NEt$_3$ complex, or an outer-sphere electron transfer from NEt$_3$ to the Rh(III) metal centre (see below). Of the three literature examples of tertiary amine dehydrogenations $^{82,91,92}$ discussed above, prior coordination of the amine is postulated for the Pd(II)$^{82}$ and Hg(II)$^{91}$ systems. For example, the dehydrogenation of the cyclic amine was thought to be facilitated by the coordination of the amine to Hg(II) as in Scheme IV.2.

In the reaction between PdCl$_2$(PhCN)$_2$ and several acyclic tertiary amines (eq. IV.6), McCrindle et al. postulated an initial coordination of the amine to the Pd(II), followed by a metal insertion into an adjacent C-H bond and a $\beta$-hydride elimination to give the enamine which complexes to PdCl$_2$ (Scheme IV.3).$^{82}$
In the absence of a vacant coordination site on the metal complex, an outer-sphere electron transfer mechanism is a possibility. The RuL$_3^{2+}$ (L = 2,2'-dipyridyl)-mediated dehydrogenation of NEt$_3$ (eq. IV.8, Scheme IV.1) probably occurs via such a mechanism because of the absence of a possible coordination site on the strongly chelated complex.

In the present work, attempts were made to isolate or at least detect a Rh(III)/NEt$_3$ intermediate and follow its decomposition path. In a $^1$H-nmr monitored reaction between RhCl$_3$(DMSO)$_3$, and -1.5 equivalents of NEt$_3$ in CDCl$_3$, the spectrum obtained ~ 5 min after the addition of NEt$_3$ to the RhCl$_3$(DMSO)$_3$ solution (Fig. IV.10.b) shows an immediate decrease in the peaks due to the major isomer mer-cis-RhCl$_3$-(DMSO)$_2$-(DMSO), accompanied by a newly developed peak due to free DMSO. The added NEt$_3$ shows two broad humps at $\delta$1.1 and 2.6, which are significantly higher than the free NEt$_3$ values (Table IV.3). These observations strongly suggest the formation of a Rh(III)/NEt$_3$ intermediate in the solution:
\[ \text{RhCl}_3(\text{DMSO})_2(\text{DMSO}) + \text{NEt}_3 \rightleftharpoons \text{RhCl}_3(\text{DMSO})_2(\text{NEt}_3) + \text{DMSO} \quad \text{IV.12} \]

\[ \text{RhCl}_3(\text{DMSO})_2(\text{NEt}_3) \xrightarrow{2\text{NEt}_3} \text{RhCl} + 2\text{NEt}_3\text{HCl} + \text{CH}_2=\text{CHNEt}_2 + 2\text{DMSO} \quad \text{IV.13} \]

The \(^1\text{H} \text{nmr}\) spectrum of a \((0.8 \text{NEt}_3 + \text{RhCl}_3(\text{DMSO})_3)\) mixture, which has a \text{NEt}_3/\text{Rh} ratio less than the stoichiometrically required 1.5 (eq. IV.5), is given in Fig. IV.11.a. The deshielding of the triplet and the quartet set due to \(-\text{NCH}_2\text{CH}_3\) and \(\text{N-CH}_2\text{CH}_3\), respectively, with respect to free \text{NEt}_3, and the sharpness of the peaks, suggest that here \text{NEt}_3 exists as \text{NEt}_3\text{H}^+ or some deshielded form. The minute peaks at \(\delta \approx 8.3\), and between 3.6-4.0 are reasonably similar to the \(^{1}\text{CH}_2-\text{CH}=^+\text{NEt}_2\) protons of the \text{Rh(III)}/ethenamine complex, 6, but the upper limit of the amount of ethenamine formed is estimated to be \(-10\%\) of the total \text{NEt}_3 added initially (the estimate is made by comparing the integrations due to \(^{1}\text{CH}_2-\text{CH}=^+\text{N}(\text{CH}_2\text{CH}_3)_2\) protons in the \(\delta 3.5-4.0\) region and the peaks due to total \text{NCH}_2\text{CH}_3 protons in the \(\delta 1.0-1.5\) region). An \text{ir} spectrum of the same solution (Fig IV.11.b) shows a well defined but relatively weak peak at 1630 cm\(^{-1}\), attributable to \(\nu_{\text{C}=-\text{N}}\) of a coordinated ethenamine (see Section IV.2). The smaller peak at 1710 cm\(^{-1}\) could be due to an enamine salt of type \text{CH}_3\text{CH}=^+\text{NEt}_2\cdot\text{Cl}^-\). The \text{ir} absorptions for such salts of pyridine-enamines are known to occur in the range 1640-1700 cm\(^{-1}\).\(^90\)

Peaks due to \(\nu_{\text{N}^+=\text{H}}\) of \text{NEt}_3\text{H}^+, expected at 2400 (br) and 2560 cm\(^{-1}\) (see Section II.4.3.3), are absent. The occurrence of \text{Rh(III)}/ethanamine unaccompanied by \text{NEt}_3\text{H}^+ is a curious observation in terms of the chemistry discussed thus far in this chapter, and will be further discussed in the next section. The absence of \text{NEt}_3\text{H}^+ is of interest
Fig. IV.11 (a) 80 MHz $^1$H nmr spectrum of RhCl$_3$(DMSO)$_3$ + 0.8 NEt$_3$ in CDCl$_3$ under Ar, and (b) an ir spectrum of the above solution in air.
since it shows that the deshielded -NCH₂CH₃ protons in Fig. IV.11a are most likely to be due to a Rh(III)/NEt₃ species. In fact, the large peak of free DMSO at δ 2.64 in the same figure, corresponding to about 30% of the total free and coordinated DMSO in solution, further supports a substitution reaction as in eq. IV.12 to give a Rh(III)/NEt₃ complex. On leaving the above reaction solution under Ar over 24 h, broad peaks attributable to νₙ⁺-H of NEt₃H⁺ appeared at ~2400-2600 cm⁻¹, and peaks due to ν₁⁻, at ~1630 cm⁻¹, increased in intensity. These data are consistent with a redox reaction as in eq. IV.13, but without the presence of excess NEt₃. Such a reaction proceeds most likely via a slow proton abstraction from the coordinated NEt₃ (eq. IV.13) by the small amount of free NEt₃ existing in solution at any time due to the equilibrium IV.12; the slowness of reaction IV.13 is attributable to the low concentration free NEt₃ available. Repeated attempts to isolate the postulated Rh(III)/NEt₃ were not successful.

No examples of Rh(III) complexes with coordinated triethylamine could be found in the literature. An unsuccessful attempt to isolate a Rh(III)/NEt₃ complex was mentioned in a report by Mori et al. on the role of tertiary amines in a RhCl₃·3H₂O catalyzed arylation of ethylene with iodobenzene; the failure was attributed to steric factors. A redox reaction, similar to that of eq. IV.5 discussed in this chapter, may have been an unnoticed complication in the Japanese work.

A likely mechanism for the redox reaction between complex 1 and NEt₃ is given in Scheme IV.4.
The suggested mechanistic pathway is analogous to that suggested by Leonard et al. (Scheme IV.2). A mechanism involving a hydride abstraction by \( \text{Rh}^{III} \) to give an intermediate \( \text{Rh}^{III}(H) \), as in the mechanism suggested for \( \text{Pd}^{II} \) systems (Scheme IV.3), is discounted in the present case on the grounds that a \( \text{Rh}^{III}(\text{NEt}_3) \) intermediate is unlikely to provide a vacant coordination site for such a \( H^- \) abstraction. In addition, no peaks attributable to \( \text{Rh}^{III-\text{H}} \) species were detected in the \( \delta 0 \) to 40 region of the \( ^1H \) nmr spectrum of a reaction solution.

IV.5 Other Routes to Dehydrogenation of \( \text{NEt}_3 \)

A dehydrogenation of about 10% of added \( \text{NEt}_3 \) without an accompanying formation of \( \text{NEt}_3H^+ \) was mentioned in the previous section. In order
to check whether this dehydrogenation was due to trace $O_2$ in the system, a reaction was carried out in air. Here it was thought that $O_2$ might act as an alternate acceptor of hydrogen, as in eq. IV.14, to give 100% conversion of the $NEt_3$ to the ethenamine.

$$\text{RhCl}_3(DMSO)_3 + NEt_3 + \frac{1}{2}O_2 \rightarrow \text{RhCl}_3(DMSO)_2(\cdot CH_2CH=^tNEt_2) + H_2O + DMSO$$

IV.14

Similar dehydrogenation reactions of amines by $O_2$ are well-documented. However, in all such cases, the amines are invariably primary or secondary amines that remain coordinated to the metal both before and after the oxidation (eqs. IV.15 and IV.16).

A reaction between $\text{RhCl}_3(DMSO)_3$ and 0.8 $NEt_3$ in CDC$_3$ in air still gave $\leq 10\%$ conversion of $NEt_3$ to ethenamine (as judged by a $^1H$ nmr spectrum of the solution), showing that trace $O_2$ was not responsible for the observed dehydrogenation.
Another plausible hydrogen acceptor in the system is DMSO. Under suitable conditions DMSO can act as a hydrogen acceptor to form DMS and H2O (eq. IV.17, see Section III.3.2.b for details).

DMSO + Rh(I) + 2H+ → DMS + H2O + Rh(III)  IV.17

In fact, the 1H nmr spectrum of a solution of RhCl₃(DMSO)₃ with 0.8 NEt₃ under Ar showed several small peaks in the δ 2.1-2.5 region (Fig. IV.11.a). The protons of Rh(III)/DMS species generally occur in this region as doublets (see Section III.4.1). The features of the peaks due to a Rh(III)/DMS by-product are more discernible in the 400 MHz ¹H nmr-monitored reaction between RhCl₃(DMSO)₃ and 1.5 NEt₃ in CDCl₃ (Fig. IV.10.d). Therefore, a slow reaction involving the reduction of DMSO (eq. IV.18) is probably the reason for the unusual dehydrogenation noted in Section IV.4.

Rh(III)/DMSO + NEt₃ → Rh(III)/DMS + H₂O + CH₂=CHNEt₂  IV.18

IV.6 Hydrolysis of the enamine ligand within the RhCl₃(DMSO)₂-(CH₂CH=NEt₂) complex, 6

The title reaction was discovered during attempts to isolate a pure species from the reaction between RhCl₃(DMSO)₃ and NEt₃. It was first thought that NEt₃ reduced all the Rh(III) to Rh(I) as in eq. IV.4,
and that the formation of the Rh(III)/ethenamine complex was due to the oxidation of the Rh(I) by excess DMSO (eq. IV.19, see also Section III.3.2.b).

\[
\text{Rh(I)} + 2\text{H}^+ + \text{DMSO} \rightarrow \text{Rh(III)} + \text{H}_2\text{O} + \text{DMS} \quad \text{IV.19}
\]

To check the possibility of such chemistry, the RhCl\(_3\)(DMSO)\(_3\) complex (200 mg, 0.45 mmol) in acetone (25 mL) was stirred under Ar in the presence of excess NEt\(_3\) (0.2 mL, 1.4 mmol) overnight and the solution concentrated to give an off-white precipitate (NEt\(_3\)-HCl) and a red-brown solution. Excess DMA·HCl (180 mg, 1.5 mmol) was added under Ar to the red-brown filtrate, and the solution was stirred overnight to obtain an air-stable, orange solution and a yellow precipitate. An ir spectrum of the crude product in Nujol showed the presence of Et\(_2\)NH\(_2^+\)(\(\nu_{N^+H}; 3140 \text{ cm}^{-1}, \text{s}\)) NEt\(_3\)H\(^+\)(\(\nu_{N^+H}; 2400-2600 \text{ cm}^{-1}, \text{s}\)) and only a weak peak due to \(^{-1}\text{CH}_2\text{-CH}^\equiv\text{NEt}_2\) \(\nu_{C-N}; 1640 \text{ cm}^{-1}, \text{w}\)). After recrystallization from CH\(_2\)Cl\(_2\)/ether in air, a complex analyzing for [NEt\(_3\)H][RhCl\(_4\)(DMSO)\(_2\)] was isolated in about 20% yield (~40 mg, 0.08 mmol). Anal. calcd. for C\(_{10}\)H\(_{28}\)Cl\(_4\)NO\(_2\)S\(_2\)Rh: C 23.86; H 5.61; N 2.78; found: C 23.35; H 5.29; N 2.71. \(^{1}\text{H} \text{nmr.} \delta(\text{CDCl}_3): 1.38, \text{t, } 9\text{H, } (\text{CH}_3\text{CH}_2)_3\text{NH}^+; 3.13, \text{q, } 6\text{H, } (\text{CH}_3\text{CH}_2)_3\text{NH}^+ \text{ (see Table IV.3)}; 3.48, \text{s, } -11\text{H, trans } (\text{CH}_3)_2\text{SO}; 3.53, \text{s, } -1\text{H, cis } (\text{CH}_3)_2\text{SO}.\) The mother-liquor from the above recrystallization step was concentrated to about 1-2 mL and left in a Schlenk tube closed with a rubber septum. After a few days, several red crystals, estimated to be ~20 mg (0.04 mmol), appeared. An ir spectrum of the crystals showed strong peaks at 3140 cm\(^{-1}\) (\(\nu_{N^+H} \text{ of } \text{R}_2\text{NH}_2^+\)) and 1128 and 1140 cm\(^{-1}\) (\(\nu_{SO} \text{ of DMSO}\)) (Fig. IV.12). X-ray analysis of the red crystals showed
Fig. IV.12
An ir spectrum \([\text{Et}_2\text{NH}]\text{[trans-RhCl}_4\text{(DMSO)}_2]\) in KBr
there to be two distinct crystal forms, both with the molecular formula \([\text{Et}_2\text{NH}_2][\text{trans-RhCl}_4(\text{DMSO})_2]\). In one type, the cation shows H-bonding with a Cl\(^-\) ligand each from two adjacent complex anions (13A, Fig. IV.13), while in the other, the interaction is with the DMSO ligands on the complex anion (13A, Fig. IV.14). On an average, the Rh-Cl bond lengths (2.331-2.346 Å) and the S=O bond lengths (1.422-1.472 Å) in 13A and 13B are slightly shorter than those reported for the complex anion in \([\text{H(DMSO)}_2][\text{trans-RhCl}_4(\text{DMSO})_2]\) (2.33-2.37 and 1.479-1.482 Å, respectively)\(^{50}\). Within the two crystal types, the effect of different H-bonding modes are reflected in their Rh-Cl and S=O bond lengths (Appendix II). The Rh(1)-Cl(1) bond length in 13A is longer than the corresponding bond length in 13B, while the reverse is true for the S(2)-O(2) bond lengths. The mother-liquor still showed \(\nu_\text{N+H}\) peaks due to \(\text{Et}_2\text{NH}_2^+\) and \(\text{Et}_3\text{NH}^+\) cations and DMSO but no further pure compounds could be isolated from the mixture. The absence of the ethenamine \(\nu_r\) peaks in the reaction mixture and the appearance of peaks due to \(\text{Et}_2\text{NH}_2^+\) suggested the possibility of reaction of HCl with the Rh(III)/ethanamine complex (e.g. as eq. IV.20).

\[
\text{RhCl}_3(\text{DMSO})_2(\text{CH}_2\text{CH}^=\text{NET}_2) + \text{HCl} \quad \rightarrow \quad [\text{CH}_3\text{CH}^=\text{NET}_2][\text{RhCl}_4(\text{DMSO})_2^-]
\]

\[
\text{H}_2\text{O} \text{ impurity}
\]

\[
\text{CH}_3\text{CHO} + [\text{Et}_2\text{NH}_2][\text{RhCl}_4(\text{DMSO})_2]
\]

IV.20
Fig. IV.13  A stereo-view ORTEP diagram of \([\text{Et}_2\text{NH}_2][\text{trans-RhCl}_4(\text{DMSO})_2]\) (crystal type A). Diagram shows an additional anion per molecule (Some structural parameters given in Appendix II)
Fig. IV.14  A stereo-view ORTEP diagram of $[\text{Et}_2\text{NH}_2][\text{trans-RhCl}_4(\text{DMSO})_2]$ (crystal type B). Diagram shows an additional anion per molecule. (Some structural parameters given in Appendix II)
The reaction between pure $\text{RhCl}_3(\text{DMSO})_2(\text{CH}_2\text{CH}=\text{NEt}_2)$, 6, (6 mg, $-0.015 \text{ mmol}$) and DMA·HCl (4 mg, $-0.03 \text{ mmol}$) in acetone-$d_6$ ($-0.6 \text{ mL}$) was thus monitored by 80 MHz $^1$H nmr. No H$_2$O was added to the system since the acetone-$d_6$ already contained $-0.04 \text{ mmol H}_2\text{O}$ as an impurity (δ2.93, Fig. IV.15.a). The original nmr peaks due to $\text{Rh(III)}/\text{CH}_2\text{CH}=\text{NEt}_2$ and DMA·HCl (Fig. IV.15.b) were replaced over 2 days by a new set of peaks (Fig. IV.15.c) assignable to $\text{Et}_2\text{NH}_2^+$ (δ1.4, t, 6H; 3.2, m, 4H), DMA (δ3.0 br, N(CH$_3$)$_2$) and $\text{-CH}_3\text{CHO}$ (δ9.8, 1H, D$_2$O stable). The peak position of DMSO remained essentially unchanged. The ir spectrum of the products in the form of a thin film, made by slow drying of a drop of the solution on a NaCl window, showed the absence of the $\nu_{\text{C-N}}$ peak at $-1640 \text{ cm}^{-1}$ and the presence of a sharp absorption at 3140 cm$^{-1}$, characteristic of $\nu_{\text{N-H}}$ of $\text{Et}_2\text{NH}_2^+$. The D$_2$O-insensitive peak at δ9.8 was assigned to CH$_3$CHO, though the expected splitting into a quartet (J=2Hz) was not discernible. The expected doublet due to CH$_3$-CHO, δ~2.2, was obscured by the acetone-$d_5$ peak and the CH$_3$CO-peak of DMA. The same reactants (6 + DMA·HCl) in CDCl$_3$ solution showed a similar but very slow reaction; after 10 days the quartet (J=2 Hz) at δ9.8 was observed. McCrindle et al. noted a similar slow decomposition of Pd$^{II}$(ethenamine) in CH$_2$Cl$_2$ containing traces of H$_2$O to give the corresponding aldehyde or ketone product.$^{82}$
Fig. IV.15  (a) 400 MHz $^1$H nmr spectra of RhCl$_3$(DMSO)$_2$(~CH$_2$CH=NEt$_2$) in acetone-$d_6$; (b) after adding one equivalent of DMA·HCl to (a); (c) 24 h after (b); x, NEt$_3$·HCl impurity
An interpretation of the data obtained by Morris\textsuperscript{50} for the reaction between \textit{RhCl}_3(DMSO)_3 and \textit{1,8-bis(dimethylamino)-naphthalene}

As discussed in the introduction to this chapter, a reaction similar to that between \textit{RhCl}_3(DMSO)_3 and \textit{NEt}_3 was discovered by Morris for another strongly basic (\textit{pK}_a 11.3) tertiary amine, \textit{1,8-bis(dimethylamino)naphthalene} (or P.S.). Morris noted that a reaction between \textit{RhCl}_3(DMSO-d_6)_3 and P.S. in CDCl\textsubscript{3} yielded PS.HCl, suggesting proton abstraction from one P.S. molecule by another. An \textit{air-stable} species, containing a P.S. derivative, was isolated in an impure form from a reaction solution containing other \textit{air-sensitive} species, but was not characterized.\textsuperscript{50}

The abstraction of protons from one \textit{NEt}_3 molecule by another was concluded in the present work to be part of a 2-electron redox reaction involving a Rh(III) metal centre (eqs. IV.2-IV.5). The reaction between \textit{RhCl}_3(DMSO)_3 and P.S., discovered by Morris, may now be explained based on the same principles. The suggested total reaction is given in eq. IV.21. The formation of an \textit{N}-carbene derivative, appearing as a ligand on the complex, 14, is invoked to accommodate a 2-electron oxidation of an \textit{N}-methyl amine. Proton Sponge scavenges protons to form mono-protonated P.S.H\textsuperscript{+} species, where the proton is strongly hydrogen-bonded to both nitrogen atoms on the molecule. In the reaction stoichiometry suggested (eq. IV.21), one proton is held as P.S.H\textsuperscript{+}, while the other proton is held by the Me\textsubscript{2}N- group on the P.S./carbene derivative as in 14. The latter type of protonation is hypothesized to accommodate the approximately 1:1 P.S./Rh stoichiometry noted by Morris.\textsuperscript{50}
2RhCl₃(DMSO)₃ + 2P.S. → RhCl₃(DMSO)₂(:CHN)⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋ düşün مع ... `-1600 cm⁻¹, since the C-N bond in a carbene is expected to show considerable double bond character, e.g.

\[
\text{Rh}^{\text{III}} (\text{C} = \text{N}) \quad \leftrightarrow \quad \text{Rh}^{\text{III}} (\text{C} = \cdot \text{N})
\]

According to Morris's IR data, the crude complex containing the P.S. derivative shows absorbances at 1605 and 1590 cm⁻¹, either of which correspond well with the literature values for the \text{Rh}^{\text{III}} carbene complexes. The \text{H} nmr data obtained by Morris (Table IV.5) are also compatible with the proposed structure, 14, although the peak assigned for the carbene proton is at a somewhat lower \delta than those reported for \text{Rh}(\text{III})/carbene complexes. For example, the carbene protons of \text{RhCl}_3(\text{PPh}_3)_2(\text{CHNEt}_2)\cdot\text{HCl}_3 and \text{RhCl}_3(\text{PET}_3)_2(\text{CHNEt}_2) appear at \delta 8.53 and 11.26, respectively. A change in the chemical shifts of the carbene ligands by 2.7 ppm for a change in the ligand environment from \text{PPh}_3 to \text{PET}_3 suggests the chemical shift of a carbene proton to be
Table IV.5

Interpretation (a) of the 100 MHz $^1$H nmr data obtained by Morris (b) for the orange crystals isolated in the reaction between RhCl$_3$(DMSO)$_3$ (1.0 mmol) and P.S. (0.8 mmol) in CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5-7.7 (5H, m)</td>
<td>H$_2$-H$_6$</td>
</tr>
<tr>
<td>7.0 (1H, dd, J = 2, 7 Hz)</td>
<td>H$_1$</td>
</tr>
<tr>
<td>5.15 (1H, s, br)</td>
<td>Rh=CH-N</td>
</tr>
<tr>
<td>3.75 (6H, s, br)</td>
<td>HCl. (CH$_3$)$_2$N-</td>
</tr>
<tr>
<td>3.44 (3H, s)</td>
<td>CH-N(CH$_3$)-</td>
</tr>
<tr>
<td>3.54 (12H, s)</td>
<td>(CH)$_2$SO (S-bonded)</td>
</tr>
</tbody>
</table>

[R.P.S.H.][RhCl$_4$(DMSO)$_2$], 15

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5-8.0 (0.2 x 6H, m)</td>
<td>aromatic protons of P.S.H$^+$ (c)</td>
</tr>
<tr>
<td>3.29 (0.2 x 12H, d, J = 2 Hz)</td>
<td>-N(CH$_3$)$_2$H$^+$ of P.S. (c)</td>
</tr>
<tr>
<td>3.50 (0.2 x 6H, s)</td>
<td>(CH$_3$)$_2$SO (S-bonded)</td>
</tr>
</tbody>
</table>

(a) Based on the structural formula 14.
(b) Ref. 50; chemical shifts given in p.p.m. Protons due to N$^+$H not observed; ascribed to the low concentration.
(c) Compares well with the values for P.S.H$^+$. $^{50}$
highly sensitive to its environment. Therefore the value of 5.15 assigned in the present case is considered reasonable. The impurity in the P.S. derivative appears to be \([\text{P.S.H}][\text{RhCl}_4(\text{DMSO})_2]\), 15, which is present in amounts up to 20%. The elemental analysis calculated for 14 (C 35.20, H 4.75 and N 4.56) agrees well with the experimental values (C 35.35, H 4.83 and N 4.61), despite the presence of the P.S.H.\(^+\) impurity, presumably because the general formulae of 14 (C\(_{14}\)H\(_{30}\)N\(_2\)O\(_2\)S\(_2\)Rh) and 15 (C\(_{14}\)H\(_{32}\)N\(_2\)O\(_2\)S\(_2\)Rh) differ only by two hydrogens. Morris reported the failure to obtain 14 in pure form.\(^{50}\) Attempts in the present work, using CH\(_2\)Cl\(_2\)/EtOH solvent, failed also to give pure products.

**IV.8 Concluding Remarks**

The dehydrogenation of tertiary amines by RhCl\(_3\)(DMSO)\(_3\) could be a more general reaction for most transition metal complexes, if suitable conditions prevail, since similar dehydrogenations with Hg(II) and Pd(II) are already known.\(^{82,91}\) Prior coordination of the amine could be a general feature, though this has not been established in the literature examples.

A relation between the basicity of the tertiary amine and its redox reactivity was noted at the outset of this chapter (see Section IV.1). This relation cannot be attributed simply to the proton affinity of the base since a strong base is not essential for the proton abstraction steps in the three suggested pathways (Schemes IV.1-IV.3). For example, in Scheme IV.2, the weak base AcO\(^-\) is used to abstract the proton from a C-H bond already weakened by coordination of the amine to
the metal. In Scheme IV.3, the metal insertion splits the C-H bond.

A contributing factor to the basicity dependence is almost certainly the differences in the bond strengths within Rh(III)/tertiary amine intermediates. For example, an interaction between a Rh(III) and a strongly basic amine should have a greater weakening effect on the N-C-H protons than an interaction with a weaker base. Therefore, proton abstraction by any base B, either directly (Schemes IV.2 and IV.4) or via a β-hydride elimination (Scheme IV.3), should be easier from a stronger base amine. For larger amines such as P.S., the concentration of the RhIII(amine) intermediate may be low but, if the weakening of the C-H bond within such an intermediate is sufficiently large, the reaction should proceed.

In terms of the arguments based on basicity of amines developed above, primary or secondary amines should show similar reactivity since they too have high pKₐ values (e.g. (C₂H₅)NH₂ 11.0; (C₂H₅)₂NH 10.6). Primary and secondary amines form stable complexes with platinum metals such as Rh(III)⁸⁰,⁹⁹,¹⁰⁰ and Ru(II).⁹⁴-⁹⁶ The amine ligands on some of these metal complexes are known to dehydrogenate in the presence of external oxidizing agents (e.g. eqs. IV.15 and IV.16 in Section IV.5).⁹⁴-⁹⁶ To our knowledge there are no reports on the dehydrogenation of primary and secondary amines in the absence of an external oxidizing agent. Whether the observed dehydrogenation of tertiary amines, via coordination to a transition metal (Section IV.4) with the metal centre acting as an effective internal oxidizing agent (eq. IV.4), is specific to tertiary amines merits further investigation.
CHAPTER V

A STUDY OF THE CATALYZED UPTAKE OF H₂/O₂ MIXTURES IN THE PRESENCE OF RhCl₃(DMSO)₃ COMPLEX IN DMA AND THE ACCOMPANYING OXIDATION OF THE SOLVENT
V A study of the catalyzed uptake of \( \text{H}_2/\text{O}_2 \) mixtures in the presence of \( \text{RhCl}_3(\text{DMSO})_3 \) complex in DMA and the accompanying oxidation of the solvent

V.1 Introduction

The potential of using \( \text{H}_2/\text{O}_2 \) mixtures in the presence of rhodium catalysts for the autoxidation of organic substrates was discussed in Section I.4. During some preliminary studies, an interesting rhodium- and \( \text{H}_2 \)-dependent autoxidation of solvent DMA in the presence of \( \text{RhCl}_3(\text{DMSO})_3 \) (1) complex was discovered. There was no autoxidation of DMA in the absence of either complex 1 or \( \text{H}_2 \), showing that both were essential for the observed catalytic activity.

Autoxidations of \( \text{N-alkyl} \) or \( \text{N,N-dialkylamides} \) are well documented.\(^{101-106} \) The studies appear to have been motivated mainly by the importance of preventing the autoxidation of industrially important amide polymers. The literature on oxidation of amides by other oxidants involves peroxysulfate,\(^{107} \) \( \text{RuO}_4 \),\(^{108} \) and alkyl hydroperoxides or peracids with or without added metal catalyst.\(^{109,110} \) Autoxidation of \( \text{N-alkyl-amides} \) generally occurs via free-radical chain mechanisms, which are initiated either photochemically at low temperatures, or thermally at \(-100-130^\circ\text{C}\). The oxidations occur at \( \text{C-H} \) bonds \( \alpha \) to the nitrogen to yield \(-\text{N-C=O}\) products (e.g. \( \text{CH}_3\text{CON(CH}_3\text{)CHO} \) (16) in DMA autoxidation) or other decomposition products. The mechanistic details of the reactions are also well documented.\(^{101,105} \) Major mechanistic pathways for DMA autoxidation are given by eqs. V.1-V.7 in Scheme V.1. At temperatures
>100°C the N-alkyl hydroperoxide (17) is the initial product, while at temperatures -0°C the termination reaction products (eqs. V.4-V.7) predominate.

Scheme V.1

Initiation:

\[ \text{CH}_3\text{CON(CH}_3\text{)}_2 \xrightarrow{\text{In.}} \text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2^· \]  

(In. = initiator)

Propagation:

\[ \text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2^· \xrightarrow{\text{O}_2} \text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2\text{O}_2^· \]  

\[ \text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2\text{OOH} \xrightarrow{} \text{CH}_3\text{CON(CH}_3\text{)}_2 \]  

Termination:

\[ 2\text{CH}_3\text{CON(CH}_3\text{)}\text{CHO} + \text{H}_2\text{O}_2 \]  

\[ 2\text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2\text{O}_2^· \xrightarrow{} [\text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2]_2\text{O}_2 + \text{O}_2 \]  

\[ \text{CH}_3\text{CON(CH}_3\text{)}\text{CHO} + [\text{CH}_3\text{CON(CH}_3\text{)}\text{CH}_2\text{OH}] + \text{O}_2 \]  

Metal-catalysis of N-alkylamide autoxidations does not appear to have received much attention. Work in our laboratory in the 1960's showed that the dimer [RhCl(COE)$_2$]$_2$ in the presence of excess LiCl in DMA at 80°C catalytically oxidized both the COE ligand and the solvent.61
V.2 Product analysis

Small amounts of solvent oxidation products were detectable by gas chromatography (Section II.5.4.c) within 0.5 h of shaking a 5.0 x 10^{-3} M solution of 1 in DMA at 50°C under a H2/O2 (2:1) mixture. For the purposes of product characterization, the reactions were allowed to proceed for at least 4-5 h to allow the accumulation of sufficient products for analysis. A gas chromatogram of the reaction mixture after 4-5 h of reaction showed a major peak with a retention time of 11.5 min and a smaller peak at 15 min accounting for <5% of the major peak. The major peak was identified as that of CH3CON(CH3)CHO (16) and the minor peak as that of CH3CON(CH3)H (20) by coinjection with authentic samples. A gc/ms of the major peak did not show the expected parent ion (m/e = 101), but three other distinct m/e values observed at 73 (40), [CH3CON(CH3)H]^+; 58 (30), [CH3CONH]^+; and 43 (100), [CH3CO]^+; matched those of authentic CH3CON(CH3)CHO (Section II.4.4). Since the parent ion in a mass spectrum of the authentic compound occurred at less than 0.1% relative intensity, the absence of the parent ion in a gc/ms of the reaction mixture was considered acceptable.

Lock and Sagar noted the decomposition of some N-alkyl hydroperoxides under high temperature (75-135°C) gas chromatographic conditions.103 Authentic CH3CON(CH3)CH2OOH (17), prepared in the present work, was also found to decompose, almost quantitatively, to CH3CON(CH3)CHO (16) under the gc conditions used for analysis (Section II.4.4). Thus, the major peak in a gas chromatogram from the product solution can be due to either 16 or 17, or both. A ^1H nmr spectrum in CDC13 of a reaction residue from a product solution after ~0.2 M total
uptake is given in Fig. V.1. The large peak at $\delta 2.1$ and the corresponding two peaks centred at $\delta 3.0$ in Fig. V.1 are assigned to DMA. The peaks at $\delta 9.2$, $3.1$, and $2.4$, which occur in an approximate 1:3:3 ratio, are assigned to $\text{CH}_3\text{CON(CH}_3\text{)CHO}$. The set of peaks at $\delta 5.15$, $3.0$ (hidden under $-\text{NCH}_3$ peak of DMA) and $2.15$, and $\delta 5.2$, $3.15$ and $2.12$ are assigned to cis and trans isomers of $\text{CH}_3\text{CON(CH}_3\text{)CH}_2\text{OOH}$, respectively. The assignments were made by comparison with $^1\text{H}$ nmr data for authentic samples (Table V.1).

Table V.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>NCH$_3$</th>
<th>NCH$_2$O$_2$/NCH$_2$OH</th>
<th>NCHO</th>
<th>OH/NH</th>
<th>CH$_3$CON</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CON(CH$_3$)H$^a$</td>
<td>2.87(d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.98</td>
</tr>
<tr>
<td>CH$_3$CON(CH$_3$)$_2$$^a$</td>
<td>3.00(d)</td>
<td>-</td>
<td>-</td>
<td></td>
<td>2.10</td>
</tr>
<tr>
<td>trans-CH$_3$CON(CH$_3$)CH$_2$OOH$^b$</td>
<td>3.19</td>
<td>5.18</td>
<td>-</td>
<td>~11(br)</td>
<td>2.15</td>
</tr>
<tr>
<td>cis-CH$_3$CON(CH$_3$)CH$_2$OOH$^b$</td>
<td>3.02</td>
<td>5.14</td>
<td>-</td>
<td>~11(br)</td>
<td>2.22</td>
</tr>
<tr>
<td>CH$_3$CON(CH$_3$)CHO</td>
<td>3.13</td>
<td>-</td>
<td>9.2</td>
<td></td>
<td>2.46</td>
</tr>
</tbody>
</table>

$^a$ Commercial Samples

$^b$ Cis:trans = 1:3; ratio estimated by $^1\text{H}$ nmr (Fig. V.2); discussion given in the text.
Fig. V.1 80 MHz $^1$H nmr spectrum in CDCl$_3$ of a reaction residue from the catalytic uptake of H$_2$/O$_2$ (-2:1) mixture by RhCl$_3$(DMSO)$_3$ in DMA ($5.0 \times 10^{-3}$ M) after ~4 h of reaction
Fig. V.2  80 MHz $^1$H nmr spectrum of $\text{CH}_3\text{CON(CH}_3)\text{CH}_2\text{OOH}$ in CDCl$_3$
(x, DMA impurity)
The occurrence of cis and trans isomers in certain N,N-alkylamides or their derivatives is well documented.\textsuperscript{104,111} The hydroperoxide derivatives generally show a greater abundance in the cis isomer (17A) than the trans isomer (17B), and this is explained in terms of a greater stability imparted to the cis isomer by internal H-bonding.\textsuperscript{104}

\begin{center}
\begin{tikzpicture}
  \node[align=center] at (-2,0) {17A};
  \draw (0,0) circle (0.8cm);
  \draw (0,0) -- (-0.5,0.8) -- (-0.8,0) -- (0,0) -- (0.5,-0.8) -- (0.8,0) -- (0,0);
  \draw (0,0) -- (0.5,0.5);
  \draw (0,0) -- (0.5,-0.5);
  \draw (0,0) -- (-0.5,-0.5);
  \draw (0,0) -- (-0.5,0.5);
  \draw (0,0) -- (0.5,0.3);
  \draw (0,0) -- (0.5,-0.3);
  \node[align=center] at (2,0) {17B};
  \draw (2,0) circle (0.8cm);
  \draw (2,0) -- (1.5,0.8) -- (1.8,0) -- (2,0) -- (1.5,-0.8) -- (2.2,0) -- (2,0);
  \draw (2,0) -- (1.5,0.5);
  \draw (2,0) -- (1.5,-0.5);
  \draw (2,0) -- (1.8,-0.8);
  \draw (2,0) -- (1.8,0.8);
  \draw (2,0) -- (1.5,-0.3);
  \draw (2,0) -- (1.5,0.3);
\end{tikzpicture}
\end{center}

A \textsuperscript{1}H nmr spectrum of authentic 17 prepared in the present work (Section II.4.4) showed two sets of peaks occurring in a \textasciitilde3:1 ratio (Fig. V.2). The set of peaks found in a greater abundance is assigned to the cis isomer based on the rationale given above. The peaks assigned to 17A and 17B, and the intensity ratio of the two isomers in CDCl\textsubscript{3} (Fig. V.1) in the \textsuperscript{1}H nmr of reaction residues, show good correspondence with those of the authentic samples. The \textsuperscript{1}H nmr spectrum of the residue showed much smaller amounts of the N-formyl (16) and H\textsubscript{2}O products since they are largely removed with the stripped solvent; a gas chromatogram of the stripped solvent shows the presence of both. The smaller peaks at \(\delta\) 2.15, 3.0 and 5.25 could be due to another peroxo derivative, perhaps some 18 shown in Scheme V.1, but this was not ascertained. The set of peaks at 3.4-3.6 are assigned to methyl protons of DMSO (Section
III.1). The D$_2$O-sensitive broad peak at $\delta$ 2.3 could be due to H$_2$O$_2$, since H$_2$O$_2$ is found as a significant product in a reaction solution after ~0.2 M H$_2$O$_2$ uptake (see later). Analysis for the total organic peroxide content in a product solution (Section II.5.2) after ~0.14 M total gas uptake gave a value of $8 \times 10^{-3}$ M. The amount of 17 in the same product solution was estimated to be about $1 \times 10^{-2}$ M, using the ratio of $^1$H integrations between the N-CH$_2$ of 17 and the phenyl protons of added internal standard DPSO in a $^1$H nmr spectrum of the reaction residue in CDC$_3$. The correspondence between the amount of organic peroxide and the amount of 17 in a product solution suggests the organic peroxide to consist essentially of the hydroperoxide 17.

The thermally unstable methylol product CH$_3$CON(CH$_3$)CH$_2$OH$^{111}$ (19) (Scheme V.1) gives the same retention time as CH$_3$CON(CH$_3$)H (20) in a gas chromatogram (Section II.5.4.b), perhaps because of decomposition to 20 under gc conditions. The methylol 19 has been detected previously as an unstable intermediate in the autoxidation of DMA by peracids.$^{112}$ In the present case, the absence of significant amounts of CH$_3$CON(CH$_3$)H in a gas chromatogram was taken as evidence for the absence of significant amounts of both 19 and 20 in a product solution.

Gas chromatograms of the product solutions failed to show other possible high-volatile oxidation products of DMA such as (CH$_3$)$_2$NH. The absence of significant amounts of HCHO, HCO$_2$H or CH$_3$CO$_2$H, or CO$_2$ was verified by colorimetry, titrimetry, and gas chromatography, respectively (Section II.5.3). Analysis for H$_2$O (Section II.5.1) and H$_2$O$_2$ (Section II.5.2) showed substantial amounts of both in a product solution (see later).
To obtain the product distribution as a function of time, product solutions were analyzed at various points up to \(-4.5\) h of reaction time. Because of the destructive nature of some analytical methods (e.g. iodometric assay for peroxides), several experiments were needed to get the time dependence of the product distribution. The results are summarized in Table V.2. The extent of the \(\text{H}_2/\text{O}_2\) reaction is given by both the time of reaction and the total uptake of gas. Plots of time vs. concentrations of the total gas uptake, \(\text{H}_2\text{O}, 16 + 17,\) and \(\text{H}_2\text{O}_2\) products are given by a-d in Fig. V.3.

The rate of total gas uptake remains essentially linear for approximately the first \(1\) h of reaction time and then falls off slowly. The product distribution up to about \(0.75\) h of reaction time is also markedly different from that found between \(0.75\) h to \(-4.5\) h of monitored reaction time.

Oxidation products of DMA (16 + 17) can be detected as early as \(0.25\) h of reaction, though it was difficult to determine accurately the concentration. Although the major oxidation product detected is the N-formyl 16, the initial product of autoxidation is almost certainly the hydroperoxide 17. The initial hydroperoxide products of N-alkyl amides (eq. V.3, Scheme V.1) decompose readily under reaction conditions to give mixtures of products.\(^{103-105}\) The decomposition of 17 to 16 (eq. V.8) is noted also in the present work (Section II.4.4); although the reaction stoichiometry is not determined, either in the literature examples or in the present work, \(\text{H}_2\text{O}\) is included in the equation as the obvious by-product.

\[
\text{CH}_3\text{CON(\text{CH}_3)CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CON(\text{CH}_3)CHO} + \text{H}_2\text{O}
\]  

V.8
Table V.2

Summary of analytical data\(^{(a)}\) for the reaction mixtures from the catalytic uptake of a \(\text{H}_2/\text{O}_2\) (2:1) mixture at 1.0 atm in the presence of \(5.0 \times 10^{-3} \text{M RhCl}_3(\text{DMSO})_3\) catalyst in DMA at 50°C

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Time of reaction, h</th>
<th>Total uptake</th>
<th>16+17 Total peroxides</th>
<th>17(b)</th>
<th>(\text{H}_2\text{O}_2)</th>
<th>(\text{H}_2\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.55</td>
<td>2.8</td>
<td>0.52</td>
<td>1.0</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>2-7</td>
<td>0.75</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0±0.3(^{(c)})</td>
</tr>
<tr>
<td>8</td>
<td>1.1</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.1</td>
<td>6.0</td>
<td>0.96</td>
<td>1.2</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>1.1</td>
<td>6.0</td>
<td>-</td>
<td>1.4</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>10.8</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>2.6</td>
<td>14.0</td>
<td>-</td>
<td>3.0</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>13</td>
<td>4.2</td>
<td>20.0</td>
<td>-</td>
<td>3.8</td>
<td>1.6</td>
<td>2.2</td>
</tr>
<tr>
<td>14</td>
<td>4.2</td>
<td>20.0</td>
<td>-</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>4.2</td>
<td>20.0</td>
<td>-</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16-19</td>
<td>4.2</td>
<td>20.0</td>
<td>3.8±0.4(^{(d)})</td>
<td>-</td>
<td>-</td>
<td>8.2±0.4(^{(e)})</td>
</tr>
<tr>
<td>20</td>
<td>4.6</td>
<td>21.4</td>
<td>4.1</td>
<td>3.8</td>
<td>1.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Details of analytical methods are given in Section II.5. All concentrations are reported in mol L\(^{-1}\) x 10\(^{2}\). A blank indicates that the particular analysis was not carried out.

\(^{(b)}\) Determined as organic peroxides (Section II.5.4); see text for rationale for assuming essentially all organic peroxides exist as the hydroperoxide 17.

\(^{(c)}\) Average of 6 sets of data: 0.7, 0.8, 0.8, 1.0, 1.0 and 1.4.

\(^{(d)}\) Average of 4 sets of data: 3.6, 3.6, 4.0, and 4.2.

\(^{(e)}\) Average of 4 sets of data: 7.8, 8.1, 8.2 and 8.5.
The plots of concentrations of (a) total $\text{H}_2 + \text{O}_2$ uptake, (b) $\text{H}_2\text{O}$, (c) $16 + 17$, and (d) $\text{H}_2\text{O}_2$, as functions of time for reaction mixtures containing $5.0 \times 10^{-3}$ M $\text{RhCl}_3(\text{DMSO})_3$ in DMA under a mixture of $\text{H}_2/\text{O}_2$ (500/260 in torr) at $50^\circ\text{C}$ (data in Table V.3).
Hydrogen peroxide occurs at a greater concentration than either H_{2}O or (16 + 17) in about the first 0.75 h of reaction time. Photo-initiated free-radical autoxidation of a simple N,N-alkyl amide such as DMA could produce H_{2}O_{2} via a termination pathway (eq. V.4, Scheme V.1). If the H_{2}O_{2} detected in the present case is due to an autoxidation of DMA, then for each equivalent of H_{2}O_{2} detected, at least two equivalents of 16 should be produced. However, if there is metal-catalyzed decomposition of H_{2}O_{2}, the observed 16: H_{2}O_{2} ratio will be greater still. Since the concentration of H_{2}O_{2} remains consistently higher than that of 16 + 17, at least upto about 2.5 h, it is almost certain that some or all of the detected H_{2}O_{2} results from a reaction other than the autoxidation of DMA.

Homogeneously catalyzed hydrogenolysis of O_{2} to yield H_{2}O_{2} (eq. V.9) is documented in some patent literature.\textsuperscript{113}

\[ \text{H}_{2} + \text{O}_{2} \rightarrow \text{H}_{2} \text{O}_{2} \] \hspace{1cm} \text{V.9}

In the few other reports available\textsuperscript{26,114-116} a net hydrogenolysis of O_{2} to H_{2}O (eq. V.10) is either verified\textsuperscript{26,115} or assumed\textsuperscript{114,116}.

\[ \text{H}_{2} + 0.5\text{O}_{2} \rightarrow \text{H}_{2}\text{O} \] \hspace{1cm} \text{V.10}

Hydrogen peroxide decomposes readily in the presence of catalysts, particularly transition metal ions (eqs. V.11-V.14).\textsuperscript{117}

\[ \text{M}^{n+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{M}^{n+} + \text{HO}^{-} + \text{HO}^{-} \] \hspace{1cm} \text{V.11}
\[ M^{n+1} + H_2O_2 \rightarrow M^{n+} + H^+ + HO_2^- \]  
\[ \text{V.12} \]

\[ \text{HO}^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  
\[ \text{V.13} \]

Adding eqs. V.11-V.13 gives

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]  
\[ \text{V.14} \]

In the patented processes, the decomposition of \( H_2O_2 \) was avoided by containing the transition-metal catalysts used, for example, \( \text{IrCl(CO)(PPh}_3)_2 \), in water immiscible solvents which are continuously extracted with water to remove promptly any \( H_2O_2 \) formed. The \( H_2O_2 \) detected in the present case almost certainly results from a metal-catalyzed hydrogenolysis of \( O_2 \) to \( H_2O_2 \), similar to those noted in the patent literature.

It was difficult to estimate the amount of \( H_2O \) formed in the early stages of the reaction (i.e. <0.5 h of reaction time), because of the low-sensitivity of the near-ir method for concentrations <0.01 M in DMA (Section II.5.1). After 0.75 h of reaction time the concentration of \( H_2O \) increases steadily (curve b, Fig. V.3). The data obtained at > 0.75 h (Table V.2) fit a linear plot with a correlation coefficient of 0.996 and an intercept equalling 0.25 h on the x-axis, suggesting the amount of \( H_2O \) in the 0-0.25 h period to be close to zero. Some or all of the \( H_2O \) observed in ~0.25-4.5 h of reaction time certainly results from the decomposition of \( H_2O_2 \) (eq. V.14) and/or the decomposition of the hydroperoxide 17 (eq. V.8). In principle, the homogeneously catalyzed hydrogenolysis of \( O_2 \) could lead to \( H_2O \) (eq. V.10), without the
intermediacy of $\text{H}_2\text{O}_2$ (eq. V.9) and its subsequent metal-catalyzed decomposition (eq. V.14). In the present case the initial product of $\text{O}_2$ hydrogenolysis is most certainly $\text{H}_2\text{O}_2$, since it is found in larger amounts than $\text{H}_2\text{O}$ in the 0-0.75 h reaction period, and the amount of $\text{H}_2\text{O}$ from 0-0.25 h is deduced to be negligible or zero. Occurrence of larger amounts of $\text{H}_2\text{O}$, and a steady state amount of $\text{H}_2\text{O}_2$ at longer reaction times, are consistent with a metal-catalyzed decomposition of $\text{H}_2\text{O}_2$ to give $\text{H}_2\text{O}$ (e.g. eq. V.14; see later for other possible modes). If the assumption that $\text{CH}_3\text{CON}($CH$_3$)$\text{CH}_2\text{OOH}$ is the initial product of DMA autoxidation is correct, the net gas uptake should correspond to the amounts of underlined atom equivalents in $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ and $\text{CH}_3\text{CON}($CH$_3$)$\text{CH}_2\text{OOH}$ products found at any time. The amount of $\text{H}_2\text{O}$ used in a calculation should be corrected, of course, for any $\text{H}_2\text{O}$ resulting from the decomposition of hydroperoxide 17 to 16 (eq. V.8). The above relation between total gas-uptake and the corresponding $\text{H}$ and $\text{O}$ atom equivalents in the products should hold true irrespective of mechanism(s) of $\text{H}_2\text{O}$ production involved, since the relation considers only the net stoichiometry of reaction.

The product distribution at $\sim4.6$ h of reaction, given in experiment 20, Table V.2, is used to test the correspondence between the total gas uptake and the product distribution, because a full analysis of a product solution is given by that set of data. The concentration of $\text{H}_2\text{O}_2$ ($2.6 \times 10^{-2}$ M) corresponds to $5.2 \times 10^{-2}$ M uptake of $\text{H}_2\text{+O}_2$ (eq. V.9) and the concentration of 16 + 17 ($4.1 \times 10^{-2}$ M) corresponds to an $\text{O}_2$ uptake of $4.1 \times 10^{-2}$ M (eq. V.15). The difference between the total of 16 + 17, and 17 amounts to $2.9 \times 10^{-2}$ M. Since the production of 16 from 17 should lead to an equivalent amount of $\text{H}_2\text{O}$ (eq. V.8), $2.9 \times$
10^{-2} \text{ M H}_2\text{O} in the product solution results from such a decomposition. The remainder of the H\text{O} (6.5 \times 10^{-2} \text{ M}) should originate from H\text{2} and O\text{2}, and therefore, corresponds to 9.8 \times 10^{-2} \text{ M uptake, according to the net stoichiometry in eq. V.10. The total uptake corresponding to the production of H\text{2O}_2, 16 + 17, and H\text{2}O, adds up to 19.1 \times 10^{-2} \text{ M}, while the total experimental uptake is 21.4 \times 10^{-2} \text{ M. The rough correspondence shows that the postulated net stoichiometries (eqs. V.9, V.10 and V.15) are consistent with the total uptake of gas.}

\[ \text{CH}_3\text{CON(CH}_3\text{)}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{CON(CH}_3\text{)CH}_2\text{OOH} \]

V.3 Mechanistic studies

V.3.1 Results

The rate of total gas uptake by a 5.0 \times 10^{-3} \text{ M solution of } \text{RhCl}_3(D\text{MSO})_3 \text{ (1) in DMA under 1 atm H}_2\text{O}_2 \text{ (2:1) at 50°C remains essentially linear in about the first 1 h of reaction and falls off slowly in the next 3.5 h of monitored reaction time (Fig. V.3.a). The maximum rate of reaction was used for kinetic analysis of the initial stage.}

The isomeric distribution of complex 1 does not appear to affect the maximum rate of the H\text{2}/O\text{2} reaction. A typical sample of complex 1 used contains about 86% of mer-RhCl\text{3}D\text{MSO})_2(D\text{MSO}) \text{ (1A+ 1C)}, ~13% of mer-RhCl\text{3}D\text{MSO})_3 \text{ (1B) and ~1% of other minor isomers. A further sample which contained ~70% of mer-cis-RhCl\text{3}D\text{MSO})_2(D\text{MSO}) \text{ (1A) and ~30% of}
mer-trans-RhCl₃(DMSO)₂(DMSO) (1c), or almost 100% of mer-RhCl₃-(DMSO)₂(DMSO), gave essentially the same rate as a typical sample (cf. experiments 1 and 2, Table V.3). The rate was unaffected also by a 20-fold excess of H₂O or 16-fold excess of hydroquinone, but was reduced by ~30% in the presence of a two-fold excess of DMSO (experiments 3-5). The rate of reaction at 2.5 x 10⁻³ M Rh is virtually unchanged by either 60-fold or 125-fold excess of HBF₄ added as DMA·HBF₄ (experiments 6-8).

The rate plots at various Rh (a-c, Fig. V.4), and H₂ and O₂ (a-c, Fig. V.5) concentrations/partial pressures remain linear for at least upto ~2000 s. The maximum rate of uptake is independent of the partial pressure of O₂ at high (540 torr) or low partial pressure of H₂ (Table V.4), but shows a linear dependence on H₂ at a total of 1 atm pressure (Table V.5, Fig. V.6). The rhodium dependence of the maximum rate is first order at lower concentrations but becomes less than first order at higher concentrations (Experiments 1-12, Table V.6; Plot a, Fig. V.7). The rate becomes first-order on rhodium in the presence of about a 50-fold excess of added DMSO (Experiments 13-15; Table V.6; plot b, Fig. V.7). The rate data at various DMSO concentrations are given in Table V.7 and the corresponding plot of (max. rate)⁻¹ vs [DMSO] in Fig. V.8.

The visible spectral changes for a 3.0 x 10⁻³ M solution of 1 in DMA under a H₂/O₂ (~2:1) mixture at 50°C are given in Figs. V.9 and V.10. The spectrum of complex 1 (curve A, Fig. V.9) changes rapidly under H₂/O₂ in the first 600 s (curves B - G) and then the spectrum remains unchanged for a further 1500 s, after which slow changes are observed. The spectra after a total of 1 h and 4 h reaction are given by curves H and J (Fig. V.10), respectively. Under O₂ alone at 50°C spectrum G changed to K within ~20 min (Fig. V.10). An ir spectrum of
Table V.3

Maximum rate of uptake of a H$_2$/O$_2$ (500/260) mixture at 1 atm by RhCl$_3$(DMSO)$_3$ (1)(a) in DMA at 50°C with or without various additives

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[Rh] x 10$^3$ M</th>
<th>Additive</th>
<th>Max. rate x 10$^5$, M s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0</td>
<td>-</td>
<td>1.49</td>
</tr>
<tr>
<td>2</td>
<td>5.0(b)</td>
<td>-</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>0.1 M H$_2$O</td>
<td>1.48</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.08 M hydroquinone</td>
<td>1.46</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>0.008 M DMSO</td>
<td>1.19</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>-</td>
<td>0.82</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>0.16 M DMA·HBF$_4$</td>
<td>0.79</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>0.31 M DMA·HBF$_4$</td>
<td>0.79</td>
</tr>
</tbody>
</table>

(a) See Table III.1 for the isomeric distribution in a typical sample.

(b) A sample RhCl$_3$(DMSO)$_2$(DMSO) containing about 70% of the mer-cis isomer (1A) and 30% of the mer-trans isomer (1C) was used.
Table V.4

Maximum rate of H₂/O₂ uptake by 5.0 x 10⁻³ M RhCl₃(DMSO)₃ in DMA at 50°C under various partial pressures (p.p.) of O₂, for a given p.p. of H₂.

<table>
<thead>
<tr>
<th>p.p. of H₂, torr</th>
<th>p.p. of H₂, torr</th>
<th>Max. rate x 10⁵, M s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>225</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1.60</td>
</tr>
<tr>
<td>160</td>
<td>600</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Table V.5

Maximum rate of H₂/O₂ uptake by 5.0 x 10⁻³ M RhCl₃(DMSO)₃ in DMA at 50°C under various partial pressures of H₂ and a total pressure of 760 torr (a)

<table>
<thead>
<tr>
<th>p.p. H₂, torr</th>
<th>Max. rate x 10⁵, M s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.89</td>
</tr>
<tr>
<td>645</td>
<td>1.79</td>
</tr>
<tr>
<td>600</td>
<td>1.79</td>
</tr>
<tr>
<td>540</td>
<td>1.67</td>
</tr>
<tr>
<td>500</td>
<td>1.49</td>
</tr>
<tr>
<td>480</td>
<td>1.41</td>
</tr>
<tr>
<td>400</td>
<td>1.17</td>
</tr>
<tr>
<td>360</td>
<td>1.16</td>
</tr>
<tr>
<td>300</td>
<td>0.94</td>
</tr>
<tr>
<td>270</td>
<td>0.90, 0.86</td>
</tr>
<tr>
<td>230</td>
<td>0.72</td>
</tr>
<tr>
<td>160</td>
<td>0.53</td>
</tr>
<tr>
<td>120</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Since the rate is independent of the partial pressure of O₂ (Table V.4), various partial pressures of O₂ were used to maintain a total pressure of 760 torr for reasons of convenience in the preparation of gas mixtures (Section II.2.6).
Table V.6

Maximum rate of uptake of a H₂/O₂ (500/260 torr) mixture by RhCl₃(DMSO)₃ in DMA at 50°C at various concentrations of Rh, with or without added DMSO

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[Rh] x 10³, M</th>
<th>Max. rate x 10⁵, M s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.0</td>
<td>1.83</td>
</tr>
<tr>
<td>2</td>
<td>5.9</td>
<td>1.68</td>
</tr>
<tr>
<td>3</td>
<td>5.4</td>
<td>1.62</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>1.49</td>
</tr>
<tr>
<td>5</td>
<td>4.4</td>
<td>1.39</td>
</tr>
<tr>
<td>6</td>
<td>4.0</td>
<td>1.34</td>
</tr>
<tr>
<td>7</td>
<td>3.1</td>
<td>0.96</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>0.82</td>
</tr>
<tr>
<td>9</td>
<td>2.2</td>
<td>0.82</td>
</tr>
<tr>
<td>10</td>
<td>1.65</td>
<td>0.56</td>
</tr>
<tr>
<td>11</td>
<td>1.10</td>
<td>0.42</td>
</tr>
<tr>
<td>12</td>
<td>0.57</td>
<td>0.23</td>
</tr>
<tr>
<td>13</td>
<td>2.5 (a)</td>
<td>0.225</td>
</tr>
<tr>
<td>14</td>
<td>4.9 (a)</td>
<td>0.435</td>
</tr>
<tr>
<td>15</td>
<td>7.2 (a)</td>
<td>0.64</td>
</tr>
</tbody>
</table>

(a) In the presence of 0.115 M added DMSO.
Table V.7

Maximum rate of uptake of a H$_2$/O$_2$ (500/260 torr) mixture by 2.5 x 10$^{-3}$ M RhCl$_3$(DMSO)$_3$ in DMA at 50°C for various concentrations of DMSO

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[DMSO]$^{(a)}$, M</th>
<th>Max. rate x 10$^6$, M s$^{-1}$</th>
<th>Max. rate$^{-1}$ x 10$^{-5}$, M$^{-1}$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;0.0025</td>
<td>8.20</td>
<td>1.22</td>
</tr>
<tr>
<td>2</td>
<td>0.027</td>
<td>4.70</td>
<td>2.13</td>
</tr>
<tr>
<td>3</td>
<td>0.082</td>
<td>2.90</td>
<td>3.45</td>
</tr>
<tr>
<td>4</td>
<td>0.092</td>
<td>2.85</td>
<td>3.51</td>
</tr>
<tr>
<td>5</td>
<td>0.105</td>
<td>2.46</td>
<td>4.06</td>
</tr>
<tr>
<td>6</td>
<td>0.115</td>
<td>2.25</td>
<td>4.44</td>
</tr>
<tr>
<td>7</td>
<td>0.145</td>
<td>2.07</td>
<td>4.83</td>
</tr>
<tr>
<td>8</td>
<td>0.165</td>
<td>1.73</td>
<td>5.78</td>
</tr>
</tbody>
</table>

(a) In experiment 1 there was no added DMSO, but a value less than the concentration of RhCl$_3$(DMSO)$_3$ is given to account for ligand dissociation in DMA (Section III.3.1.a). The [DMSO] given in experiments 2-8 refer to [DMSO] added only, since the effect of ligand dissociation is minimal at high concentrations 33 DMSO.
Fig. V.4 The rate of total $\text{H}_2/\text{O}_2$ (500/260 in torr) uptake by solutions of RhCl$_3$(DMSO)$_3$ in DMA at 50°C at various concentrations of Rh: (a) $4.0 \times 10^{-2}$, (b) $3.1 \times 10^{-3}$, (c) $1.7 \times 10^{-3}$ M
Fig. V.5  The rate of total H₂/O₂ uptake by 5.0x10⁻³ M solutions of RhCl₃(DMSO)₅ in DMA at 50°C at various partial pressures of H₂; (a) 645, (b) 300, (c) 160 torr total pressure 760 torr
Fig. V.6  Plot of maximum rate vs. partial pressure (p.p.) of H₂ for 5.0×10⁻³ M RhCl₃(DMSO)₃ in DMA at 50°C under H₂/O₂ at a total pressure of 760 torr (data in Table V.5)
V.7 (a) Plot of maximum rate vs. the concentration of Rh for RhCl₃(DMSO)₃ in DMA at 50°C under a H₂/O₂ (500/260 in torr) mixture; (b) same conditions as (a), but with added 0.115 M DMSO

Fig. V.7

(a) Plot of maximum rate vs. the concentration of Rh for RhCl₃(DMSO)₃ in DMA at 50°C under a H₂/O₂ (500/260 in torr) mixture; (b) same conditions as (a), but with added 0.115 M DMSO

Fig. V.8
Plot of maximum rate⁻¹ vs. [DMSO] for RhCl₃(DMSO)₃ in DMA at 50°C under a H₂/O₂ (500/260 in torr) mixture (data in Table V.7)
solution G (meaning the solution corresponding to spectrum G in Figs. V.9 or V.10) does not show any significant new bands in the narrow 650-950 cm\(^{-1}\) window available for DMA solvent in the 250-1700 cm\(^{-1}\) region (Fig. V.10.1); see below for other details. Hydrogen uptake plots for freeze-thaw degassed solutions G and J are given by curves b and c in Fig. V.11, respectively. The uptake plot for solution G (curve b) is essentially the same as that of complex 1 under analogous conditions (curve a; see also Section III.3.2). Solution J takes up H\(_2\) much more slowly than either G or complex 1 in DMA. It was not possible to obtain the total reaction stoichiometry for either solution G or J, because of metal precipitation on prolonged exposure (>2500 s) to H\(_2\).

Some comparative studies on the rate of autoxidation of DMA under various conditions are summarized in Table V.8

V.3.2 Discussion

(a) Initiation reaction

The rapid visible spectral changes in about the first 600 s of reaction and the relative stability of the spectrum for at least a further 1500 s (Fig. V.9) suggest that the catalytically active species is generated in the first 600 s. An uptake plot obtained under conditions analogous to those in Fig. V.9 (plot b, Fig. V.4) does not show an induction period, but the total gas uptake at ~600 s corresponds to ~2 equivalents of total gas per an equivalent of Rh. The uptake data are consistent with an initiation reaction as in eq. IV.16 to give an
Table V.8

Rate of oxidation of DMA solvent\(^{(a)}\) by 1.0 atm O\(_2\) at 50°C with or without added RhCl\(_3\)(DMSO)\(_3\) complex (5.0 x 10\(^{-3}\)M) under various conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Additive</th>
<th>Average rate of oxidation x 10(^6), M s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)O(_2) (-3 x 10(^{-2}) M) and CH(_3)CON(CH(_3))CH(_2)OOH (17) (-1 x 10(^{-2}) M)(^{(b)})</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>H(_2)O(_2)(^{(c)}) (4 x 10(^{-2}) M)</td>
<td>0.4±0.1(^{(d)})</td>
</tr>
<tr>
<td>4</td>
<td>H(_2)O(_2)(^{(c)}) (4 x 10(^{-2}) M) + 1</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>t-BuOOH (4 x 10(^{-2}) M) + 1</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>6</td>
<td>t-BuOOH (4 x 10(^{-2}) M) + 1</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>H(_2) (500 torr) with 1(^{(e)})</td>
<td>2.5±0.2(^{(f)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Defined as the amount of (CH\(_3\)CON(CH\(_3\))CHO, 16 + CH\(_3\)CON(CH\(_3\))CH\(_2\)OOH, 17), detected by gas chromatography (Section II.5.4.c) after a reaction period of ~4 h.

\(^{(b)}\) A sample of a product solution from a H\(_2\)/O\(_2\) reaction corresponding to experiment 20 in Table V.2 was used. The given concentrations for H\(_2\)O\(_2\) and 17 in the product solutions were estimated by analogy with the analytical data for experiment 20.

\(^{(c)}\) H\(_2\)O\(_2\) added as a 34% aqueous solution.

\(^{(d)}\) Some CH\(_3\)CON(CH\(_3\))H (20) approximating to about 15% of total products was detected; the given rates refer to the formation of 16 + 17 + 20

\(^{(e)}\) The partial pressure of O\(_2\) in experiment 7 was 260 torr.

\(^{(f)}\) Deduced from plot C in Fig. V.3.
Fig. V.9  Visible spectral changes for a 3.0x10^{-3} M solution of RhCl_3(DMSO)_3 in DMA at 50°C under a H_2/O_2 (500/260 in torr) mixture within 0-2000 s of reaction (A, spectrum of 1 in DMA)
Fig. V.10  Visible spectral changes (A $\rightarrow$ G) over 4 h for a 3.0x10$^{-3}$ M solution of RhCl$_3$(DMSO)$_3$ in DMA at 50°C under a H$_2$/O$_2$ (500/260 in torr) mixture (A: 1 in DMA; K and L: ~20 min and ~6 h, respectively, after leaving G under O$_2$ (1 atm) at 50°C
initial Rh\textsuperscript{I} species by reaction between complex 1 and H\textsubscript{2}, and a subsequent rapid reaction between the Rh\textsuperscript{I} species and O\textsubscript{2}.

\[
\text{Rh}^{\text{III}} + \text{H}_2 \xrightarrow{\text{slow}} \text{Rh}^{\text{I}} \xrightarrow{\text{fast}} \text{Rh}^{\text{I}}\cdot\text{O}_2
\]

The H\textsubscript{2} reaction of complex 1 is postulated to yield a Rh\textsuperscript{I} species which rapidly reacts with O\textsubscript{2} to give a Rh\textsuperscript{I}\cdotO\textsubscript{2} adduct (Section III.3.2.a); a full characterization of the species was not possible because of its instability. The visible spectrum of the catalytically active species in DMA (curve G, Fig. V.9) is similar to the spectrum of the postulated Rh\textsuperscript{I}O\textsubscript{2} species in Section III.3.2.a (curve D, Fig. III.4) in that both show increased \(\varepsilon\) (extinction coefficients) over the 400-600 nm range with respect to the spectrum A of complex 1 in DMA. Species D shows a higher \(\varepsilon\) than G in the range 400-435 nm. The discrepancy between the visible spectra of species D and G is not surprising considering that species D in Fig. III.4 is postulated to be a mixture \(-60\%\) of Rh\textsuperscript{I}O\textsubscript{2}, \(-20\%\) of unreacted 1, and \(-20\%\) of a Rh\textsuperscript{III}(DMS) species (Section II.3.2.a). Because of the nucleophilicity of the dioxygen ligand, the Rh\textsuperscript{I}\cdotO\textsubscript{2} species may exist in association with 1 and/or Rh\textsuperscript{III}(DMS) species. The dimeric [RhCl(O\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2} complex (21)\textsuperscript{118a} is thought to form via a nucleophilic attack by the dioxygen ligand of a RhCl(O\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} species on the metal centre of another (eq. V.17, E \textsubscript{=} RhCl(O\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2}).\textsuperscript{119} By analogy, a Rh\textsuperscript{I}\cdotO\textsubscript{2} species could form (Rh\cdotO\textsubscript{2})\textsubscript{2} or (Rh)\textsubscript{2}O\textsubscript{2} species via nucleophilic attacks by coordinated O\textsubscript{2} of Rh\textsuperscript{I}\cdotO\textsubscript{2} on another Rh\textsuperscript{I}\cdotO\textsubscript{2} or on \(-40\%\) of unreacted 1 or Rh\textsuperscript{III}(DMS) species,
respectively; a dioxygen bridged \((\text{Rh})_2\text{O}_2\) is postulated to be the intermediate in a reaction between \(\text{KO}_2\) and the formally \(\text{Rh}^{\text{III}}\) complex \([\text{Rh}(\text{C}_3\text{H}_5)_2\text{Cl}]_2\) (eq. V.17.1).\(^{118b}\)

\[
\begin{align*}
\text{Rh} & + E \rightarrow \text{Rh} - E \rightarrow \text{Rh(OOH)}
\end{align*}
\]

An IR spectrum of the species \(G\) (b, Fig. V.10.1) is essentially the same as the spectrum of complex 1 in DMA (a, Fig. V.10.1), except that the peak at 930 cm\(^{-1}\) appears broader and there is a new absorption at -950 cm\(^{-1}\). Subtracting spectrum (a) from spectrum (b) gives a weak
Fig. V.10.1 FT IR spectra of: (a) 4x10^{-2} \text{ M} solution of RhCl_3(DMSO)_3 in DMA; (b) a solution resulting from the H_2/O_2 (500/260 in torr) reaction of (a) at 50^\circ\text{C} for ~2000 s (path length of KBr windows, 0.5 mm)
Fig. V.11  H₂ uptake plots for: (a) 1.0x10⁻² M RhCl₃(DMSO)₃ in DMA; (b) solution (a) after reaction at 50°C under H₂/O₂ (500/260 in torr) for ~2000 s; (c) solution (a) after reaction at 50°C under H₂/O₂ (500/260 in torr) for ~4 h
broad band at -895 cm\(^{-1}\) which may be due to a O—O stretch, but the evidence is not compelling.

Although the spectral data available are insufficient to characterize the catalytically active species G, the observed 2:1 gas:rhodium ratio required to generate the catalytically active species G is best interpreted in terms of a stepwise reaction between 1 and \(\text{H}_2\) and then \(\text{O}_2\) (eq. IV.16). The similarity between the \(\text{H}_2\) reaction of complex 1 in DMA and species G in DMA, in their reaction rates and stoichiometry (curves a and b, respectively, in Fig. V.11) suggests the \(\text{Rh}^{\text{III}}\cdot\text{O}_2\) species resembles complex 1 in DMA in electronic and structural properties. The inverse dependence of the rate on the concentration of DMSO (Fig. V.8) suggests that the rate determining step(s) involve(s) a DMSO dissociation from G. A \(\text{Rh}^{\text{III}}\) peroxo complex containing DMSO ligands such as \(\text{Rh}^{\text{III}}\text{Cl(O}_2\text{)(DMSO)}_3\) is consistent with the observed properties of species G in DMA. In principle, the peroxide ligand is replacing two Cl\(^{-}\) ligands, and thus the similarity with complex 1 in DMA. Although the visible spectral data clearly indicate a change from complex 1 to species G under the catalytic conditions (Fig. V.9), the rate of \(\text{H}_2/\text{O}_2\) uptake (Figs. V.4 and V.5) remains essentially linear during the corresponding periods of time, consistent with the above proposed similarity between species G and complex 1 in DMA.

The net stoichiometry of the \(\text{H}_2/\text{O}_2\) reaction of 1 (eq. V.16) requires that two protons are generated for each equivalent of species G formed. Dioxygen adducts of \(\text{M}^{\text{V}}\)(M=Pd,Pt) are known to react with acids (HX) to yield \(\text{MX}_2\) species and \(\text{H}_2\text{O}_2\) via a postulated \(\text{M}^{\text{II}}\text{(OOH)}\) intermediate (e.g. eq. V.18).\(^{120a}\) An analogous protonation of a Rh-O\(_2\) complex has also been reported (eq. V.18.1).\(^{120b}\)
The absence of a significant effect on the catalytic H₂/O₂ reaction by either a 60- or 125-fold excess of HBF₄ over rhodium (experiments 7 and 8, Table V.3) suggests that such a protonation step(s) is not involved in the rate determining step(s) of the catalytic cycle(s). It is likely that any such protonation is inhibited by DMA solvent. If E in eq. V.17 is equivalent to a proton, an analogous mechanism can be proposed for protonation of Rh⁺⁺⁺O₂ in DMA (eq. V.19).

Solvent DMA is likely to compete with the O₂ ligand and thus inhibit the protonation of the dioxygen ligand (cf. eq. III.11, p. 85). (However, rapid protonation of dioxygen ligands under the reaction conditions cannot be totally ruled out. For example, if the protons generated in the H₂ reaction of Rh⁺⁺⁺ (eq. IV.16) remain in the coordination sphere of the metal during a rapid reaction between Rh⁺ and O₂, solvent effects,
as discussed above, would be minimal. The possibility of rapid protonation under reaction conditions is considered later in this section).

(b) Catalysis

The rate data and the product distribution in the initial phase of the catalytic reaction are tentatively, but best, interpreted in terms of a mechanistic scheme involving a Rh\textsuperscript{III}-peroxo intermediate (Scheme V.2). The requirement of a predissociation of a DMSO ligand (eq. V.20) is invoked to explain the DMSO dependence of the rate. The dissociation

Scheme V.2

\[
K \quad \text{Rh}^\text{III}(\text{O}_2^-)(\text{DMSO}) + \text{DMA} \rightleftharpoons \text{Rh}^\text{III}(\text{O}_2^-)(\text{DMA}) + \text{DMSO} \quad \text{V.20}
\]

\[
\begin{array}{c}
\text{Rh}^\text{III}(\text{O}_2^-)(\text{DMA}) \\
\text{H}_2 \quad k_1 \quad \text{O}_2 \quad \text{fast} \quad k_2 \quad \text{CH}_3\text{CON(CH}_3)_2\text{CH}_2\text{OOH} \\
\text{H}_2\text{O}_2 \\
\text{Rh}^\text{I} \\
\end{array}
\]
is given as a substitution of DMSO by solvent DMA (Section III.3.2). Subsequent H\textsubscript{2} reaction of the Rh\textsuperscript{III}(O\textsubscript{2})(DMA) species (path A) may or may not require a predissociation of a DMA ligand: the possibility of a DMA ligand dissociation is discussed later.

If the total concentration of rhodium is [Rhp] and rate of reaction is defined as the rate of total uptake, the mechanism in Scheme V.2 yields the rate law,

\begin{align*}
\text{rate} &= 2k_1 [\text{Rh}^{III}(O_2)(DMA)] [H_2] + k_2 [\text{Rh}^{III}(O_2)(DMA)] \\
&= \frac{2k_1K'[Rhp][H_2]}{K' + [\text{DMSO}]} + \frac{k_2K'[Rhp]}{K' + [\text{DMSO}]}
\end{align*}

\[ V.21 \]

where, \( K' = K[\text{DMA}] \) \[ V.22 \]

At sufficiently low rhodium concentrations, \([\text{DMSO}] < K'\) and the rate law in eq. \( V.21 \) leads to a first-order dependence on \([Rhp]\); at the higher rhodium concentrations, \([\text{DMSO}] > K'\) and in the absence of added DMSO is equated to \([\text{Rh}^{III}(O_2^-)(DMA)]\) (which is given by \((K'[\text{Rhp}])^{1/2}\)). Thus the rate law then becomes:

\[ \text{rate} = 2k_1 (K'[Rhp])^{1/2}[H_2] + k_2 (K'[Rhp])^{1/2} \]

The complex dependence on Rh (plot a, Fig. V.7) is thus accounted for by the \( K \) equilibrium, i.e. in terms of the relative magnitudes of \( K \) and \([\text{DMSO}]\) in the denominator of eq. \( V.21 \) as \([Rhp]\) increases. In the presence of sufficient added DMSO \(([\text{DMSO}] \gg K\) in eq. \( V.21 \)), a first-order dependence on catalyst is obtained (plot b, Fig. V.5).
The rate dependence on added DMSO can be analyzed by taking the reciprocal form of eq. V.21 (eq. V.23) and plotting \((\text{rate})^{-1}\) vs. [DMSO] (Fig. V.8).

\[
(\text{rate})^{-1} = \frac{[\text{DMSO}]}{K'(2k_1[H_2] + k_2[Rh_T])} + \frac{1}{(2k_1[H_2] + k_2)[Rh_T]} \quad \text{V.23}
\]

Analysis of various rate dependences using eqs. V.21 and V.23 lead to internally consistent values for \(k_1\), \(k_2\) and \(K'\). The slope of rate vs. [Rh_T] in the presence of 0.115 M added DMSO (Fig. V.7.b) is given by

\[
\frac{(2k_1[H_2] + k_2)K'}{K' + 0.115} = 8.9 \times 10^{-4} \text{ s}^{-1} \quad \text{V.24}
\]

and the slope of \((\text{rate})^{-1}\) vs [DMSO] (Fig. V.8) yields a value of

\[
(2k_1[H_2] + k_2)K' = 1.4 \times 10^{-4} \text{ M s}^{-1} \text{ for } r = 0.998 \quad \text{V.25}
\]

Dividing equation V.24 by V.25 leads to a \(K' = 0.042 \text{ M}\). A plot of rate vs [H_2] gives a linear plot (Fig. V.6), the slope of which leads to

\[
\frac{2k_1K'[Rh_T]}{K' + [\text{DMSO}]} = 9.6 \times 10^{-3} \text{ s}^{-1} \text{ for } r = 0.994 \quad \text{V.26}
\]

Using the value of \(K'\) derived above, [DMSO] is calculated to be \(4.5 \times 10^{-3} \text{ M}\) at \(5.0 \times 10^{-3} \text{ M [Rh_T]}\), and thus \(k_1 = 1.05 \text{ M}^{-1} \text{s}^{-1}\) is obtained from eq. V.26. Substituting values for \(K'\) and \(k_1\) in eqs. V.25 or V.24 yields
\[ k_2 = 5.0 \times 10^{-4} \text{ s}^{-1}. \] The intercept in Fig. V.6 equals 0.17 x 10^{-5} and yields \[ k_2 = 3.7 \times 10^{-4} \text{ s}^{-1}, \] while the intercept in Fig. V.8 equals 1.1 x 10^{-5} M s^{-1} and yields \[ K' = 0.039 \] via the intercept:slope ratio (eq. V.23). The values of \( k_2 \) and \( K' \) derived using the intercepts will be less accurate than those derived using the slopes.

The value of \( K' = 0.042 \text{ M} \) derived above yields \( K = 0.004 \) via eq. V.22; the density of DMA expressed in mol L^{-1} is used for [DMA]. The \( K \) value derived corresponds well with the \( K = 0.01 \pm 0.005 \) value reported for the analogous equilibrium of complex 1 in CDCl\(_3\)\(^{23} \) (see also Section III.3.1). According to the rate expression in eq. V.21, the intercept in the \( H_2 \)-dependence plot (Fig. V.5) should give the rate of autoxidation of DMA at \([\text{Rh}_T] = 5.0 \times 10^{-3} \text{ M}\). The value of \(-0.2 \times 10^{-5} \text{ M s}^{-1}\) derived from Fig. V.5 corresponds well with the rate of production of oxidized DMA (16 + 17) equalling \( 0.25 \times 10^{-5} \text{ M s}^{-1}\), derived from plot c in Fig. V.3.

The internal consistency of the derived \( k_1, k_2 \) and \( K \) values and the correspondence of derived \( k_2 \) and \( K' \) with independent measurements lend strong support to the postulated mechanism in Scheme V.2.

### Hydrogenolysis of \( O_2 \)

The reaction pathways A and B in Scheme V.2 require elaboration. In path A, the \( H_2 \) reaction of a Rh\(^{III}\)-peroxo intermediate is postulated to lead to the production of \( H_2O_2 \) and a Rh\(^{I}\). Mechanistic details of the hydrogenolysis of \( O_2 \) to water or hydrogen peroxide, whether homogeneously or heterogeneously catalyzed, remain largely unknown.\(^{115} \) In
the Cu\textsuperscript{2+}-catalyzed hydrogenolysis of O\textsubscript{2} to H\textsubscript{2}O in aqueous media at high temperatures and pressures, first-order dependences on the catalyst and on H\textsubscript{2}, and zero-order dependence on O\textsubscript{2}, were reported, but the suggested mechanism (eqs. V.27-V.29) did not consider the details of the O\textsubscript{2} reduction (eq. V.29).\textsuperscript{114}

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2 & \xrightleftharpoons[k_1]{k_{-1}} \text{CuH}^+ + \text{H}^+ & \text{V.27} \\
\text{CuH}^+ + \text{Cu}^{2+} & \rightarrow 2\text{Cu}^+ + \text{H}^+ & \text{V.28} \\
\text{Cu}^+ + \frac{1}{2}\text{O}_2 + 2\text{H}^+ & \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O} & \text{V.29}
\end{align*}
\]

In the report by Vaska et al. on the hydrogenolysis of O\textsubscript{2} to H\textsubscript{2}O in toluene solvent under ambient conditions by several Pt metal catalysts containing phosphine ligands, complex rate dependences on metal, and first-order dependences on H\textsubscript{2} and O\textsubscript{2} were noted and the catalytically active species were postulated to be metal hydrides such as IrH(CO)-(PPh\textsubscript{3})\textsubscript{3} and IrH\textsubscript{3}(CO)(PPh\textsubscript{3})\textsubscript{2}.\textsuperscript{115}

The mechanism suggested in the present work postulates H\textsubscript{2}O\textsubscript{2} to be the initial product of a Rh catalyzed hydrogenolysis of O\textsubscript{2}. The occurrence of relatively larger amounts of H\textsubscript{2}O\textsubscript{2} over H\textsubscript{2}O in the initial phase of the H\textsubscript{2}/O\textsubscript{2} reaction suggests the initial product to be H\textsubscript{2}O\textsubscript{2}, and the smaller amount of H\textsubscript{2}O detected to result from the decomposition of hydroperoxide (17) product (eq. V.8). The good rate dependences obtained within about the first 2000 s suggest that production of H\textsubscript{2}O
and O₂ via a metal catalyzed decomposition of H₂O₂ (eqs. V.11-V.14) is not significant within this time.

To our knowledge there are no precedents in the literature for H₂ reactions with metal-peroxides. Hydrogen reactions of Rh³⁺ complexes containing halide ligands (eqs. V.30 and V.32) are well documented.¹²¹,¹²²

\[
\text{Rh}^{III}\text{Cl}_6^{3-} + \text{H}_2 \rightarrow \text{Rh}^I\text{Cl}_4^{3-} + 2\text{HCl} \quad \text{V.30}
\]

\[
\text{RhCl}_3(\text{DES})_3 + \text{H}_2 \rightarrow \text{Rh}^I\text{Cl}(\text{DES})_3 + 2\text{HCl} \quad \text{V.31}
\]

A similar reaction where a peroxide ligand acts essentially as two Cl⁻ ligands could presumably produce H₂O₂ and Rh⁺ in a H₂ reaction with Rh³⁺-peroxide. Hydrogen reduction of Rh³⁺Clₙ species are thought to occur via Rh³⁺(H) intermediates,¹⁵⁷ but the mechanism of the H₂ activation is not clear.¹²³ The requirement of a vacant coordination site is invoked in one study¹²² but not in another.¹²¹ A mechanism involving a predissociation of a ligand is given in Scheme V.3. If equilibrium K₂ is important, the k₂ (measured) in a catalytic H₂/O₂ reaction (Scheme V.3) is actually the value of k₂K₂.

Autoxidation of DMA

According to path B in Scheme V.2 autoxidation of DMA occurs via a metal-centred transfer of peroxidic dioxygen to a coordinated DMA. The
The proposed mechanism is based on kinetic evidence. Solvent DMA is not effectively autoxidized in the absence of complex 1 or H₂.

Scheme V.3

(experiment 1, Table V.8). The rate of peroxide-initiated autoxidations with or without complex 1 amounts only to about (0.3-0.6) x 10⁻⁶ Ms⁻¹ (experiment 2-6), while in the presence of H₂ the rate of autoxidation of DMA remains essentially linear in the 4.5 h of reaction at 2.5 x 10⁻⁶ Ms⁻¹ (curve c, Fig. V.3). A 15-fold excess of the free-radical scavenger hydroquinone has no effect on the rate of H₂/O₂ uptake for about 2000 s of monitored reaction time, showing that there are no significant free-radical chain autoxidations in this period (experiment 4, Table V.3); hydroquinone has been used previously with success to
inhibit photo-initiated autoxidation of DMA.\textsuperscript{106} The rate data (Tables V.4-V.7) are also consistent with a Rh-dependent total reaction (eq. V.19).

Ng suggested a metal-centred transfer of \( \text{O}_2 \) to a coordinated DMA to explain an observed slow autoxidation of solvent DMA in the presence of \([\text{RhCl(COE)}_2]_2\) complex and excess LiCl at 80\(^\circ\)C (Scheme V.4)\textsuperscript{124a}. A homolytic pathway via a radical abstraction from coordinated DMA was postulated to occur via a \( \text{Rh}^{\text{II}}(\text{O}_2^-) \) form of a \( \text{Rh}^{\text{I}}\text{O}_2 \) adduct; about 3\% of the \( \text{Rh}^{\text{I}}\text{O}_2 \) adduct was postulated to exist as \( \text{Rh}^{\text{II}}\text{O}_2^- \) based on an e.s.r. study.\textsuperscript{124b}

Since the above work, more information on the coordination mode of DMA has become available. Dimethylacetamide protonates at the carbonyl oxygen; for example, within the DMA·HCl adduct protonation at the oxygen gives a polarized molecule (22).\textsuperscript{75}
Coordination through the oxygen atom was postulated for $\text{Rh}_2\text{Cl}_6(\text{DMA})_2$, the only DMA complex of Rh$^{\text{III}}$ reported in the literature, but further structural data are not available. However, DMA is now considered to bind invariably through the oxygen.

A plausible mechanism for the autoxidation of DMA by $\text{Rh}^{\text{III}}(\text{O}_2^-)$-(DMA) (23) species, where the DMA is coordinated via the oxygen atom, is given in Scheme V.5.

Scheme V.5
A polarization of the molecule similar to structure 22 will make the N-CH₃ protons sufficiently acidic for a proton abstraction by the peroxidic O₂ ligand to give an intermediate -N-CH₂⁻ species: the N-methyl groups in amides are known to react via N-CH₂⁻ moieties under suitable conditions. The proposed mechanism assumes a slow proton abstraction by the nucleophilic peroxide ligand to give an intermediate RhIII complex containing an N-methylene ligand, possibly via a 5-membered metallocycle (24). Reductive elimination of the NCH₂⁻ and HO₂⁻ ligands would yield CH₃CON(CH₃)CH₂OOH, with concomitant generation of an O₂-sensitive Rh¹ species; rapid reaction of Rh¹ with O₂ regenerates the catalytically active RhIII(O₂⁻) complex (23). Precedents for metal-centred proton abstraction from N-CH₃ groups are found in Chapter IV, where the coordination of tertiary amines to RhIII metal centres are postulated to render the N-CH₂⁻ proton sufficiently acidic for proton abstraction.

In principle, if a rapid protonation(s) of the peroxide ligand occurs under the reaction conditions (see p. 183), the reactive intermediate could be a RhIII(OOH) (eq. V.32), or a RhIII species which does not contain a peroxo ligand (eq. V.33).

\[
\begin{align*}
\text{Rh}^{III} (O_2^-) & \xrightarrow{H^+ \text{ fast}} \text{Rh}^{III} (OOH)^{2+} & \text{V.32} \\
\text{Rh}^{III} (O_2^-) & \xrightarrow{H^+ \text{ fast}} [\text{Rh}^{III} (OOH)]^{2+} \xrightarrow{H^+ \text{ fast}} \text{Rh}^{III} + H_2O_2 & \text{V.33}
\end{align*}
\]

In either case, subsequent reaction with H₂ could lead to a catalytic hydrogenolysis of O₂ via a mechanism analogous to Scheme V.3, but a
mechanism for DMA oxidation via a \( \text{Rh}^{\text{III}}(\text{OOH}) \) or \( \text{Rh}^{\text{III}} \) species is not readily conceivable. Some \( \text{Mn}^{2+} \) or \( \text{Mn}^{3+} \) complexes are reported to catalyze the oxidation of N-alkyl amides to the respective keto derivatives by alkyl hydroperoxides (eq. V.34) but mechanistic details are not available.\textsuperscript{110}

\[
\begin{align*}
\text{Mn}^{\text{II}} \text{ or Mn}^{\text{III}} + 2\text{ROOH} & \rightarrow \text{H}_2\text{O} + \text{ROH} \\
\text{NR}'+(\text{CH}_2)_n\text{NR}' & \rightarrow \text{CH}_2\text{C}(\text{CH}_2)_n\text{NR}'
\end{align*}
\]

V.34

Results from 'blank' reactions in the present study (experiments 2-6, Table V.8) show that \( \text{Rh}^{\text{III}}\text{Cl}_3(\text{DMSO})_3 \) in the presence of \( \text{H}_2\text{O}_2 \) cannot oxidize DMA at the same rate as the \( \text{H}_2/\text{O}_2 \) reaction.

(c) The role of \( \text{H}_2 \) in the autoxidation of DMA

According to path B, Scheme V.2, or Scheme V.5, it should be possible to catalyze the autoxidation of DMA by the \( \text{Rh}^{\text{III}}(\text{O}_2=) \) intermediate even in the absence of \( \text{H}_2 \), but such catalysis is not realized. When a reaction solution containing the postulated \( \text{Rh}^{\text{III}}(\text{O}_2=) \) intermediate (for example, a solution corresponding to spectrum G in Fig. V.9 or V.10) is put under 1 atm of \( \text{O}_2 \) at 50\degree\text{C}, rapid, visible spectral changes (\( \text{G} \rightarrow \text{K} \), Fig. V.10) are observed, but there is no
discernible uptake of gas for at least 1 h. There were further slower spectral changes with time to give a stable spectrum L (Fig. V.10) after a few hours. Attempts to isolate characterizable species from reaction solutions corresponding to spectrum L (for [Rh] = 3 × 10⁻³ or 1 × 10⁻² M) were not successful.

A study on immobilized, solid-supported organosulfide complexes of Rh for autoxidation of olefins, reported by Nyberg and Drago,¹²⁷ has been based on the assumption that the relatively short life times of rhodium catalysts in autoxidations¹⁷,¹⁸ result from processes that are multiordered in rhodium. Read and coworkers reported¹²⁸ that the decomposition of RhCl(O₂)(PPh₃)₃ species in benzene solution under anaerobic conditions leads to dimeric Rh species and PPh₃O (eq. V.35).

\[
4\text{RhCl(O}_2\text{)(PPh}_3\text{)}_3 \longrightarrow [\text{RhCl(PPh}_3\text{)}_2]_2 + \text{[RhCl(O}_2\text{)(PPh}_3\text{)}_2]_2 + 4\text{PPh}_3\text{O} \quad \text{V.35}
\]

The changes G —> K in the visible spectrum of the Rh³⁺(O₂⁻) species in solution (Fig. V.10), in the absence of H₂, could involve similar dimerization processes. The proposed mechanism for the autoxidation of DMA (Scheme V.5, p. 184) requires that the O₂ ligand be nucleophilic. Since dimeric [RhO₂]₂ species (e.g. 21, p. 179) are known to be unreactive towards electrophiles,¹²⁹ dimerization of Rh³⁺(O₂⁻) species in solution will render the reaction solution catalytically inactive towards autoxidation of DMA.

At any given time a reaction solution containing Rh³⁺(O₂⁻) species will have 2 equivalents of protons per equivalent of Rh³⁺(O₂⁻) (p. 182). Dioxygen ligands on monomeric dioxygen complexes of Rh and Pt
complexes are known to protonate readily, but such a protonation does not appear to be a factor in the catalytic inactivity of postulated $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ species in solution. For example, a $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ model system, made of labile $[\text{RhCl(COE)}_2]_2$ dimer, and 2 equivalents of LiCl and 3 equivalents of DMSO per equivalent of Rh in DMA, is also catalytically inactive towards the uptake of $\text{O}_2$ (p. 80) although the system does not contain protons.

Under $\text{H}_2/\text{O}_2$ mixtures the postulated $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ intermediate remains stable for $\sim$1400 s (Fig. V.10), after which it changes slowly. The apparent stability of $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ species under $\text{H}_2$ for $\sim$1400 s is most likely a result of constant regeneration of $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ species from its inactive forms in the presence of $\text{H}_2$. If the inactive form is a $[\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})]_2$ dimeric species as postulated above, $\text{H}_2$ reaction of such species could give $\text{Rh}^{\text{I}}$ species (eq. V.36), which will then react rapidly with $\text{O}_2$ to regenerate the catalytically active $\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})$ species.

$$[\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})]_2 + 2\text{H}_2 \xrightarrow{-2\text{H}_2\text{O}_2} 2\text{Rh}^{\text{I}} \xrightarrow{2\text{O}_2} 2[\text{Rh}^{\text{III}}(\text{O}_2^{\text{2-}})]$$

V.36

The low nucleophilic reactivity of the bridging dioxygen ligands in a dimeric species, in principle, should not have a direct effect on the $\text{H}_2$ activation by the formally $\text{Rh}^{\text{III}}$ metal centres (also see p. 189).
(d) Later stages of the reaction

After \(-1400\) s of reaction under \(\text{H}_2/\text{O}_2\) mixtures, the visible spectrum of the catalytically active Rh\(^{\text{III}}(\text{O}_2^{-})\) species (spectrum \(G\), Fig. V.10) changes slowly (\(G \rightarrow J\)), suggesting a slow decomposition of the catalytically active species even under \(\text{H}_2\). A solution after from \(-4\) h of reaction (or the solution corresponding to spectrum \(J\)) takes up \(\text{H}_2\) much more slowly than the initial Rh\(^{\text{III}}(\text{O}_2^{-})\) species (cf. curves (a) and (b) in Fig. V.11), consistent with the decomposition of Rh\(^{\text{III}}(\text{O}_2^{-})\) species to other \(\text{H}_2\)-inactive or low-active form(s). The decomposition could occur via several paths. Some data for an analogous Rh-dioxygen species, which is formed via the stoichiometric \(\text{H}_2/\text{O}_2\) reaction of complex 1 in \(-60\%\) purity, are given in Chapter III (p. 74). The reaction mixture obtained from the above solution on leaving it under Ar or \(\text{O}_2\) showed evidence for an \(-\text{OH}\) species (broad \(\text{D}_2\text{O}\)-sensitive band in the \(^1\text{H}\) nmr spectrum of reaction residue in \(\text{CDCl}_3\), Fig. III.5.b). Although protonation reactions were postulated to be slow for the Rh\(^{\text{III}}(\text{O}_2^{-})\) species in the presence case (see p. 183), such protonations may become significant at longer reaction times.

Another plausible explanation for the deactivation of Rh\(^{\text{III}}(\text{O}_2^{-})\) species is the accumulation of \(\text{H}_2\text{O}_2\) and/or \(\text{CH}_3\text{CON(CH}_3\text{)CH}_2\text{OOH}\) products in the course of the catalytic \(\text{H}_2/\text{O}_2\) uptake. After about \(0.75\) h of reaction time (Fig. V.3), the concentration of \(\text{H}_2\text{O}_2\) in the system approaches a steady state and the concentration of \(\text{H}_2\text{O}\) increases steadily, most certainly as a result of metal-catalyzed decomposition of \(\text{H}_2\text{O}_2\) (eqs. V.11-V.14). As the concentration of \(\text{H}_2\text{O}_2\) increases, reaction between \(\text{H}_2\text{O}_2\) and Rh species will compete with the \(\text{H}_2\) and/or \(\text{O}_2\) reactions.
of the metal (Scheme V.2). For example, the steady state concentration of \( \text{H}_2\text{O}_2 \) in the system (curve c, Fig. V.3) is about 20 times greater than the concentration of \( \text{O}_2 \) (<1 x 10^{-3} M) at any time. Therefore at later stages, reaction between \( \text{Rh}^I \) and \( \text{H}_2\text{O}_2 \) may compete with the fast reaction between \( \text{Rh}^I \) and \( \text{O}_2 \) in Scheme V.2 to lead to catalytically inactive Rh species (eq. V.37).

\[
\text{Rh}^I + \text{H}_2\text{O}_2 \rightarrow \text{Rh}^{II} + \text{HO}^- + \text{HO}^-
\]

As shown in the above equation, such reactions also generate \( \text{HO}^- \) free-radicals. Therefore, at later stages of the catalytic \( \text{H}_2/\text{O}_2 \) reaction, free-radical autoxidations of DMA will play a significant role. Visible spectral changes (Fig. V.10) suggest the deactivation of catalyst, but the autoxidation rate of DMA (curve c, Fig. V.3) remains essentially linear, consistent with increased contributions from free-radical autoxidations at later stages of the reaction.

V.4 Implications for further work

(a) Hydrogenolysis of \( \text{O}_2 \)

Homogeneously catalyzed hydrogenolysis of \( \text{O}_2 \) to give \( \text{H}_2\text{O} \) or \( \text{H}_2\text{O}_2 \) is documented, but the mechanistic information on such systems is limited,\textsuperscript{114,115} or is not reported at all.\textsuperscript{26,113,116} Theoretically, the hydrogenolysis of \( \text{O}_2 \) could lead either to \( \text{H}_2\text{O}_2 \), where it may be further decomposed to \( \text{H}_2\text{O} \) (eq. V.38), or directly to \( \text{H}_2\text{O} \) without the release of
H$_2$O$_2$ (eq. V.39). In the present study, hydrogenolysis of O$_2$ within Rh systems is proposed to occur via the direct H$_2$ reaction of a RhIII(peroxo) complex to give H$_2$O$_2$; production of H$_2$O is thought to result from a metal-catalyzed decomposition of the initial H$_2$O$_2$ product (eq. V.37). In all the Journal literature reports (i.e. with the exception of the patent literature), H$_2$O is the only observed product and the reactions are represented as concerted hydrogenolysis reactions of O$_2$ to give H$_2$O (eq. V.39). In biological systems, the cytochrome oxidase enzyme carries out a concerted 4-electron reduction of O$_2$ to H$_2$O without the release of intermediary H$_2$O$_2$; the 4e + 4H$^+$ requirement of the enzyme system (eq. V.40) is stoichiometrically equivalent to two hydrogens required in the hydrogenolysis of O$_2$ to give H$_2$O (eq. V.39). Cytochrome oxidase is a multicomponent enzyme system containing two heme porphyrins and two copper centres. Although the mechanism of the reaction is poorly understood, the four redox centres are thought, perhaps, to be involved in the storage and transfer of the required four electrons.\textsuperscript{11a}

\[
\begin{align*}
H_2 + O_2 & \xrightarrow{M} H_2O_2 \xrightarrow{M} H_2O + 1/2O_2 & \text{V.38} \\
2H_2 + O_2 & \xrightarrow{M} 2H_2O & \text{V.39} \\
4H^+ + 4e + O_2 & \xrightarrow{\text{Cyto. oxidase}} 2H_2O & \text{V.40}
\end{align*}
\]
The in vitro catalyst systems, which yield H2O from H2 and O2, are relatively simple and are comprised of monomeric Pt-metal complexes containing phosphine,115 porphyrin,116 or cyclooctadiene ligands26 in non-aqueous solvents, or of copper salts in water.114 In such systems, 2-electron reduction of O2 to initial H2O2 product appears more likely. The evidence for H2O2 production via metal-catalyzed hydrogenolysis, suggested in the patent literature and in the present study, supports such a hypothesis, but further studies are required before any generalizations can be made.

Further mechanistic studies to understand the details of hydrogenolysis of O2 are important in the context of H2O2 production and fuel-cell technology. Hydrogen peroxide is used widely in industry as a non-polluting oxidizing agent. It is manufactured commercially, mainly by the autoxidation of anthroquinol (eq. V.41); the anthroquinone co-product is then hydrogenated back to the quinol using supported Pd or Ni catalyst (eq. V.42).131

\[ \text{OH} \quad \xrightarrow{\text{O}_2} \quad \text{O} \quad + \text{H}_2\text{O}_2 \quad \text{V.41} \]

\[ \text{O} \quad \xrightarrow{\text{Pd/H}_2} \quad \text{OH} \quad \text{V.42} \]
A second process for H$_2$O$_2$ production developed by Shell$^{131}$ involves the oxidation of isopropanol to acetone and H$_2$O$_2$ in either vapor or liquid phase with 15 to 20 atm of O$_2$ at ~100$^\circ$C (eq. V.43).

\[
\begin{align*}
\text{CH}_3\text{CH(OH)}_2 & \xrightarrow{\text{O}_2} \text{CH}_3\text{C(OOH)}_2 \xrightarrow{} \text{CH}_3\text{CO} + \text{H}_2\text{O}_2 \\
& \text{V.43}
\end{align*}
\]

Hydrogen peroxide can also be formed directly by the thermal, electric discharge, or metal-activated reaction of H$_2$ and O$_2$.$^{131}$ Silent electric discharge processes have been patented and a process piloted in Germany, but the power requirements are too high for commercial use.$^{131}$ The recent patent activity in the area of metal-catalyzed homogeneous hydrogenolysis of O$_2$ indicates an increasing interest in such reactions as viable alternatives to methods presently used.$^{131}$ An understanding of the mechanism of hydrogenolysis should enable the design of cheaper and/or improved catalysts.

On the other hand, the practical need to reduce dioxygen to H$_2$O without the release of H$_2$O$_2$ is important in fuel-cell technology,$^{11a}$ while the photo-initiated splitting of H$_2$O (the reverse of the hydrogenolysis reaction in eq. V.39) demands much current interest.$^{132}$ Increased understanding of the metal-catalyzed hydrogenolysis will provide some insights into the 4-electron reduction of O$_2$. 
(b) Metal-centred transfer of $O_2$ to C-H bonds

Metal-centred oxygen transfers are postulated in metal-catalyzed autoxidations of terminal olefins using Rh catalysts. Metal-mediated autoxidations are reported also for phenolic substrates, where Cu, Mn and Co catalysts are used to obtain quinone products (see also Section 1.3). To our knowledge, metal-centred activation and transfer of $O_2$ to C-H bonds to give C-OOH species is not documented except for the study by Ng on Rh-catalyzed autoxidation of DMA. Enzymic oxidations are known to lead to hydroperoxide intermediates via pathways which may or may not involve active metal-centres (e.g. eq. V.44).

\[ \text{lipoxigenase} \]

\[ R_1CH=CHCH_2CH=CHR' + O_2 \xrightarrow{\text{lipoxigenase}} R_1CH=CHCH(\text{O}_2\text{H})R' \quad \text{V.44} \]

Sheldon and Kochi suggest that the hydroxylation of phenolic substrates mediated by nonheme iron and copper monooxygenases proceeds also via the initial incorporation of a dioxygen molecule across the aromatic C-H bond (eq. V.45).
The findings in the present study suggest that a metal-centred incorporation of a dioxygen molecule across a C-H bond is a feasible reaction, though the hydroperoxide products formed in such reactions could initiate free-radical chain autoxidations (see Section I.1).

(c) Role of reducing co-substrates in autoxidations

The requirements of added co-substrates (e.g. PPh$_3$) or alcohol solvent are noted in almost all the successful autoxidation catalyst systems reported, but the role of the co-substrate or the solvents remains generally unclear.

In the report by Read and Walker the rhodium-catalyzed autoxidation of oct-1-ene to octan-2-one in the presence of excess PPh$_3$ is accompanied by oxidation of the phosphine to PPh$_3$O, and the reaction mixture after 3 h contains about a 6-fold excess of PPh$_3$O over the ketone product of interest. Similarly, in a recent report on the autoxidation of terminal olefins to ketones by cationic Rh$^I$ complexes in EtOH or MeOH solvent, the aldehyde product of solvent autoxidation is present in about a 5-fold excess over the olefin oxidation product after 7 h of reaction. In the present Rh/DMA work, the rates of production of CH$_3$CON(CH$_3$)CH$_2$OOH and H$_2$O$_2$ are about 2 x 10$^{-6}$ M s$^{-1}$ and 6 x 10$^{-6}$ M s$^{-1}$, respectively, in the initial 0.5 h of reaction for a 5 x 10$^{-3}$ M catalyst in DMA at 50°C under a 1 atm of H$_2$/O$_2$ (2:1) (Fig. V.2). According to the mechanistic interpretation, the requirement of H$_2$ co-substrate in the autoxidation of DMA could be avoided if measures were taken to prevent the deactivation of the catalyst. It is possible
that the co-substrates or the reducing solvents in other related systems
act in a similar manner, i.e. by regenerating species active for oxygen
transfer. Systematic studies on the role of reducing agents, and the
reasons for catalyst deactivation in such systems, would be useful in
the design of autoxidation catalysts that do not require the employment
of co-substrates, since these consume a large proportion of the oxidant
in wasteful side-reactions.
CHAPTER VI

OTHER AUTOXIDATION CATALYST SYSTEMS UTILIZING H₂/O₂ MIXTURES
VI. Other autoxidation catalyst systems utilizing H₂/O₂ mixtures

VI.1 Introduction

Hydrogenolysis of O₂ by RhCl₃(DMSO)₃ catalyst in DMA leads to the production of H₂O₂ and an accompanying autoxidation of the solvent (Chapter V). In the presence of suitable substrate(s), it should be possible to utilize the H₂O₂ formed in such catalysis towards the in situ autoxidation of a substrate S to SO (eq. VI.1).

\[
\text{H}_2 + \text{O}_2 \xrightarrow{\text{metal}} [\text{H}_2\text{O}_2] \xrightarrow{S} \text{H}_2\text{O} + \text{SO} \quad \text{VI.1}
\]

Thioethers (R-S-R') are oxidized readily to the corresponding sulfoxides (R-SO-R') by H₂O₂ or alkylhydroperoxides\(^{135}\). This chapter describes some attempts at catalytic autoxidation of thioether substrates utilizing H₂/O₂ mixtures. Several other systems which do not contain added substrates are also described.

VI.2 Results and Discussion

The rates of H₂/O₂ uptake by RhCl₃(DMSO)₃ in DMA systems, with or without added thioether substrates, are summarized in Table VI.1. The rate of catalytic H₂/O₂ uptake by RhCl₃(DMSO)₃ complex in DMA

- 206 -
Table VI.1

Maximum rate of gas uptake from an approximately 2:1 mixture of \( \text{H}_2 \) and \( \text{O}_2 \) at 1 atm by \( \text{RhCl}_3(\text{DMSO})_3 \) (1.0 x \( 10^{-2} \) M), with or without thioether substrates, at 50°C in DMA

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Added substrate</th>
<th>maximum rate x ( 10^5 ), M s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>DPS (4 x ( 10^{-2} ) M)</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>DPS (~1 M)</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>DES (~1 M)</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>DMS (~1 M)</td>
<td>no uptake</td>
</tr>
</tbody>
</table>

(experiment 1) is unaffected by a 4-fold excess of DPS over rhodium (experiment 2) but was decreased by ~50% in the presence of a 100-fold excess (experiment 3). Similar suppression in rate was observed with excess DES or DMS (experiments 4 and 5, respectively, Table VI.1). The effect of added thioethers on the reaction rates probably results from changes in the coordination sphere of the rhodium. Dimethylsulfide readily displaces DMSO ligands from complex 1 to give \( \text{Rh}^{\text{III}}(\text{DMS}) \) species (Section II.2.3), and \( \text{Rh}^{\text{III}} \) complexes of DES are known.\(^{35} \) The observed suppression in rates could result from a suppression of DMA autoxidation rate (path B, Scheme V.2, p. 184) due to a lower effective concentration of the catalytically active \( \text{Rh}^{\text{III}}(\text{O}_2^-) \) species in the presence of the
thioether (eq. VI.2), and/or from a lower reactivity of a thioether-substituted Rh$^{III}$ complex towards H$_2$ (eq. VI.3, cf. path A, Scheme V.2).

\[
\text{Rh}^{III}(O_2^-)(\text{DMA}) + R_2S \rightleftharpoons \text{Rh}^{III}(O_2^-)(R_2S) + \text{DMA} \quad \text{VI.2}
\]

\[
\text{Rh}^{III}(O_2^-)(R_2S) + H_2 \rightarrow \text{Rh}^{I}(R_2S) + H_2O_2 \quad \text{VI.3}
\]

In the DPS systems, diphenylsulfoxide (DPSO), H$_2$O, and CH$_3$CON(CH$_3$)CHO (16) and/or CH$_3$CON(CH$_3$)CH$_2$OOH (17) are detected as reaction products at DPS concentrations of 0.2-1 M, after reaction times of 3.5-5.5 h (Table VI.2). Significantly, no H$_2$O$_2$ was detected in a reaction mixture after 5.5 h of reaction (experiment 4, cf. with corresponding systems in the absence of DPS where H$_2$O$_2$ is detected, Table V.2, p. 158). In addition, solutions containing 0.2 M DPS, and 4 x 10$^{-2}$ M H$_2$O$_2$ added as a 35% aqueous solution, under Ar, also showed ~3 x 10$^{-2}$ M DPSO after ~4 h reaction, with or without added complex 1 (at 5 x 10$^{-3}$ M); 4 x 10$^{-2}$ M H$_2$O$_2$ was used in the latter reaction since such a concentration is of the same order as that found in a catalyst system in the absence of added thioether substrates (Table V.2). Therefore it is highly probable that the observed DPSO product results from the oxidation of DPS by the H$_2$O$_2$ generated by the catalytic hydrogenolysis of O$_2$.

An analogous autoxidation of thioethers by in situ generated H$_2$O$_2$ was reported recently.\textsuperscript{21} The H$_2$O$_2$ was postulated to result from an effective reduction of O$_2$ by alcohol solvent, catalyzed by Ru$^{II}$(DMSO) complexes (eq. VI.4).
Table VI.2

Product analysis\(^{(a)}\) after a catalytic uptake of a \(\text{H}_2/\text{O}_2\) (2:1) mixture at 1 atm, at 50°C in the presence of 0.010 M \(\text{RhCl}_3(\text{DMSO})_3\) or \(\text{RhCl}_3(\text{DES})_3\) catalyst in DMA with added DPS substrate

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Catalyst</th>
<th>[DPS], M</th>
<th>Time of reaction, h</th>
<th>Total gas uptake, M</th>
<th>DPSO, M</th>
<th>(\text{H}_2\text{O}), M</th>
<th>16+17(^{(b)})</th>
<th>(\text{H}_2\text{O}_2), M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{RhCl}_3(\text{DMSO})_3)</td>
<td>1.1</td>
<td>5.5</td>
<td>0.20</td>
<td>-0.04</td>
<td>&gt;1(^{(c)})</td>
<td>-(\text{(d)})</td>
<td>-(\text{(c)})</td>
</tr>
<tr>
<td>2</td>
<td>(\text{RhCl}_3(\text{DMSO})_3)</td>
<td>0.24</td>
<td>3.5</td>
<td>0.12</td>
<td>-0.04</td>
<td>&gt;1(^{(c)})</td>
<td>-(\text{(d)})</td>
<td>-(\text{(c)})</td>
</tr>
<tr>
<td>3</td>
<td>(\text{RhCl}_3(\text{DMSO})_3)</td>
<td>1.1</td>
<td>5.5</td>
<td>0.18</td>
<td>0.04</td>
<td>0.074</td>
<td>0.02</td>
<td>-(\text{(c)})</td>
</tr>
<tr>
<td>4</td>
<td>(\text{RhCl}_3(\text{DMSO})_3)</td>
<td>1.1</td>
<td>5.5</td>
<td>0.20</td>
<td>-(\text{(d)})</td>
<td>-(\text{(e)})</td>
<td>-(\text{(d)})</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>(\text{RhCl}_3(\text{DES})_3)</td>
<td>0.24</td>
<td>4.6</td>
<td>0.13</td>
<td>0.06</td>
<td>0.04</td>
<td>-(\text{(d)})</td>
<td>-(\text{(c)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) See Section II.5.4 for details of analytical methods.

\(^{(b)}\) Detected and/or quantified by gas chromatography as \(\text{CH}_3\text{CON}(\text{CH}_3)\text{CHO}\) (16) (see Section V.2 for details).

\(^{(c)}\) Analyses were done before the satisfactory method described in Section II.5.1 was fully developed.

\(^{(d)}\) Detected but not quantified.

\(^{(e)}\) Not analyzed for.
The mechanism proposed includes a direct electron transfer from Ru\textsuperscript{II} to O\textsubscript{2} to yield Ru\textsuperscript{IV} and O\textsubscript{2}\textsuperscript{-} (eq. VI.5), and a reduction of the Ru(IV) species by the alcohol to regenerate Ru\textsuperscript{II} (eq. VI.6). The mode of electron transfer in eq. VI.5, i.e. whether outer-sphere or inner-sphere, is not specified.

\[
\text{Ru}^{\text{II}} + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Ru}^{\text{IV}} + \text{O}_2^{-} \quad \text{VI.5}
\]

\[
\text{Ru}^{\text{IV}} + \text{R}_1\text{R}_2\text{CHOH} \rightarrow \text{Ru}^{\text{II}} + \text{R}_1\text{R}_2\text{CO} + 2\text{H}^+ \quad \text{VI.6}
\]

The above mechanism is similar in principle to that proposed in the present work for the Rh-catalyzed hydrogenolysis of O\textsubscript{2} by H\textsubscript{2} to yield H\textsubscript{2}O\textsubscript{2} (Scheme V.3, p. 190), although the latter mechanism involves an inner-sphere electron transfer from H\textsubscript{2} to O\textsubscript{2}\textsuperscript{-} to yield 2H\textsuperscript{+} and O\textsubscript{2}\textsuperscript{-}. In the Ru system, turnover numbers (t.n.) from 1 to 19 mol product (mol catalyst\textsuperscript{-1} h\textsuperscript{-1}) have been obtained for thioether autoxidations. For example, trans-RuBr\textsubscript{2}(DMSO)\textsubscript{4} in methanol at 100°C under O\textsubscript{2} (100 psi) gives a t.n. of 19 for the selective autoxidation of decyl methyl sulfide to the corresponding sulfoxide.\textsuperscript{21} The catalytic oxidation of DPS to DPSO under H\textsubscript{2}/O\textsubscript{2} (2:1, 1 atm) at 50°C in the present work gives a t.n. of \(-1\). A major problem in the present system is the accompanying autoxidation of the DMA solvent. For example, in the presence of 1.1 M
DPS, autoxidation products of DMA (16 + 17) accounts for about 33% of total organic products (experiment 3, Table VI.2).

In an effort to find an alternative to DMA solvent, catalysis in \( \text{C}_2\text{H}_4\text{Cl}_2 \) was investigated. Because of its relatively high boiling point (83.5°C), \( \text{C}_2\text{H}_4\text{Cl}_2 \) is a suitable solvent for gas-uptake studies.

There was no \( \text{H}_2/\text{O}_2 \) (2:1) uptake by \( \text{RhCl}_3(\text{DMSO})_3 \), \( \text{RhCl}_3(\text{DES})_3 \), or \( \text{RhCl}_3(\text{DMSO})_2(\sigma\text{-CH}_2\text{CH}=\text{NEt}_2) \) complexes in \( \text{C}_2\text{H}_4\text{Cl}_2 \) solvent, and added base did not initiate any reactivity with complex 1 (experiments 1-4, Table VI.3). In contrast, complexes 1, \( \text{RhCl}_3\cdot3\text{H}_2\text{O} \) and \( \text{RhCl}_3(\text{DES})_3 \) in DMA showed catalytic gas uptake from \( \text{H}_2/\text{O}_2 \) (2:1) mixtures (experiments 5-7, Table VI.3). Another Rh system containing \([\text{RhCl}(\text{COE})_2]_2 \) as a labile Rh\(^I\) precursor, together with 3 equivalents of DMA+HCl and 2 equivalents of DMSO in \( \text{C}_2\text{H}_4\text{Cl}_2 \), gave an initial rapid uptake which corresponded roughly to one equivalent of gas per rhodium, but there was no uptake over the next 0.5 h (experiment 8). Essentially the same reactivity was observed when LiCl was used in place of DMA+HCl (experiment 10). However, analogous systems in DMA solvent gave catalytic uptake of \( \text{H}_2/\text{O}_2 \) at rates (experiments 9 and 11) close to that found for complex 1 in DMA.

The necessity of DMA solvent for catalytic activation suggests, perhaps, that the reactions proceed via the activation of \( \text{H}_2 \) by \( \text{Rh}^{\text{III}}(\text{O}_2^{-}) \) in a heterolytic mode which requires a basic solvent (see p.p. 64 and 189). The 'catalytic inactivity' of Rh\(^I\) species in \( \text{C}_2\text{H}_4\text{Cl}_2 \) towards \( \text{H}_2/\text{O}_2 \) contrasts with the reported catalytic activity of other low-valent Pt metal complexes such as \( \text{Pt}(\text{PPh}_3)_4 \), \( \text{RhCl}(\text{CO})(\text{PPh}_3)_2 \) and \( \text{IrCl}(\text{CO})(\text{PPh}_3)_2 \), to give \( \text{H}_2\text{O} \). The latter systems at 2 x 10^{-3}M are reported to produce \( \text{H}_2\text{O} \) from \( \text{H}_2/\text{O}_2 \) mixtures (2:1) at rates of 13.2 x
**Table VI.3**

Maximum rate of gas uptake\(^{(a)}\) from an approximately 2:1 mixture of \(\text{H}_2\) and \(\text{O}_2\) at 1 atm by Rh catalyst systems \((1.0 \times 10^{-2} \text{ M in Rh})\), at 50°C in various solvents

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Catalyst</th>
<th>solvent</th>
<th>added base/ligand</th>
<th>max. rate (\times 10^5), (\text{M s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{RhCl}_3)(DMSO)(_3) ((1))</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>-</td>
<td>no uptake</td>
</tr>
<tr>
<td>2</td>
<td>(\text{RhCl}_3)(DMSO)(_3) ((1))</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>2,6-di-t-butyl-pyridine(^{(b)}) ((0.1 \text{ M}))</td>
<td>no uptake</td>
</tr>
<tr>
<td>3</td>
<td>(\text{RhCl}_3)(DES)</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>-</td>
<td>no uptake</td>
</tr>
<tr>
<td>4</td>
<td>(\text{RhCl}_3)(DMSO)(-\text{-CH}_2\text{CH}-\text{NET}_2))</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>-</td>
<td>no uptake</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>DMA</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>(\text{RhCl}_3)(DES)(_3)</td>
<td>DMA</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>(\text{RhCl}_3\cdot3\text{H}_2\text{O})</td>
<td>DMA</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>([\text{RhCl}(\text{COE})_2]_2)</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>DMA-HCl ((3\times10^{-2} \text{ M})) DMSO((3\times10^{-2} \text{ M}))</td>
<td>no catalytic uptake(^{(c)})</td>
</tr>
<tr>
<td>9</td>
<td>([\text{RhCl}(\text{COE})_2]_2)</td>
<td>DMA</td>
<td>&quot;</td>
<td>1.8</td>
</tr>
<tr>
<td>10</td>
<td>([\text{RhCl}(\text{COE})_2]_2)</td>
<td>(\text{C}_2\text{H}_4\text{Cl}_2)</td>
<td>LiCl ((2\times10^{-2} \text{ M})) DMSO ((3\times10^{-2} \text{ M}))</td>
<td>no catalytic uptake(^{(c)})</td>
</tr>
<tr>
<td>11</td>
<td>([\text{RhCl}(\text{COE})_2]_2)</td>
<td>DMA</td>
<td>&quot;</td>
<td>1.7</td>
</tr>
</tbody>
</table>

\(^{(a)}\) All uptakes, unless otherwise stated, were catalytic with respect to rhodium.

\(^{(b)}\) Stronger bases such as P.S. and NEt\(_3\) were not used because they gave complicating side reactions with 1 (Ch. 3).

\(^{(c)}\) A rapid uptake corresponding to one equivalent of gas per rhodium was observed initially.
10^{-6}, 9.6 \times 10^{-6} and 6.9 \times 10^{-6} \text{ M sec}^{-1}, \text{ respectively}, \text{ at } 25^\circ \text{C in toluene. Phosphine and/or CO ligands in such systems markedly increase the reactivity of Rh}^I \text{ species towards H}_2 \text{ and/or O}_2. \text{ If H}_2\text{O}_2 \text{ is really the initial product of hydrogenolysis in those systems and the observed H}_2\text{O product is a result of the decomposition of H}_2\text{O}_2, it should be possible to utilize the intermediate H}_2\text{O}_2 \text{ to oxidize added thioether substrates.}
CHAPTER VII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK
VII. Conclusions and Suggestions for Further Work

The general aim of the work described in this thesis was to obtain a suitable Rh catalyst for the autoxidation of organic substrates by H₂/O₂ mixtures. Dimethylacetamide (DMA) was chosen as a solvent, because of its known ability to promote formation of monohydrides from reaction of platinum metal complexes with H₂. However, it soon became clear that the amide solvent itself underwent oxidation under H₂/O₂ mixtures, and this system was then investigated. This autoxidation catalyzed by RhCl₃(DMSO)₃ yielded useful information on the hydrogenolysis of O₂ to H₂O₂, the feasibility of metal-centred dioxygen transfer to substrates, and a potential role of H₂ in such catalysis.

Both the Rh complex and H₂ are essential for the observed effective autoxidation of DMA. Rate data obtained are consistent with a metal-centred autoxidation of DMA in a Rh⁺¾⁺(O₂⁻⁻)(DMA) (23) intermediate and an independent hydrogenolysis of O₂ via the same intermediate. Although the proposed structure for the catalytically active intermediate, and the postulated details of the mechanistic pathways, (Schemes V.2, V.3 and V.5; p. 184-192) are tentative, the overall internal consistency of the data lends strong support to the proposed mechanism. The catalytic inactivity of 23 towards the autoxidation of DMA under O₂ alone is attributed to the instability of such species in solution. Species 23 is postulated to give inactive [Rh⁺¾⁺(O₂⁻⁻)]₂ type products via dimerizations and the H₂ cosubstrate is thought to regenerate Rh⁺¹ species, hence 23 (eq. V.36, p. 196), from such products. Slow deactivation of the catalyst, and the participation of H₂O₂ product
in other autoxidation pathways of DMA, limit the mechanistic interpretation to the kinetically analyzed initial phase of the reaction that lasts about 2000 s.

The findings in the present study raise several possible areas of further work. For example, systematic studies on the metal-catalyzed hydrogenolysis of O$_2$ will be important in the development of catalysts for commercial production of H$_2$O$_2$ from H$_2$ and O$_2$ (see p. 43). Secondly, H$_2$O$_2$ generated from such autoxidations could be used for in situ autoxidation or organic substrates (Chapter VI). Screening various known hydrogenolysis catalyst systems$^{113-116}$ for such catalytic activity will be a first step in such an investigation. Thirdly, the proposed role of H$_2$ in the autoxidation of DMA suggests that the use of H$_2$ or any other co-substrates in autoxidations will be unnecessary, if measures are taken to prevent the deactivation of catalysts. In this respect, studies on deactivation pathways of metal-dioxygen adducts should lead to the development of robust catalysts for autoxidations.

The complex RhCl$_3$(DMSO)$_3$ (1) was found to undergo facile reduction to Rh$^{III}$(DMS) species by CO, but yielded a Rh$^I$ species as the major reduction product under H$_2$ in DMA (Chapter III). Dimethylsulfoxide was readily reduced by Rh$^I$ in the presence of added acids in CH$_2$Cl$_2$, but the reaction was slow in DMA. The stability of the Rh$^I$/2H$^+$, DMSO redox couple in DMA was attributed to the proton affinity of solvent DMA.

The investigations into the reactions of tertiary amines and RhCl$_3$(DMSO)$_3$ (1) (Chapter IV) revealed interesting redox processes between 1 and the tertiary amines, NEt$_3$ or P.S. The proposed redox reactions are represented in eqs. VII.1 and VII.2, although the observed final reaction stoichiometries (see eqs. IV.5 (p. 121) and IV.21 (p.
144), respectively) are more complicated, because of secondary reactions between the dehyrogenated amines and complex I.

\[
\text{RhCl}_3 + 3\text{NEt}_3 \rightarrow \text{RhCl} + 2\text{NEt}_3^+ + \text{CH}_2=\text{CHNEt}_2 \quad \text{VII.1}
\]

\[
\text{RhCl}_3 + 2 \text{P.S.} \rightarrow \text{RhCl} + \cdot \text{P.S.}\text{HCl} + \cdot \text{CHN} \quad \text{VII.2}
\]

The above redox reactions are, in principle, analogous to the more familiar reactions between Rh\textsuperscript{III} and alcohols to yield aldehydes (e.g. eq. VII.3).\textsuperscript{56}

\[
\text{RhCl}_3 + \text{HOCH}_2\text{R} \rightarrow \text{RhCl} + 2\text{HCl} + \text{O=CHR} \quad \text{VII.3}
\]

Tertiary amines are widely used as cocatalysts in Rh-catalyzed reactions and are generally thought to act as proton scavengers in such systems.\textsuperscript{78-81} The facile redox reactions discovered in the present work suggest that tertiary amines should be considered also as potential 2-electron reducing agents, and that any discussions on the role of amines in catalysis should consider this feature.

To our knowledge, the isolated Rh\textsuperscript{III}-ethenamine complex (6) is the first recorded for this metal, although analogous Pt\textsuperscript{II} and Pd\textsuperscript{II} complexes are known.\textsuperscript{82-86} The proposed redox reaction between Rh\textsuperscript{III} and an N-CH\textsubscript{3} group of P.S. (eq. VI.5; see also Section IV.7) may provide a useful synthetic route to Rh-carbene complexes from strongly basic tertiary amines containing N-CH\textsubscript{3} groups, for example, trimethylamine.
CHAPTER VIII

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(c) F. Moseley and P.N. Dyer, ibid., 111978y.

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117. Ref. 3, p. 35 and references therein.


119. Ref. 10, p. 36.


129. Ref. 10; p. 51.


    (b) M. Gratzel, K. Kalyanasundaram and J. Kiwi, Structure and Bonding, 49, 37 (1982).
    (c) H. Tributsch, Structure and Bonding, 49, 127 (1982).


Appendix I

Some structural parameters for mer-cis-RhCl$_3$(DMSO)(^CH$_2$CH=NEt$_2$)

Table I

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh -Cl(1)</td>
<td>2.3342(6)</td>
</tr>
<tr>
<td>Rh -Cl(2)</td>
<td>2.3480(5)</td>
</tr>
<tr>
<td>Rh -Cl(3)</td>
<td>2.3578(5)</td>
</tr>
<tr>
<td>Rh -S(1)</td>
<td>2.2800(5)</td>
</tr>
<tr>
<td>Rh -S(2)</td>
<td>2.3906(5)</td>
</tr>
<tr>
<td>Rh -C(1)</td>
<td>2.125(2)</td>
</tr>
<tr>
<td>S(1)-O(1)</td>
<td>1.472(2)</td>
</tr>
<tr>
<td>S(1)-C(7)</td>
<td>1.771(3)</td>
</tr>
<tr>
<td>S(1)-C(8)</td>
<td>1.780(3)</td>
</tr>
<tr>
<td>S(2)-O(2)</td>
<td>1.476(2)</td>
</tr>
<tr>
<td>S(2)-C(9)</td>
<td>1.770(3)</td>
</tr>
<tr>
<td>S(2)-C(10)</td>
<td>1.785(4)</td>
</tr>
<tr>
<td>N -C(2)</td>
<td>1.291(3)</td>
</tr>
<tr>
<td>N -C(3)</td>
<td>1.475(3)</td>
</tr>
<tr>
<td>N -C(5)</td>
<td>1.481(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.439(3)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.511(4)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.503(4)</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Angle(deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)-Rh -Cl(2)</td>
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<td>Cl(1)-Rh -Cl(3)</td>
<td>90.44(2)</td>
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<tr>
<td>Cl(1)-Rh -S(1)</td>
<td>89.98(2)</td>
</tr>
<tr>
<td>Cl(1)-Rh -S(2)</td>
<td>92.23(2)</td>
</tr>
<tr>
<td>Cl(1)-Rh -C(1)</td>
<td>86.06(7)</td>
</tr>
<tr>
<td>Cl(2)-Rh -Cl(3)</td>
<td>89.33(2)</td>
</tr>
<tr>
<td>Cl(2)-Rh -S(1)</td>
<td>90.42(2)</td>
</tr>
<tr>
<td>Cl(2)-Rh -S(2)</td>
<td>90.48(2)</td>
</tr>
<tr>
<td>Cl(2)-Rh -C(1)</td>
<td>89.22(6)</td>
</tr>
<tr>
<td>Cl(3)-Rh -S(1)</td>
<td>179.30(2)</td>
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<tr>
<td>Cl(3)-Rh -S(2)</td>
<td>85.52(2)</td>
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<td>Cl(3)-Rh -C(1)</td>
<td>92.19(6)</td>
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<tr>
<td>S(1)-Rh -S(2)</td>
<td>95.03(2)</td>
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<tr>
<td>S(1)-Rh -C(1)</td>
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</tr>
<tr>
<td>S(2)-Rh -C(1)</td>
<td>177.69(6)</td>
</tr>
<tr>
<td>Rh -S(1)-O(1)</td>
<td>116.84(7)</td>
</tr>
<tr>
<td>Rh -S(1)-C(7)</td>
<td>112.42(12)</td>
</tr>
<tr>
<td>Rh -S(1)-C(8)</td>
<td>112.21(11)</td>
</tr>
<tr>
<td>O(1)-S(1)-C(7)</td>
<td>107.3(2)</td>
</tr>
<tr>
<td>O(1)-S(1)-C(8)</td>
<td>106.80(14)</td>
</tr>
<tr>
<td>O(1)-C(7)-S(1)</td>
<td>99.8(2)</td>
</tr>
<tr>
<td>Rh -S(2)-O(2)</td>
<td>117.17(8)</td>
</tr>
<tr>
<td>Rh -S(2)-C(9)</td>
<td>111.90(15)</td>
</tr>
<tr>
<td>Rh -S(2)-C(10)</td>
<td>110.78(11)</td>
</tr>
<tr>
<td>O(2)-S(2)-C(9)</td>
<td>107.4(2)</td>
</tr>
<tr>
<td>O(2)-S(2)-C(10)</td>
<td>108.8(2)</td>
</tr>
<tr>
<td>C(9)-S(2)-C(10)</td>
<td>99.3(2)</td>
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<tr>
<td>C(2)-N -C(3)</td>
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<tr>
<td>C(2)-N -C(5)</td>
<td>120.3(2)</td>
</tr>
<tr>
<td>C(3)-N -C(5)</td>
<td>116.8(2)</td>
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<tr>
<td>Rh -C(1)-C(2)</td>
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<tr>
<td>N -C(2)-C(1)</td>
<td>126.7(2)</td>
</tr>
<tr>
<td>N -C(3)-C(4)</td>
<td>111.8(2)</td>
</tr>
<tr>
<td>N -C(5)-C(6)</td>
<td>112.8(2)</td>
</tr>
</tbody>
</table>
Appendix II

Some structural parameters for \([\text{Et}_2\text{NH}_2][\text{trans-RhCl}_4(\text{DMSO})_2]\)\(^{(a)}\)

### Table I

**Bond lengths (Å) with estimated standard deviations in parentheses**

<table>
<thead>
<tr>
<th>Bond</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(1)-Cl(1)</td>
<td>2.3459(4)</td>
<td>2.3309(12)</td>
</tr>
<tr>
<td>Rh(1)-C(2)</td>
<td>2.3452(5)</td>
<td>2.3371(13)</td>
</tr>
<tr>
<td>Rh(1)-S(1)</td>
<td>2.3173(5)</td>
<td>2.3124(10)</td>
</tr>
<tr>
<td>Rh(2)-Cl(3)</td>
<td>2.3400(5)</td>
<td>2.3330(11)</td>
</tr>
<tr>
<td>Rh(2)-C(4)</td>
<td>2.3429(5)</td>
<td>2.3339(11)</td>
</tr>
<tr>
<td>Rh(2)-S(2)</td>
<td>2.3294(5)</td>
<td>2.3318(11)</td>
</tr>
<tr>
<td>S(1)-O(1)</td>
<td>1.463(2)</td>
<td>1.463(2)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.783(2)</td>
<td>1.783(2)</td>
</tr>
<tr>
<td>S(2)-O(2)</td>
<td>1.422(2)</td>
<td>1.472(4)</td>
</tr>
<tr>
<td>S(2)-C(3)</td>
<td>1.773(3)</td>
<td>1.779(6)</td>
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<td>S(2)-C(4)</td>
<td>1.786(4)</td>
<td>1.777(6)</td>
</tr>
<tr>
<td>N-C(5)</td>
<td>1.482(3)</td>
<td>1.493(8)</td>
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<td>N-C(7)</td>
<td>1.499(3)</td>
<td>1.497(11)</td>
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<tr>
<td>C(5)-C(6)</td>
<td>1.495(4)</td>
<td>1.492(11)</td>
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<tr>
<td>C(7)-C(8)</td>
<td>1.486(4)</td>
<td>1.485(11)</td>
</tr>
</tbody>
</table>

### Table II

**Bond angles (deg) with estimated standard deviations in parentheses**

<table>
<thead>
<tr>
<th>Bonds</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)-Rh(1)-C(2)</td>
<td>89.61(2)</td>
<td>90.24(6)</td>
</tr>
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<td>87.75(2)</td>
<td>94.42(4)</td>
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<td>Cl(2)-Rh(1)-S(1)</td>
<td>92.51(2)</td>
<td>90.11(5)</td>
</tr>
<tr>
<td>Cl(3)-Rh(2)-C(1)</td>
<td>89.76(2)</td>
<td>90.09(5)</td>
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<tr>
<td>Cl(3)-Rh(2)-S(2)</td>
<td>90.59(2)</td>
<td>89.89(4)</td>
</tr>
<tr>
<td>Cl(4)-Rh(2)-S(2)</td>
<td>91.61(2)</td>
<td>86.14(4)</td>
</tr>
<tr>
<td>Rh(1)-S(1)-O(1)</td>
<td>115.23(8)</td>
<td>115.85(15)</td>
</tr>
<tr>
<td>Rh(1)-S(1)-C(1)</td>
<td>111.78(9)</td>
<td>111.3(2)</td>
</tr>
<tr>
<td>Rh(1)-S(1)-C(2)</td>
<td>110.92(10)</td>
<td>112.5(2)</td>
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<td>O(1)-S(1)-C(1)</td>
<td>108.16(12)</td>
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<tr>
<td>O(1)-S(1)-C(2)</td>
<td>109.88(14)</td>
<td>107.4(3)</td>
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<tr>
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<td>99.74(14)</td>
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<td>110.8(2)</td>
<td>107.5(3)</td>
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<tr>
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<td>100.1(4)</td>
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<td>C(5)-N-C(7)</td>
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<td>113.9(5)</td>
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<tr>
<td>N-C(5)-C(6)</td>
<td>111.8(2)</td>
<td>111.5(6)</td>
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<tr>
<td>N-C(7)-C(8)</td>
<td>111.8(2)</td>
<td>110.5(6)</td>
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</table>

\(\text{(a)}\) Found in two crystal forms, termed type A and B (Figs. IV.13 and IV.14 respectively), both triclinic. See also p. 138.