SYNTHESIS OF DICHLORO-SULPHOXIDE COMPLEXES
OF RUTHENIUM(II) AND THEIR USE AS CATALYSTS
FOR HOMOGENEOUS ASYMMETRIC HYDROGENATION

by

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ABSTRACT

Syntheses of a number of chiral and non-chiral sulfoxides and corresponding Ru(II) sulfoxide compounds are described, as well as significant reactions of some of these complexes with molecular hydrogen, olefins, and carbon monoxide.

The new sulfoxides presented are: (S,R;S,S)-(+)2-methylbutyl methyl sulphoxide, (MBMSO), (2R,3R)-(−)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane·H₂O, (Dios), and (2R,3R)-(−)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(benzyl sulphinyl)butane·H₂O, (BDios). These sulfoxides are prepared as mixtures of diastereomers. Other sulfoxides discussed are: dimethyl (DMSO), methyl n-propyl, (MeₙprSO), methyl phenyl, (MPSO), and R-(+)methyl p-tolyl sulfoxide, (MPTSO) and (2R,3R)-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane, (DDios).

The previously unknown complexes, [NH₂Me₂][RuCl₃(DMSO)₃], [NH₂Me₂][RuCl₃(MeₙprSO)₃], [RuCl₂(MBMSO)₂]₃, [RuCl₂(MPTSO)₂]₃, [RuCl₂(MPSO)₂]ₙ, RuCl₂(Ddios)₂·2H₂O, RuCl₂(Dios)(DDios) and RuCl₂(DDios)(DMSO)(MeOH) have been prepared using newly developed synthetic routes. The previously prepared compounds, RuCl₂(DMSO)₄ and RuBr₂(DMSO)₄ are more fully described and in collaboration with A. Mercer and J. Trotter of this department the structures of the chloro-complex and the [NH₂Me₂][RuCl₃(DMSO)₃] compound were determined by x-ray crystallography.

Both [NH₂Me₂][RuCl₃(DMSO)₃] and RuCl₂(DMSO)₄ react readily with molecular hydrogen in N,N'-dimethylacetamide (DMA) in the presence of a strong base, proton sponge. The net heterolytic cleavage of H₂.
results in hydride species which although not well characterized have anomalously high $^1$H n.m.r. hydride chemical shifts at least for Ru(II).

The anionic DMSO complex catalyses the hydrogen reduction of activated olefins in DMA at 60°C under 1 atm $H_2$ and kinetic and spectral studies indicate the following mechanism:

$$\begin{align*}
\text{Ru}^{II}\text{Cl}_3(\text{DMSO})_3^{-} + H_2 & \stackrel{k_1}{\rightarrow} \frac{k_1}{k^{-1}} \text{HRu}^{II}\text{Cl}_2(\text{DMSO})^{-} + \text{HCl} \\
\text{Ru}^{II}\text{Cl}_3(\text{DMSO})^{-} + \text{DMSO} & \stackrel{k_2}{\rightarrow} \frac{k_2}{k^{-2}} \text{HRu}^{II}\text{Cl}_2(\text{DMSO})_2^{(\text{olefin})}^{-} \\
H_2 & \stackrel{k_4}{\rightarrow} \frac{k_4}{k^{-4}} \text{HRu}^{II}\text{Cl}_2(\text{DMSO})^{-} + \text{olefin} \stackrel{k_5}{\rightarrow} \text{Ru}^{II}\text{Cl}_2(\text{DMSO})_2^{(\text{alkyl})}^{-} \\
\text{HRu}^{II}\text{Cl}_2(\text{DMSO})^{-} + \text{olefin} & \stackrel{k_5}{\rightarrow} \frac{k_5}{k^{-5}} \text{Ru}^{II}\text{Cl}_2(\text{DMSO})_2^{(\text{alkyl})}^{-} \\
\text{Ru}^{II}\text{Cl}_3(\text{DMSO})_2^{(\text{olefin})}^{-} & \stackrel{k_6}{\rightarrow} \frac{k_6}{k^{-6}} \text{HCl} \\
\text{Ru}^{II}\text{Cl}_3(\text{DMSO})_2^{-} + \text{Sat. Product} &
\end{align*}$$

Activation of $H_2$ is thought to occur by net heterolytic cleavage of molecular hydrogen and this and an olefin insertion step are considered to be rate determining, ($k_3$ and $k_4$). Reduction proceeds by two pathways, one olefin-dependent and the other olefin-independent; the final step involves protonolysis of a $\sigma$-alkyl complex.

Catalytic hydrogenation of acrylamide in DMA at 70°C using $[\text{RuCl}_2(\text{MMBSO})_2]_3$ is described and the postulated mechanism is summarized below:
As with the anion system a two-path reduction occurs, one olefin-dependent and one olefin-independent, with the $H_2$-activation steps rate determining, ($k_1$ and $k_4$); however, $H_2$ activation is this time via oxidative addition.

Asymmetric hydrogenation studies using the catalysts $[\text{RuCl}_2(\text{MBMSO})_2]^3$, $[\text{RuCl}_2(\text{MPTSO})_2]^3$, $\text{RuCl}_2(\text{DDios})_2\cdot2\text{H}_2\text{O}$, $\text{RuCl}_2(\text{Dios})(\text{DDios})$, and $\text{RuCl}_2(\text{DDios})(\text{DMSO})(\text{MeOH})$ are presented. The largest optical purities obtained are 25 and 15%, for the $\text{RuCl}_2(\text{Dios})(\text{DDios})$-itaconic acid and $[\text{RuCl}_2(\text{MBMSO})_2]^3$-itaconic acid systems, respectively.

The preparation of carbonyl derivatives of $[\text{RuCl}_2(\text{MBMSO})_2]^3$ and $[\text{RuCl}_2(\text{MPTSO})_2]^3$ are described; these derivatives have anomalously high $\nu(\text{CO})$ values.
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ABBREVIATIONS

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

A absorbance
Acryl acrylamide, CH₂=CHCONH₂
atm atmosphere
BDios (2R,3R)-(-)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(benzyl sulphonyl)butane as a mixture of three diastereomers

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

bipy 2,2'-bipyridine
B.P. boiling point
Bu Butyl
DDios (2R,3R)-2,3-dihydroxy-1,4-bis(methyl sulphonyl)butane as a mixture of three diastereomers

\[
\begin{array}{c}
\text{HO} \\
\text{HO}
\end{array}
\]

\[
\begin{array}{c}
\text{HO} \\
\text{HO}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{CH₂SOCH₃}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{CH₂SOCH₃}
\end{array}
\]
Diop  (2S,3S)-(+)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

Dios  (2R,3R)-(-)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis-(methyl sulphinyl)butane as a mixture of three diastereomers

DMA  N,N'-dimethylacetamide  CH₃CON(CH₃)₂
DMAC  N,N'-dimethylacetamide hydrochloride  CH₃CON(CH₃)₂·HCl
DMF  N,N'-dimethylformamide  HCON(CH₃)₂
DMSO  dimethyl sulphoxide  (CH₃)₂SO
DSS  sodium 2,2-dimethyl-2-silapentone-5-sulphonate
e.e.  enantiomeric excess
eqn.  equation
Et  ethyl
fig.  figure
hr  hour
I.R.  infrared
L ligand
M molar or metal atom
MBMSO (S,R,S,S)-(+)-2-methylbutyl methyl sulphoxide
\[ \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CH}_2\text{S(O)CH}_3 \]
Me methyl
Me\(^n\)prSO methyl n-propyl sulfoxide \[ \text{CH}_3(\text{CH}_2)_n\text{S(O)CH}_3 \]
Men (-)-menthol
m.p. melting point
MPSO methyl phenyl sulfoxide \[ \text{CH}_3\text{S(O)C}_6\text{H}_5 \]
MPTSO R-(+)-methyl p-tolyl sulfoxide \[ \text{C}_7\text{H}_7\text{S(O)CH}_3 \]
M.W. molecular weight
\[^T\] refractive index measured at the sodium D line
\[ \text{nm} \] nanometer \( (10^{-9} \text{ meter}) = 1 \text{ millimicron (mu)} \)
N.M.R. nuclear magnetic resonance
ol olefin
O.R.D. optical rotary dispersion
P phosphine
p pressure
Ph phenyl
PPh\(_3\) triphenylphosphine
ppm parts per million
R alkyl or aryl group or Rate
R.T. room temperature
S sulfoxide
s or sec second
T  temperature

t  time

TMS  tetramethysilane

Tosyl  C₇H₇SO₂⁻

U.V.  ultraviolet

Vis  visible

vpc  vapor phase chromatography

X  halogen

[α]_D^T  specific rotation measured at the sodium D line

Λ^T  molar conductance, cm²ohm⁻¹mol⁻¹

δ  chemical shift, ppm

ε  molar extinction coefficient

λ  wavelength

μ eff  corrected magnetic moment in Bohr Magnetrons, B.M.

ν  frequency, cm⁻¹

φ  phenyl

χ M corr  corrected molar susceptibility
ACKNOWLEDGMENTS

I wish to thank Dr. B.R. James for his expert guidance and continual encouragement throughout the course of this work.

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CHAPTER I
INTRODUCTION

1.1. General Introduction

Historically the first report of catalytic homogeneous hydrogenation of an organic substrate, that of benzoquinone in the presence of quinoline solutions of cupric acetate, occurred in 1938\(^1\). Since this time many homogeneous catalytic systems have been studied and their mechanisms deduced. Maintained interest in homogeneous catalysts generally arises from their specificity towards reduction of particular substrates, (ie., high selectivity), their ability to function under generally mild reaction conditions, their ease of study, and their industrial applicability. Indeed some industrially-used processes include the Wacker process\(^2\), the Oxo process\(^3\), some Ziegler-Natta systems\(^4\), and methanol carbonylation\(^5\).

Since 1970, interest in catalytic hydrogenation has spread to asymmetric synthesis. Use of catalytic complexes containing chiral ligands, (especially phosphines), can lead to induced optical activity in the saturated product, for example\(^6-8\);

\[
\begin{align*}
R_1R_2C=CH_2 + H_2 &\rightarrow R_1R_2CH-CH_3 \\
R_1R_2C=O + H_2 &\rightarrow R_1R_2CH-OH
\end{align*}
\]
In addition, reports by Pino et al.\textsuperscript{9} on asymmetric hydroformylation have recently appeared. A comprehensive summary of this rapidly expanding field of homogeneous hydrogenation, complete upto and including 1972, has recently been published in a text by James\textsuperscript{10}.

1.2. \textbf{Aim of Work}

Earlier studies in this laboratory\textsuperscript{11} and elsewhere\textsuperscript{12} had shown the feasibility of synthesizing DMSO complexes of Ru(II). In view of the known ability of many Ru(II) complexes to activate molecular H\textsubscript{2} (including complexes with simple halide ligands\textsuperscript{13}, phosphine and arsine ligands\textsuperscript{14}, and nitrogen ligands\textsuperscript{15}), and the vast range of metal complexes that have been reported to catalytically hydrogenate, there seemed a good possibility that sulphoxide complexes could be "made" to activate H\textsubscript{2}.

Sulphoxide ligands have special interest in that bonding may occur via sulphur or oxygen, and also, since they are pyramidal, sulphoxides of the type R\textsubscript{1}R\textsubscript{2}S=O will exhibit chirality at the sulphur. This suggested the possibility of catalytic asymmetric hydrogenation using Ru(II) complexes containing chiral sulphoxide ligands. Catalytic synthesis using chiral sulphoxide ligand systems had not been reported prior to the studies described in this thesis.

The aim of the work then was to develop syntheses of Ru(II) complexes containing sulphoxides and test them as catalysts for hydrogenation; development of the synthesis of the ligands themselves, especially if chiral, was also envisaged. In view of the importance of asymmetric
and non-asymmetric homogeneous hydrogenation to this thesis, a short discussion of these two aspects of catalysis is included below.

1.3. Homogeneous Hydrogenation of Olefinic Compounds

It is generally believed that hydrogenation of olefins requires prior activation by co-ordination of both the hydrogen and olefin molecules\(^1\). Hydrogen activation is thought to occur in three ways\(^{16-19}\) depending on the metal complex employed.

An overall heterolytic cleavage, reaction (1,1)\(^20\), involves

\[
\text{Ru}^{\text{III}}\text{Cl}_6^{-3} + H_2 \rightleftharpoons \text{Ru}^{\text{III}}\text{HCl}_5^{-3} + H^+ + \text{Cl}^- \quad (1,1)
\]

substitution of a hydride ligand, and is aided by the loss of $H^+$ and $\text{HCl}$, and thus by addition of a base\(^{15}\). Co-ordination of an olefin to this hydride may result in subsequent insertion of the olefin into the Ru-hydride bond to give a Ru-alkyl complex. A Ru(II) example of this has been described\(^{21}\) for hydrogenation of some unsaturated olefinic acids. The reaction is:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C}
\end{align*} \quad \text{Ru-\text{-}} \quad \text{Ru-\text{-}} \quad \text{Ru-\text{-}}
\]

Electrophilic attack by a proton at the carbon attached to the metal (protonolysis)\(^{22}\) results in the saturated product and can regenerate the Ru(II) catalyst.
Homolytic splitting of hydrogen by a metal complex results in the co-ordination number and oxidation state of the metal increasing by one\textsuperscript{16}. An example of such a process is shown by aqueous solutions of \([\text{Co(CN)}_5]^{-3}\)\textsuperscript{23}:

\[
2[\text{Co(CN)}_5]^{-3} + \text{H}_2 \rightleftharpoons 2[\text{HCo(CN)}_5]^{-3} \quad (1,3)
\]

For this case, an alkyl complex formed by olefin insertion reacts with another hydride species to yield the saturated product:

\[
[\text{(CN)}_5\text{Co-alkyl}]^{-3} + [\text{HCo(CN)}_5]^{-3} \rightarrow 2[\text{Co(CN)}_5]^{-3} + \text{saturated product} \quad (1,4)
\]

The third method of hydrogen activation is oxidative addition of \(\text{H}_2\) to the metal, resulting in an increase in oxidation state and co-ordination number by two. Ruthenium(I) chloride complexes in DMA activate hydrogen this way, a so-called hydride path\textsuperscript{24}:

\[
\text{Ru}^I + \text{H}_2 \rightleftharpoons \text{Ru}^{\text{III}}\text{H}_2 \quad (1,5)
\]

A co-ordinated olefin may be reduced by consecutive transfer of two hydride ligands to initially form a \(\sigma\)-alkyl hydride intermediate and then the saturated product:

\[
\text{H}_2\text{Ru}^{\text{III}}\text{olefin} \rightarrow \text{HRu}^{\text{III}}\text{alkyl} \rightarrow \text{Ru}^I + \text{saturated product} \quad (1,6)
\]
A better documented system reacting by the hydride route is that involving RhCl(PPPh$_3$)$_2$. The same systems$^{25}$ may also activate olefin and H$_2$ by oxidative addition to a previously formed olefin complex, the so-called unsaturate path:

$$\text{Rh}^I\text{Cl}P_3 + \text{olefin} \rightleftharpoons \text{Rh}^I\text{Cl}P_2(\text{olefin}) + P \quad (1,7)$$

$$\text{Rh}^I\text{Cl}P_2(\text{olefin}) + H_2 \rightleftharpoons H_2\text{Rh}^{III}\text{Cl}P_2(\text{olefin}) \quad (1,8)$$

The remaining steps to saturated product are as for the hydride path of the type shown in eqn. (1,6).

1.4. Asymmetric Hydrogenation

The interest in this area of hydrogenation stems from the desire to synthesize chirally pure products especially some naturally occurring ones, eg., amino acids, from their precursor olefins. The predominance of work in this area has been with Rh(I) phosphine systems as catalysts which Knowles et al.$^6$ have utilized with remarkable success to produce $\alpha$-amino acids in a high state of optical purity. Very recently a comprehensive review on asymmetric homogeneous hydrogenation in general, and one dealing specifically with chiral rhodium-phosphine catalysts, have been published$^{26,27}$.

Only a little work in this area has been done with ruthenium complexes. Apparently the first asymmetric hydrogenation with a chiral ruthenium catalyst was that reported by Hirai and Furuta$^7$ using an in situ generated ruthenium(III) complex of poly-L-methylethylamines. They
reduced methylacetoacetate to methyl-3-hydroxybutyrates with an enantiomeric enhancement of about 5%. A Ru(II)-(+)\-diop complex, \([\text{Ru}_2\text{Cl}_4(\text{diop})_3]\) has been reported\(^{28}\) to catalyse the hydrogenation of \(\alpha\)-acetamidoacrylic acid to N-acetylaspartic acid with a product of optical purity = 60%.

Little is known about the actual stereoselective hydrogenation process. Pino et al.\(^{29}\) have postulated fairly detailed mechanisms for some asymmetric hydroformylation reactions, but they admit that the mechanism of asymmetric induction is only speculation. Some of the factors which are thought to influence asymmetric induction are; interaction between substrate and chiral transition metal atoms, the face of the olefin attacked by hydrogen, and the choice of carbon atom initially attacked (Markownikoff or anti-Markownikoff addition). The size of coordinated ligands, the presence of groups on these ligands capable of H-bonding (for example, \(-\text{CH}_3\)), the nature of the functional groups on the substrate, temperature and pressure all play a role in influencing asymmetric induction. Thermodynamic equilibria governing the reaction intermediates formed and activation energies in the reaction steps influence the eventual product distribution.

Greater effort is required to clarify the relative influence of the thermodynamic and kinetic effects as well as the effect of steric structure of the catalytic complex before the origin of asymmetric induction can be completely determined.
1.5. Homogeneous Hydrogenation Using Ruthenium Complexes

Reports on homogeneous hydrogenation of olefinic substrates using ruthenium complexes began appearing in 1961 with studies of ruthenium(II) chloride complexes in aqueous acid solutions. These solutions were found to catalytically hydrogenate some substituted ethylenes such as maleic, fumaric, and acrylic acids, (see Section 1.3.). More recently, systems involving triphenylphosphine complexes of Ru(II), have been investigated thoroughly, in particular using RuCl$_2$(PPh)$_3$ and RuClH(PPh$_3$)$_2$. Extension of this work toward asymmetric hydrogenation by using chiral phosphines has also been accomplished in this laboratory, (see Section 1.4.). Other ruthenium systems capable of activating H$_2$ for hydrogenation have been reviewed in some detail.

The premier Ru(II) complex containing co-ordinated DMSO ligand to be used as a homogeneous hydrogenation catalyst was reported by Ogata et al. in 1970. The complex, formulated as C$_6$H$_6$RuCl$_2$(DMSO), catalysed the hydrogenation of maleic acid at 25°C and 20 atm H$_2$. In 1971 the DMSO complexes, RuX$_2$(DMSO)$_4$, (X = Cl, Br), were reported; however, these compounds were found to be inactive towards the reduction of olefinic substrates in DMSO and other solvents under the conditions employed.

1.6. Thesis Contents

A new preparative route was developed for the RuX$_2$(DMSO)$_4$, (X = Cl, Br), compounds and this led to isolation of a new complex, [NH$_2$Me$_2$][RuCl$_3$(DMSO)$_3$]. Both chloro-compounds were found to catalytically...
hydrogenate activated olefins under mild conditions in DMA. Chapters IV, V and VI describe the preparative routes, the compounds and their characterization, and the kinetics of hydrogenation, respectively. In order to develop further Ru(II) hydrogenation catalysts and to extend this work to asymmetric hydrogenation, new sulphoxides were synthesized; this aspect is described in Chapter III. New Ru(II) compounds made with these new sulphoxides are described in Chapters VII, X, and XI, while hydrogenation kinetics for one such catalyst system appears in Chapter VIII. Asymmetric hydrogenation studies using some of the catalysts with chiral sulphoxides are presented in Chapters IX and XII. General conclusions and thoughts on possible extension of the work presented in this thesis occupy Chapter XIII.
CHAPTER II
APPARATUS AND EXPERIMENTAL PROCEDURE

2.1. Instrumentation

Infrared spectra were recorded on a Perkin Elmer 225 or 457 spectrophotometer, as nujol or hexachlorobutadiene mulls between CsI plates. Solution spectra were obtained in CC\textsubscript{4} solvent in NaCl or polyethylene cells.

N.M.R. spectra were recorded on a Varian T60 or XL100 spectrometer in CC\textsubscript{4}, CDC\textsubscript{3}, or D\textsubscript{2}O solvent at 35°C with Tetramethylsilane or sodium 2,2-dimethyl-2-silapentone-5-sulphonate as reference. Ultra violet and visible spectra were obtained on either a Perkin Elmer 202 or Cary 14 spectrophotometer, with 1 mm or 1 cm path length quartz or glass cells. Both spectrophotometers could be fitted with thermostated cell holders.

Magnetic moments were determined by the Gouy or Faraday method, at 22°C. Molecular weights were determined by freezing point depression.

High pressure liquid chromatographic separations were effected on a Waters Associates ALC 202 equipped with a differential U.V. detector and Corasil II, Carbowax and Cellulose columns. My thanks to Dr. J. Kutney for the use of this machine.

Optical rotation data were collected on a Perkin Elmer 421 polarimeter at room temperature using a one decimeter microcell with a volume of 0.5 ml.
Conductivity data were obtained at room temperature with a dip type conductivity cell connected to a Thomas Serfass conductivity bridge. For air sensitive solutions Ar gas was used to blanket the cell. Melting points were recorded using a Fisher-Johns or Gallenkempt apparatus, and are uncorrected.

Gas chromatographic analysis was conducted on a Perkin Elmer 900 with a flame ionization detector and a Chromosorb 103 column or a Bechman GC-2A unit with a thermal conductivity detector and a Poropak W, Carbowax 1000, or Chromosorb 103 column.

2.2. Gas-Uptake Apparatus

The constant pressure apparatus, (Fig. 2.1), was used for kinetic and for stoichiometric experiments. A flexible glass spiral tube connected a capillary monometer D at tap C to a pyrex two necked reaction flask equipped with a dropping side arm bucket. The reaction flask was thermostated in an oil bath and shaken by means of a piston-rod and driven by an offset wheel connected to a Welch variable speed electric motor. The manometer D contained n-butylpthalate and was connected to a gas measuring burette consisting of a mercury reservoir E and a 10 ml pipette of known diameter. The gas burette was connected via an Edwards high vacuum metering valve, M, to the gas-handling part of the apparatus. This part consisted of a mercury manometer F, gas inlet Y, and vacuum pump G. The capillary manometer and gas burette were thermostated at 25°C in a perspex water bath. Thermostating of the oil bath and water bath was controlled by
Figure 2.1. Constant pressure gas-uptake apparatus
Jumo thermo-regulators and Merc to Merc relay control circuits, with heating accomplished by a 40 watt elongated light bulb. The baths were well stirred, and the oil bath insulated. The temperature was held to ±0.05°C. A vertical mounted cathetometer followed the gas uptake in the burette, and time was recorded with a Labchron 1400 timer.

2.3. Gas-Uptake Experimental Procedure

In a typical gas-uptake experiment 5 ml of solvent was placed in the 25 ml reaction flask. Weighed substrates were added to the solvent directly and weighed catalyst via the bucket after the solvent was degassed and the flask filled with reactant gas. Degassing for DMA solvent was effected by pumping on the solvent while shaking. For higher vapour pressure solvents the freeze thaw under static vacuum technique was employed. For both methods a degas-refill cycle was repeated three times. Initially the reaction flask was filled with reactant gas at a pressure somewhat less than that required for the experiment, at 0, (fig. 2.1.). The taps C and D were then closed and the reaction flask complete with spiral disconnected from 0 and attached to H and the shaker rod. The whole system up to tap C was then pumped down with taps H, K, L, J and M open. Reactant gas was admitted to this part of the system at a pressure greater than that in the reaction flask but less than that desired for the reaction. After thermal equilibration of the reaction flask was attained (≈15 min.) tap C was opened and the pressure of the whole system adjusted to the desired reaction pressure by introduction of gas through Y.
Shaking of the reaction vessel was then done to saturate the solvent with gas at the reaction pressure (=5 min.). An experimental run was then started by dropping the catalyst bucket, starting the shaker, closing taps K and L and starting the timer. Gas-uptake was indicated by a difference in oil levels in manometer D. The manometer was balanced by admitting gas into the burette through the metering valve M. Corresponding changes in mercury levels in the pipette N were translated to volume changes of gas reacted, per unit time.

Diffusion control of the reactions was eliminated by using fast shaking rates and a large indented reaction flask.

2.4. Anerobic Spectrophotometric Solution Cells

Two types of anerobic cell were employed for recording U.V. and visible spectra of air sensitive solutions or of solutions undergoing anerobic gas reactions.

Fig. 2.2 shows one type of cell. A solid compound was put in the L tube and a solvent in the cell and the two mixed under the appropriate anerobic conditions. The quartz cell had a 1 cm path length. Fig. 2.3 shows an anerobic cell designed to facilitate the recording of the simultaneous gas uptake and U.V., visible spectra of a solution. A solid was added to the stirred solvent by means of the side arm bucket. The stirrer was driven by a magnetic stirrer held directly above the cell. The circulation time of the solution through the cell window was less than ten seconds. The cell window was pyrex of approximately 2 mm path length. The solution as well as the gas above the solution was thermostatable. The gas-
Figure 2.2. Anerobic spectral cell
Figure 2.3. Gas-uptake spectral cell
uptake was recorded with a gas burette similar to that described previously.

2.5. Procedure for Spectrophotometric Experiments with Anerobic Cells

2.5.1. Simple Anerobic Solution Cell

With the cell shown in fig. 2.2, kinetic and equilibrium experiments were conducted. In a typical experiment a sample of solid was weighed into the L tube. The solvent (DMA, 4 ml) and any substrate were placed in the cell, which was assembled with a DMA resistant Viton O-ring and O-ring clamp. The cell was evacuated and filled with argon or hydrogen three times. The cell and its contents were allowed to temperature equilibrate and a baseline spectrum recorded. The solid and solution were then quickly mixed and spectra run.

2.5.2. Gas-Uptake Spectrophotometric Cell

With the gas-uptake spectrophotometer cell, the procedure was similar to above for the cell. A sample of solid was weighed into the glass bucket and the cell assembled with the solvent and any substrate in the cell. The stirrer was operated while degassing and filling with gas was done. The pressure of gas at the last fill was set to approximately 5 cm below the desired reaction pressure. The solution was then temperature equilibrated, with stirring, the pressure in the cell and gas burette set to reaction pressure and a baseline spectrum run. The bucket was then dropped, the gas burette taps K and L closed and the timer started. Spectra with corresponding gas-uptakes were then recorded with time; gas-uptakes as described previously with a gas-uptake experiment.
2.6. Hydrogenation of Substrates

2.6.1. Low Pressure

For pressure up to 1 atm., reactions were carried out using the same apparatus and in the same way as described for kinetic gas-uptake experiments.

2.6.2. Medium Pressure

Reactions using between 1 to 4 atms. \( \text{H}_2 \) were carried out using a Vortex Hydrogenation apparatus, (fig. 2.4.). A 5 ml solution of catalyst (0.025 M) and substrate (1 M), in degassed DMA, was placed in a glass thimble (15 mm x 80 mm), with a teflon coated spin bar, under an Ar blanket. The apparatus was then assembled as per diagram 2.5. The reaction bottle and thimble were evacuated, flushed with hydrogen three times and finally filled to the approximate desired pressure with hydrogen. The reaction vessel was then heated, and stirred, and the reaction pressure and temperature recorded when temperature equilibrium was attained (\( \approx 0.5 \) hr). Reactions were allowed to continue for four to ten days.

2.6.3. High Pressure

Reactions at between 80 and 145 atms. \( \text{H}_2 \) were carried out in a stainless steel Parr high pressure (3000 psi) reaction bomb, (fig. 2.6.). 5 ml solutions analogous to those used for the medium pressure reactions were placed in a 35 mm x 110 mm glass sleeve under an Ar blanket. The glass sleeve with spin bar was placed into the bomb and the bomb assembled. The reaction bomb was filled directly from a high pressure hydrogen cylinder and the gas
Figure 2.4. Vortex gas reaction apparatus
Figure 2.5. Vortex gas reaction bottle
Figure 2.6. Parr gas reaction bomb
bled off. This was repeated once and the bomb filled. Gas was then bled off to the desired pressure and the reaction solution stirred by a stirrer hot plate. Pressure and temperature were recorded when thermal equilibration was attained. Reactions were continued for five to ten days.

2.7. Work Up of Hydrogenation Reactions

Low, medium, and high pressure reactions were all worked up in the same way, with variation in technique depending on the substrate involved. All reaction solutions were pumped to dryness at 0.2 mm pressure and 40°C to leave a gummy residue. If metal was present this was filtered off first through celite. The gummy residue was then worked up as follows:

a) Acrylamide substrate; white crystals of propanamide sublimed out of the residue at 0.2 mm and 100°C.

b) Itaconic acid, atropic acid, and α- and β-methylcinnamic acid; the residue was dissolved in 25 ml of 10% NaOH solution and filtered through celite. The filtrate was extracted with chloroform (5 x 25 ml) to remove sulphoxide, and catalyst and then made just acidic with 10% HCl. The products, α-methysuccinic acid, 2-phenylpropanoic acid, 2-methyl-3-phenyl propanoic acid, and 3-phenyl butanoic acid, respectively, and unreacted substrate were then extracted from the aqueous phase with diethyl ether (5 x 25 ml) and dried over MgSO₄. Reduction in volume of ether yielded the product and substrate.

c) 2-acetamidoacrylic acid; the residue was dissolved in 25 ml of water, filtered, and extracted with chloroform as with previous substrates. Removal of the water left a brown oil which on addition of 15 ml of diethyl
ether and cooling gave white microcrystals of N-acetylanaline and unreacted substrate.

The above product and substrate mixtures were used without further purification for \(^1H\) n.m.r. determination of % product purity and optical rotation in the appropriate solvents. Optical rotations of N-acetylanaline, and \(\alpha\)-methylsuccinic acid, were measured in \(H_2O\) and 95% EtOH respectively. For \(^1H\) n.m.r. spectra CDCl\(_3\) was used in every case, except for the acetoamido-acrylic/acetylanaline system when D\(_2O\) was used.

2.7.1. **Determination of the Enantiomeric Excesses of the Hydrogenated Substrates**

The enantiomeric excesses of the hydrogenated substrates were determined by two methods. Comparison of the specific rotation of the hydrogenated substrate samples with that for the pure chiral substrate gives the enantiomer excess, where:

\[
\text{Specific rotation} = [\alpha]^T_D = \frac{100\alpha^T}{\lambda c}
\]

and \([\alpha]^T_D\) is the optical rotation of the sample at the NaD line at temperature \(T\), \(\lambda\) is the path length in decimeters and \(c\) is the concentration in grams/100 ml solvent.

\[
\text{Enantiomer Excess} = \text{e.e.} = \frac{[\alpha]^T_D \text{ of substrate sample x 100}\%}{[\alpha]^T_D \text{ of the pure chiral substrate}}
\]

Use of the chiral shift reagent Kiralshift R-E7, in CC\(_4\), with the hydrogenated substrate samples gave \(^1H\) n.m.r. spectra with resolved peaks for the enantiomers. For acid substrate samples that were insoluble in CC\(_4\), the
methyl esters were made and their spectra with shift reagent recorded. Integration of peak areas for each enantiomer gave the amount of each enantiomer present. From this information the enantiomeric purity was calculated.

\[
\text{Enantiomeric Purity} = \frac{(F^+ - F^-)}{(F^+ + F^-)} \times 100\%
\]

where \( F^+ \) and \( F^- \) are the mole fractions of each enantiomer with \( F^+ \) in excess.

In conjunction with the specific rotation of the hydrogenated substrate sample, the stereoisomeric configuration of the excess enantiomer could be assigned.

2.8. Materials

2.8.1. Gases

Prepurified hydrogen and CP grade carbon monoxide were obtained from the Matheson Gas Co., while purified nitrogen and argon were from the Canadian Liquid Air Ltd. For kinetic experiments the hydrogen was passed through a Deoxo Hydrogen Purifier.

2.8.2. Solvents

Spectral grade or analytical grade solvents were supplied by MCB, Mallinckrodt, Eastman or Fisher Chemical Co.'s and used without further purification. DMA was supplied by Fisher Chemical Co., and was refluxed over calcium hydride, vacuum distilled and stored under nitrogen before use in kinetic experiments.
2.8.3. **Olefinic Substrates**

Olefinic substrates were obtained as CP grade reagents. Acrylamide and 1-hexene were supplied by K & K Laboratories Inc., itaconic acid by Eastman Chemical Co., α-methylcinnamic acid, and methylvinyl ketone by Aldrich Chemical Co., and 2-acetamidoacrylic acid by Fluka Chemical Co. These substrates were used without further purification.

2.8.4. **Sulphoxide Ligands**

2.8.4.1. **Dimethyl Sulphoxide**

This liquid was supplied by Continental Bio-Systems Ltd., as analytical grade, and was used as such for all experiments.

2.8.4.2. **Methyl Phenyl Sulphoxide**

This liquid was used as supplied by K & K Laboratories.

2.8.4.3. **Methyl n-Propyl Sulphoxide, I**

2.8.4.3i. **Methyl n-Propyl Sulphide**

1.025 mole of NaOH was dissolved in 250 ml of water in a 1 l. three-necked flask equipped with a dropping funnel, reflux condenser, teflon gland and motor-driven stirrer. 1 mole (76.2 g, 90.7 ml) of n-propyl mercaptan was added slowly to the vigorously stirred basic solution. When all the mercaptan had reacted 1 mole of methyl iodide (62.25 ml) was added as fast as the resulting exothermic reaction would allow. As the methyl iodide was being added the product sulphide formed a layer on top of the basic solution. On completion of the addition, the stirred reaction mixture was refluxed, by
external heating for three hours\(^\dagger\). The product was then steam distilled from the reaction mixture, washed with 3 x 100 ml portions of water, 3 x 100 ml of 10% NaOH (aq) and 100 ml of H\(_2\)O and dried over calcium chloride. Distillation from a helix filled fractionating column yielded 85 g (95%) of pure sulphide.

\(\delta_{^1}C\)\(_{Cl}\) 0.98 (triplet, 3H, -CH\(_3\)), 1.25 - 1.80 (multiplet, 2H, -CH\(_2\)-), 2.0 (singlet, 3H, CH\(_3\)-S), 2.39 (triplet, 2H, S-CH\(_2\)-).

2.8.4.3ii. **Methyl n-Propyl Sulphoxide**

0.92 mole (83.1 g) of the sulphide, II, 150 ml of acetone and 104 g of 30% H\(_2\)O\(_2\) were allowed to react in a 500 ml R.B. flask, at 5°C for one hour, and let stand overnight at R.T. The solvent was removed at reduced pressure and the remaining liquid dried over BaO and vacuum distilled (b.p. = 47°C @0.2 mm) to give a colorless liquid, 91 g, (93%). \(\delta_{^1}C\)\(_{Cl}\) 1.10 (triplet, 3H, CH\(_3\)-), 1.45 - 2.00 (multiplet, 2H, -CH\(_2\)-), 2.60 (triplet, 2H, -CH\(_2\)-S), 2.50 (singlet, 3H, S-CH\(_3\)). \(v_{\text{max}}\)\(^{\text{neat}}\) 1050 cm\(^{-1}\) (S=O).

2.8.4.4. **Enantiomerically Pure Methyl n-Propyl Sulphoxide**

2.8.4.4i. **Methanesulphinyl Chloride**\(^{35}\), III

0.5 mole of methyl lithium (Alfa) in ether was transferred under nitrogen to a 1 l. three-necked flask equipped with a teflon gland, mechanical stirrer, calcium chloride drying tube and a gas-inlet tube, and contained in a dry ice bath. 25 ml (=35 g, 0.55 mole) of SO\(_2\) was condensed in a trap with a dry ice-acetone bath. After cooling the methyl lithium solution to approximately -70°C the liquid SO\(_2\) was allowed to warm up slowly and introduced

\(^\dagger\) A vapour tight stirrer gland is required here to prevent loss of sulphide vapour.
as \( \text{SO}_2 \) gas above the methyl lithium solution in a nitrogen stream. A white solid, lithium methanesulphinate, formed immediately. After all the \( \text{SO}_2 \) was added through the inlet tube, stirring was continued for 0.5 hour. With nitrogen flushing, 300 g (2.5 moles) of thionyl chloride was added to the reaction mixture maintained at \(-15^\circ\) to \(-20^\circ\)C. The mixture changed from white to yellow during this addition, as the sulphinate reacted to give methane-sulphinyl chloride and LiCl precipitated. After the addition was completed the mixture was allowed to warm up to room temperature, and stirring continued for four hours. The LiCl was filtered off under nitrogen and washed with benzene. The solvent, ether and benzene and thionyl chloride, in the filtrate were removed at reduced pressure (flash evaporator, \( \approx 50 \text{ mm} \)) at 30°C until infrared absorption of the residue at 1225 cm\(^{-1}\) (\( \text{SOCl}_2 \)) was very weak compared to absorption at 1150 cm\(^{-1}\) (\( \text{CH}_3\text{SO}_2\text{Cl} \)). The distillate was light yellow in colour due to methanesulphinyl chloride which does co-distill with the solvent to a small extent. The yield of sulphinyl chloride was 33.5 g (67%) and was used as such in the next step.

2.8.4.4ii. (\(-\))Menthyl Methanesulphinate, IV

51.6 g (0.33 mole) of (\(-\))menthol (Aldrich) 95% optically pure in 60 ml of anhydrous pyridine was added dropwise to a nitrogen flushed solution of 33 g (0.33 mole) of methanesulphinyl chloride, III, in 150 ml of ether cooled to \(-75^\circ\)C. (Dry Ice - acetone bath). The addition was slow enough to

\[ \begin{array}{l}
\text{\# Lower pressure and higher temperature leads to greater co-distillation.}
\end{array} \]
maintain the temperature of the solution below -70°C. During addition pyridinium hydrochloride precipitated. Stirring was continued for 3 hours after addition was finished as the reaction mixture was allowed to warm up slowly. The pyridinium hydrochloride was dissolved by adding 250 ml of water and the ether layer was washed with water (1 x 150 ml), 1% aqueous hydrochloric acid until the washings were acidic, aqueous sodium bicarbonate (saturated solution) until the washings were neutral, and finally with water (1 x 150 ml). The ethereal solution was dried over anhydrous sodium sulphate and the ether removed at reduced pressure at room temperature. The yield of crude menthyl methanesulphinate was 53.5 g (69%). The ester was a viscous yellow orange liquid.

2.8.4.4iii. Stereochemical Calibration

The crude ester was stereochemically calibrated by the formation of methyl p-tolyl sulfoxide. A solution of 2.5 g (0.012 moles) of methyl methanesulphinate in 20 ml of anhydrous ether was added to the Grignard reagent, p-tolyl magnesium bromide, so that vigorous refluxing occurred. The Grignard reagent was prepared from 5.15 g (0.30 mole) of p-bromotoluene (Eastman), 2.16 g (0.090 mole) of magnesium shavings and 11.3 g (0.60 mole) of 1,2 dibromoethane. It was found necessary to use an entraining agent to activate the magnesium. Addition of the Grignard reagent to the menthyl methanesulphinate caused the reaction mixture to become cloudy. After stirring for 5 minutes, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride. The crude reaction mixture was extracted with water (5 x 50 ml). The combined aqueous extracts were extracted with petroleum ether, 30 - 60°C, (5 x 50 ml) to remove traces of menthol, saturated with sodium chloride and extracted with chloroform (5 x 50 ml). The combined chloroform extracts were
dried over anhydrous magnesium sulphate and the solvent removed at reduced pressure. Hot box horizontal sublimation at 0.05 mm yielded 1.2 g (65%) of methyl p-tolyl sulphoxide. \([\alpha]^{22}_D = +31.2^\circ, \ (C = 5.1 \text{ acetone}), \ 21\% \text{ enantiomeric excess.} \ [\alpha]^{25}_D = +145.5^\circ \ (C = 1, \text{ acetone}) \text{ for (R)-(+)-methyl p-tolyl sulphone}\text{.} \]

2.8.4.4iv. Resolution of (-)Menthy1 Methanesulphinate

Separation of the diastereotopic mixture was attempted using liquid chromatography. Cyclohexane, chloroform, carbon tetrachloride, benzene, methanol and ethyl acetate were used as eluting solvents on neutral alumina and silica gel columns. High pressure liquid chromatography on Corasil II, Carbowax, and Cellulose columns with chloroform, methanol, cyclohexane, and mixtures of these solvents as elutants was tried. Paper chromatography with ethyl acetate, benzene, carbon tetrachloride and chloroform was also utilized. Lastly, gas phase chromatography with Carbowax, Apiezon J, SF 90, SE 30, and HMPF columns was tried. None of the above techniques achieved separation of the diastereomers on the preparative scale. On a smaller scale the high pressure liquid chromatography using chloroform eluting from a Corasil II column showed some separation, two overlapping peaks. V.P.C. with SF 90 showed the same effect.

2.8.4.5. (R)-(−)-Methyl p-Tolyl Sulphone, V

2.8.4.5i. p-Toluene sulphinyl Chloride, VI

96 g (0.45 mole) of sodium paratoluene sulphinyl (Eastman) was slowly added to 220 ml of thionyl chloride in a \(N_2\) flushed 500 ml three-necked flask equipped with a mechanical stirrer, and gas-inlet tube. The exothermic reaction gave an orange-yellow mixture containing a precipitate of NaCl. After
stirring overnight excess thionyl chloride was distilled off at reduced pressure (flash evaporator) and p-toluenesulphinyl chloride distilled from the reaction mixture. B.p. 86 - 88°C, 0.01 mm. Yield 77.7 g, (99%) of orange viscous air and water sensitive liquid.

2.8.4.5ii. (-)Menthyl p-Toluenesulphinate, VII

The preparation of the methyl diastereomers was done in anhydrous conditions under nitrogen. A solution of 64 g (0.41 mole) of (-)menthol in 100 ml of anhydrous ether and 36 ml of pyridine, dried over BaO, in a 500 ml three-necked flask equipped with a gas-inlet tube, mechanical stirrer and equilizing addition funnel was cooled to dry ice-acetone temperature. A solution of 71.1 g (0.41 mole) of p-toluenesulphinyl chloride in 100 ml of anhydrous ether was slowly added and the reaction mixture stirred and allowed to warm up to room temperature over 1 hr. 100 ml of 1N aqueous HCl solution was added, the ether layer extracted with water, (2 x 100 ml), and the aqueous layer with ether (1 x 100 ml). The combined ether extracts were dried over anhydrous magnesium sulphate and the ether pumped off (flash evaporator). The oily residue was dissolved in 30 ml of hot petroleum ether (60 - 80°C) and the resulting solution stored at 0°C for one day. 30.3 g of solid was collected and washed with petroleum ether (30 - 60°C). The combined filtrate was taken to dryness, 20 ml of petroleum ether (60 - 80°C) added along with a crystal from the first crop, and anhydrous HCl gas slowly bubbled through the solution until crystallization began. After cooling 51 g of product separated. A further 7.3 g was obtained by repeating the above process with the second crop filtrate. The total product 88.6 g (0.25 mole) (60%) was recrystallized from hot acetone, 2 ml per gram of product, as colourless rods and stored at 4°C.
to prevent decomposition. \([\alpha]_{D}^{25} = -197\) (C = 1, acetone) lit. \([\alpha]_{D}^{25} = -199^\circ\), acetone.

2.8.4.5iii. (R)-(+-)-Methyl p-Tolyl Sulphoxide

Preparation of this compound was accomplished by reaction of the optically pure menthyl p-toluenesulphinate prepared above with methyl magnesium iodide. The Grignard reagent was prepared under nitrogen in a 250 ml three-necked flask equipped with an equilizing addition funnel and reflux condenser with drying tubes, and a gas-inlet tube. To 5.3 g (0.22 mole) of magnesium shavings in 100 ml of anhydrous ether was added 35 g (0.25 mole) of methyl iodide\(^\dagger\). The Grignard solution was added dropwise under nitrogen to a well stirred solution of 30 g (0.17 mole) of menthyl p-toluenesulphinate in 250 ml of anhydrous ether at 0°C, in a 1 l. two-necked flask equipped with a gas-inlet tube, and a gas-equilization addition funnel with drying tube. After addition was complete the solution was stirred at room temperature for 0.5 hr then hydrolyzed with 150 ml of a saturated ammonium chloride solution. The aqueous phase was then immediately made just basic with aqueous ammonium hydroxide\(^\ddagger\). The ether layer was separated, dried over anhydrous magnesium sulphate, taken to dryness, diluted with 50 ml of ACS Hexanes, and cooled to 0°C overnight to yield 6.4 g of crude sulphoxide. The aqueous phase was extracted thoroughly with ether (6 x 200 ml), and the combined ether extracts treated as with the initial ether layer to yield 5 g of sulphone. The

\(\dagger\) 1,2 dibromoethane may be needed to initiate reactions, if any moisture is present or the magnesium is coated with impurity.

\(\ddagger\) This prevents decomposition of the sulphone to a yellow material.
combined crude sulphoxide fractions (0.074 mole, 42%) were recrystallized from hot cyclohexane\(^\ddagger\) (7 ml/g) to give lustrous white flakes. \([\alpha]_{D}^{25} = +143^\circ\) (C = 1, acetone), lit.\(^{36}\) \([\alpha]_{D}^{25} = +145.5^\circ\) (acetone). Found; C (62.52), H (6.64), O (10.53), S (20.82); Calc. for \(C_{8}H_{10}SO\); C (62.34), H (6.49), O (10.39), S (20.78). \(\delta_{\text{CDCl}_3}^{\text{TMS}}\) 2.45 (singlet, 3H, \(\text{CH}_3\)), 2.74 (singlet, 3H, \(\text{CH}_3\)-S), 7.46 (quartet, 4H, ArH). \(\nu_{\text{nujol}}^{\text{max}} = 1055\text{ cm}^{-1}\) (S=S).

2.8.4.6. (S,R,S,S)-(+) -2-Methylbutyl Methyl Sulphoxide, VIII

2.8.4.6i. (S)-1-Bromo-2-methylbutane, IX

100 g of (S)-(−)-2-methylbutan-1-ol (K & K) was dried over anhydrous magnesium sulphate, refluxed, and distilled from magnesium metal activated with iodide to give 82 g of pure alcohol. The distillate was 95% optically pure; \([\alpha]_{D}^{25} = -5.6^\circ\) lit.\(^{38}\) \([\alpha]_{D}^{20} = -5.9^\circ\). Bromination of the alcohol was done in two batches of 50 and 32 g. In a 1 l. three-necked flask equipped with a nitrogen gas-inlet tube, a thermometer, a gas-equilization funnel and a magnetic stirrer was mixed in a nitrogen atmosphere 50 g (0.57 mole) of the dry alcohol, 159 g (0.61 moles) of triphenylphosphine and 500 ml of DMF dried over and distilled from BaO. Bromine, dried over phosphorous pentoxide, was added over a 45 min period while the reaction mixture temperature was maintained below 55°C. Addition of bromine was stopped when 2 drops persisted in giving the solution an orange tint. The bromide, unreacted alcohol, and DMF were removed from the triphenylphosphine oxide by vacuum distillation into a Dry Ice cooled receiver. One litre of cold water was added to the distillate and 73 g (85%) of (S)-1-bromo-2-methylbutane separated. The liquid product

\(\ddagger\) Charcoal is required to remove yellow impurity.
was removed and dried over anhydrous magnesium sulphate. \( \frac{n}{D}^{20} = 1.4428 \),  
\[ \text{b.p.} = 120 - 122 \text{ (lit.} \frac{n}{D}^{20} = 1.4451, \text{b.p.} 121.6). \]

2.8.4.6ii. (S)-1-Mercapto-2-methylbutane, \( \text{X} \)

In the preparation 120 g (0.795 mole) of bromide, \( \text{IX} \), 60.5 g (0.795 mole) of thiourea, and 400 ml of 95% ethanol were refluxed for 12 hours in a 1 l three-necked flask equipped with a mechanical stirrer, addition funnel and reflux condenser. A solution of 47.7 g (1.19 mole) of sodium hydroxide in 300 ml of water was added and the mixture refluxed for 4 hours. During refluxing the mercaptan separated out as an oil. The layers were separated and the aqueous layer made acidic with 14 ml of conc. sulphuric acid in 200 ml of water. On acidification some mercaptan separated and this was combined with the previous mercaptan layer. The aqueous layer was then extracted with benzene (1 x 100 ml). The extract was added to the crude mercaptan layer and the whole washed with water (2 x 200 ml) and dried over anhydrous sodium sulphate. The solvent was removed and the residual oil distilled through a vigreux column to give 63 g (0.60 mole) (70%) of a clear liquid. \[ \text{b.p.} 116 - 118^\circ\text{C} \text{ (lit.} \frac{n}{D}^{39} \text{ b.p.} = 118.2^\circ\text{C}). \]

2.8.4.6iii. (S)-2-Methylbutyl Methyl Sulphide, \( \text{XI} \)

This compound was prepared by the analogous method described for methyl n-propyl sulphide, \( \text{II} \) by using 62.7 g (0.60 mole) of mercaptan, 24.8 g (0.62 mole) of sodium hydroxide in 150 ml of water, and 85.8 g (0.60 mole) of iodomethane. The iodomethane was added over one hour and the resulting mixture refluxed for 3 hours. Steam distillation gave 48 g (68%) of clear liquid.  
\( \delta_{\text{TMS}}^{\text{CDCl}_3} 0.90 - 1.70 \) (multiplet, 9H, \( \text{CH}_3\text{-CH}_2\text{-CH} \)), 2.1 (singlet, 3H, \( S\text{-CH}_3 \)), 2.78 - 2.60 (multiplet, 2H, \( \text{-CH}_2\text{-S} \)).
2.8.4.6iv. **(S,R;S,S)-(+)-2-Methylbutyl Methyl Sulphoxide**

As described for the preparation of methyl n-propyl sulphoxide, 1, 48 g (0.40 mole) of the sulphide, XI and 43 ml of 30% hydrogen peroxide in 160 ml of acetone were allowed to react overnight. The vacuum distillate fraction (65 - 70°C, 0.2 mm) was dried over barium oxide and vacuum-distilled to give 44 g (82%) of clear oily sulphoxide. B.p. 63°C, 0.1 mm. Micro-distillation of this clear oil gave; [α]_{D}^{25} = +20.3; neat, ρ = 0.993 g/ml.

Found; C (53.90), H (10.64); Calc. for C_{6}H_{14}SO; C (53.68), H (10.51).

\[ \delta_{\text{CDCl}_{3}}^{\text{TMS}} \]

- 0.90 - 1.20 (multiplet, 8H, CH\text{S} = CH\text{S}), 1.25 - 1.60 (multiplet, 1H, -CH-), 2.40 - 2.80 (triplet, 2H, -CH_{2}-S), 2.55 (singlet, 3H, S-CH_{3}).

\[ \nu_{\text{max}}^{\text{nujol}} \]

- 1025 cm\textsuperscript{-1}, (S=0). \[ \lambda_{\text{max}}^{\text{iso-octane}} \]

(loge) 205 nm (3.55).

2.8.4.7. **(2R,3R)-(−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane - H_{2}O (Dios), XII**

2.8.4.7i. **Diethyl-L-g-tartrate**\textsuperscript{40}, XIII

500 g (3.23 mole) of L-g- (+)-tartaric acid, 100% optically pure ([α]_{D}^{25} = +12.8, C = 17, water; lit. [α]_{D}^{20} = +12.7, C = 17.4, water), was converted to the diethyl ester by azeotropic distillation. The acid, 535 g (11.6 mole) of 99.9% ethanol, 20 g of proton charged cation exchanger and 700 ml of petroleum ether 30 - 60° were mixed into a 3 l. two-necked flask equipped with a teflon gland, mechanical stirrer, and a Dean-Stark tube with condenser. The reaction mixture was stirred and refluxed for seven days, while =300 ml of a water-ethanol azeotrope was removed. The cation exchanger was filtered off, solvent removed at reduced pressure and the resulting yellow
oil vacuum distilled to give 450 g (66%) of the colourless diester.\(^\dagger\)

B.p. 130°, 0.02 mm lit. \(^{40}\) b.p. 138°, 4 mm. \(^{\delta_{^1}C_{DCI}\_TMS}\) 1.33 (triplet, 3H, -CH\(_3\)), 3.55 (singlet, 2H, -OH), 4.34 (quartet, 2H, -CH\(_2\)\(\_\)), 4.57 (singlet, 2H, -CH). 

\(n^D_{25} = 1.4449, [\alpha]^D_{26} = +8.6, \) neat (lit. \(^{40}\) \(n^D_{25} = 1.4454, [\alpha]^D_{16} = +7.9\) neat).

2.8.4.7ii. **Diethyl-2,3-O-Isopropylidene-Lg-(+)-tartrate\(^43\), XIV**

A solution of 450 g (2.18 mole) of diethyl-Lg-(+) tartrate, 229 g (2.61 mole) of 2,2-dimethoxypropane (Eastman), one litre of sodium dried benzene and 1 g of p-toluenesulphonic acid monhydrate was placed in a 3 l. R.B. flask equipped with a helix filled distillation column. The yellow solution was refluxed while the benzene-methanol azeotrope, b.p. 88°C, was removed at the top of the column. After 9 hrs the temperature of the refluxing vapour was 78°C. The acid catalyst was neutralized by adding 2.5 g of anhydrous potassium carbonate to the orange reaction mixture and stirring overnight. The solvent and unreacted 2,3-dimethoxypropane were removed under reduced pressure and the product mixture vacuum distilled to give 478 g (91%) of light yellow liquid, b.p. 88 - 96 (0.04 mm); 67% diethyl ester, 30% ethyl methyl ester, and 3% dimethylester. \(^{\delta_{^1}C_{DCI}\_TMS}\) 1.35 (triplet, 3H, C-OC-CH\(_3\)), 1.51 (singlet, 6H, C(CH\(_3\))\(_2\)), 3.83 (singlet, 6H, C-OCH\(_3\)), 4.30 (quartet, 4H, C-OCH\(_2\)\_), 4.76 (singlet, 2H, CH).

2.8.4.7iii. **2,3-O-Isopropylidene-Lg-threitol\(^44\), XV**

A suspension of 32.4 g of LiAlH\(_4\) in 350 ml of anhydrous diethyl ether

\(^\dagger\) An analogous preparation with 227 g tartaric acid, 17 g ion exchanger and 350 ml of benzene as the azeotroping agent gave after six days 300 g (96%) of diethyl tartarate.
was refluxed for 30 min with vigorous stirring in a 2 l. three-necked R.B. flask. The flask was equipped with a reflux condenser, an addition funnel, and stirred with a glass stirrer with a 5" x 3" teflon paddle passed through a water cooled mercury sealed stirrer gland and turned with an enclosed explosion proof electrical motor. The condenser and funnel employed drying tubes filled with anhydrous CaCl₂. 79.4 g (0.33 mole) of the above tartrates, XIV in 350 ml of anhydrous diethyl ether was added dropwise over a 3 hour period, so that gentle refluxing resulted. After the addition was finished, the reaction mixture was refluxed for 2 hr, cooled to room temperature, 50 ml of ethyl acetate added carefully, and the mixture cooled to 0 - 5°C. 32 ml of water, 32 ml of 15% NaOH, and finally 96 ml of water were added cautiously and successively and the resulting white inorganic precipitate removed by filtration, washed with warm diethyl ether and Soxhlet extracted for 24 hr. The ethereal extracts were dried over MgSO₄ and evaporated under reduced pressure. Vacuum distillation of the residual yellow oil yielded a clear liquid, 40 g (74%), b.p. 99 - 102°C (1 mm) [lit. b.p. 96 - 96.5°C (0.5 mm)], nD 25 1.4606 (lit. nD 25 1.4347), [α]D 22 +1.9° (C = 5, CHCl₃) [lit. αD 26 -3.1 (C = 5, CHCl₃) for D enantiomer]. δDMSO TMS 1.34 (singlet, 6H, C(CH₃)₂), 3.33 - 3.60 (multiplet, 4H, -CH₂-,), 3.60 - 3.82 (multiplet, 2H, CH), 4.77 (triplet, 2H, OH).

N.B. This LiAlH₄ reduction is potentially a dangerous reaction. During addition of the tartrates the reaction mixture takes on the consistency of very thick Scottish porridge. The use of a stirrer with a 2"x1" paddle leads to inadequate stirring. The use of a non-enclosed explosion proof electrical motor further compounds the situation. During one such reduction with the latter stirrer and motor an explosion and fire resulted. The cause of this catastrophe was determined to be "bumping" ether touched off by a spark from the motor or heat from the hot stirrer gland.
2.8.4.7iv. 1,4-Ditosyl-2,3-O-isopropylidene-L-g-threitol\(^{44}\), XVI

50 g (0.31 mole) of the alcohol XV and 330 ml of dry freshly distilled pyridine were placed in a 2 l. R.B. flask and cooled to -10°C. 125 g (0.65 mole) of finely powdered, p-toluenesulphonyl chloride, recrystallized from hexane, was added in total. The mixture was shaken until homogeneous\(\dagger\) and held at 0°C for 12 hours. Crystallization of the product was induced by the slow addition of water. Once crystals began to form, water was added more rapidly until a total of at least 540 ml had been added. Crystallization was allowed to proceed overnight. After filtering and drying in vacuo the crude white solid weighed 143 g (98%). Recrystallization from 375 ml of absolute ethanol gave 140 g (96%) of compact white needles; m.p. 77 - 78.\([\alpha]_{D}^{24} -24.0 (C = 4, CHC\textsubscript{3}) \) \cite{45} m.p. 80.8 - 82.0; \([\alpha]_{D}^{24} -12.4° (C -5, CHC\textsubscript{3})\). \(\text{CDCl}_3\) 1.30 (singlet, 6H, C(CH\textsubscript{3})\textsubscript{2}), 2.43 (singlet, 6H, CH\textsubscript{3}), 3.83 - 4.18 (multiplet, 6H, -CH\textsubscript{2}, CH), 7.21 (doublet, 4H, ArCH-C-C), 7.65 (doublet, 4H, ArCH-C-S).

2.8.4.7v. S,S-Diacety1-2,3-O-isopropylidene-1,4-dithio-L-g-threitol\(^{45}\), XVII

A mixture of 140 g (0.30 mole) of the ditosylate XVI, 77 g (0.675 mole) of potassium thiolacetate, and 750 ml of absolute ethanol was refluxed and stirred under dry nitrogen in a three-necked 2 l. R.B. flask. During the refluxing, white potassium tosylate precipitated out. After ten hours refluxing, the mixture was cooled, filtered, and the solid tosylate washed with diethyl

\(\dagger\) At this point pyridinium hydrochloride precipitates out of solution.
ether. The ether wash was combined with the ethanol filtrate and the resulting solution concentrated, diluted with diethyl ether and filtered. The solution was again concentrated, diluted with ether and filtered. The solution was stripped of solvent and the remaining yellow liquid distilled under reduced pressure, b.p. 100 - 115°C (0.02 mm), to give 75 g (90%) of a yellow liquid.

\[\nu_{\text{max}} \text{neat} = 5.92 \mu(C = 0). \delta_{\text{TMS}}^{\text{CCl}_4} = 1.34 \text{ (singlet, 6H, C(CH}_3)_2), 2.35 \text{ (singlet, 6H, -CH}_3), 2.97 - 3.16 \text{ (multiplet, 4H, -CH}_2), 3.58 - 3.84 \text{ (multiplet, 2H, -CH).} \]

\[\alpha_{D}^{25} = -39.6 \text{ (C = 3.5, CHCl}_3) [\text{lit.}^{43} \nu_{\text{max}} \text{neat} = 5.91 \mu(C = 0); \delta_{\text{TMS}}^{\text{CCl}_4} \text{ as found above; } \alpha_{D}^{22} = -39.3^\circ \text{ (C = 3.1, CHCl}_3)]. \]

2.8.4.7vi. 2,3-0-Isopropylidene-1,4-dithio-L-gl-threitol \(^{43}\), XVIII

75 g (0.27 mole) of S,S-diacetyl-2,3-0-isopropylidene-1,4-dithio-L-gl-threitol was added to a 250 ml R.B. flask containing 50 mg of sodium in 100 ml of dry methanol. Over a period of 8 hours, the methanol, methylacetate azeotrope (b.p. 54 - 56°C) was removed through a 15 cm Vigreux column. 50 mg of sodium dissolved in 40 ml of methanol was then added and the distillation continued for 4 hr. The remaining solvent was then removed and the yellow liquid residue vacuum-distilled to yield 42 g (80%) of colourless liquid; b.p. 60°C (0.10 mm). \[\alpha_{D}^{24} = 1.4^\circ \text{ (C = 3.3, CHCl}_3) \]. \[\delta_{\text{TMS}}^{\text{neat}} = 1.38 \text{ (singlet, 6H, C(CH}_3)_2), 1.24 \text{ (triplet, } J = 8 \text{ cps, 2H, -SH), 2.58 - 2.95 \text{ (multiplet, 4H, -CH}_2), 3.76 - 4.05 \text{ (multiplet, 2H, CH).} \]

[\text{lit.}^{43}, \alpha_{D}^{23} = 13.0^\circ \text{ (C = 3.2, CHCl}_3); \delta_{\text{TMS}}^{\text{neat} \text{ as found above}]. \]

2.8.4.7vii. \((2R,3R)-(-)-2,3-0-Isopropylidene-2,3-dihydroxy-1,4-bis(methylthio)-butane\), \(XIX\)

To a 250 ml three-necked R.B. flask equipped with a gas-inlet tube, a reflux condenser, an addition funnel and internal stirring was added 12.7 g
(0.32 mole) of NaOH in 75 ml of water. 30 g (0.15 mole) of 2,3-O-isopropylidene-1,4-dithio-L-g-threitol was slowly added to the vigorously stirred, nitrogen flushed solution. When this reaction was complete, 43.8 g (0.31 mole) of iodomethane was added as rapidly as the resultant exothermic reaction would allow. On completion of this addition the stirred reaction mixture was refluxed for 4 hr. The sulphide layer was separated from the reaction mixture, washed with water, 10% sodium hydroxide solution and finally water before drying with calcium chloride. The aqueous layer of the reaction mixture was extracted with pet. ether (30 - 60°) (4 x 100 ml), washed with water, 10% sodium hydroxide solution, water, and the solvent then stripped off. The liquid residue was washed with 10% sodium hydroxide solution, water and dried over calcium chloride. The two dried sulphide fractions were then combined and vacuum-distilled to give 20.6 g (60%) of clear colourless liquid, b.p. 66°C, (0.02 mm). 

$[\alpha]_{D}^{25} = -6.8 \ (C = 4.9, CHCl_3)$. $\delta^{TMS}_{CCl_4}$ 1.37 (singlet, 6H, C(CH$_3$)$_2$), 2.17 (singlet, 6H, -CH$_3$), 2.58 - 2.80 (multiplet, 4H, -CH$_2$-), 3.77 - 4.05 (multiplet, 2H, -CH).

$\nu_{\text{nujol}}^{\text{max}}$ 9.6 $\mu$ (S=0).

2.8.4.7viii. (2R,3R)-(-)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(methylsulphanyl)butane·H$_2$O, (Dios)

20.2 g (0.091 mole) of XIX and 50 ml of acetone were placed in a 250 ml R.B. flask. 9.6 ml (0.18 mole) of 30% hydrogen peroxide was added slowly to the cooled (5°C) stirred solution. After stirring overnight the solvent was flash evaporated with the final traces of water removed at the

† At this point some white solid pptd. out. On addition of iodomethane this ppt. dissolved.
vacuum pump. The resulting clear oil solidified over a period of one week, to give a hygroscopic white solid, (18.9 g (82%), m.p. 63 - 85° in vacuo). Found; C (39.24), H (7.05); Calc. for C₉H₂₀O₅S₂; C (39.68), H (7.40). [α]²³D = -85.8° (C = 5.2, CHCl₃). δCDCl₃ TMS 1.43 (singlet, 6H, C(CH₂)₂), 2.66 (singlet, 6H, -CH₃), 2.90 - 3.35 (multiplet, 4H, -CH₂-), 4.05 - 4.02 (multiplet, 2H, -CH).

δd₆-Acetone TMS 3.0 (singlet, 2H, H₂O).

2.8.4.8. (2R,3R)-(−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(benzyl sulphinyl)butane-H₂O (BDios), XX

2.8.4.8i. (2R,3R)-(−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(benzylthio)-butane, XXI

11.3 g (0.058 mole) of 2,3-O-isopropylidene-1,4-dithio-Lg-threitol was added to an aqueous sodium hydroxide solution (4.76 g, 0.12 mole NaOH in 30 ml water) in a nitrogen purged 100 ml R.B. three-necked flask equipped with an addition funnel, reflux condenser, gas-inlet tube and internal stirring. After dissolution was complete, 19.9 g (0.12 mole) of α-bromotoluene was added with vigorous stirring. On completion of this addition the reaction mixture was heated to reflux for 3 hr. During this time the sulphide layer formed. Diethyl ether (400 ml) was added to the cooled reaction mixture to dissolve the sulphide. The two layers were then separated and the aqueous layer extracted with diethyl ether (3 x 75 ml). The ether fractions were combined, washed with water, 10% sodium hydroxide solution and water, and dried over anhydrous calcium chloride. Removal of the ether solvent gave a white solid.

Recrystallization from carbon tetrachloride gave a white solid, (18.3 g (84%), m.p. 86 - 88°C). [α]²⁵D = -56.7° (C = 2.7; CHCl₃). δCDCl₃ TMS 1.38 (singlet, 6H, C(CH₂)₂), 2.50 - 2.70 (multiplet, 4H, -CH₂-), 3.65 - 3.95 (multiplet, 2H, -CH), 3.72 (singlet, 4H, ArCH₂-), 7.22 (singlet, 10H, Ar-H).
2.8.4.8ii. (2R,3R)-(−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(benzyl sulphinyl)butane·H$_2$O (BDios)

15.93 g (0.043 mole) of XXI and 50 ml of acetone were placed in a 100 ml R.B. flask. 9.0 ml (0.086 mole) of 30% H$_2$O$_2$ was added slowly to the cooled (5°C), stirred solution. Overnight a white solid precipitated; the mixture filtered and the mother liquor flash-evaporated to give a clear colourless oil which upon addition of 50 ml of diethyl ether gave more white precipitate. The ether precipitates were combined, washed with petroleum ether (30 - 60°C) and vacuum dried, (10.5 g, 50%, m.p. 158 - 168 with decomposition, in vacuo). Found; C (59.51), H (6.71); Calc. for C$_{21}$H$_{28}$O$_5$S$_2$: C (59.41), H (6.65).

\[\begin{align*}
\alpha = -15.0 \text{ (C = 1.5, CHCl}_3) & \quad \nu_{\text{max}} \text{ (SO), 1605 cm}^{-1}, 1591 \text{ cm}^{-1} \\
(C = C) & \quad \delta^\text{d}_{6}\text{-Acetone} \\
\text{TMS} & \quad 1.30 - 1.50 \text{ (multiplet, 6H, C(CH}_3}_2) & \quad 2.90 - 3.10 \\
\text{(multiplet, 6H, -CH}_2,-, H}_2O & \quad 4.0 - 4.5 \text{ (multiplet, 2H, -CH), 4.0 - 4.1} \\
\text{(multiplet, 4H, ArCH}_2,-) & \quad 7.32 \text{ (singlet, 10H, Ar-H).}
\end{align*}\]

2.8.5. Ruthenium Compounds

2.8.5.1. Ruthenium Trichloride Trihydrate

This was supplied on loan from Johnson Matthey Co.; The % Ru varied from 37 - 42% depending upon the batch.

2.8.5.2. Methanolic "Blue Ruthenium(II) Solutions"

These solutions were produced by taking ruthenium trichloride

†Dried, degassed reagent grade solvents were used in all reactions which were also carried out under anerobic conditions, except where noted. Work up of products was done under a nitrogen or argon atmosphere. $^1$H n.m.r. spectra of compounds and respective ligands are contained in figs. 2.7.-2.10.
trihydrate, (0.75 - 3.0 g) in 50 ml of methanol, in a three-necked flask equipped with gas-inlet tube, reflux condenser and magnetic stirrer. Upon refluxing under H₂ (1 atm) for eight hrs a deep blue coloured solution resulted. These solutions were used directly for some preparations of Ru complexes.

2.8.5.3i. Dimethylammonium Trichlorotris(dimethyl sulphoxide)ruthenate(II),

1 g of ruthenium trichloride trihydrate (39% Ru) and 1 ml of dimethyl sulphoxide were heated at 80°C in 20 ml of DMA under H₂ (1 atm) for 4 hrs, in a 100 ml two-necked flask equipped with a reflux condenser, a gas-inlet tube and a magnetic stirrer. The resulting red solution was set aside overnight (or concentrated to 10 ml and cooled) to give a bright yellow product which was washed with acetone and ether, and vacuum dried. Recrystallization from DMA, as cubes, yielded 1.23 g (66%). M.p. 195°C (decomp. in vacuo). Found; C (19.6), H (5.3), Cl (21.6), N (2.6); Calc. for C₁₈H₂₆Cl₃No₃RuS₃; C (19.7), H (5.4), Cl (21.6), N (2.9). δCDCl₃ 2.68 (triplet, 6H, (CH₃)₂N), 3.51 (singlet, 18H, CH₃-S). νmax nujol 1100 cm⁻¹ (S=O) 347,293 (Ru-Cl). λmax (logε), 368 nm (2.76), 325 nm (2.58) shoulder. λ²² = 43.8 (C = 10⁻³, DMA) cm²ohm⁻¹mol⁻¹.

2.8.5.3ii. Dimethylammonium Trichlorotris(d₆-dimethyl sulphoxide)-ruthenate(II), 2

This compound was prepared in an analogous way as the preceding complex, but using d₆-DMSO.
2.8.5.4. Dimethylammonium Trichlorotris(methyl n-propyl sulfoxide)-ruthenate(II), 3

This compound was prepared in the same way as 1 with 3 g of ruthenium trichloride (39%) and 5 ml of methyl n-propyl sulfoxide. The resulting brown reaction mixture was concentrated under vacuum to an oil, and stored in vacuo at 5°C for 48 hr, during which time a yellow powder crystallized out. The product was washed with acetone and diethyl ether to remove the remaining oil and vacuum dried. Recrystallization from DMA gave 1.07 g (16%) of bright yellow powder. Found; C (29.19), H (6.70), Cl (18.02), N (2.70); Calc. for C_{38}H_{58}Cl_{13}N_{3}O_{3}RuS_{3}; C (29.39), H (6.70), Cl (18.59), N (2.45). δ_{C{DCl}_{3}} 1.08 (triplet, 3H, -CH₃), 1.50 - 2.40 (multiplet, 2H, -CH₂-), 2.68 (triplet, 6H, N(CH₃)₂), 3.42 (singlet, 3H, CH₃-C-S), 3.25 - 4.40 (multiplet, 2H-, S-CH₂-). ν_{max} 1105 cm⁻¹ (S=O), 355, 290 cm⁻¹ (Ru-Cl). λ_{max} 377 nm (2.77), 328 nm (2.50) shoulder. Λ_{22} = 46.0 (C = 10⁻⁴, DMA) cm²·ohm⁻¹·mol⁻¹.

2.8.5.5. Dichlorotetrakis(dimethyl sulphoxide)ruthenium(II), 4

2.8.5.5i.

As for the synthesis of compound 1 ruthenium trichloride trihydrate (3 g, 41% Ru), 5 ml of DMSO and 20 ml of DMA were heated together under hydrogen at 65°C overnight. Reduction in volume of the orange reaction mixture gave 3.4 g (58%) of yellow powder. Found; C (19.76), H (4.72); Calc. for C_{8}H_{24}Cl_{2}O_{4}RuS_{4}; C (19.83), H (4.99), Cl (14.63). δ_{C{DCl}_{3}} 2.60 (singlet, CH₃-S, uncoordinated), 2.73 (singlet, =1 DMSO, CH₃-S), 3.33, 3.42, 3.49, 3.52 (singlets, 3 DMSO, CH₃-S). ν_{max} 1110, 1090, 930, (S=O). λ_{max} 358 nm (2.69), 309 nm (2.55).
2.8.5.5ii.

To the blue methanolic solution produced from 1 g of ruthenium trichloride trihydrate (39% Ru) was added 4 ml of dimethyl sulfoxide. Refluxing under H\textsubscript{2} (1 atm) was continued for 12 hours yielding a red solution. Upon cooling 1.1 g (59%) of yellow cubes formed. M.p. 208°C (decomp. in vacuo). Found; C (19.76), H (5.10), Cl (14.43). \( \Lambda^22 = 0.70 \) (C = 10\textsuperscript{-3}, DMA) cm\textsuperscript{2}ohm\textsuperscript{-1}mol\textsuperscript{-1}. I.r. and \textsuperscript{1}H n.m.r. data were the same as those recorded for samples prepared by the previous method.

2.8.5.6. **Dibromotetrakis(dimethyl sulfoxide)ruthenium(II), 5**

0.5 g of ruthenium tribromide, 2 ml of DMSO in 20 ml of DMA were reacted as in the preparation of dimethyl ammonium trichlorotris(dimethyl sulfoxide)ruthenate(II), 1. Reduction in volume of the resulting orange solution yielded 0.2 g (24%) of orange powder. Found; C (17.23), H (4.19); Calc. for C\textsubscript{8}H\textsubscript{24}Br\textsubscript{2}O\textsubscript{4}RuS\textsubscript{4}; C (16.75), H (4.22). \( \delta_{\text{TMS}}^\text{CDCl}_3 \) 2.62 (singlet, 1 DMSO, CH\textsubscript{3}-S), 3.52 (singlet, 3 DMSO, CH\textsubscript{3}-S). \( \nu_{\text{max}} \) 1080, 944 (S=0).

2.8.5.7. **Dichlorobis(methyl phenyl sulphoxide)ruthenium(II), 6**

1.30 g of methyl phenyl sulphoxide was added to the methanolic blue solution (formed from 0.75 g (41.33% Ru) of ruthenium trichloride trihydrate), and refluxing under H\textsubscript{2} (1 atm) was continued overnight. During this period a gold coloured solid separated from a red solution. The product was filtered, washed with 100% ethanol, and acetone and vacuum dried to give 0.87 g (63%) of a gold solid. Found; C (56.94), H (3.70), Cl (15.90); Calc. for C\textsubscript{14}H\textsubscript{16}Cl\textsubscript{2}O\textsubscript{2}RuS\textsubscript{2}; C (37.17), H (3.56), Cl (15.67). \( \nu_{\text{max}} \) 1130 cm\textsuperscript{-1} (S=0), 330 cm\textsuperscript{-1} (Ru-Cl).
2.8.5.8. Ruthenium(II)dichloro-complexes of (S,R;S,S)-(+)-2-Methylbutyl Methyl Sulphoxide

2.8.5.8i. Ether-solvated Dichlorobis[(S,R;S,S)-(+)-2-methylbutyl methyl sulphoxide]ruthenium(II), 7

In a preparation analogous to that of 6, 4 ml of (S,R;S,S)-(+)-2-methylbutyl methyl sulphoxide was added to a methanolic blue solution produced from 2.0 g (41.33% Ru) of ruthenium trichloride trihydrate and refluxing continued for 48 hr under H₂ (1 atm). The resulting yellow brown solution was pumped down to a brown oil and diethyl ether added. The resulting yellow brown solution was cooled to 5°C for 3 hr, 0.5 g of small yellow crystals were filtered off and washed with ether. The mother liquor was cooled to 5°C for 96 hr yielding 0.6 g of green-tinted yellow crystals. Found; C (38.70), H (7.73), Cl (14.1); Calc. for C₁₂H₂₈Cl₂O₂RuS₂C₄H₁₀O; C (37.35), H (7.44), Cl (13.78). δ^CDCl₃ TMS 0.90 - 1.80, 1.82 - 2.60 (multiplets, 24H, CH₃-CH₂-CH(CH₃), CH₃-(ether)), 2.72 (singlet, 3H, CH₃-S), 2.80 - 3.80 (multiplets, 14H, -CH₂-S-CH₃, -CH₂-ether)). ν_max ν_jujol 1105 cm⁻¹, (S=O), 347 (Ru-C1). λ_CHCl₃ 364 nm (2.63), 450 nm (1.84) (shoulder). Λ²₂ = 4.5 (C = 10⁻³, DMA) cm²·ohm⁻¹·mol⁻¹.

2.8.5.8ii. Dichlorobis[(S,R;S,S)-(+)-2-methylbutyl methyl sulphoxide]ruthenium(II) Trimer, 8

As for the preparation of 6, 1.1 ml of (S,R;S,S)-(+)-2-methylbutyl methyl sulphoxide was added to the methanolic blue solution formed from 1 g (41.38% Ru) of ruthenium trichloride trihydrate and refluxing under H₂ (1 atm) continued for 48 hr. The resulting yellow brown solution was filtered from metal and the methanol solvent pumped off, leaving a
brown oil. 40 ml of benzene was added and the resulting solution freeze-dried to give 1.75 g (97%) of a gold-coloured powder. Found C (33.13), H (6.56), Cl (16.2), S (14.76). Calc. for \([\text{C}_{12}\text{H}_{28}\text{Cl}_2\text{O}_2\text{RuS}_2]\); C (32.72), H (6.41), Cl (16.1), S (14.56). M.w. 1273 g/mole (benzene).

\[\delta_{\text{TMS}}^\text{CCl}_4\] 0.7 - 1.75 (multiplet, 16H, \text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3), 1.85 - 2.5 (multiplet, 2H, -\text{CH}-), 2.8 - 4.2 (multiplet, 10H, \text{CH}_3-\text{S}-\text{CH}_3), 2.80 - 3.00 (multiplet, 10H, -\text{CH}_2-\text{S}-\text{CH}_3).

\[\nu_{\text{nujol}}^\text{max}\] \(1105\) cm\(^{-1}\) (S=0), 330 (Ru-Cl). \(\lambda_{\text{max}}^\text{C_6H_6}\) (loge as trimer), 351 nm (3.41), 446 nm (2.98) shoulder; \(\lambda_{\text{max}}^\text{CHCl}_3\) 351 nm (3.44), 445 nm (3.01) shoulder. \(\lambda_{\text{max}}^{22}\) = 7.2 (C = \(10^{-4}\), DMA) cm\(^2\) ohm\(^{-1}\) mol\(^{-1}\).

### 2.8.5.9. Dichlorodicarbonylbis(\(S,R;S,S\)-\(+\)-2-methylbutyl methyl sulfoxide) ruthenium(II), 9

0.35 g of 8 was refluxed in benzene (40 ml) under CO (1 atm) for twelve hours. During this time the solution went from dark brown to light yellow in colour. On freeze-drying the reaction mixture a dark oil resulted. Carbon tetrachloride (20 ml) was added to effect solution of the oil and n-hexane until the solution became cloudy. On cooling to -20°C white crystals (cubes) separated. \(\delta_{\text{TMS}}^\text{CCl}_4\) 0.8 - 1.9 (multiplet, 18H, \text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3), 2.80 - 3.00 (multiplet, 10H, -\text{CH}_2-\text{S}-\text{CH}_3).

\[\nu_{\text{nujol}}^\text{max}\] 2135, 2059 cm\(^{-1}\) (C = 0), 930 cm\(^{-1}\) (S=0), 320, 295 cm\(^{-1}\) (Ru-Cl).

### 2.8.5.10. Dichlorobis(\(R\)-\(+\)-methyl p-tolyl sulfoxide)ruthenium(II) Trimer, 10

1.33 g of (R)-\(+\)-methyl p-tolyl sulfoxide was added to a methanolic blue solution formed from 1.0 g (41.49% Ru) of ruthenium trichloride trihydrate. Refluxing under \(\text{H}_2\) (1 atm) was continued for 96 hr. At this point the brown solution was pumped to dryness and 15 ml of chloroform
added to dissolve the residue. The solution was filtered and diethyl ether added to precipitate a yellow solid. The solid was filtered and dissolved in 15 ml of chloroform. Slow precipitation with diethyl ether, filtering, and washing with diethyl ether resulted in 1.2 g (61%) of a yellow powder. Found; C (40.44), H (4.41), Cl (14.54); Calc. for C$_{16}$H$_{20}$Cl$_2$O$_2$RuS$_2$: C (40.00), H (4.20), Cl (14.76). M.W. 1358 g/mole (benzene). $\delta^\text{CDCl}_3$ 2.04 - 2.58 (multiplet, 6H, CH$_3$-Ar), 3.34 - 3.96 (multiplet, 6H, S-CH$_3$), 6.44 - 7.90 (multiplet, 8H, Ar-H). $\nu_{\text{max}}$ 1110 cm$^{-1}$ (S=O). $\lambda^{22} = 4.6$ (C = 10$^{-4}$, DMA) cm$^2$ohm$^{-1}$mol$^{-1}$.

2.8.5.11. Dichlorobis[(2R,3R)-2,3-dihydroxy-1,4-bis(methyl sulphinyl)-butane]ruthenium(II) Dihydrate, Dichlorobis(D Dios) ruthenium (II) Dihydrate, 11

2.8.5.11i.

To a methanolic blue soln. formed from 0.75 g ruthenium trichloride trihydrate (41.83% Ru) was added 1.56 g of Dios. Refluxing under H$_2$ (1 atm) was continued for another 12 hr. During this time a faint green solid precipitated (0.90 g, 46%) and this was filtered and washed with methanol. The reaction filtrate was concentrated (10 ml) and a yellow precipitate filtered off (0.52 g, 27%). Combination of the solids and precipitation from a water solution with acetone yielded 1.33 g (68%) of pale yellow solid. Found; C (22.70), H (4.62), Cl (11.30); Calc. for C$_{12}$H$_{32}$Cl$_2$O$_2$RuS$_4$: C (22.6), H (5.07), Cl (11.14). $\delta^{D_2O}$ 3.25 - 4.30 (multiplet, 26H, DDios). $\nu_{\text{max}}$ 3370 cm$^{-1}$ (-OH, H$_2$O), 1095 cm$^{-1}$ (S=O). $\lambda^{22} = 7.6$ (C = 10$^{-4}$M, DMA) cm$^2$ohm$^{-1}$mol$^{-1}$.

† In one preparation, benzene was used in place of CHCl$_3$, the solution filtered and freeze-dried to give the yellow product.
2.8.5.11iiii.

The compound was also prepared from RuCl$_2$(DMSO)$_4$ (0.50 g) and Dios (0.63 g) by allowing them to react in refluxing methanol (40 ml) overnight. During the reaction a yellow precipitate formed. Reduction in volume to 15 ml, and cooling to 3°C yielded, after washing with acetone and drying in vacuo, 0.45 g (69%) of a yellow powder.

2.8.5.12. Dichloro[(2R,3R)-(-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane][(2R,3R)-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane] ruthenium(II), Dichloro(Dios)-

RuCl$_2$(DMSO)$_4$ (0.94 g) and Dios (0.80 g) in CHCl$_3$ (50 ml) were refluxed for 120 hr. During this period the solution changed from an initial yellow colour to golden. The chloroform was removed from the reaction solution and the residue dissolved in acetone (15 ml), filtered and ether (50 ml) added slowly to the filtrate. The resulting yellow precipitate was filtered off, dissolved in acetone (10 ml) and ether (60 ml) added slowly to the resulting solution to precipitate a light yellow solid. The solid was filtered off, washed with ether (25 ml x 2) and vacuum dried to give 0.57 g (46%) of a pale yellow solid. Found; C (28.30), H (5.13), Cl (11.04); Calc. for C$_{15}$H$_{32}$Cl$_2$O$_8$RuS$_4$: C (28.12), H (5.03), Cl (11.07). $\delta^{1}$CDC$_{13}$ TMS 1.42 (singlet, 6H, (CH$_3$)$_2$C), 2.58 (singlet, 3H, S-CH$_3$, uncoordinated), 2.61 - 2.90 (multiplet, 5H, -CH$_2$SCH$_3$), 3.07 - 3.80 (multiplet, 17H, -CH$_2$SCH$_3$, -OH), 3.90 - 4.70 (multiplet, 4H, -CH). $\nu_{\text{max}}$ cm$^{-1}$: 3500 (-OH), 1065 (C-OH), 1100, 932 (S=O), 335 (Ru-Cl). $\lambda_{\text{max}}$ cm$^{-1}$ (log e): 309 nm (2.67), 356 nm (2.74). $\Lambda^{22} = 2.6$ (C = 10$^{-4}$, H$_2$O) cm$^{-1}$ mol$^{-1}$. 
2.8.5.13. Dichloro[(2R;3R)-2,3-dihydroxy-1,4-bis(methyl sulphinyl)]-butane][dimethyl sulphoxide][methanol]ruthenium(II),

Dichloro(DDios)(DMSO)(MeOH)ruthenium(II), 13

RuCl$_2$(DMSO)$_4$ (1.0 g) and Dios (0.57 g) were allowed to react together with refluxing in 50 ml of methanol. After 18 hr a yellow solid began precipitating out of the reaction solution. At the end of 42 hr the reaction mixture was allowed to cool and a lemon yellow powder filtered off, washed with methanol, and ether and vacuum dried to yield 0.90 g (88%). Recrystallization from DMA gave yellow microcrystals.

Found; C (21.69), H (4.68), Cl (14.57); Calc. for C$_9$H$_{24}$Cl$_2$O$_6$RuS$_3$; C (21.77), H (4.87), Cl (14.24). $\delta_{DSS}^{D_2O}$ 3.52, 3.60, 3.63, 3.75 (singlets, 19H, CH$_3$-CH$_2$, CH$_3$S, CH$_3$O), 3.9 - 4.1, 4.2 - 4.4 (multiplets, 5H, OH, CH). $\nu_{\text{nujol}}^{\max}$ 3400 cm$^{-1}$ (O-H), 1123, 1100 cm$^{-1}$ (S=O), 325, 305 cm$^{-1}$ (Ru-Cl).

$\Lambda^{22} = 4.4$ (C = 10$^{-4}$, DMA) cm$^2$ ohm$^{-1}$ mol$^{-1}$. 
Figure 2.7. $^1$H n.m.r. spectra of some sulphoxide ligands;
1) Me$^n$prSO, 2) MBMSO, 3) Dios, 4) MPTSO,
5) BDios
Figure 2.8. $^1$H n.m.r. spectra of some DMSO complexes of Ru(II); 1) $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$ in CDCl$_3$, 2) " in D$_2$O, 3) RuCl$_2$(DMSO)$_4$ in CDCl$_3$, 4) " in D$_2$O, 5) RuBr$_2$(DMSO)$_4$ in CDCl$_3$, 6) " in D$_2$O
Figure 2.9. $^1$H n.m.r. spectra of some sulphoxide complexes of Ru(II); 1) Ether-solvated RuCl$_2$(MBMSO)$_2$ in CDCl$_3$, 2) [NH$_2$Me$_2$][RuCl$_3$(Me$_n$prSO)$_3$] in CDCl$_3$, 3) RuCl$_2$(DDios)$\cdot$2H$_2$O in D$_2$O, 4) RuCl$_2$(DDios)(DMSO)(MeOH) in D$_2$O.
Figure 2.10. $^1$H n.m.r. spectra of some sulphoxide complexes of Ru(II);

1) $[\text{RuCl}_2(\text{MBMSO})_2]_3$ in CDCl$_3$,
2) $\text{RuCl}_2(\text{CO})_2(\text{MBMSO})_2$ in CCl$_4$,
3) $[\text{RuCl}_2(\text{MPTSO})_2]_3$ in CDCl$_3$,
4) $\text{RuCl}_2(\text{Dios})(\text{DDios})$ in CDCl$_3$. 
CHAPTER III
PROPERTIES AND PREPARATION OF SULPHOXIDE LIGANDS

3.1. Structure and Bonding

The sulphur of sulphoxides is sp\textsuperscript{3} hybridized\textsuperscript{46} with a non-bonding pair of electrons of the sulphur occupying one position of the tetrahedron. The result is a pyramidal-shaped molecule. Fig. 3.1. shows the structure of dimethyl sulphoxide\textsuperscript{47}. The angle OSC is 107° while the angle CSC is 98°. The S-C bond length is 1.80 - 1.82 Å. Replacement of one methyl group with another alkyl or aryl group will affect the bond angles and C-S bond lengths due to steric and inductive effects, as will replacement of both methyls.

![Figure 3.1. Structure of DMSO](image_url)

Figure 3.1. Structure of DMSO
The sulphur-oxygen bond consists of a sigma bond formed from overlap of a sp$^3$ orbital on sulphur and a p$_x$ orbital on oxygen, along with two pi bonds of the type d$_{xz}$-p$_z$ and d$_{xy}$-p$_y$. Such d-p pi overlap is not very effective. The overall result is that the oxygen remains electronegative compared to the sulphur and the bond strength is on the order of common double bonds. The three resonance structures for the S-O bond are shown below; structure II is dominant:

\[ \overset{+}{S} - \overset{2}{O} \quad \overset{2}{S} = \overset{2}{O} \quad \overset{2}{S} \equiv \overset{2}{O} \]

Figure 3.2. Resonance structures of sulfoxides

3.2. Co-ordination of Sulfoxides

Both the sulphur and oxygen have unpaired electrons enabling the sulfoxide to act as a Lewis base. Co-ordination to Lewis acids can occur through the hard oxygen to class a metal ions or through the soft sulphur to class b metal ions.
On co-ordination through the sulphur atom to Ru(II), the resulting geometry about the sulphur atom is the expected distorted tetrahedral. With DMSO the O-S-C and C-S-C angles, SO and SC bond lengths are similar to those found in the free ligand.\(^{50}\) Co-ordination through the oxygen does not alter the geometry about the sulphur atom to any extent, the geometry remaining pyramidal, however the SO bond length is longer than if sulphur bonded, 1.56 \(\text{Å}\) as compared to 1.48 \(\text{Å}\).\(^{51}\)

3.3. Effect of Co-ordination of Sulphoxide Ligand on \(\nu(\text{SO})\)

I.r. and \(^1\text{H} \text{ n.m.r.}\) are two spectroscopic tools which are available to help elucidate the nature of the bonding of the sulphoxide ligand. Co-ordination through the oxygen atom decreases the SO bond order by enhancing the contribution of resonance structure (I), (fig. 3.2), due to the withdrawal of electrons from oxygen. This will result in a lowering of the SO stretching frequency, by approximately 100 \(\text{cm}^{-1}\).\(^{48,52}\) Co-ordination through the sulphur atom increases the SO bond order by enhancing the contribution of resonance structure (III), thus raising the \(\nu(\text{SO})\). Experimentally this has proven correct and is on the order of approximately 70 \(\text{cm}^{-1}\).\(^{12,48,50}\)

3.4. Effect of Co-ordination on \(^1\text{H} \text{ N.M.R. Chemical Shifts}\)

Co-ordination of sulphoxides to metal centres causes the adjacent proton nuclei to resonate at lower field positions. Methyl protons of
DMSO and other methyl alkyl and methyl aryl sulphoxides are deshielded =1 p.p.m. on co-ordination to Ru(II) through sulphur and =0.1 p.p.m. on co-ordination through oxygen.

3.5. Determination of Stereochemistry at the Sulphur Centre in Sulphoxide Ligands

The stereochemical configuration at the sulphur atom of free sulphoxide ligands can be determined by the combination of two methods. The correlation of the Cotton effect with the sulphur stereochemistry has been achieved by Mislow. For methyl alkyl sulphoxides a negative Cotton effect centred at the strong n-d electronic transition, at approximately 205 nm (isooctane), indicates an R configuration at sulphur. This method gives the configuration but not the amount of each enantiomer or diastereomer present. The second method involves the use of a chiral lanthanide n.m.r. shift reagent. One particular shift reagent is Kiral-shift, E7, tris[3-(heptafluorobutyryl)-d-camphorato]europium(III). This reagent used in an equal molar ratio with DMSO co-ordinates to the sulphoxide and causes the methyl proton singlet to split into two equal area singlets separated by 0.40 p.p.m. For methyl alkyl or aryl sulphoxides the methyl resonance of each enantiomer or diastereomer will occur at different chemical shifts, (fig. 3.3.). The area under the respective peak then gives the amount of each isomer present. This method in conjunction with the O.R.D. method, above, will give the amount of
Figure 3.3. $^1$H n.m.r. spectrum of MBMSO with added Kiralshift$^R$
each isomer present and its stereochemical configuration. Because of the limitation of the O.R.D. method to methyl alkyl sulfoxides only, absolute stereochemical information is available for these sulfoxides only.

3.6. **Preparation of Sulphoxide Ligands**

Sulphoxides are generally made by the oxidation of the corresponding sulphide, which in turn has usually been made from a mercaptan and alkyl iodide. This general procedure has been followed in the preparation of most sulphoxides reported in this work. In one case, the synthesis of methyl n-propyl sulphoxide was attempted using a diasteromeric mixture of (-) menthyl methanesulphinates. The preparation for chiral (R)-(+) -methyl p-tolyl sulphoxide was achieved from a diasteromerically pure (-) menthyl-p-toluene sulphinate. For the general procedure most of the synthetic work involved preparation of the appropriate mercaptan for subsequent reaction with methyl iodide to give the alkyl-, or aryl-methyl sulfoxide. The general preparative scheme for this mercaptan to sulphide to sulfoxide procedure is shown below:

\[
\text{RSH} \xrightarrow{1)} \text{NaOH/H}_2\text{O} \xrightarrow{2)} \text{CH}_3\text{I} \ \rightarrow \ \text{RSCH}_3 \xrightarrow{\text{H}_2\text{O}_2/\text{acetone}} \ \rightarrow \ \text{RS(O)CH}_3
\]

RSH = n-propyl and (S)-2-methylbutyl mercaptan and 2,3-O-isopropylidene-1,4-dithio-L-g-threitol.

The mercaptan was converted to the sulphide in a two-step process, according to the procedure of Fidler et al.\textsuperscript{34}. Aqueous sodium
hydroxide caused the mercaptan to dissolve and dissociate with formation of RS\(^-\) and H\(^+\) ions. Addition of methyl iodide (to this solution) results in displacement of the iodide by the RS\(^-\) anion, presumably by an S\(_2\)N\(_2\) substitution. Steam distillation of the reaction mixture gives a product contaminated with mercaptan; however, washing with aqueous sodium hydroxide solution followed by fractional distillation removes most of the contaminant. This procedure was modified somewhat for the Dios and BDios syntheses, since the sulphide was difficult to steam distil. In these cases the crude sulphide layer of the reaction mixtures was separated and the aqueous layer extracted with petroleum ether (for Dios) or diethyl ether (for BDios).

After solvent removal, the combined layers were treated as for the other sulphides above, except BDios which was not distilled. Oxidation of the sulphide to the sulphoxide was accomplished by the action of a stoichiometric amount of hydrogen peroxide\(^{55}\). This reagent smoothly gave the product in high yield after vacuum distillation (or crystallization). The liquid product sulphoxides were stored over molecular sieves 5 A. The oxidation process gave sulphoxides which were racemic at the sulphur atom as shown by the use of \(^1\)H n.m.r. and examining the S(O)CH\(_3\) moiety with a co-ordinated chiral europium n.m.r. shift reagent, and where applicable by the absence of a Cotton curve.

3.6.1. Methyl n-Propyl Sulphoxide

This ligand was prepared in 87% overall yield from commercial n-propyl mercaptan as a racemic liquid by the route outlined previously.
The ligand was a clear liquid at room temperature, soluble in water, alcohols, acetone, diethyl ether, and halogenated solvents but insoluble in hexanes.

3.6.2. Enantiomerically Pure Methyl n-Propyl Sulphoxide

A procedure for preparing this ligand enantiomerically pure was worked out based on a modification of work done by Mislow and Jacobus. The preparative route is shown below:

\[
\begin{align*}
\text{SO}_2(g) & \xrightarrow{\text{ether}} \text{CH}_3\text{S(O)OLi} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{S(O)Cl} \\
\text{CH}_3\text{S(O)n-pr} & \xleftarrow{n-pr\text{MgBr}} \text{CH}_3\text{S(O)Omen}
\end{align*}
\]

The nucleophilic attack of methyl lithium on sulphur dioxide resulted in production of lithium methanesulphinate which was then reacted in situ with thionyl chloride to give methanesulphinyl chloride. Esterification of this product with naturally occurring (-) menthol gave a diastereomeric mixture of two menthyl methanesulphinates in the ratio of 61/39, R/S at the sulphur atom. The abundance of each isomer was determined by reacting the diastereomer mixture with p-tolyl magnesium bromide to give an enantiomerically enriched mixture of methyl p-tolyl sulphoxide. This Grignard reaction proceeds by direct inversion at the sulphur centre to give the sulphoxide. The diastereomeric ratio of the esters is then equal to the enantiomeric ratio of the sulphoxides. Comparison of the specific rotation of the mixture to the absolute
rotation of (R)-(+)-methyl p-tolyl sulfoxide, gives the enantiomeric excess and enantiomer ratio. Production of enantiomerically pure methyl n-propyl sulfoxide required that the liquid diastereomeric mixture of menthyl methanesulphinate be separated into its two diastereomers.

Many attempts to effect this resolution of isomers failed. The following techniques were used; liquid column chromatography, paper chromatography, gas phase chromatography, fractional distillation, and high pressure liquid chromatography. With both V.P.C. and the latter technique there was some separation of isomers but not enough to be useful even on the micro-preparative scale. Clearly if the diastereomeric mixture was composed of solids and not liquids, resolution by fractional crystallization could have been employed. This was the technique used for the following sulfoxides.

3.6.3. (R)-(+)-Methyl p-Toly1 Sulfoxide

The procedure below used for preparation of this enantiomerically pure sulfoxide and the experimental detail described previously was worked out by Dr. Heather Boucher and is a modification of work by Holloway et al.\textsuperscript{56} and Mislow and Jacobus\textsuperscript{57}. The synthetic route employed was as follows:

\[
\begin{align*}
\text{p-CH}_3\phi\text{S(0)ONa} \cdot \text{2H}_{2}\text{O} & \xrightarrow{\text{SOCl}_2} \text{p-CH}_3\phi\text{S(0)}\text{Cl} \\
\text{R-(-)-p-CH}_3\phi\text{S(0)CH}_3 & \xrightarrow{\text{CH}_3\text{MgI}} \text{p-CH}_3\phi\text{S(0)Omen}
\end{align*}
\]
Chlorination of sodium p-toluenesulphinate gave p-toluenesulphinyl chloride which on reaction with (-) menthol gave a diastereomer mixture. Fractional crystallization gave one diastereomer which on reaction with methyl magnesium iodide gave the solid chiral sulphoxide in an overall yield of 25% and optical purity of 96% R(+). By variation of the Grignard reagent, chiral t-butyl p-tolyl sulphoxide and o-tolyl p-tolyl sulphoxide were also made.

These ligands are white solids at room temperature and have similar solubility properties as DMSO and methyl n-propyl sulphoxide; however, the tolyl sulfoxides are soluble in hexanes.

3.6.4. Preparation of (S,R;S,S)-(+)−2-Methylbutyl Methyl Sulphoxide

This ligand was prepared as a mixture of two diastereomers. The 2-methylbutyl moiety contained an S centre at the "2" carbon in 95% optical purity as determined by the specific rotation of the initial starting reagent (S)-(−)-2-methyl-1-butanol. As no chemistry was done at this carbon atom the chirality at this carbon centre was not altered during the reactions to produce the sulphoxide. As the oxidation process from the sulphide to the sulphoxide is not stereospecific the two diastereomers are the (S,R) and (S,S) isomers. As shown by the use of a chiral $^1$H n.m.r. shift reagent the abundance of each isomer is equal, (fig. 3.3.). No Cotton effect was observed for this sulphoxide in the region 200 to 350 nm. As the sulphoxide is a liquid, preparative resolution of the diastereoisomers was not attempted. (S)-2-methylbutyl mercaptan was prepared by the following route:
Bromination of the starting chiral alcohol was accomplished smoothly using the method of Chung et al. The alcohol was essentially titrated with bromine in dry DMF. Conversion of the chiral bromide to the mercaptan was achieved using a two step process. Thiourea in ethanol converted the bromide to an isothiourea hydrobromide salt which was then decomposed to the mercaptan with aqueous sodium hydroxide. The mercaptan was then converted to the sulphoxide in 36% overall yield, by the general route outlined previously. This ligand mixture is a clear, colourless, odourless, viscous oil at room temperature. The solubility characteristics are as for DMSO and methyl n-propyl sulphoxide (except for a very limited solubility in water).

3.6.5. (2R,3R)-(-)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(methyl sulphinyl)butane, (Dios) and (2R,3R)-(-)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(benzyl sulphinyl)butane, (BDios)

These ligands were prepared by the scheme shown below in an overall yield of 15%, and 13% respectively.

Naturally occurring Lg(+)~tartaric acid, which was 100% optically pure as determined by its specific rotation, was used in the synthesis. The acid was converted easily to the diethyl ester by azeotropic distillation. The following five steps of the synthetic route, from the diethyl ester to the mercaptan, were worked out by Cormack and Kelley. The
Figure 3.4. Synthetic Scheme for Dios and BDios.
diketal linkage was obtained by azeotropic distillation with dimethoxypropane, to form the diacetal, the three possible products were obtained, in the following abundance, as determined by $^1$H n.m.r.; diethyl ester; 67%, ethylmethyl; 30%, and dimethyl ester; 3%. Reduction of the diester mixture to the diol was accomplished with lithium aluminium hydride. The ditosyl derivative of the threitol was easily obtained (by electrophilic attack of the sulphonyl chloride on the alcohol) as the lower melting polymorphic form. Nucleophilic displacement of the tosyl groups by potassium thiolacetate resulted in the dithioacetate.

The sulphur-carbonyl linkage of the moiety was then cleaved with sodium methoxide to give the mercaptan, 2,3-O-isopropylidene-1,4-dithio-L-g-threitol. Up to and including this product, all spectroscopic and optical rotation data confirmed the proper product formation and their accompanying optical purity. None of the reactions had altered the stereochemical configuration of the chiral carbons. Conversion to the sulphoxides was completed using the general format described previously, with two exceptions. The sulphide reactions were done under a nitrogen atmosphere to prevent the formation of a dithioketal, and the sulphide product was extracted and not steam distilled from the reaction mixture as noted previously. Use of a chiral lanthanide shift reagent on Dios failed to show the ratio of diasteromers produced. The proton shifts for each isomer were small and overlapping and as a result the abundance of each diastereomer could not be determined. Since the oxidation process from the sulphide to the sulphoxide is not stereospecific for any other sulphoxide produced by this method it can be assumed that this
process is not stereospecific during the production of Dios. Dios should then be a mixture of four diastereomers; (2R,S;3R,S), (2R,R;3R,R), (2R,R;3R,S) and (2R,S;3R,R), in equal abundance. Because the molecule possesses a C₂ axis the last two diastereomers are equivalent. Dios is a white hydroscopic solid which is soluble in water, alcohols, acetone, halogenated hydrocarbons, benzene and diethyl ether, and is slightly soluble in hexanes. For the same reason as presented for the Dios ligand, the exact ratio of diastereomers comprising BDios could not be determined experimentally. Due to the non stereospecific oxidation process the diastereomers should be as for Dios. BDios is a white non-hygroscopic solid with similar solubility properties as Dios except for insolubility in hexanes, and a slight solubility in benzene and diethyl ether. Both Dios and BDios are produced with one associated molecule of water, as shown by ¹H n.m.r. and elemental analysis data. The water molecule could possibly be hydrogen-bonded to one of the sulphone oxide oxygen atoms.
CHAPTER IV
PREPARATIVE ROUTES TO CHLOROSULPHOXIDE
COMPLEXES OF RUTHENIUM(II)

Chlorosulphoxide complexes of ruthenium(II) were made by three general synthetic routes. One route utilized the methanolic "blue ruthenium(II) solutions". Commercially available RuCl$_3$·3H$_2$O, a mixture of Ru(III) and Ru(IV), containing oxy- and hydroxy-chloro species$^{60,61}$ was reduced in methanol to the blue solutions under reflux with H$_2$ (1 atm).

These blue solutions are thought to contain chlororuthenate(II) species$^{62}$, but the exact nature of the species present is a matter of some controversy$^{62-64}$. The solutions were first prepared and used synthetically by Wilkinson et al.$^{65}$ to prepare a number of compounds. This group prepared the blue solutions in the presence of platinum black or Adam's catalyst under 2 atm of hydrogen$^{62}$. We have found that production of these solutions requires no external catalyst, and can be accomplished under 1 atm of hydrogen in refluxing methanol. Reduction of the Ru(III) and Ru(IV) is almost certainly done catalytically involving ruthenium(III) hydride species, which are known to be present during the hydrogenation of Ru(III) and Ru(IV) in aqueous HCl solutions and DMA solutions$^{64}$. The synthetic route is then:
Addition of the ligands to the "blue solution" with continued refluxing under hydrogen (1 atm) afforded the dichlororuthenium(II) compounds.

The second preparative route, using RuCl$_3$·3H$_2$O or RuBr$_3$, is shown below:

\[ \text{RuCl}_3 \cdot 3\text{H}_2\text{O} + \text{L}^1 \xrightarrow{\text{H}_2, 80^\circ\text{C}} \text{DMSA}_6 \rightarrow [\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{L}^1)_3] \]

\[ + \text{L}^2 \xrightarrow{\text{H}_2, 60^\circ\text{C}} \text{DMSA}_6 \rightarrow \text{RuCl}_2(\text{L}^2)_4 \]

\[ \text{RuBr}_3 + \text{L}^2 \xrightarrow{\text{H}_2, 80^\circ\text{C}} \text{DMSA}_6 \rightarrow \text{RuBr}_2(\text{L}^2)_4 \]

\( \text{L}^1 \equiv \text{DMSO, d}_6\text{DMSO and Me}^n\text{PrSO}; \text{ L}^2 \equiv \text{DMSO} \)

**SYNTHETIC ROUTE 2**

Use of stoichiometric amounts of ligand at 80°C or 60°C under 1 atm hydrogen easily yields the ionic or neutral complexes respectively. The hydrogen reduction of the ruthenium(III,IV) to ruthenium(II) in DMA with production of protons is well known. In this acidic reaction solution at 80°C formation of the dimethyl ammonium cation apparently stabilizes the RuCl$_3$(L$_3^1$)$^-$ anions. The presence of acetic acid and
dimethyl amine, hydrolysis products of DMA, in the reaction mixture was confirmed by gas chromatography. Hydrolysis of DMA is known to occur at high temperatures, ca. 350°C, but this process could be catalysed at 80°C by the ruthenium. An extra equivalent of ligand results in the tetrakis ligand route.

The third preparative route uses as a ruthenium(II) source dichlorotetrakis(dimethyl sulphoxide)ruthenium(II) prepared either from synthetic route 1 or 2 or by the method of Wilkinson et al. This group have already reported the successful use of this compound as a source of ruthenium(II) complexes. The third route is then:

\[
\text{RuCl}_2(\text{DMSO})_4 + L^1 \xrightarrow{\text{N}_2, \text{MeOH}} \text{RuCl}_2(L^2)_2; \text{RuCl}_2(L^2)(\text{DMSO})(\text{MeOH})
\]

\[
+ L^1 \xrightarrow{\text{N}_2, \text{CHCl}_3} \text{RuCl}_2(L^1)(L^2)
\]

\[L^1 \equiv \text{Dios}; \quad L^2 \equiv \text{DDios}\]

SYNTHETIC ROUTE 3

These exchange reactions proceed easily in methanol or chloroform, with however, different results. This aspect will be discussed later.
CHAPTER V

DICHLOOROTETRASIS(DIMETHYL SULPHOXIDE)RUTHENIUM(II),
DIMETHYAMMONIUM TRICHLOROTRIS(DIMETHYL SULPHOXIDE)RUTHENATE(II)
AND RELATED COMPOUNDS

5.1. Introduction

While a number of ruthenium(II) complexes containing DMSO are known, for example the cationic species $\text{[Ru(NH}_3)_5(\text{DMSO})]^2+$, and a possible dimeric species $(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{DMSO})$, the most investigated complex is $\text{RuCl}_2(\text{DMSO})_4^-$, reported first by Rempel et al.$^{11}$ and subsequently by Wilkinson et al.$^{12}$ and Stephenson et al.$^{67}$. Although all three research groups employed different preparative methods, the products appear to be similar, with three S-bonded DMSO ligands and one O-bonded ligand. Whether the cis or trans isomers are prepared is less clear. Wilkinson et al.$^{12}$ reported their product to be a mixture of cis and trans isomers while Rempel et al.$^{11}$ reported the trans isomer only. Mixed S- and O-bonding is known for other DMSO complexes, notably the cationic species $\text{Pd(DMSO)}_4^{+2}$, and such. This type of co-ordination for Ru(II) is not surprising considering this metal centre is on the borderline of class a/class b (hard/soft) character.$^{39}$

Reports of halosulphoxide complexes as catalysts for hydrogenation of unsaturated organics are non-existent, and indeed it is well
known that sulphur donors poison heterogenous systems. Nevertheless, this chapter reports on three such hydrogenation catalysts: RuCl₂(DMSO)₄ and two anionic ruthenium(II) halosulphoxide complexes, [NH₂Me₂][RuCl₃(DMSO)₂], and [NH₂Me₂][RuCl₃(Me²prSO)₃], all of which reduce acrylamide, and methylvinyl ketone at 60°C, under 1 atm H₂; anionic complexes containing sulphoxide ligands have not been reported previously.

5.2. [NH₂Me₂][RuCl₃(DMSO)₂], 1 and [NH₂Me₂][RuCl₃(d₆-DMSO)₂], 2

Compound 1 is prepared as an analytically pure bright yellow powder in a 66% yield. Use of d₆-DMSO gives the analogous deuteriated complex, 2. Crystallization of 1 as powder from DMA gives bright yellow cubes. Determination of the magnetic moment of complex 1 by the Gouy method gives a zero μ_eff consistent with a diamagnetic Ru(II) complex. Conductivity in DMA under N₂ indicates two ions in solution, with a value of Λ²² = 43.8 cm²ohm⁻¹mol⁻¹, which remains unchanged for 48 hr. In aqueous solution, the initial conductivity (Λ²² = 134 cm²ohm⁻¹mol⁻¹). This corresponds to two ions, but slowly increases over 48 hr to that corresponding to the presence of three to four ions, (Λ²² = 327 cm²ohm⁻¹mol⁻¹). This change in conductivity can be explained if the complex rapidly dissociates one chloride, giving a neutral ruthenium species plus two ions in solution (cation and chloride). The visible spectral data (see later) are consistent with this interpretation. Slower dissociation of the remaining chloride ligands results in the higher conductivity. If the

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† The compounds are reported elsewhere ⁵⁰.
complex is dissolved in aqueous silver nitrate, rapid precipitation of silver chloride occurs followed by slower precipitation until after 90 hr, 96% of the total chloride present in the complex has been precipitated (as determined gravimetrically). The ruthenium species present in solution could then be \([\text{Ru(Me}_2\text{SO)}_3(H_2\text{O})_3]^+\) which is analogous to cationic species formed from the \(\text{RuCl}_2(\text{DMSO})_4\) complex\(^{12}\).

Compound \(\_\) is very soluble in water, DMA, and methanol, soluble in chloroform, slightly soluble in benzene and acetone, and insoluble in ether and alkanes. It is relatively air-stable in the solid state but undergoes air-oxidation in DMA, slowly in the presence or more slowly in the absence of light, to give a green solution. The action of light on an anerobic DMA solution of \(\_\) does not give the green solution.

5.2.1. I.r. Spectra

From accepted data for DMSO and its transition metal complexes\(^{11,12,48,56,70}\) the i.r. bands of \(\_\) and \(\_\) can be assigned (Table 5.1). The spectra of both complexes have a strong band at 1100 cm\(^{-1}\) which is indicative of sulphur-bonded DMSO. The absence of a band at \(\approx 930\) cm\(^{-1}\) indicates no O-bonded DMSO\(^{12}\). The Ru-Cl stretches in the far i.r. can be assigned from the strength and position of the bands \(^{71,72}\) \(\nu(\text{Ru-Cl})\) are at 347 and 293 cm\(^{-1}\) in the spectrum of \(\_\) and 335 and 292 cm\(^{-1}\) in that of \(\_\), the presence of two \(\nu(\text{Ru-Cl})\) bands indicating a fac-isomer\(^{71}\). The corresponding mer-isomer would be expected to have three \(\nu(\text{Ru-Cl})\) bands in the region 360 - 250 cm\(^{-1}\). The observed spectra in this region are similar to that of fac-\([\text{RuCl}_3(\text{py})_3]\) which has two \(\nu(\text{Ru-Cl})\) bands at 346 and 301 cm\(^{-1}\)\(^{173}\). The band at 266 cm\(^{-1}\) in the spectrum of \(\_\) is
Table 5.1.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Assignment$^a,b$</th>
<th>Frequency</th>
<th>Assignment</th>
<th>$\nu(CH)/\nu(CD)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3125br,S</td>
<td>$\nu$(NH)</td>
<td>3125br,S</td>
<td>$\nu$(NH)</td>
<td></td>
</tr>
<tr>
<td>3015s</td>
<td>$\nu$(CH) cation</td>
<td>3015s</td>
<td>$\nu$(CH) cation</td>
<td></td>
</tr>
<tr>
<td>2975s</td>
<td>$\nu$(CH)</td>
<td>2975m</td>
<td>$\nu$(CH) cation</td>
<td>1.32</td>
</tr>
<tr>
<td>2925s</td>
<td>$\nu$(CH)</td>
<td>2125m</td>
<td>$\nu$(CD)</td>
<td>1.38</td>
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<td>1605w</td>
<td>$\delta_d$(NH)</td>
<td>1605w</td>
<td>$\delta_d$(NH)</td>
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<tr>
<td>1570w</td>
<td>$\delta_d$(NH)</td>
<td>1570w</td>
<td>$\delta_d$(NH)</td>
<td></td>
</tr>
<tr>
<td>1465w</td>
<td>$\delta_d$(CH) cation</td>
<td>1465w</td>
<td>$\delta_d$(CH) cation</td>
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<td>1430w</td>
<td>$\delta_d$(CH) cation</td>
<td>1430w</td>
<td>$\delta_d$(CH) cation</td>
<td></td>
</tr>
<tr>
<td>1465s</td>
<td>$\delta_d$(CH)</td>
<td>1082m</td>
<td>$\delta_d$(CD)</td>
<td>1.35</td>
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<td>$\delta_d$(CH)</td>
<td>1020m</td>
<td>$\delta_d$(CD)</td>
<td>1.40</td>
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<tr>
<td>1400s</td>
<td>$\delta_d$(CH)</td>
<td>1010sh</td>
<td>$\delta_d$(CD)</td>
<td>1.39</td>
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<td>1310s</td>
<td>$\delta_d$(CH)</td>
<td>not obs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1287s</td>
<td>$\delta_d$(CH)</td>
<td>not obs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1250w</td>
<td>$\nu$(CN)</td>
<td>1250w</td>
<td>$\nu$(CN)</td>
<td></td>
</tr>
<tr>
<td>1100br,s</td>
<td>$\nu$(SO)S-bond</td>
<td>1100s</td>
<td>$\nu$(SO)S-bond</td>
<td></td>
</tr>
<tr>
<td>1025s</td>
<td>$\rho$(CH)</td>
<td>819s</td>
<td>$\rho$(CD)</td>
<td>1.25</td>
</tr>
<tr>
<td>975m</td>
<td>$\rho$(CH)</td>
<td>785m</td>
<td>$\rho$(CD)</td>
<td>1.24</td>
</tr>
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cont'd......
Table 5.1 (cont'd...)

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Assignment(^{a,b})</th>
<th>Frequency</th>
<th>Assignment</th>
<th>(\nu(CH))/(\nu(CD))</th>
</tr>
</thead>
<tbody>
<tr>
<td>930(m)</td>
<td>(\rho r(CH))</td>
<td>765(m)</td>
<td>(\rho r(CD))</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>895(w)</td>
<td>Cation</td>
<td></td>
</tr>
<tr>
<td>843(w)</td>
<td>Cation</td>
<td>840(w)</td>
<td>Cation</td>
<td></td>
</tr>
<tr>
<td>820(m)</td>
<td>Cation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>714(m)</td>
<td>(\nu_a(CS))</td>
<td>625(m)</td>
<td>(\nu_a(CS))</td>
<td>1.14</td>
</tr>
<tr>
<td>675(m)</td>
<td>(\nu_s(CS))</td>
<td></td>
<td>Not obs.</td>
<td></td>
</tr>
<tr>
<td>422(s)</td>
<td>(\delta_s(CSO))</td>
<td>390(s)</td>
<td>(\delta_s(CSO))</td>
<td>1.08</td>
</tr>
<tr>
<td>386(m)</td>
<td>(\delta_a(CSO))</td>
<td>360(m)</td>
<td>(\delta_a(CSO))</td>
<td>1.07</td>
</tr>
<tr>
<td>347(m)</td>
<td>(\nu(Ru-Cl))</td>
<td>335(m)</td>
<td>(\nu(Ru-Cl))</td>
<td></td>
</tr>
<tr>
<td>293(m)</td>
<td>(\nu(Ru-Cl))</td>
<td>292(m)</td>
<td>(\nu(Ru-Cl))</td>
<td></td>
</tr>
<tr>
<td>266(m)</td>
<td></td>
<td></td>
<td>Not obs.</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Subscripts: \(\nu_a = \text{asym. str.}, \nu_s = \text{sym. str.}, \delta_d = \text{degenerate def.},\)
\(\delta_s = \text{sym. def.}, \delta_a = \text{asym. def.}, \rho r = \text{rocking}.\)

\(^{b}\) \(s = \text{strong}, m = \text{medium}, w = \text{weak}, sh = \text{shoulder}, br = \text{broad}.\)
unassigned but could be due to a methyl torsion mode \(^{70,72}\). The absence of a band at ca. 480 cm\(^{-1}\) in the spectra of \(1\) and \(2\), combined with the presence of such a band in the spectra of \(\text{RuCl}_2(\text{DMSO})_4\) \(^{11,12}\) makes possible a tentative assignment of this band as \(v(\text{Ru-O})\). This band in the spectrum of \(\text{RuCl}_2(\text{DMSO})_4\), where mixed S-and O-bonding occurs, has been previously assigned \(^{12}\) as either \(v(\text{Ru-O})\) or \(v(\text{Ru-S})\). Bands are assigned to the cation by comparison with those for known compounds \(^{74}\), although assignment of the exact vibrational mode is not possible in all cases.

5.2.2. Visible Spectra

Inspection of the solid state and solution spectra and use of the i.r. assignment, shows that the fac-isomer persists in both chloroform and DMA solutions (Table 5.II.). In water the initial solution spectrum of \(1\) is different and also slowly changes with time. On addition of chloride ion, the spectrum rapidly becomes the same as for the complex in chloroform or DMA. These data, together with the conductivity and the \(^1\text{H} \text{n.m.r.} \) data (Table 5.III.) indicate that on dissolution of the complex in water, rapid loss of chloride ligand occurs to give \(\text{RuCl}_2(\text{DMSO})_3(\text{H}_2\text{O})\), followed by slow loss of further chloride to give cationic ruthenium(II) species. Addition of chloride at any state regenerates the anion of \(1\).
Table 5.11.
Visible Spectra \(^a\) (nm) of \(\text{I}\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorbance max (log(c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid State(^b)</td>
<td>370, 330 sh</td>
</tr>
<tr>
<td>DMA</td>
<td>369(2.76), 325(2.47) sh</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>368(2.76), 325(2.58) sh</td>
</tr>
<tr>
<td>H(_2)O(6M-HCl)(^c)</td>
<td>369(2.76), 325(2.50) sh</td>
</tr>
<tr>
<td>H(_2)O(^d)</td>
<td>346(2.60), 215(2.51) sh</td>
</tr>
</tbody>
</table>

\(^a\) At R.T.

\(^b\) Nujol mull.

\(^d\) Cl\(^-\) added to suppress dissociation.

\(^e\) Initial spectrum, taken after dissolution.
5.2.3. \(^1\)H n.m.r. Spectra, (Table 5.III)

In CDCl\(_3\) the spectrum of the complex, \(\text{I}\) shows a singlet at 63.51 attributed to the eighteen equivalent methyl protons of the S-bonded DMSO ligands\(^{12,66}\). The presence of the singlet and the integration ratio of this peak to that due to the six methyl protons of the cation (a triplet at 62.68) indicate that in CDCl\(_3\) solutions the fac-isomer is present exclusively, and this is consistent with the visible spectral data. In D\(_2\)O the immediate spectrum of the complex after dissolution is different from that of the complex in CDCl\(_3\); the S-bonded DMSO ligands have peaks at 63.48, and 3.39 in a ratio of 2:1, and the cation has a peak at 62.71. Addition of chloride ion, as KCl or DCI, generates the same spectrum in the S-bonded DMSO region, as found for the complex dissolved in CDCl\(_3\). These spectral changes are consistent with those observed for the visible spectra. The two singlets observed in D\(_2\)O are due to a RuCl\(_2\)(DMSO)\(_3\)(D\(_2\)O) species, where two DMSO ligands are equivalent. Addition of chloride regenerates the fac-anion.

The DMSO ligands can be exchanged with d\(_6\)-DMSO ligands. Addition of ca. 10% by volume of d\(_6\)-DMSO to a CDCl\(_3\) solution of the complex results in the slow disappearance of the singlet due to the three S-bonded DMSO ligands. After 8 hr. the exchange is complete with the spectrum now consisting of a triplet at 62.68 due to the cation and a singlet at 62.60 due to free DMSO. The same exchange, only slower, occurs in D\(_2\)O with added chloride ion, the total exchange taking 16 hr.

\(^{\dagger}\) See also Chapter II, for spectral diagrams, (fig. 2.8.).
Table 5.III.

$^1$H n.m.r. Spectra of $^1$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$(Me)</th>
<th>Integration Ratio</th>
<th>Peak Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>3.51</td>
<td>3</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.68</td>
<td>1</td>
<td>t</td>
</tr>
<tr>
<td>D$_2$O(6M-DC1, in D$_2$O)$^a$</td>
<td>3.51</td>
<td>3</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.76</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td>D$_2$O$^b$</td>
<td>3.48</td>
<td>2</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>3.39</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.71</td>
<td>1</td>
<td>s</td>
</tr>
</tbody>
</table>

$^a$ Cl$^-$ added to suppress dissociation.

$^b$ Initial spectrum taken after dissolution.

s = singlet, t = triplet.
5.2.4. **Crystal Structure**

The solid state structure of the complex 1 is shown in fig. 5.1. Two crystallography non-equivalent anions are linked by two non-equivalent cations. The anions all have approximate octahedral co-ordination with three S-bonded DMSO ligands in a fac configuration, as predicted by the $^1$H n.m.r., and i.r. spectra. There is slight distortion of the octahedral environment, possibly due to steric interference between the DMSO groups; the Cl-Ru-Cl angles are slightly smaller than 90° (mean 87.6°), while those for S-Ru-S are slightly larger (mean 92.6°).

The strong trans-influence of S-bonded DMSO ligands is illustrated in the Ru-Cl distance (mean 2.426 Å) which is significantly longer than those for the mutually trans-chlorine atoms (mean 2.390 Å) in the octahedral complex $[\text{RuCl}_3(\text{N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2] \cdot \text{Me}_2\text{O}$. 77

5.3. $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{Me}^n\text{prSO})_3] \cdot 3$

This compound was prepared in an analogous way to 1, giving a bright yellow solid; recrystallization from DMA gave yellow cubes. The complex is a 1:1 electrolyte in DMA, under $N_2$ ($\Lambda^{22} = 46.0 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}$) and like the analogous DMSO compound, 1, the conductivity remains unchanged for 48 hr. The solubility characteristics of this complex are the same as for complex 1.

I wish to thank Anthony Mercer for this structure.
Figure 5.1. ORTEP drawing for $[\text{NH}_2\text{Me}_2]_2[\text{RuCl}_3(\text{DMSO})_3]$. 1
5.3.1. **I.r. Spectra, (Table 5.IV)**

The i.r. spectrum of the recrystallized complex is similar to that of complex 1. The presence of a strong band at 1105 cm\(^{-1}\) indicates S-bonded methyl n-propyl sulfoxide ligand, (for the free sulfoxide \(\nu(SO)=1050\) cm\(^{-1}\)). It is difficult to detect O-bonded sulfoxide since the region 930 - 970 cm\(^{-1}\) of the spectrum is complicated by the presence of bands due to methyl rocking modes\(^{11}\).

Deuteriated methyl n-propyl sulfoxide was not available to help simplify this region of the spectrum. Bands at 355 and 290 cm\(^{-1}\) indicate the complex is again the fac-isomer. A strong band at 3110 cm\(^{-1}\), assigned to \(\nu(NH)\) by comparison with complex 1, shows the presence of the \([\text{NH}_2\text{Me}_2]^+\) cation.

5.3.2. **\(^1\text{H n.m.r. Spectrum}^\dagger\), (Table 5.V)**

The \(^1\text{H n.m.r.}\) spectrum of the complex in CDCl\(_3\) confirms the structural data implied from the i.r. data. A singlet at 63.42 due to the methyl protons adjacent to the sulphur atom indicates S-bonded sulfoxide ligands while the integration ratio of this peak to that for the cation at 62.68 indicates that only S-bonded ligands are present. The singlet also indicates that the fac-isomer is present exclusively. The methylene protons of the carbon \(\alpha\) to the sulphur occur in the S-bonded region of the spectrum as a multiplet at 63.25 - 4.40. The methylene protons of the

\dagger See also Chapter II, (fig. 2.9.).
### Table 5.IV.

Selected i.r. spectral data (cm\(^{-1}\)) for 
\[ \text{[NH}_2\text{Me}_2\text{][RuCl}_3\text{(Me}^n\text{prSO)}_3] \]

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Assignment(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3110br,s</td>
<td>(\nu(\text{NH}))</td>
</tr>
<tr>
<td>1105s</td>
<td>(\nu(\text{SO}))(^b) S-bond</td>
</tr>
<tr>
<td>355m</td>
<td>(\nu(\text{Ru-Cl}))</td>
</tr>
<tr>
<td>290m</td>
<td>(\nu(\text{Ru-Cl}))</td>
</tr>
</tbody>
</table>

\(^a\) \(s = \text{strong, m = medium.}\)

\(^b\) Free ligand: \(\nu(\text{SO}) = 1050\).
Table 5.V.
N.m.r. \textsuperscript{a} spectrum of 3 and Me\textsuperscript{3}prSO

<table>
<thead>
<tr>
<th>δ (Assignment)</th>
<th>Integration Ratio for 3</th>
<th>Peak Type \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.42 (aCH\textsubscript{3})</td>
<td>2.50</td>
<td>s</td>
</tr>
<tr>
<td>3.25-4.40 (a-CH\textsubscript{2}-)</td>
<td>2.60</td>
<td>m</td>
</tr>
<tr>
<td>1.50-2.40 (β-CH\textsubscript{2}-)</td>
<td>1.45-2.00</td>
<td>m</td>
</tr>
<tr>
<td>1.08 (γCH\textsubscript{3})</td>
<td>1.10</td>
<td>t</td>
</tr>
<tr>
<td>2.68 (CH\textsubscript{3} cation)</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In CDC\textsubscript{13}.

\textsuperscript{b} s = singlet, t = triplet, m = multiplet
carbon are shifted downfield ca. 0.15 p.p.m. with respect to the free sulfoxide ligand and appear in the spectrum as a multiplet at 61.50 - 2.40. The γ carbon methyl group shows a small shift. As stated earlier, the downfield shift of the protons, on sulphur co-ordination becomes less with increasing distance from the sulphur atom; α-carbon > β-carbon > γ-carbon (=zero shift).

5.4. **Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II),** 4

As outlined previously, this compound is prepared by two methods; from the methanolic "blue solutions", and by H₂-reduction of RuCl₃·3H₂O in DMA in the presence of DMSO. Since both preparative routes give similar products only that from the methanolic "blue solutions" will be described in detail.

5.4.1. **RuCl₂(DMSO)₄** from a Methanolic "Blue Solution"

The crystalline solid, obtained from the reaction solution, can be recrystallized from methanol to give yellow cubes. Conductivity in DMA 69; (Λ²² = 0.70 cm²ohm⁻¹mol⁻¹) indicates a non-electrolyte, however the conductivity measured in air does increase with time to a value of ca. 28 cm²ohm⁻¹mol⁻¹ (48 hr). The solution is now dark green and the increased conductivity must be due to formation of some cationic Ru(II) and Ru(III) species. Air oxidation to give a green, presumably Ru(III) solution occurs with [NH₂Me₂][RuCl₃(DMSO)₃], RuBr₂(DMSO)₄ 67, and RuCl₂(DMSO)₄ as prepared by James et al. 11.
The compound 4 is quite air stable in the solid state, and its solubility characteristics are similar to those of 1. The former is much more soluble in chloroform and benzene.

5.4.2. I.r. Spectral Data

As the i.r. spectrum of compound 4 is virtually identical to that recorded for a supposedly cis-trans isomer mixture of RuCl\(_2\)(DMSO)_4, the i.r. band assignment of this can be used to assign some bands in our compound; these at 1120 and 1090 cm\(^{-1}\) indicate the presence of S-bonded DMSO ligands while a band at 920 cm\(^{-1}\) indicates O-co-ordinated DMSO.

Comparison of the spectrum of 4, in the region 370 - 295 cm\(^{-1}\), with that of RuBr\(_2\)(DMSO)_4 (this work and that of James et al.\(^{11}\)) allows the assignment of vibrations due to metal-chloride bonds, and one band at 344 cm\(^{-1}\) can be unambiguously assigned as \(\nu(\text{Ru-Cl})\). For a dichloro-complex two bands are expected for a cis-isomer and one for a trans-isomer. The presence of only one Ru-Cl band in complex 4 would indicate that the recrystallized product is exclusively the trans-isomer. However, this will be shown later to be incorrect, and the complex is in fact a cis-isomer.

5.4.3. \(^1\)H n.m.r. Spectra\(^+\)

The proton n.m.r. spectrum of compound 4 in CDCl\(_3\) is identical to that found by Wilkinson et al.\(^{12}\). Four singlets due to the methyl protons of the sulphur-bonded DMSO ligands occur at δ3.33, 3.42, 3.49, and

\(^+\) See also Chapter II, (fig. 2.8.).
3.52. The equivalent methyl protons of O-co-ordinated and free DMSO are observed at δ2.73 and 2.60 respectively. The integration ratio of the downfield singlets to the upfield pair indicate that compound 4 contains three S-bonded and one O-bonded DMSO ligand. The presence of four singlets for the S-bonded DMSO ligands may be readily rationalized. S-bonded ligands trans to Cl- or O-bonded DMSO could give two different methyl resonances. Extra methyl resonances could also result from a mixture of isomers of five-co-ordinate trigonal bipyramidal and square pyramidal structures. Wilkinson et al. suggests that some degree of methyl inequivalence could also be present, but this is not necessary to explain the four singlets. The closely spaced four singlets can not be unambiguously integrated to provide further information on the matter.

In D₂O, compound 4 has a more simple spectrum. In the S-bonded region there are two singlets at δ3.48 and 3.40 with a peak height ratio of about 2:1. There is a singlet at δ2.70 attributed to the equivalent methyl protons of free DMSO, and this assignment is confirmed by the addition of DMSO to the solution, with subsequent increase in the height of this peak. The integration ratio of the downfield pair of singlets to the free DMSO peak is 3:1, confirming that in D₂O the O-bonded DMSO dissociates. All possible octahedral RuCl₂(DMSO)₃(D₂O) isomers would give rise to the observed spectrum with the observed 2:1 integration ratio of S-bonded DMSO ligands.

The spectrum of compound 4 in 38% DC1/D₂O or on addition of 38% DC1 to the compound in D₂O consists of two singlets at δ3.47 and 3.13, with an integration ratio of 3:1 respectively. Addition of DMSO causes the
peak at 63.13 to increase in height. The peak at 63.47 can be attributed to the equivalent methyl protons of the fac-RuCl$_3$(DMSO)$_3^-$ anion. The peak at 63.13 is thought to be due to a DMSO·DCl adduct. The formation of the fac-trichloro isomer suggests that cis-RuCl$_2$(DMSO)$_3$(D$_2$O) is present in D$_2$O implying that compound 4 is cis-RuCl$_2$(DMSO)$_4$; this assumes that no rearrangement occurs in D$_2$O during the substitution of O-bonded DMSO by Cl$^-$.

5.4.4. **Crystal Structure**

The crystal structure of recrystallized compound 4 shows it to be the cis-isomer, with three S-bonded and one O-bonded DMSO ligands, (fig. 5.2.). The O-bonded sulphoxide is trans to a S-bonded DMSO.

The strong trans-influence of the S-bonded DMSO is apparent in this compound$^{51}$, as in compound 1. The Ru-Cl bond lengths (2.435 Å) are again significantly greater than would be expected if DMSO was purely a σ donor. The effect of S- and O-bonding on the S-O bond lengths and hence the multiple bond character of the S-O bond is clearly shown in this structure. The S-O bond length for S-bonded DMSO is 1.435 Å compared to 1.557 Å for the O-bonded case, while the estimated S-O single bond length is (1.70 Å)$^{51}$.

5.5. **Comparison of Different RuCl$_2$(DMSO)$_4$ Products**

As outlined, RuCl$_2$(DMSO)$_4$ has been prepared to date by five different preparative routes by four different research groups. The compound seems an important precursor for the synthesis of a wide range
Figure 5.2. ORTEP drawing for RuCl$_2$(DMSO)$_4$, 4
of ruthenium(II) complexes, and it is worthwhile to evaluate any differences in the products from the different preparations. Available spectral data for all the products are presented in Table 5.VI.

The i.r., $^1$H n.m.r. and visible spectral data presented show that the products from preparations I, IV, and V are the same, i.e., the cis-isomer with three S-bonded and one O-bonded DMSO ligands. Although one expects two $\nu$(Ru-Cl) bands for the cis-isomer only one band, at 344 cm$^{-1}$, has been assigned unambiguously to date. Spectra of I, II, IV and V contain weak bands at 330 cm$^{-1}$ and 295 cm$^{-1}$, either of which could be the second Ru-Cl band. The spectrum of RuBr$_2$(DMSO)$_4$ (see later), also contains a weak band at 330 cm$^{-1}$, and the assignment of this band as the second $\nu$(Ru-Cl) as done by Wilkinson et al.$^{12}$ is incorrect. $\nu$(Ru-Cl) bands at ca. 344 and 295 cm$^{-1}$ is similar to that found for $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$. Preparations I, II, IV and V give the same isomer product, however, preparation III appears to be a mixture of isomers; the additional methyl resonances in the $^1$H n.m.r. at 63.38 and 2.69 may be due to either a cis-chloride isomer with the O-bonded DMSO ligand trans to a chloride, or to a trans-chloride isomer.

5.6. RuBr$_2$(DMSO)$_4$  

This compound was prepared by the H$_2$ reduction of ruthenium(III) bromide in DMA solution containing excess DMSO. The preparation follows that for RuCl$_2$(DMSO)$_4$, except that a larger mole ratio of DMSO ligand to the ruthenium is used for the bromide. The $[\text{NH}_2\text{Me}_2][\text{RuBr}_3(\text{DMSO})_3]$ complex,
Table 5.VI.

Selected spectral data for RuCl$_2$(DMSO)$_4$

(I) Rempel, et al.$^{11}$, (II) Wilkinson, et al.$^{12}$, (III) Stephenson, et al.$^{67}$, (IV) This work from Methanolic "Blue Solutions"$^a$, (V) This work, from Reduction of RuCl$_3$·3H$_2$O in DMA.

<table>
<thead>
<tr>
<th></th>
<th>I.R.$^b$</th>
<th>1$^h$ n.m.r.$^c$ (CH$_3$)</th>
<th>Visible$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v(SO)</td>
<td>v(Ru-Cl)</td>
<td>S-bond</td>
</tr>
<tr>
<td>(I)</td>
<td>1100-1120</td>
<td>930</td>
<td>345,295</td>
</tr>
<tr>
<td>(II)</td>
<td>1120,1090</td>
<td>928</td>
<td>345,330, 295</td>
</tr>
<tr>
<td>(III)</td>
<td>-</td>
<td>930</td>
<td>-</td>
</tr>
<tr>
<td>(IV)</td>
<td>1110,1090</td>
<td>930</td>
<td>344,295</td>
</tr>
<tr>
<td>(V)</td>
<td>1110,1090</td>
<td>930</td>
<td>344,295</td>
</tr>
</tbody>
</table>

$^a$ Shown by crystal structure to be cis isomer.

$^b$ In cm$^{-1}$; nujol mull.

$^c$ In CDCl$_3$ relative to TMS.

$^d$ In nm; CHCl$_3$ solvent.

$^e$ A new band found on re-examination of the preparation.

$^f$ This band is not reported by the authors as v(Ru-Cl).
would probably be formed using a 3:1 stoichiometric amount of DMSO.

The product, \( 5_\)_, is an orange powder which has similar solubility and physical properties to \( \text{RuCl}_2(\text{DMSO})_4 \).

5.6.1. I.r. Spectrum

The i.r. spectrum of complex \( 5_\) has strong bands at 1080 and 944 cm\(^{-1}\) which on comparison with \( \text{RuCl}_2(\text{DMSO})_4 \) can be assigned as \( \nu(\text{SO}) \) (S-bonded), and \( \nu(\text{SO}) \) (O-bonded), respectively. The far i.r. contains a weak band at 330 cm\(^{-1}\), which could be due to a ligand methyl torsion mode.

5.6.2. \( ^1\text{H} \) n.m.r. Spectra

The \( ^1\text{H} \) n.m.r. spectrum of compound \( 5_\) in CDCl\(_3\) contains two singlets at 63.52 and 2.62 with an integration ratio of 2:1 respectively, Table 5.VII. Assignment of the peaks can be done on comparison with \( \text{RuCl}_2(\text{DMSO})_4 \) and previous work\(^67\); the 62.62 peak is then assigned to the six equivalent methyl protons of free DMSO, and the singlet at 63.52 is due to the eighteen equivalent methyl protons of the three S-bonded DMSO ligands. Addition of d\(_6\)-DMSO (ca. 10% by volume) to the CDCl\(_3\) solution of complex \( 5_\) results in the very rapid (<2 min) decrease in the peak at 63.52, a resultant growth in the peak at 62.62 and the growth of a new peak at 62.72. This new peak at 62.72 must be due to O-bonded DMSO. On dissolution of complex \( 5_\) in CDCl\(_3\) the O-bonded DMSO rapidly (<2 min) dissociates to give a \( \text{RuBr}_2(\text{DMSO})_3 \) species. The five co-ordinate

\(^*\) See also Chapter II, (fig. 2.8.).
Table 5.VII.

$^1\text{H n.m.r. spectra of } \text{RuBr}_2(\text{DMSO})_4$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$(Me)</th>
<th>Integration Ratio</th>
<th>Peak Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>3.52</td>
<td>3</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.62</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td>CDCl$_3^a$</td>
<td>2.72</td>
<td>-</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.62</td>
<td>-</td>
<td>s</td>
</tr>
<tr>
<td>D$_2$O$_b$</td>
<td>3.43</td>
<td>3</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td>4</td>
<td>s</td>
</tr>
</tbody>
</table>

$^a$ d$_6$-DMSO (10% by volume) added.

$^b$ Initial spectrum taken after dissociation.

s = singlet
species has a single S-bonded resonance and the structure of the species could be trigonal bipyramidal with the sulfoxides in the equatorial plane. Such a structure satisfies the steric requirements of the sulfoxide ligands, with the least steric interaction resulting for the sulfoxides in the equatorial plane. The site preference for axial and equatorial positions in a trigonal bipyramidal structure has been established. Axial bromides (σ-donor) and equatorial S-bonded sulfoxides (σ-donor, π-acceptor) satisfy this generality. Alternate explanations of the single S-bonded resonance for the five co-ordinate species are possible. Rapid equilibrium between two square pyramidal isomers through a trigonal bipyramidal intermediate could result in the observed spectra, as could rapid equilibrium between monomer and dimeric species. One would expect these spectra to consist of a broad singlet, (the square pyramidal and dimer species would result in two closely spaced singlets) rather than the observed sharp singlet.

The addition of the d₆-DMSO results in the formation of RuBr₂(d₆-DMSO)₃(DMSO), which appear to be in rapid equilibrium with RuBr₂(d₆-DMSO)₄ through the five co-ordinate species RuBr₂(d₆-DMSO)₃. If rapid exchange did not occur the only six co-ordinate species would be RuBr₂(d₆-DMSO)₄ and no singlet at 62.72 would be observed. Resonances in the S-bonded region are not present with added d₆-DMSO which implies that exchange with the S-bonded ligands is much less rapid. That the S-bonded are more substitution inert than O-bonded DMSO can be seen from the initial spectrum where the O-bonded DMSO is completely dissociated. With RuCl₂(DMSO)₄ addition of d₆-DMSO causes rapid loss of O-bonded DMSO
and a slower loss of S-bonded DMSO showing that O-bonded DMSO is more labile than the S-bonded DMSO. Comparison of the d₆-DMSO exchange rates \(^{12}\) of \(\text{RuCl}_2(\text{DMSO})_4\) and \(\text{RuBr}_2(\text{DMSO})_4\) shows that the S-bonded DMSO are more substitution inert in the chloro-complex. Since O-bonded d₆-DMSO rapidly exchanges with O-bonded DMSO in \(\text{RuBr}_2(\text{d}_6-\text{DMSO})_4\) and not in \(\text{RuCl}_2(\text{d}_6-\text{DMSO})_4\), the O-bonded ligand is less labile in the dichloro-complex. Thus all the sulphoxide ligands in \(\text{RuBr}_2(\text{DMSO})_4\) are more labile than in \(\text{RuCl}_2(\text{DMSO})_4\). The increased lability would appear to be an indication of the greater kinetic trans-effect of \(\text{Br}^-\) compared to \(\text{Cl}^-\). In rhodium(III) octahedral complexes\(^{79,80}\) this has been rationalized in terms of a greater degree of charge transfer to the rhodium from the softer \(\text{Br}^-\), resulting in a greater polarisability of the metal, or a softer or more class b character. The more covalent bond partially deprives the bond trans to it of \(\sigma\)-bonding orbitals\(^{81}\), and thus weakens that bond. It seems likely that the ruthenium sulphoxide system can be rationalized in terms of this same explanation. For \(\text{RuCl}_2(\text{DMSO})_4\) an \(S_{N1}\) mechanistic exchange goes via a trigonal pyramid or the more stable square pyramid intermediate\(^{82}\); the latter requiring rearrangement to ensure complete exchange. The pentagonal bipyramid intermediate of an \(S_{N2}\) mechanism is another possibility for complete exchange.

It is interesting to note that the spectrum of \(\text{RuBr}_2(\text{DMSO})_4\) in \(\text{CDCl}_3\) as reported by Stephenson et al.\(^{67}\) is composed of four singlets in the S-bonded region at 63.51, 3.48, 3.44, and 3.39, and one for free DMSO at 62.61, with relative intensity of the S-bonded to free DMSO being 3:1. The resonance at 63.51 corresponds to that we obtained; the extra
resonances could be due to some polymeric \( \text{RuBr}_2(\text{DMSO})_2 \) and \( \text{RuBr}_2(\text{DMSO})_4 \) (all S-bonded) species which would preserve the 3:1 integration ratio. This would be consistent with their findings, that the S-bonded peak intensities change with added DMSO; the i.r. spectrum was equivocal concerning the presence of O-bonded DMSO.

The \(^1\text{H} \text{n.m.r.} \) spectrum of complex 5 in \( \text{D}_2\text{O} \) is more complicated than that for \( \text{CDCl}_3 \). There are three singlets present at \( \delta 3.43, 3.33 \) and 2.70. The first two are due to S-bonded DMSO while the singlet at \( \delta 2.70 \) (in comparison with the spectrum of \( \text{RuCl}_2(\text{DMSO})_4 \) in \( \text{D}_2\text{O} \)) is due to free DMSO. The intensity ratio of the peaks is 3:1:4. This could best be explained by the presence of two species in solution; trans-\( \text{RuBr}_2(\text{DMSO})_2(\text{D}_2\text{O})_2 \) and cis-\( \text{RuBr}_2(\text{DMSO})_2(\text{D}_2\text{O})_2 \) (all ligands cis).

5.7. Reaction of [\( \text{NH}_2\text{Me}_2 \)]\( \text{[RuCl}_3(\text{DMSO})_3 \)] \text{and RuCl}_2(\text{DMSO})_4 \text{with Molecular Hydrogen}

In terms of potential use for catalytic hydrogenation both compound 1 and compound 4 were found to react with \( \text{H}_2 \) (1 atm) at 60°C in DMA, although the extent of the reaction was never more than 10%, (assuming a Ru: \( \text{H}_2 \) stoichiometry of 1:1). For complex 1 the total extent of hydrogen uptake was completed by 1500 secs, (\([\text{Ru}^{\text{II}}]=0.0195\text{M}, \text{and } [\text{H}_2]=0.97\times 10^{-3}\text{M}\)). For a similar solution, (\([\text{Ru}^{\text{II}}]=0.0108\text{M}, \text{and } [\text{H}_2]=0.95\times 10^{-3}\text{M}\)), equilibrated at 60°C under Ar, the extent of \( \text{H}_2 \) uptake was 14.8%. Similar solutions, (\([\text{Ru}^{\text{II}}]=0.03\text{M}, [\text{H}_2]=0.95\times 10^{-3}\text{M}\)), with added LiCl, (0.30M), or p-toluenesulphonic acid, (0.015M) had no measurable reaction with \( \text{H}_2 \). With the addition of a 3-fold excess of "Proton Sponge" \(^R\) (1,8-bis(dimethylamino)napthalene)\(^83\) a remarkably strong base in water (\( pK_a 12.34 \)), the extent of the reaction varied from 85-100% and is very rapid (<2000 sec., \([\text{Ru}]=10^{-2}\text{M}\)). These data strongly imply the possible formation of a ruthenium(II) hydride via the
heterocyclic cleavage of \( \text{H}_2 \):

\[
[RuCl_n(L)_{6-n}]^{2-n} + \text{H}_2 \rightleftharpoons [RuCl_{n-1}H(L)_{6-n}]^{2-n} + \text{HCl}
\]  

\( L \equiv \text{DMA or DMSO} \)

The addition of a strong base would cause the equilibrium to shift to the right. During the reactions the solutions change from a lemon yellow to a bright orange colour. At the end of the reaction the DMA could be pumped off to give a red oil which dissolved in \( d_6 \)-DMSO to give a red solution; the \( ^1\text{H} \) n.m.r. of the solution was recorded. The \( d_6 \)-DMSO was then pumped off, 5 ml of DMA added to give an orange solution, and ether added to precipitate a bright orange solid. After dissolving in acetone and filtering, the orange precipitate could be reprecipitated with more ether; this process removed some of the soluble proton sponge. The i.r. and \( ^1\text{H} \) n.m.r. of the orange solid were then recorded. The spectral data are presented in Table 5.VIII., and spectra in figs. 5.3 and 5.4. The n.m.r. of a reaction residue (after removal of DMA and dissolution in \( d_6 \)-DMSO) and the corresponding isolated orange solid in \( d_6 \)-DMSO, were the same.

The product from \( \text{RuCl}_2(\text{DMSO})_4 \) is similar to that from the anionic ruthenium(II) species; both have a group of resonances centred at ca. \( \delta \approx 22.6 \), a single resonance at ca. \( \delta \approx 27.6 \), and resonances due to free DMSO (\( \delta 26.1 \)) and S-bonded DMSO (ca. 63.4).

The i.r. spectrum of the orange product isolated from the \( \text{RuCl}_2(\text{DMSO})_4 \) system showed the presence of both S-bonded and O-bonded DMSO. The peaks at 1980 cm\(^{-1}\) and 2258 cm\(^{-1}\) are in the region for ruthenium(II) terminal hydrides \(^{84,85}\) although 2258 cm\(^{-1}\) seems an exceptionally high frequency. No evidence of a bridging hydride (ca. 1400 ± 200 cm\(^{-1}\)) could
Figure 5.3. $^1$H n.m.r. spectra of some hydride derivatives of $[\text{NH}_2\text{Me}_2]\text{[RuCl}_3(\text{DMSO})_3]$, 1 and RuCl$_2$(DMSO)$_4$, 4; 1) hydrides formed from 1 in $d_6$-DMSO ($n\text{H}_2/n\text{Ru} =1:1$), 2) the same solution after six days.
Figure 5.4. $^1$H n.m.r. spectra of some hydride derivatives of $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$, $\text{1}$ and $\text{RuCl}_2(\text{DMSO})_4$, $\text{4}$; 1) low field spectrum of hydrides formed from $\text{4}$ in $d_6$-DMSO ($n\text{H}_2/n\text{Ru} = 1:1$), 2) low field spectrum of hydrides formed from $\text{1}$ in $d_6$-DMSO ($n\text{H}_2/n\text{Ru} = 1:1$), 3) high field spectrum of hydrides formed from $\text{4}$ in $d_6$-DMSO ($n\text{H}_2/n\text{Ru} = 1:1$)
Table 5.VIII.

Spectral data for hydride derivatives of
(I) RuCl$_2$(DMSO)$_4$ and (II) [NH$_2$Me$_2$][RuCl$_2$(DMSO)$_3$]

<table>
<thead>
<tr>
<th></th>
<th>(I)</th>
<th>(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.r.$^a$</td>
<td>1980(w), 2258(w)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100(s), 935(s)</td>
<td>-</td>
</tr>
<tr>
<td>$^1$H n.m.r.$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>high field</td>
<td>$^d$ -24.56(4)$^c$, -22.68(1)</td>
<td>-27.70(4), -22.85(1), -22.65(1)</td>
</tr>
<tr>
<td></td>
<td>-22.48(1), -22.34(2)</td>
<td>-</td>
</tr>
<tr>
<td>ii) $^e$</td>
<td>-27.56(2), -22.68(1)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-22.48(1), -22.34(2)</td>
<td>-</td>
</tr>
<tr>
<td>iii) $^f$</td>
<td>-</td>
<td>-27.70(1), -22.85(1), -22.65(1), -22.45(4)</td>
</tr>
<tr>
<td>low field</td>
<td>3.35, 3.55, 3.69, 2.61</td>
<td>3.38, 3.45, 2.61</td>
</tr>
</tbody>
</table>

$^a$ In cm$^{-1}$; nujol mull.

$^b$ In d$_6$-DMSO; p.p.m. relative to TMS; for either isolated orange solid or initial reaction mixture residue. All peaks are singlets. Solutions under Ar.

$^c$ Relative Peak Intensity in parentheses.

$^d$ Reaction complete nH$_2$/nRu = 1:1

$^e$ Reaction 50% complete nH$_2$/nRu = 0.5:1

$^f$ Solution spectrum of II measured again after six days.

s = strong, w = weak
be found, although this region of the spectrum is obscured with other bands.

The low field n.m.r. is indicative of S-bonded DMSO ligands. The 62.61 peak is due to either S-bonded or O-bonded DMSO ligands that have exchanged with d₆-DMSO. Whether O-bonded ligands are present cannot be discerned from these n.m.r. data. The high-field n.m.r. spectra contain exceptionally high-field hydride resonances. The usual range for ruthenium hydrides is 7 - 20 p.p.m. above T.M.S.⁸⁴, although complexes of other metals with high hydride shifts exist, e.g., the complex HRhCl₂(PBu₂Me)₂ with δ-30 has been reported by Masters et al.⁸⁶

They attribute the high chemical shift to a very short metal-hydrogen distance for a hydride in the apical position of a square pyramidal structure. Johnson et al.⁸⁷ have suggested that, for derivatives of the same metal, the resonance of bridging hydrogen appears at higher field than that of terminally bonded hydrogen. Comparison of H₂Mn(CO)₅, δ - 7.5, and H₃Mn₃(CO)₁₂, δ - 24.0 would appear to bear this out. Bridging hydrides are known to be present in α-H₄Ru₄(CO)₁₂, where the hydride shift is δ - 17.6. Kaesz and Saillant⁸⁴ suggest that a hydride trans to a ligand of low trans-influence has a higher chemical shift than one trans to a ligand of high trans-influence. Compare for example, H₂RuCl(PPh₃)₃, δ - 17.44, where the hydride is trans to Cl⁻ and cis-H₂RuCO(PPh₃)₃, δ - 6.69, where the hydride is trans to phosphine or carbonyl. Thus a hydride trans to chloride or O-bonded sulphoxide would have a higher chemical shift than a hydride trans to S-bonded sulphoxide. Utilizing the above data, one can speculate on the nature of the chlorohydridoruthenium(II) species, although the system is clearly complex. The high field resonance,
ca. δ - 27, could be due to bridging hydride possibly trans to a chloride or O-bonded DMSO, while the lower field resonance, ca. δ - 22, could be due to a terminal hydride again with the hydride possibly trans to chloride or O-bonded DMSO. Since the extent of reaction determines the relative intensity of the lower to higher field resonances, one would have to postulate the existence of both bridging- and terminal-hydride species. The disappearance of the δ - 27 resonance with time with concomitant growth of a peak at ca. δ - 22 could be consistent with a process involving dissociation of a bridging hydride species into a species containing a terminal hydride. The presence of more than one resonance at ca. δ - 22 could be due to different isomers of the terminal hydride species, although it is surprising that the integration ratio is invariant with time. This discussion of the hydride systems is clearly highly speculative and difficult to justify and a detailed interpretation of the data would require considerable more work. The only real conclusion is that hydrides are formed.

5.8. Catalytic Hydrogenation of Some Olefins with Some Anionic and Neutral Sulphoxide Complexes

The \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\) complex, the corresponding methyl n-propyl sulphoxide complex and \(\text{RuCl}_2(\text{DMSO})_4\) all catalytically hydrogenate acrylamide to proponamide under mild conditions (1 atm \(\text{H}_2\), 60°C) in DMA. The proponamide was isolated from the reaction mixture and identified by n.m.r. Under comparable conditions, i.e., similar concentrations of olefins, catalyst and hydrogen, all three catalysts have similar hydro-
genation rates. The catalyst systems display similar hydrogen uptake curves, (fig. 6.4; Chapter VI); an initial faster reaction, gradually slows down to give linear uptake, the rates of which are given in Table 5.IX. The kinetics and mechanism for the hydrogenation of acrylamide with the $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$ catalyst is presented in detail in Chapter VI.
Table 5.IX.

Hydrogenation rates\(^a\) for \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\),
\([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{Me}^n\text{prSO})_3]\), and \(\text{RuCl}_2(\text{DMSO})_4\)
in DMA with acrylamide substrate

<table>
<thead>
<tr>
<th></th>
<th>pH(_2) mm</th>
<th>[acrylamide]</th>
<th>[Ru(^{II})]</th>
<th>10(^6) linear rate, Ms(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I)</td>
<td>728</td>
<td>0.50</td>
<td>0.0050</td>
<td>1.24</td>
</tr>
<tr>
<td>II)</td>
<td>730</td>
<td>0.54</td>
<td>0.0050</td>
<td>1.18</td>
</tr>
<tr>
<td>III)</td>
<td>704</td>
<td>0.50</td>
<td>0.0053</td>
<td>1.32</td>
</tr>
</tbody>
</table>

I) \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\).
II) \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{Me}^n\text{prSO})_3]\).
III) \(\text{RuCl}_2(\text{DMSO})_4\).

\(^a\) Linear uptake region; at 60°C in DMA (5 ml).
CHAPTER VI

HOMOGENEOUS HYDROGENATION OF ACRYLAMIDE

USING DIMETHYLAMMONIUM TRICHLOROTRIS(DIMETHYL SULPHOXIDE)RUTHENATE(II) AS CATALYST

6.1. Introduction

The title catalyst is effective for the hydrogenation of some unsaturated organic substances. In DMA at 60°C at hydrogen pressures less than 1 atm, acrylamide and methylvinyl ketone are hydrogenated to proponamide and ethylmethyl ketone, respectively. Under the same conditions, hex-1-ene and cyclohexene are not hydrogenated. In aqueous solution under the same mild conditions the activated substrates are not hydrogenated, although the ruthenium complex is readily soluble. The physical properties of the catalyst are described in the previous chapter.

6.2. Determination of the Equilibrium Constant for the DMSO Dissociation from the Complex

In DMA at 60°C under 1 atm argon the title catalyst was found to dissociate dimethyl sulphoxide. Fig. 6.1. shows the U.V./Visible spectral changes of the catalyst with time, while fig. 6.2. shows the equilibrium spectrum with various amounts of added DMSO; addition of Cl did not alter this equilibrium spectrum. The dissociation of DMSO is very
Figure 6.1. U.v./visible spectral changes of $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$, 1 in DMA at 60°C; $[\text{Ru}]_T = 0.00118M$, pAr = 655mm; time after solution attained; 1) 80 sec, 2) 1050 sec, 3) 3200 sec, 4) 11,200 sec. b = DMA baseline.
Figure 6.2. Effect of added DMSO on the spectrum of 1 in DMA at 60°C; 1) \([Ru]_T = 0.00102 \text{M at } 25^\circ\text{C, [DMSO]} = 0.0,\)

2) \([Ru]_T = 0.00118 \text{M, [DMSO]} = 0.0,\) 3) \([Ru]_T = 0.00120 \text{M, [DMSO]} = 0.006 \text{M},\)

4) \([Ru]_T = 0.00112 \text{M, [DMSO]} = 0.0012 \text{M}.\)

\(\text{pAr} = 650 \text{mm.} \quad b = \text{DMA baseline.}\)
slow, (ca. 12,000 sec) with relatively small spectral changes; analysing the spectrophotometric data of fig. 6.2., according to eqn. (6.1) gives a $K_D$ value of $(1.9 \pm 0.2) \times 10^{-3} \text{M}$, (see below).

\[
\begin{align*}
\text{RuCl}_3(\text{DMSO})_3^- & \underset{K_D}{\overset{}{\rightleftharpoons}} \text{RuCl}_3(\text{DMSO})_2^- + \text{DMSO} \\
\text{(I)} & \text{(II)}
\end{align*}
\]

An iterative method of determining $K_D$ was employed since only the extinction coefficients of species I were known; these values were obtained at room temperature with the knowledge that dissociation is extremely slow at this temperature. The extinction coefficients were taken to be approximately constant between 20°C and 60°C. The method for calculating the dissociation constant is presented below.

Before dissociation $[I] = \text{Ru}_T; [II] = 0; [\text{DMSO}] = D_0$;
at equilibrium $[I] = \text{Ru}_T - [II]; [\text{DMSO}] = D_0 + [II]$.
The total equilibrium absorbance $A$ is given by;

\[
A = \epsilon_1[I] + \epsilon_2[II]; \quad A = A_0 + \Delta\epsilon[II] \quad \text{and}
\]

\[
\Delta A = \Delta\epsilon[II] \quad \text{where} \quad \Delta\epsilon = \epsilon_2 - \epsilon_1,
\]

$\Delta A = A - A_0$, and $\epsilon_1$ and $\epsilon_2$ are the molar extinction coefficients of species I and II, respectively.

Using

\[
K_D = \frac{[II](D_0 + [II])}{\text{Ru}_T - [II]} \]

gives

\[
\frac{\text{Ru}_T}{\Delta A} = \frac{(D_0 + \Delta A/\Delta\epsilon)}{\Delta\epsilon K_D} + (\Delta\epsilon)^{-1}. \quad (6.2)
\]
Experimental data were collected for equilibria at an approximately constant total ruthenate concentration with varying amounts of added dimethyl sulfoxide ligand. Mathematically a value of $\Delta \varepsilon$ is guessed and a linear plot of $\text{Ru}^{4+}/\Delta A$ versus $(D_0 + \Delta A/\Delta \varepsilon)$ is constructed. The slope of the plot (eqn. 6.2) gives $K_D$ and the intercept $\Delta \varepsilon$. With this new $\Delta \varepsilon$ a new plot of $\text{Ru}^{4+}/\Delta A$ vs $(D_0 + \Delta A/\Delta \varepsilon)$ is done resulting in a new value of $\Delta \varepsilon$ and $K_D$. This process was repeated until successive $K_D$'s were within 2% of each other. Table 6.I. lists experimental data, and 6.II. the determined values of $K_D$ and extinction coefficients. The % dissociation of species I at the concentration used ($=10^{-3}M$) varied from 69% with no added DMSO to 53% with 0.0012 M added DMSO. This satisfies the criterion that reliable values of equilibrium constants are obtained only if the extent of dissociation in the experiments is between 20% and 80%. The determination of the equilibrium constant is subject to some errors. The long times required to establish equilibria produce a base line drift due to evaporation of DMA; however, a fairly good isosbestic point is obtained at ca. 420 nm and 365 nm for each dissociation experiment, fig. 6.1.† With no added DMSO the first order dissociation rate constant, measured from initial rate data, was $2.6 \times 10^{-4} s^{-1}$; using the value for $K_D$ the reverse DMSO complexation rate constant was $0.14 M^{-1} s^{-1}$.

† With larger amounts of added DMSO good isosbestic points were not obtained, perhaps due to formation of some tetrakis(DMSO) species.
TABLE 6.1.

Spectrophotometric data for the dissociation of DMSO from the RuCl$_3$(DMSO)$_3^-$ anion

<table>
<thead>
<tr>
<th>$10^3 D_0$ (M)</th>
<th>$10^3 Ru_T$ (M)</th>
<th>450 nm</th>
<th>460 nm</th>
<th>350 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>$A_0$</td>
<td>$A$</td>
</tr>
<tr>
<td>0</td>
<td>1.18</td>
<td>.19</td>
<td>.04</td>
<td>.19</td>
</tr>
<tr>
<td>0.60</td>
<td>1.20</td>
<td>.17</td>
<td>.04</td>
<td>.18</td>
</tr>
<tr>
<td>1.20</td>
<td>1.12</td>
<td>.15</td>
<td>.04</td>
<td>.14</td>
</tr>
</tbody>
</table>
**TABLE 6. II.**

Equilibrium constant and extinction coefficients for the RuCl$_3$(DMSO)$_3^-$ anion system

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\varepsilon_1$ (cm$^{-1}$M$^{-1}$)</th>
<th>$\varepsilon_2$ (cm$^{-1}$M$^{-1}$)</th>
<th>$10^3$ $K_D$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>460</td>
<td>23.5</td>
<td>219</td>
<td>2.0</td>
</tr>
<tr>
<td>450</td>
<td>33.5</td>
<td>214</td>
<td>2.2</td>
</tr>
<tr>
<td>350</td>
<td>371</td>
<td>613</td>
<td>1.6</td>
</tr>
</tbody>
</table>
6.3. **Spectral Observations on the RuCl₃(DMSO)₃⁻ Anion**

In the presence of a large excess of acrylamide (0.4 M), RuCl₃(DMSO)₃⁻ (0.001 M) showed the same spectral changes as observed under the same conditions without acrylamide, (fig. 6.1.). The catalyst (0.001 M) under 1 atm H₂ also showed the same spectral changes. These data suggest that little reaction occurs between the catalyst species, either (I) or (II) with either H₂ or acrylamide separately. A rapid reaction of the catalyst with H₂ to a small extent, (as monitored by gas-uptake), was observed with a more concentrated catalyst solution, (see Section 5.7., Chapter V).

In the presence of both acrylamide (0.4 M) and H₂ (1 atm), however, the catalyst solution (0.001 M) exhibits significantly larger spectral changes, (fig. 6.3.). Most of the change occurs before 3300 secs and is especially noticeable in the region 350 to 390 nm. In the region 400 to 500 nm the spectral changes are similar to those observed for the loss of the DMSO ligand. Consideration of these data together with the kinetic data, (see Section 6.4.), suggests a possible interpretation in terms of formation of a Ru-hydrido-olefin and/or Ru-alkyl complex (following DMSO dissociation), which reaches a near constant concentration after about 3300 secs.

---

† Comparison of these times with those for the gas-uptake experiments must be done with caution since the spectral measurements and these reactions could be in part diffusion controlled as the solutions were not continually agitated.
Figure 6.3. Effect of added acryl and \( \text{H}_2 \) on the spectrum of 1 in DMA at 60°C; \([\text{Ru}]_T = 0.00103\text{M}, \text{[acryl]} = 0.39\text{M}, \text{pH}_2 = 670\text{mm};\) time after reactants combined; 1) 80 sec, 2) 530 sec, 3) 1410 sec, 4) 3300 sec, 5) 4950 sec. \(b\) = DMA baseline.
6.4. Catalytic Hydrogenation of Acrylamide

The kinetics of acrylamide hydrogenation using DMA solutions of $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$, (0.005 - 0.05 M), were studied under varying conditions of substrate concentrations, hydrogen pressure, catalyst concentrations and added DMSO and acid concentrations, by measuring the gas-uptake rate of the reaction solution. The gas-uptake experiments were conducted as outlined previously in Chapter II. The total uptake of hydrogen indicated complete reduction of acrylamide, while n.m.r. identified the product as proponamide. Fig. 6.4., shows gas-uptake plots under varying conditions; the curves have an initial non-linear region followed by a linear region. The linear region extends to about 60% of the total uptake and then the rate begins to fall off slowly. The initial non-linear region lasts≈1500 secs, and in all cases except with added chloride and DMAHCl involves a decreasing rate of uptake with time. With added chloride and DMAHCl the non-linear region involves increasing rate with time, (autocatalytic type). The linear uptake rates were measured usually between 2000 and 8000 secs and are tabulated in Table 6.III.

6.4.1. Dependence on Dimethyl Sulphoxide Concentration

A plot of the linear rate of acrylamide hydrogenation against the added concentration of DMSO with other parameters fixed is shown in fig. 6.5. The rates vary inversely with added DMSO concentration and at high $[\text{DMSO}]$ approach a limiting value. A plot of the reciprocal rate versus the added DMSO concentration is linear, (fig. 6.6.).
Figure 6.4. H₂ uptake plots for the reduction of acryl using Ru in DMA at 60°C.
TABLE 6.III.

Linear hydrogenation rates for the reduction of acrylamide in DMA at 60°C using 

\[ (\text{NH}_2\text{Me}_2)[(\text{RuCl}_3(\text{DMSO})_3)] \]

<table>
<thead>
<tr>
<th>[RuII] x10³</th>
<th>pH₂</th>
<th>[H₂] x10³</th>
<th>[acrylamide]</th>
<th>Linear Rate x10⁷ Ms⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.01</td>
<td>728</td>
<td>2.06</td>
<td>0.011</td>
<td>3.84</td>
</tr>
<tr>
<td>5.00</td>
<td>728</td>
<td>2.06</td>
<td>0.011</td>
<td>4.11</td>
</tr>
<tr>
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<td>0.026</td>
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<tr>
<td>5.00</td>
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<td>0.053</td>
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<tr>
<td>4.98</td>
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<td>2.06</td>
<td>0.179</td>
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<td>1.88</td>
<td>12.34</td>
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<tr>
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<tr>
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<tr>
<td>21.9</td>
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Table 6.III. (cont'd)

<table>
<thead>
<tr>
<th>[RuII] x10³</th>
<th>pH₂ nm</th>
<th>[H₂] x10³</th>
<th>[acrylamide]</th>
<th>Linear Rate x10⁷ Ms⁻¹</th>
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<td>7.73ᵏ</td>
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<tr>
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<td>728</td>
<td>2.06</td>
<td>0.478</td>
<td>3.60¹</td>
</tr>
</tbody>
</table>

Added DMSO: ᵃ 0.036 M; ᵇ 0.065 M; ᶜ 0.190 M.
Added LiCl: ᵈ 0.033 M; ᵉ 0.067 M; ᶠ 0.104 M; ᵍ 0.132 M; ʰ 0.631 M.
Added p-toluene sulphonie acid: ⁱ 0.023 M; ʲ 0.096 M; ᵏ 0.191 M.
Added DMAHCl; ¹ 0.043 M.
Figure 6.5. Dependence of linear rate on added DMSO; 
[\text{Ru}]_T = 0.005 \text{M}, [\text{acryl}] = 0.49 \text{M}, \text{pH}_2 = 728 \text{mm}

Figure 6.6. Plot of (linear rate)$^{-1}$ vs added [DMSO]; 
[\text{Ru}]_T = 0.005 \text{M}, [\text{acryl}] = 0.49 \text{M}, \text{pH}_2 = 728 \text{mm}
6.4.2. Dependence on Acrylamide Concentration

The uptake rates at constant hydrogen and total catalyst concentration with the absence of added DMSO and acid vary non-linearly with increasing acrylamide concentration to a constant value (fig. 6.7.), indicating that the olefin dependence varies between first and zero order. With added acid, the rate dependence on [acrylamide] from 0.46 to 1.04 M, becomes greater than zero order. An unusual feature of the substrate dependence is that the rate extrapolated to zero olefin concentration appears to give a positive intercept of ≈3 x 10⁻⁷ Ms⁻¹, and (fig. 6.8.), a "reciprocal plot" of rate⁻¹ versus [acrylamide]⁻¹, tends to support this, since such plots are commonly linear when used to analyse for an olefin dependence which starts at the origin and goes from first to zero order.

6.4.3. Dependence on Hydrogen Pressure

At 0.005 M Ru(II), and 0.47 M acrylamide the variation of rate with hydrogen pressure is non-linear, (fig. 6.9.). The dependence is going from first to zero order with increasing hydrogen pressure up to 1 atm. Fig. 6.10, a plot of (rate)⁻¹ vs [H₂]⁻¹ is linear. At 0.005 M Ru(II) and 0.011 M substrate the rate is now first order in hydrogen up to 1 atm. (fig. 6.11.).

6.4.4. Dependence on Catalyst Concentration

Plots of rate vs catalyst concentration at constant high concentration of hydrogen and two high concentrations of acrylamide are non-
Figure 6.7. Dependence of linear rate on [acryl]; [Ru]_T = 0.005M, pH_2 = 728mm
Figure 6.8. Plot of \((\text{linear rate})^{-1}\) vs \([\text{acryl}]^{-1}\); \([\text{Ru}]_T = 0.005\text{M},\) \(\text{pH}_2 = 728\text{mm}\)
Figure 6.9. Dependence of linear rate on $[H_2]$; $[Ru]_T = 0.005M$, [acryl] = 0.47M

Figure 6.10. Plot of $(\text{linear rate})^{-1}$ vs $[H_2]^{-1}$; $[Ru]_T = 0.005M$, [acryl] = 0.47M
Figure 6.11. Dependence of linear rate on $[\text{H}_2]$; $[\text{Ru}]_T = 0.005\text{M}, [\text{acryl}] = 0.011\text{M}$.
linear, (fig. 6.12.). The initial first order dependence up to 0.015 M total catalyst concentration drops towards zero order at higher concentrations of catalyst, and this decrease in order occurs at lower concentration of catalyst when the substrate concentration is lower. The inverse plot, \((R^{-1} \text{ vs } [\text{Ru}^{II}]_{T}^{-1})\), at 0.52 M substrate concentration, shows a slight curvature, (fig. 6.13.), while that at 1.10 M acrylamide is linear, (fig. 6.14.).

6.4.5. Dependence on Added Acid

Fig. 6.15 shows that there is a very small inverse dependence of rate on added p-toluenesulphonic acid at constant total catalyst = (0.005 M), acrylamide = (0.48 M), and hydrogen = (.00206 M), concentrations. Plots of Rate\(^{-1}\) vs \([\text{H}^+]\)\(^{-1}\) were not linear and this implies a non-regular inverse dependence of rate on added p-toluenesulphonic acid. Under the same catalyst and hydrogen concentrations but with [acrylamide] = 0.085 M and added \([\text{H}^+]\) = 0.030 M, (p-toluenesulphonic acid), a total inhibition of hydrogenation occurred.

With the same catalyst and hydrogen concentrations as used above but with [acrylamide] = 0.478 M and [DMAHCl] = 0.043 M the hydrogenation rate was \(3.60 \times 10^{-7} \text{ Ms}^{-1}\), lowered from the value for a comparable experiment without added DMAHCl, implying an inverse acid dependence.

6.4.6. Dependence on Added LiCl

Addition of 0.03 M LiCl to the catalyst solutions in the presence of 0.5 M acrylamide, (see Table 6.III.), resulted in a small rate
Figure 6.12. Dependence of linear rate on $[\text{Ru}^{\text{II}}]_T$; $\text{pH}_2 = 728 \text{mm}$, $\square [\text{acryl}] = 0.52 \text{M}$, $\circ [\text{acryl}] = 1.10 \text{M}$
Figure 6.13. Plot of \((\text{linear rate})^{-1}\) vs \([\text{Ru}^{II}]_T\); 
\[\text{pH}_2 = 728 \text{mm}, [\text{acryl}] = 0.52 \text{M}\]

Figure 6.14. Plot of \((\text{linear rate})^{-1}\) vs \([\text{Ru}^{II}]_T\); 
\[\text{pH}_2 = 728 \text{mm}, [\text{acryl}] = 1.10 \text{M}\]
Figure 6.15. Dependence of linear rate on added p-toluenesulphonic acid; [Ru]$^+_T=0.005\text{M}$, [acryl] =0.48M, pH$_2$ =728mm
increase (ca. 1.1 times). Further addition up to 0.10 M LiCl resulted in a maximum rate increase (1.4 times), and further increase up to 0.63 M LiCl resulted in rate decrease. The overall effect of added chloride is small.

6.5. Discussion of Kinetic Results

As shown in Chapter V, (Section 5.7.), the RuCl$_3$(DMSO)$_3$ anion does react rapidly to a small extent with hydrogen and the promotion of the reaction in the presence of added base and the complete inhibition of the reaction in the presence of chloride or acid indicates a net heterolytic splitting of the H$_2$. This, together with the inverse acid dependence, and the shape of the initial H$_2$ uptake curve in the presence and absence of acrylamide suggests a "hydride path" reduction i.e., the transfer of hydrogen to the olefin occurs via a process involving addition of olefin to a ruthenium(II) hydride, (eqn. (6,3)).

\[
\text{Ru}^{II} + H_2 \underset{K_1}{\overset{}{\rightleftarrows}} \text{RuH}^- + \text{HCl} \\
\text{RuH}^- + \text{olefin} \underset{K_2}{\overset{}{\rightleftarrows}} \text{Ru-alkyl} \overset{H^+}{\rightarrow} \text{Products} \quad (6,3)
\]

Using the gas-uptake data of Section 5.7., an approximate maximum value for $K_1$, the equilibrium constant for the H$_2$ reaction with the [RuCl$_3$(DMSO)$_3$]$^-$ anion, (eqn. (6,3)), is calculated to be 0.1; it is assumed that a negligible amount of [RuCl$_3$(DMSO)$_2$]$^-$ species are involved in this reaction due to the long times required for sulphone disassociation and the short period over which gas-uptake is measured.
The visible spectral evidence also shows a fairly rapidly formed intermediate, possibly a hydrido-olefin or alkyl complex, implying that both the equilibria for hydride formation and subsequent olefin complexation are rapidly established.

Hydrogen could also be activated via an "unsaturate path", in which an olefin complex reacts correspondingly with hydrogen, eqn. (6,4).

\[ \text{Ru}^{II} + \text{olefin} \rightleftharpoons K' \quad \text{Ru olefin} \quad \overset{\text{H}_2}{\text{-HCl}} \quad \text{Ru alkyl} \rightleftharpoons \text{products} \quad (6,4) \]

Such a heterolytic cleavage of hydrogen could also give rise to the observed inverse acid dependence. Processes such as;

\[ \text{Ru}^{II}(\text{olefin}) + \text{H}_2 \rightleftharpoons \text{H}_2\text{Ru}^{IV}(\text{olefin}) \]

\[ \overset{\uparrow \text{olefin}}{\text{Ru}^{II}} + \text{products} \rightleftharpoons \overset{\downarrow}{\text{HRu(alkyl)}} \quad (6,5) \]

or the corresponding hydride route;

\[ \text{Ru}^{II} + \text{H}_2 \rightleftharpoons \text{H}_2\text{Ru}^{IV} \overset{\text{olefin}}{\rightleftharpoons} \text{H}_2\text{Ru}^{IV}(\text{olefin}) \quad (6,6) \]

as written show no acid dependence. There is as yet no precedent in the literature for such processes involving Ru(II) complexes, (see Chapter VIII). There is no visible spectral evidence for the olefin equilibrium \((K')\) in a process shown in eqn. (6,4). Both reactions (6,3) and (6,4) are written as involving loss of HCl rather than a solvated proton; this seems highly likely whether the processes involve a direct hydride substitution, or an initial oxidative addition followed by reductive elimination,
since the HCl can be stabilized as the DMA·HCl adduct\(^{15}\). The dependence on added DMSO as well as the visible spectral evidence, suggests that at least one active catalyst species in solution has lost a DMSO ligand. The positive intercept of the rate vs [acrylamide] plot, (fig. 6.7.), implies that a catalyst species functions by a path independent of the amount of substrate present in solution. Scheme 6-A, involving the hydride pathways of eqn. (6,3) is the most satisfactory for accounting for the observed kinetic and spectra data.

\[
\begin{align*}
(I) & \quad \text{RuCl}_3S_3^- + H_2 \xrightarrow{\text{fast}} \frac{K_1}{K_D} \xrightarrow{\text{fast}} \text{HRuCl}_2S_3^- + HCl \\
(II) & \quad \text{RuCl}_3S_2^+ + S \xrightarrow{\text{slow}} \xrightarrow{k_4} \text{HRuCl}_2S_2^- + \text{olefin} \\
(V) & \quad \text{HRuCl}_2S_2^- + \text{olefin} \xrightarrow{\text{fast}} \text{RuCl}_2S_2^- + \text{alkyl} \\
(VI) & \quad \text{HRuCl}_2S_2^- + \text{olefin} \xrightarrow{\text{fast}} \xrightarrow{k_6} \text{HCl} \\
(IV) & \quad \text{RuCl}_2S_2^- + \text{sat. product}
\end{align*}
\]

SCHEME 6-A

(solvent molecules excluded; \(S = \text{DMSO}\))

\(K_1\) is the equilibrium constant for hydride formation, \(K_D\) is the equilibrium constant for sulphoxide dissociation, (see Section 6.2.), \(K_2\)
is the equilibrium constant for olefin binding to give a hydrido-olefin complex (III), $k_3$ is the rate constant for a process involving isomerization of (III) and hydride transfer steps, $k_4$ is the rate constant for a rate determining $H_2$ addition to the bis-sulphoxide species (V), $k_5$ is the rate constant for the process of olefin complexation to (VI) and subsequent insertion into the metal-hydride bond, and $k_6$ is the rate constant for the final protonolysis step yielding saturated product and regenerated catalyst species (V). The mechanistic pathways, when steady concentrations of species (I-III) and (V) have built up, (linear uptake region), leads to the following rate expression;

$$\text{Rate} \equiv R = \frac{-d[H_2]}{dt} = k_3[III] + k_4[V][H_2] \quad \text{(6,7)}$$

$$R = \frac{k_1k_2k_3[I][H_2][\text{olefin}]}{[\text{HCl}][S]} + \frac{k_Dk_4[I][H_2]}{[S]} \quad \text{(6,8)}$$

The total ruthenium(II) concentration, $[\text{Ru}^{II}]_T$, is given by;

$$[\text{Ru}^{II}]_T = [I + II + III + V] \quad \text{(6,9)}$$

the concentrations of species IV and VI are negligible due to the fast reaction steps governed by $k_5$ and $k_6$.

Eqn. (6,9) can be rewritten to give;

$$[\text{Ru}^{II}]_T = [I] \left(1 + \frac{K_1[H_2]}{[\text{HCl}]} + \frac{K_1k_2[H_2][\text{olefin}]}{[\text{HCl}][S]} + \frac{K_D}{[S]}\right) \quad \text{(6,10)}$$
Hence:

\[ R = \frac{K_1K_2K_3[Ru^{II}]_T[H_2][olefin]}{[HCl][S] + K_1[H_2][S] + K_1K_2[H_2][olefin] + K_D[HCl]} \]

\[ + \frac{K_Dk_4[Ru^{II}]_T[H_2]}{[S] + \frac{K_1[H_2][S]}{[HCl]} + \frac{K_1K_2[H_2][olefin]}{[HCl]} + K_D} \]  

(6,11)

Eqn. (6,11) is exact for conditions of olefin concentration where the concentration of species(III) is negligible compared to the concentration of free olefin, [olefin]. At low concentrations of total added olefin, [olefin]_T, the following expression holds;

\[ [olefin]_T = [olefin](1 + \frac{K_1K_2[H_2][I]}{[HCl][S]}) \]  

(6,12)

Rewriting eqn. (6,11) in terms of (6,12) gives;

\[ R = \frac{K_1K_2K_3[Ru^{II}]_T[H_2][olefin]_T}{[HCl][S]+K_1[H_2][S]+\frac{K_1K_2[H_2][olefin]_T}{K_1K_2[H_2][I]} + K_D[HCl]+K_1K_2[H_2][I]+[II]+[III]+[V]} \]

\[ + \frac{K_Dk_4[Ru^{II}]_T[H_2]}{[S] + \frac{K_1[H_2][S]}{[HCl]} + \frac{K_1K_2[H_2][olefin]_T}{K_1K_2[H_2][I]} + K_D} \]  

(6,13)

where ([I] + [II] + [III] + [V]) is of course equal to [Ru^{II}]_T, (eqn. (6,9). Equation (6,13) is the exact rate expression for all concentrations
of olefin. Over the range of acrylamide concentrations employed at 

\[ [\text{Ru}^{	ext{III}}]_T = 0.005 \text{ M} \]

the concentration of hydrido-olefin complex (III) should be small compared to the concentration of added acrylamide. The maximum value of [III] is 0.005 M which should only occur at very high [acrylamide]. At [acrylamide] = 0.011 M the amount of species (III) present should be small compared to 0.011 M. For all practical purposes then, eqn. (6,11) can be used accurately with [olefin] = [olefin]_T. At higher concentrations of total catalyst the amount of species (III) could be significant compared to the added olefin concentration and as a result eqn. (6,11) would be inaccurate. Rate expression (6,11) has two terms corresponding to the two pathways, (I \rightarrow II \rightarrow III \rightarrow IV \rightarrow V) and (I \rightarrow V \rightarrow VI \rightarrow IV \rightarrow V), respectively. The first term is an olefin-dependent path, while the second term represents an olefin-independent path, (the names are assigned on the basis of their olefin-dependence neglecting the denominator terms in [olefin]).

The olefin-dependent term of (6,11) increases in value up to a constant value as the concentration of olefin is increased, i.e., this describes a first-to zero-order dependence on [olefin]_T since the denominator term \( K_1 K_2 [H_2][\text{olefin}]_T \) at constant \([H_2]\) becomes large compared to the other denominator terms. The dominance of this term at high constant [olefin]_T results in a first to zero order dependence of the first term rate with increasing \([H_2]\) at high constant [olefin]_T. The olefin-independent term decreases in relative value compared to the olefin-dependent term as the concentration of olefin is increased; at high olefin and \( H_2 \) concentrations the relative contribution of this term
to the total rate should be negligible; the maximum value of this term, according to the plot of fig. 6.7, is ca. $3 \times 10^{-7}$ Ms$^{-1}$ at zero $[\text{olefin}]_T$ and ca. 1 atm $H_2$. The rate expression (6,11) is clearly complex although limiting forms can be derived. One mathematical limit of eqn. (6,11) becomes evident at some very high olefin and hydrogen concentration when the total rate becomes:

$$R = k_3[Ru^{II}]_T$$

(6,14)

ie., the rate is independent of hydrogen and olefin concentrations (as observed experimentally), due to the olefin complex (III) being fully formed. Fig. 6.12 shows that the rate is first order in $[Ru^{II}]_T$ at low $[Ru^{II}]_T$ and higher acrylamide concentrations. Using eqn. (6,14) and data from fig. 6.7., a value of $k_3$ can be calculated to be $\approx 2.5 \times 10^{-4}$ s$^{-1}$.

At lower olefin concentrations the relative contributions of both the olefin-dependent and independent paths to the total rate are significant. As well, the $K_1K_2[H_2][\text{olefin}]_T$ term in the denominators of eqn. (6,1) are now not dominant and this can reduce to:

$$R = \frac{K_1K_2k_3[Ru^{II}]_T[H_2][\text{olefin}]_T}{([\text{HCl}][S] + K_D[\text{HCl}])} + \frac{K_Dk_4[Ru^{II}]_T[H_2]}{([S] + K_D)}$$

(6,15)

corresponding to the predominance of species (I) and (V). Here again the first term of eqn. (6,15) is for the olefin-dependent path and the second for the olefin-independent path. The experimentally observed dependence
on \([\text{olefin}]_T\), (fig. 6.7.), at lower \([\text{olefin}]_T\) is consistent with this expression as is the first order dependence on \([H_2]\), (fig. 6.11.) if the concentrations of HCl and S are relatively constant with varying \([H_2]\). If the olefin-independent path is predominant at 0.011 M acrylamide the second term of eqn. (6.15) gives the rate. In this path the concentration of DMSO produced will be constant at a constant concentration of olefin; (increasing the concentration of olefin will decrease the concentration of species (V) by increasing that of (I), (II) and (III) and result in a varying \([\text{DMSO}]\)). An approximate value of \(k_4\) can be calculated from this term, using a slope value from fig. 6.11 (a plot of rate vs \([H_2]\) at 0.011 M acrylamide), a previously calculated value of \(K_D\) (see Section 6.2.), a value of \([S]\) calculated from \(K_D\), and a value of \([\text{Ru}^{\text{II}}]_T = 0.005\ M\). The slope of \(1.92 \times 10^{-4}\ \text{s}^{-1}\) gives a value of \(k_4 \approx 0.08\ M^{-1}\text{s}^{-1}\).

Extrapolating to zero \([\text{olefin}]_T\) on fig. 6.7., gives the intercept rate for the olefin-independent term of eqn. (6.15). This equation can be used to obtain an approximate value of \(k_4\) at zero olefin concentration. Using the same values as used in the \(k_4\) calculation above and a rate of \(3 \times 10^{-7}\ \text{Ms}^{-1}\) for zero \([\text{olefin}]_T\), gives a value for \(k_4\) of \(=0.06\ M^{-1}\text{s}^{-1}\), in good agreement with the previously obtained value for \(k_4\).

In general, any concentration changes which can reverse the equilibria governed by \(K_1\) and \(K_2\), will result in a decrease in rate of the olefin-dependent path and thus increase the relative contribution of the olefin-independent path to the total observed rates; added DMSO will,
however, decrease the rates of both paths.

6.5.1. Dependence on DMSO Concentration

Added DMSO should affect the hydrogenation pathways by reversing somewhat the equilibria governed by the constants $K_1$, $K_2$ and $K_D$; this lowers the concentrations of (II), (III), and (V) and increases that of (I). The net result will be an overall rate decrease. Eqn. (6,11) can be rewritten to give;

$$ R^{-1} = [S] \cdot \frac{([\text{HCl}] + K_1[\text{H}_2])}{(K_1K_2k_3[\text{olefin}]_T + K_Dk_4[\text{HCl}])[\text{Ru}^{\text{II}}]_T[\text{H}_2]} $$

$$ + \frac{K_1K_2[\text{H}_2][\text{olefin}]_T + K_D[\text{HCl}]}{(K_1K_2k_3[\text{olefin}]_T + K_Dk_4[\text{HCl}])[\text{Ru}^{\text{II}}]_T[\text{H}_2]} $$

(6,16)

A plot of $R^{-1}$ vs added [DMSO] at high [acrylamide]$_T$ is found to be linear with a positive intercept of $7.8 \times 10^5$ M$^{-1}$s and slope of $9.3 \times 10^6$ M$^{-2}$s, (fig. 6.6.). The slope and intercept of eqn. (6,16) both contain [HCl] terms, although in the numerator of the intercept the $K_D[\text{HCl}]$ term should be negligible compared to $K_1K_2[\text{H}_2][\text{olefin}]_T$. The concentration of HCl at any time should be equal to the concentrations of (II) plus (III), (Scheme 6-A); the maximum value of the [HCl] is $[\text{Ru}^{\text{II}}]_T$, in these experiments 0.005 M. The observed rate decrease with added DMSO (a factor of one-third with [DMSO] = 0.19 M) is largely due to a decrease in the [III] by one-third, (eqn. (6,7)), implying a maximum decrease in the [HCl] of one-third ie., the [HCl] decreases from 0.005 M with no added...
DMSO to a minimum of 0.0017 M, the actual decrease depending upon $K_1$ and $K_2$. The linear plot of fig. 6.6. implies that the fluctuation in the [HCl] is small enough to result in an essentially constant slope value. By neglecting the small numerator term, $K_D[HCl]$, and the denominator term $K_Dk_4[HCl]$ from the intercept expression, (eqn. (6.16), a value of $k_3$ can be calculated to be $2.6 \times 10^{-4} \text{ s}^{-1}$, in good agreement with the value obtained previously from the maximum rate data, (eqn. (6.14)); this suggests that the contribution from the olefin-independent path to the total rate under these conditions is small, (ie., $K_Dk_4[HCl] \ll K_1K_2k_3[\text{olefin}]_T$).

6.5.2. Dependence on Substrate Concentration

Inspection of eqn. (6.11) shows that the reciprocal of the rate is a complex function of $[\text{olefin}]_T^{-1}$, due to the contribution of both olefin-dependent and -independent terms except at high olefin concentrations. A limiting form of the reciprocal rate expression at higher $[\text{olefin}]_T$ can be derived (assuming the olefin-independent path is insignificant at these high olefin concentrations):

$$ R^{-1} = \frac{1}{[\text{olefin}]_T} \cdot \frac{([\text{HCl}][S] + K_1[H_2][S] + K_D(\text{HCl}))}{K_1K_2k_3[Ru^{II}]_T[H_2]} $$

$$ + \frac{1}{k_3[Ru^{II}]_T} $$  \hspace{1cm} (6.17)
Fig. 6.8 is a plot of $R^{-1}$ vs $[\text{olefin}]^{-1}_T$ which at high $[\text{olefin}]_T$ approaches a limiting slope of $4.2 \times 10^4$ s and has a positive intercept of $7 \times 10^5$ M$^{-1}$s. With increasing $[\text{olefin}]^{-1}_T$, the slope approaches zero due to the growing contribution of the olefin-independent path to the total rate. Here again the $[\text{S}]$ and $[\text{HCl}]$ vary with the $[\text{olefin}]^{-1}_T$ causing a minor variation in the numerator of the slope term of eqn. (6,17). A value of $k_3$ can be obtained from the intercept of the curve of fig. 6.8, and eqn. (6,17) and is found to be $2.9 \times 10^{-4}$ s$^{-1}$, in good agreement with the previously found values, (see Section 6.5. and 6.5.1.).

6.5.3. Dependence on Hydrogen Concentration

Eqn. (6,11) can be rewritten to give;

$$R^{-1} = \frac{1}{[H_2]} \cdot \frac{([\text{HCl}][\text{S}] + K_D[\text{HCl}])}{(K_1K_2k_2[\text{olefin}]_T + K_Dk_4[\text{HCl}])[\text{Ru}^{II}]_T} + \frac{K_1[S] + K_1K_2[\text{olefin}]_T}{(K_1K_2k_3[\text{olefin}]_T + K_Dk_4[\text{HCl}])[\text{Ru}^{II}]_T} \tag{6,18}$$

The plot of $R^{-1}$ vs $[H_2]^{-1}$ at high $[\text{olefin}]_T$, (fig. 6.10.), is linear with a slope of $6.7 \times 10^2$ s and a positive intercept of $4.6 \times 10^5$ M$^{-1}$s. A decrease in $[H_2]$ could increase the relative significance of the olefin-independent path, if the effect of decreasing $[H_2]$ on the olefin-dependent path equilibria ($K_1$, $K_2$) is smaller than the effect on the olefin-independent path rate determining step ($k_4$). If the relative contribution of the olefin-independent path to the total rate at this
high acrylamide concentration (0.47 M), is insignificant at high $[H_2]$, then the intercept term of eqn. (6,18) approximates to $1/k_3[Ru^{II}]_T$; by neglecting the $K_1[S]$ term, a $k_3$ value of $4.4 \times 10^{-4}$ s$^{-1}$ is obtained, which is in reasonable agreement with the previously obtained values.

It would be expected that the slope term of eqn. (6,18) would not be constant due to the $[HCl]$ and $[S]$ dependence on $[H_2]$. However, the linear plot obtained in fig. 6.10., implies that the numerator of the slope term is relatively constant. This could occur if the $[S]$ increases somewhat as the $[HCl]$ and the $[H_2]$ decreases. Decreasing the concentration of $H_2$ decreases the $[S]$ for the olefin-dependent path but could increase the $[S]$ from the olefin-independent path.

6.5.4. Dependence on Catalyst Concentration

This dependence is again complex owing to the non-zero contribution of the olefin-independent path to the total rate at the higher total catalyst concentration. The dependence appears to be initially first order in total catalyst concentration and then decreasing in order with increasing $[Ru^{II}]_T$. At these higher catalyst concentrations, the olefin substrate to total catalyst ratio is decreasing, and the amount of substrate present is not large enough to fully form complex (III). This results in a decreasing $[III]:[Ru^{II}]_T$ ratio, and a decreasing order dependence of rate on $[Ru^{II}]_T$. Concomitant with the decreasing extent of formation of (III) is the growing significance of the olefin-independent path to the total rate.
Eqn. (6,11) can be rearranged to give;

\[
R^{-1} = \frac{1}{[\text{Ru}^{\text{II}}]^T} \cdot \left( \frac{([\text{HCl}][S]+K_1[H_2][S]+K_1K[H_2][\text{olefin}]^T+K_0[HCl])}{(K_1K_2k_3[\text{olefin}]^T + K_0k_4[HCl])[H_2]} \right)
\]  \hspace{1cm} (6,19)

Figs. (6.13.) and (6.14.) show plots of (rate$^{-1}$) vs [Ru$^{\text{II}}$]$^{-1}$ for two different acrylamide concentrations. The plot at [acryl]$^T = 0.52$ M, (fig. 6.13.), is slightly curved presumably due to the variation of [S] and [HCl] with [Ru$^{\text{II}}$]$^T$, as well as the presence of the olefin-independent path. The linear plot at 1.10 M acrylamide, (fig. 6.14.) implies that complex (III) is more fully formed, the contribution from the olefin-independent path is less and the $K_1K_2[H_2][\text{olefin}]^T$ and $K_1K_2k_3[H_2][\text{olefin}]^T$ terms are predominant. At these conditions the slope of eqn. (6,19) reduces to $1/k_3$. The slope value, $(7.65 \times 10^{-3} \text{ s})$ of this plot gives a value of $k_3 = 2.7 \times 10^{-4} \text{ s}$, in good agreement with previously obtained values.

Both plots of $R^{-1}$ vs [Ru$^{\text{II}}$]$^T$, (figs. 6.13. and 6.14.) have positive intercepts implying that eqn. (6,19) should have an intercept term. As was stated earlier, eqn. (6,11) is inaccurate at higher total catalysts concentrations; the exact rate expression of eqn. (6,13) can be rewritten in the form of eqn. (6,19) to give an intercept term of $1/k_3[\text{olefin}]^T$. The intercept corresponds to an infinite concentration of total catalyst where the maximum rate would be equal to $k_3[\text{III}] = k_3[\text{olefin}]^T$. From the intercept value $(7.9 \times 10^4 \text{ M}^{-1}\text{s})$ of the plot of $R^{-1}$ vs [Ru$^{\text{II}}$]$^{-1}$ (fig. 6.14.) a value of $k_3 = 1.2 \times 10^{-5} \text{ s}^{-1}$ is obtained. This value is in poor
agreement with previously obtained values; however, the intercept and hence the \( k_3 \) value is subject to error created by extrapolation.

6.5.5. Dependence on Added Acid

Experimentally, the reaction rates decrease slightly at high substrate concentrations and much more at lower substrate concentrations with added p-toluenesulphonic acid. Addition of DMAHCl under comparable conditions at high substrate concentration decreases the reaction rate far greater than does added p-toluenesulphonic acid. Addition of HCl causes the reversal of the equilibrium governed by \( K_1 \), causing a lowering of the concentrations of species (II) and (III). Added HCl should have little effect on the olefin-independent path, resulting in an enhancement of this path's contribution to the overall rate. The limit in rate lowering with added HCl should be the olefin-independent rate which, from the rate vs olefin plot, (fig. 6.7.) is about \( 3 \times 10^{-7} \) Ms\(^{-1}\). The rate measured at 0.043 M DMAHCl, \( (3.6 \times 10^{-7} \) Ms\(^{-1}\)\) is very close to this value suggesting that \( K_1 K_2 \) is quite small (of the order of 0.01) i.e., very little of species (II) and (III) are present under these conditions.

The marked smaller effect on rate due to p-toluenesulphonic acid as compared to DMAHCl implies that the \( K_1 \) equilibrium is reversed by added HCl, not just by the \( H^+ \) as supplied by the sulphonic acid. The observed non-regular inverse rate dependence on sulphonic acid also suggests this equilibrium is not effectively reversed by addition of this acid without addition of Cl\(^-\) as well. This non-regular acid dependence
makes it impossible to quantitatively analyse the p-toluenesulphonic acid dependence data.

With added DMAHCl, (0.043 M) little dissociation to H\(^+\) and Cl\(^-\) occurs\(^{32}\) so that virtually all the added DMAHCl is available as HCl to reverse the K\(_1\) equilibrium.

The complete inhibition of hydrogenation at relatively low acrylamide concentration, (0.085 M) with added p-toluenesulphonic acid is not readily explained; co-ordination of the acid to the catalysts could occur.

6.5.6. Dependence on Added Chloride

As was seen earlier, (see Section 5.7. and 6.5.) addition of chloride inhibited the reaction of catalyst with H\(_2\) by reversing equilibria such as that governed by K\(_1\) (Scheme 6-A). Addition of chloride to the acrylamide system caused small rate increases, (see Section 6.4.6.). This could be due to the large excess of chloride forming some tetra-chloro species and these could be somewhat more active; however, spectral evidence, (see Section 6.2.) does not suggest formation of these species. This possibility was not studied further.

6.6. The Nature of the Non-Linear Region Reaction Rates

As stated previously the gas-uptake plots, (fig. 6.4.), showed an initial non-linear region. This region can be accounted for by the catalytic system approaching an equilibrium state where the concentrations
of species (I - V) have become constant. The initial region is then attributed to the reaction of species (I) with hydrogen to produce (II) which subsequently reacts with olefin to produce species (III), (IV) and (V). Initially when no complex (III) is present the reaction rate of (I) with \( H_2 \) to produce (III) is large (as evident by gas-uptake data in the absence of olefin), but as the concentration of complex (III) builds up the observed rate slows down somewhat until it becomes constant with a steady state concentration of complex (III) and (V). With added chloride or DMAHCl the reaction of species (I) with hydrogen is inhibited, (see Section 5.7. and 6.5.). Slow dissociation of sulphoxide from species (I) to form (V) must occur (as evident by spectral data) as well as the reaction of (I) with \( H_2 \) to form some (II) and (III). The eventual build-up of species (III) and in particular (V) could result in an increasing rate as more of these species are produced. Eventually again a steady state equilibrium concentration of (III) and (V) is achieved and the rate becomes constant. An inhibition of the overall hydrogenation rate by added chloride would be expected due to the suppression of equilibrium \( K_1 \); however the linear rate is in fact increased somewhat. Thus a contribution from a more active tetrachloro-species seems likely.

6.7. Discussion

The mechanistic scheme, 6-A, fits the observed kinetic data at least qualitatively and semi-quantitatively. The values of \( k_3 \) obtained are reasonably consistent, adding credence to the proposed mechanism. The presence of two non-equivalent kinetic pathways makes analysis for other rate and equilibrium constants generally unattainable with the available data; however values for \( k_4 \) were obtained.

Both pathways of Scheme 6-A involve activation of hydrogen and olefin via initial formation of a metal-hydride complex and decomposition
of a common metal-alkyl species via protonolysis. This hydrogen and olefin activation process is well known, in particular for the systems involving $\text{HRuCl(PPh}_3)_3$, $[\text{RuCl}_3(\text{bipy})]^{-2}$, $\text{HRh(CO)(PPh}_3)_3$, $[\text{PtCl}_2(\text{SnCl}_3)_2]^{-2}$, and $\text{HIrCl}_2(\text{DMSO})_3$. However, only in the case of the Ir and Pt systems has protonolysis of the metal-alkyl intermediate to form the saturated product been postulated. The reaction of hydrogen with $\text{RuCl}_3S_3^-$ or $\text{RuCl}_3S_2(\text{DMA})^-$ can proceed by either "direct substitution" of hydride anion for chloride, or oxidative addition of $\text{H}_2$ to form an eight-co-ordinate species followed by reductive elimination of $\text{HCl}$. For the olefin-dependent pathway the reaction of $\text{RuCl}_3S_3^-$ with $\text{H}_2$ is written as a fast equilibrium step while the corresponding reaction of $\text{RuCl}_3S_2(\text{DMA})^-$ is a slower rate determining step; this could be rationalized in terms of the extra sulphoxide ligand acting as a $\pi$-acid (relative to DMA), and thereby stabilizing hydride formation. Scheme 6-A can be expanded to show both kinetic pathways in more detail. The olefin-dependent pathway is shown below;

$$\text{RuCl}_3S_3^- + \text{H}_2 \xrightarrow{K_1} \text{HRuCl}_2S_3^- + \text{HCl} \ (6,20)$$

$$\text{HRuCl}_2S_3^- \xrightarrow{K_2'} \text{HRuCl}_2S_2(\text{DMA})^- + S \ (6,21)$$

$$\text{HRuCl}_2S_2(\text{DMA})^- + \text{olefin} \xrightarrow{K_2''} \text{trans-HRuCl}_2S_2(\text{olefin})^- \ (6,22)$$

$$\text{trans-HRuCl}_2S_2(\text{olefin})^- \xrightarrow{k_3} \text{cis-HRuCl}_2S_2(\text{olefin})^- \ (6,23)$$

$$\text{cis-HRuCl}_2S_2(\text{olefin})^- \xrightarrow{K_3'} \text{RuCl}_2S_2\text{alkyl}^- \ (6,24)$$
Since hydride has a high trans-labilizing effect, reaction (6,21) will result in the loss of a sulphoxide trans to the hydride. Equilibrium (6,22) should result in an olefin co-ordinated trans to the hydride ligand. For insertion of the olefin into the metal hydride bond to occur, (eqn. 6,24), the olefin has to be co-ordinated cis to the hydride ligand. The isomerization step, (eqn. 6,23), is thought to be the slow step of the pathway, since isomerization of a six-co-ordinate species should be relatively difficult. A few hydrido-olefin complexes are known but their stereochemistry is uncertain.

Reports of kinetic studies on the insertion process involving trans-hydrido-olefin complexes of platinum(II) have shown that for such square-planar complexes, isomerization to the cis-isomer can occur via co-ordination of an olefin, solvent molecule or counter-anion to form a five-co-ordinate intermediate which rearranges and dissociates a ligand to form the cis-square planar complex. This complex then undergoes insertion of the olefin to form the metal-alkyl. The rate determining step for these systems was thought to be the insertion step and not the trans-cis isomerization.

With the present six-co-ordinate DMSO species, trans to cis isomerization could proceed via either a five-co-ordinate, or less likely, a seven-co-ordinate intermediate. The olefin-independent path of Scheme 6-A is shown in more detail below;

\[
\text{RuCl}_3\text{S}_3^- + S \xrightarrow{K_D \text{ fast}} \text{RuCl}_3\text{S}_2\text{(DMA)}^- + S \quad (6,25)
\]
\[ \text{RuCl}_3\text{S}_2(\text{DMA})^- + \text{H}_2 \xrightarrow{k_4} \text{HRuCl}_2\text{S}_2(\text{DMA})^- + \text{HCl} \] (6,26)

\[ \text{HRuCl}_2\text{S}_2(\text{DMA})^- + \text{olefin} \xrightarrow{k_5'} \text{cis-HRuCl}_2\text{S}_2(\text{olefin})^- \] (6,27)

\[ \text{HRuCl}_2\text{S}_2(\text{olefin})^- \xrightarrow{k_5''} \text{RuCl}_2\text{S}_2\text{alkyl}^- \] (6,28)

Kinetic data require that the monohydride complexes formed in the olefin-dependent and -independent paths, (eqns. (6,21) and (6,26)), respectively be different isomers. Further, co-ordination of olefin to these complexes (eqns. (6,22) and (6,27)), respectively, must produce a trans- and cis-hydrido-olefin isomer respectively, i.e., the data exclude any crossing of the olefin-independent path into the olefin-dependent path via monohydride or hydrido-olefin complexes. It is impossible that the slow step, (eqn. (6,26)) could involve isomerization to produce a solvated hydride complex perhaps with a hydride ligand trans to a sulphoxide; when the olefin replaces DMA in the co-ordination sphere all isomers with hydride trans to sulphoxide would yield cis-hydrido-olefin complexes. The insertion step, (eqns. (6,24) and (6,28)), involves promotion of the electrons of the metal-hydride bond into the olefin anti-bonding orbitals, and transfer of the hydrogen to form the alkyl derivative. Promotion of the electrons into the olefin anti-bonding orbital becomes more difficult with increasing electron density in this anti-bonding orbital. An octahedral Ru(II)-olefin complex is likely to have considerable electron density within the olefin anti-bonding orbital due to effective \( \pi \)-backbonding from the metal. As this transfer step is usually fast\textsuperscript{22} some electronic redistribution is likely occurring to
facilitate insertion. With "activated" olefins such as acrylamide, hydrogen transfer (as hydride) to the more positive Y carbon atom is probably more favoured than transfer to the other olefin carbon atom. This polarization of the olefin could well promote the insertion reaction;

\[
\text{CH}_2=\text{CH-CONH}_2 + \text{H-Ru} \rightarrow \text{CH}_3-\text{CH-CONH}_2 \quad (6,29)
\]

Such a rationale also explains the non-hydrogenation of simple terminal olefins such as hex-1-ene. The question of the direction of addition of a metal-hydride across an olefin link (Markownikoff or anti-Markownikoff), is in general a complex problem \(^96\).

As stated, the last step of Scheme 6-A is the rapid protonolysis step by HCl. Electrophilic attack of HCl on the metal-bonded carbon atom yields the saturated product as well as the catalyst species, either as the mer or fac chloride isomers.
CHAPTER VII
(S,R;S,S)-(+)2-METHYLBUTYL METHYL SULPHOXIDE
COMPLEXES OF RUTHENIUM(II)

7.1. Introduction

Homogeneous catalytic asymmetric hydrogenation using compounds containing chiral phosphine ligands has been known for some time\textsuperscript{6,28,97,98}, and high enantiomeric excesses have been achieved particularly with \(\alpha\)-acetamido amino acid substrates\textsuperscript{98}. The following studies present the first asymmetric hydrogenation catalysts containing a chiral sulphoxide. This chapter describes the physical characteristics of the compounds, while later chapters describe the kinetics of hydrogenation, and asymmetric hydrogenation using one of the catalysts, dichloro((S,R;S,S)-(+)2-methylbutyl methyl sulphoxide)ruthenium(II), 8. A rather poorly characterized ether-solvated dichlorobis-sulphoxide complex 7, and the products of the reaction of compound 8 with carbon monoxide will also be discussed. Complex 8 is the first of a series of three bis-sulphoxide polymer species. The remaining two will be discussed later.

7.2. Ether-Solvated Dichlorobis(MBMSO)ruthenium(II), 7

This compound was prepared by adding (R,S;S, S)-(+)2-methylbutyl methyl sulphoxide to a methanolic "blue solution" (nMBSO/nRu = 3.6/1).
In the presence of ether the reaction residue yielded green-tinted yellow crystals. The amount of ether present in the product, which could not be removed in vacuo varied with the preparation. The elemental analysis of one preparation shows diethyl ether impurity, ca. 19%.

Compound 7 is a neutral complex in DMA, (\(A = 4.5 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}\)), the solution in air turns green slowly, likely giving a ruthenium(III) species. The green tint of the solid could be due to traces of the oxidized product. The complex is soluble in water and polar organic and halogenated solvents, but insoluble in ether and alkanes.

7.2.1. I.r. Spectrum

The i.r. spectrum contains a strong band at 1100 cm\(^{-1}\) assigned to the SO stretch of S-bonded sulphone, (free MBMSO, \(\nu(\text{SO}) = 1025 \text{ cm}^{-1}\)). A band due to possible O-bonded sulphone could not be detected due to ligand absorbances. Strong bands due to diethyl ether are present at 842, 1120, and 1300 cm\(^{-1}\). The far i.r. has a broad band at 347 cm\(^{-1}\), which is assigned to \(\nu(\text{Ru-Cl})\).

7.2.2. \(^1\text{H n.m.r. Spectrum}\)

Compound 7 in CDCl\(_3\) has a complicated \(^1\text{H n.m.r. spectrum. In the region } \delta 0.9 - 1.4 \text{ there are large peaks due to the protons of the } \beta, \gamma \text{ and } \delta \text{ carbons of the sulphone as well as the methyl groups of diethyl ether. In the region } \delta 2.9 - 3.8 \text{ there are both broad and sharp}

\(\dagger\) See also Chapter II, (fig. 2.9.).
peaks due to the protons of the \( \alpha \) carbons of S-bonded sulphoxide and the methylene protons of diethyl ether respectively. At 62.7 - 2.9 there is a singlet and a broad peak due to the protons of the \( \alpha \) carbon of O-bonded sulphoxide. An exact integration ratio between the peaks due to S and O-bonded sulphoxides is not possible due to the presence of the diethyl ether peaks, however a rough integration indicates predominantly sulphur co-ordination.

7.2.3. Discussion

Collective data for the complex suggest a dichloro bis-sulphoxide complex, with predominantly S-bonded sulphoxide, but also containing O-bonded sulphoxide. The sulphoxide to ruthenium ratio of the compound (2:1) compared to that of the reaction solution (ca. 3.6:1), is indicative of the steric interference that would be present in a dichlorotris- or tetrakis- sulphoxide complex, (species that are readily formed with for example DMSO). The low co-ordination number of ruthenium, excluding ether, (which shows no sign of co-ordination according to the i.r and n.m.r. spectra) suggests that the compound is not monomeric and could be dimeric or polymeric with possibly bridging chlorides, although the i.r. shows terminal chlorides are definitely present as well. In analogy to a dichlorobis(MBMSO)ruthenium(II) trimer 8 (see later) compound 7 could similarly be a trimer with diethyl ether solvated in the crystals. Molecular weight studies for compound 7 were not carried out however.
7.3. **Dichlorobis(MBMSO)ruthenium(II) trimer 8**

Compound 8 is again prepared from a methanolic "blue solution" with a reaction mole ratio of 2:1 for sulphoxide to ruthenium. The reaction residue was freeze-dried from benzene to yield the product. Attempts at recrystallizing this compound from various solvent systems, in particular, CH₂Cl₂-n-hexane, gave oils. During the freeze-drying, residual methanol and water are presumably pumped off, together with excess chloride as HCl. The compound varies in colour, depending on the preparation, from tan to gold. Anerobic elution of the compound on an alumina column (grade III) with chloroform, methanol or a mixture of the two results in a light yellow solid which has the same elemental analysis (C,H,Cl) as the parent compound. A non-moving green band remains on the column; since the parent compound in CCl₄, benzene, or CHCl₃ turns green readily in air, this band likely contains ruthenium(III) species. After a few days in air the green solution deposits green crystals, possibly a ruthenium(III) sulfoxide complex, although this was not studied further.

In benzene the compound shows a degree of association of 2.9 (M.W. = 1273 g/mole) indicating a probable trimer in the solid state. A measured \( \mu_{\text{eff}}^{22°} \) of 0.57 ± .17 B.M. per trimer (Gouy method) which, in view of the air sensitivity of the compound, is consistent with a diamagnetic ruthenium(II) complex with some paramagnetic ruthenium(III) impurity, (see discussion).

The conductivity in DMA, (\( \Lambda^{22°} = 7.2 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1} \)), indicates an essentially non-ionic complex. Compound 8 is soluble in organic solvents except alkanes and diethyl ether where it is insoluble, and slightly soluble in water.
7.3.1. I.r. Spectrum

The i.r. spectrum of compound 8 contains a strong band at 1105 cm\(^{-1}\) attributed to \(v(SO)\) of S-bonded sulfoxide. Again the detection of an O-bonded sulfoxide band is not possible due to other ligand absorbances. The far i.r. has a broad strong band centred at 330 cm\(^{-1}\) attributed to terminal Ru-Cl stretches.

7.3.2. \(^1\)H n.m.r. Spectra†

The proton n.m.r. spectrum of compound 8 in CCl\(_4\) or CHCl\(_3\) is complicated, consisting of broad peaks. Peaks due to the sulfoxide protons of the \(\gamma\) and \(\delta\) carbons are found in the region \(\delta0.7 - 1.75\) while peaks of the \(\beta\) carbon protons are at \(\delta1.85 - 2.50\). In the region \(\delta2.8 - 4.2\) are peaks due to the protons of the \(\alpha\) carbons of the sulfoxides. The peak areas show that mainly S-bonded sulfoxides are present however the possibility of some O-bonded sulfoxide cannot be entirely ruled out, due to the close proximity of the peaks. Integration of the region \(\delta0.7 - 2.7\) and \(\delta2.8 - 4.2\) yields the proton ratio \(1.75:1\), similar to the ratio of the \(\beta\), \(\gamma\), and \(\delta\) carbon's protons to the \(\alpha\) carbon protons for the free ligands \((1.80:1)\). The broadness of the peaks can be explained by the many different chemical environments of the ligand protons. Since the compound is associated in solution, even in polar DMA (kinetic data, see later), the number of different environments is compounded. The long

† See also Chapter II, (fig. 2.10.).
alkyl tail of the sulphoxide ligand could rotate about somewhat, giving
a variable chemical environment and broad peaks.

Dissolution of compound 8 in $d_6$-DMSO gives a simple spectrum. The spectrum, 5 min after solution, is essentially that of free MBMSO and the solution eventually deposits yellow crystals, presumably of RuCl$_2$(d$_6$-DMSO)$_4$. Addition of varying amounts of d$_6$-DMSO to a CCl$_4$ solution of compound 8 gives equally simple spectra. Addition of 1% (by weight) of d$_6$-DMSO results in 50% exchange. As well as peaks due to the protons of the $\beta$, $\gamma$ and $\delta$ carbons of free and co-ordinated MBMSO there is a singlet at 62.52 due to a methyl protons of the free MBMSO ligand. In the S-bonded region there are a methyl singlets at 63.12, 3.40, and 3.52. Addition of a further 1% of d$_6$-DMSO results in 75% exchange with singlets in the S-bonded region at 63.12 and 3.40. Addition of a further 2% of d$_6$-DMSO results in complete exchange. The singlets in the S-bonded region are due to the $\alpha$ methyl protons of the different sulphoxide ligands of the trimer or of perhaps monomers with the composition RuCl$_2$(d$_6$-DMSO)$_n$-(MBMSO)$_m$ ($n + m \leq 4$). The rate of exchange of d$_6$-DMSO with MBMSO is of the order of that found for DMSO in RuBr$_2$(DMSO)$_4$.

7.3.3. Discussion

Association of co-ordinatively unsaturated monomers is a convenient way of alleviating deficiency in co-ordination. One can envisage two possible structures for the trimer, utilizing chloride bridges and S-bonded sulphoxide ligands, (fig. 7.1.). The two possible structure types are linear (I) and triangular (II), along with isomers of
each, although sufficient data are not available to definitely assign the

```
I
Cl—Ru—Cl
| |
S—Cl  S—Cl  S—Cl
| |
Cl—Ru—Cl

II
S—Cl  S—Ru—Cl
S—Cl  S—Cl
S—Cl
```

Figure 7.1. Possible structures of [RuCl$_2$(MBMSO)$_2$]$^3$.

structure. The sulphoxide ligands are distributed evenly to give the
least steric interference. Of the two structures the linear form gives
more chemically different sulphoxide ligands (cf. n.m.r. data). The
trimer 8 is related in some ways to the ruthenium cluster compounds
reported by Rose and Wilkinson, and Spencer and Wilkinson. The
compound is made from a methanol blue solution which the former report
as containing the cluster anion Ru$_5$Cl$_{12}$$^-2$. They suggest that these blue
solutions on the addition of Cs$^+$ yield salts of the trinuclear anion
Ru$_3$Cl$_9$$^-3$ which is thought to consist of a triangle of ruthenium atoms while
the pentanuclear species is thought to have a trigonal bipyramidal
structure of ruthenium(II) atoms. Both these species are formulated as
having metal-metal bonds with terminal chlorides.
Trinuclear ruthenium(II) and (III) carboxylates, both with and without a central oxygen atom and containing bridging carboxylates, are known. The ruthenium(III) oxo species has a $\mu_{\text{eff}} = 1.77$ B.M., while $[\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]$ is diamagnetic and $[\text{Ru}^{\text{II}}_3(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]$ and its derivatives are weakly paramagnetic, (the trisaquo complex has a $\mu_{\text{eff}} = 0.4$ B.M., per Ru$^3$). Trimer 8 appears to be similar to the ruthenium(II) acetate complexes with a similar magnetic moment and could perhaps on oxidation produce an oxo species, although there is no evidence for this species. In summary it would appear that cluster complexes of co-ordinatively unsaturated ruthenium(II) or (III) may not be particularly rare, (see also Chapter X).

7.4. The Reaction of $[\text{RuCl}_2(\text{MBMSO})_2]_3$ with Carbon Monoxide

In order to help elucidate the structure of the trimer 8 and to develop new hydrogenation or hydroformylation catalysts, the reaction of carbon monoxide with the trimer 8 in methanol, benzene and toluene, was studied. In toluene at 42°C under 660 mm CO the reaction is stoichiometric with a 2:1 mole ratio of CO to Ru. The reaction solution changes from an initial dark brown colour to orange and finally pale yellow during the course of the reaction. Spectral data for these reactions are collected in Table 7.1.

7.4.1. Discussion

An even distribution of CO in the reaction products would suggest the formation of a monomer; $\text{RuCl}_2(\text{CO})_2(\text{MBMSO})$. Isomers with cis-
TABLE 7.1.
Spectral data for carbonyl derivatives of $[\text{RuCl}_2(\text{MBMSO})_2]_3$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ν(CO)</th>
<th>δ(MCO)</th>
<th>ν(SO)</th>
<th>ν(Ru-Cl)</th>
<th>δ(CH$_3$)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>2070,2058,</td>
<td>-</td>
<td>1130,</td>
<td>-</td>
<td>3.3,2.9,</td>
</tr>
<tr>
<td>I</td>
<td>2008,1985</td>
<td></td>
<td>938</td>
<td></td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>2070,2058,</td>
<td>615,575</td>
<td>1130,</td>
<td>310,</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2008,1985</td>
<td>485</td>
<td>928</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>2130sh,2058</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>2133,2059</td>
<td>620,580</td>
<td>932</td>
<td>320,</td>
<td>-</td>
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<td>297</td>
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</tr>
<tr>
<td>III</td>
<td>2130sh,2052</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I) Oily residue after MeOH removed for the reaction of 8 with CO in MeOH.
II) Crystals from the reaction of CO with 8 in benzene.
III) Oily residue following toluene removal after the stoichiometric reaction of CO with 8 in toluene.

a In cm$^{-1}$; CC$_4$ solution in NaCl cells except I2, which is neat between CsI plates, and II2 a nujol mull between CsI plates.

b In CDCl$_3$, relative to T.M.S., (fig. 2.10.).

sh = sharp.
carbonyls should have two $v(CO)$ bands, $(a_1 + b_2)$, and three $\delta(MCO)$ bands, $(a_1 + b_1 + b_2)$, active in the i.r.\textsuperscript{70}, while isomers with trans-carbonyls will have one $v(CO)$ band, $(b_{1u})$ and two $\delta(MCO)$ bands, $(b_{2u} + b_{3u})$.

The i.r. spectrum of the crystalline product II, from the reaction of CO with trimeric 8, has two $v(CO)$ bands, three $\delta(MCO)$ bands and two $v(Ru-Cl)$ bands indicating two cis-carbonyl and cis-chloride ligands; (the assignment of the $\delta(MCO)$ bands are made to the strongest bands in this region of the spectrum, but must be considered somewhat tentative due to the presence of other sulphoxide ligand bands). The band at 932 cm$^{-1}$ and a sharp singlet resonance at 62.95 indicate only O-bonded sulphoxide. Collectively these data suggest the following structure for cis-RuCl$_2$(CO)$_2$(MBMSO)$_2$, (fig. 7.2).

![Structure of cis-RuCl$_2$(CO)$_2$(MBMSO)$_2$](image)

OS = MBMSO, O-bonded

(I)

Figure 7.2. Possible structure of RuCl$_2$(CO)$_2$(MBMSO)$_2$

A confirmation of the empirical formula is not available as analytic data were unfortunately not obtained for this crystalline product due to lack of sample. Repeats of the preparation have so far only yielded oils, which do, however, have the same spectra as the crystalline product. Compounds of the type RuCl$_2$(CO)$_2$P$_2$ have been
previously prepared, where $P = \text{PEt}_3^{100}, \text{PEt}_2\text{Ph}^{100}$, and $\text{PPh}_3^{101,102}$. The isomer which is thought to have cis-carbonyls, chlorides and trans-$\text{PPh}_3$ has $\nu(\text{CO})$ bands at 2064, and 2001 cm$^{-1}$\textsuperscript{100-102}. A compound with the the same empirical formula, but with perhaps an all cis structure, has $\nu(\text{CO})$ bands at 2042 and 1967 cm$^{-1}$\textsuperscript{102}. Decreasing the electron density on the phosphorus atom by aromatic substitution in the phosphine ligand results in increased $\pi$- acidity of the triphenylphosphate and an increase in CO stretching frequencies\textsuperscript{103,104}. The same arguments have been presented for corresponding $\text{FeCl}_2(\text{CO})_2\text{P}_2$ systems\textsuperscript{105}. Replacing the $\pi$-acid phosphines with O-bonded MBMSO, essentially a $\sigma$-donor (and perhaps $\pi$-donor, cf. $\text{H}_2\text{O}$, and $\text{OH}^-$), should result in an increase in $\pi$-donation from the metal to the $\pi^*$ orbitals of the carbonyls and a lowering of the CO stretching frequencies. The compound of structure (I), fig. 7.2, would thus be expected to have two $\nu(\text{CO})$ bands in the region ca. 2050 - 1900 cm$^{-1}$. The experimentally observed bands at ca. 2130 and 2059 cm$^{-1}$ are thus contradictory to structure (I), although the other spectral data are consistent with this structure. A compound of structure (I) with S-bonded sulphoxide could possibly give the observed $\nu(\text{CO})$ bands if such a ligand were a stronger $\pi$-acid than triphenyl phosphine. The presence of S-bonded sulphoxide is however contradictory to the i.r. and n.m.r. data. A crystal structure determination is required to elucidate the problem. The appearance of an additional $\nu(\text{CO})$ band at 2010 cm$^{-1}$ for reaction III indicates that another isomer is present in the reaction mixture. Presumably the isomer could also be formed in the benzene reaction but is not present in the crystalline product.
Reaction I has two groups of ν(CO) bands centred at ca. 2064 and 1996 cm⁻¹ with each group split into two bands. This splitting is not a solid state site symmetry effect as it is also present in the solution spectra. The probable cause is a mixture of two similar isomers of the same compound, perhaps with cis-CO's trans to chloride or sulphone. The observed stretching frequencies are similar to those observed for the chlorocarbonyl phosphine complexes mentioned earlier, and to those reported by Wilkinson et al.¹², for the poorly characterized RuCl₂(CO)₂(DMSO)₂, (ν(CO), 2082 and 2036 cm⁻¹).

The possibility of dichlorotris carbonyl(MBMSO)ruthenium(II) species being produced in reaction I, II, and III can not be entirely ruled out, since a fac-carbonyl isomer of the above composition would also be expected to have two ν(CO) bands and three δ(MCO) bands.⁶⁰

The products of carbonylation of the trimer ₈ may be a mixture and the CO stretches appear to be anomalous when compared to some analogous phosphine complexes. The systems are worthy of more detailed study although the synthetic problems are not trivial.
CHAPTER VIII
HOMOGENEOUS CATALYTIC HYDROGENATION OF ACRYLAMIDE
USING TRIMERIC DICHLORO[(S,R; S,S)-(−)-2-METHYLBUTYL METHYL SULPHOXIDE]RUTHENIUM(II)

8.1. Introduction

Kinetic studies of the title catalyst were undertaken with a relatively simple substrate in order to help elucidate the hydrogenation mechanism as an aid to understanding systems involving asymmetric hydrogenation.

Trimeric readily hydrogenates acrylamide to proponamide at 70°C and hydrogen pressures <1 atm; however, the pro-chiral substrates employed were found to require higher pressures to effect reduction, and these systems were less suitable for mechanistic study.

8.2. The Reaction of [RuCl₂(MBMSO)₂]₃ with Hydrogen

Trimer was found to react with molecular hydrogen at 1 atm pressure in DMA at 70°C, hydrogen uptake being complete after 2100 sec. The extent of the reaction as monitored by gas-uptake was 5%, (total uptake = (4 ± 1) x 10⁻⁵ moles of H₂ for a 5 ml solution) based on a 1:1 reaction uptake with the catalyst trimer, (ie., H₂ = Ru = 1:1, [Ru] =
0.018 M, \([H_2] = 1.24 \times 10^{-3} \text{M}) . \\

The resulting yellow solutions had essentially the same spectrum as solutions which had not been subjected to \(H_2\), and indeed the spectral changes observed at 70°C during the \(H_2\) treatment were the same as those observed in the absence of \(H_2\), under Ar, (see Section 8.3., and fig. 8.1.).

The presence of DMA-HCl did not alter the extent of \(H_2\) reaction discussed above, ([\(Ru^{II}\] = 0.017 M, \([H_2] = 1.24 \times 10^{-3} \text{M}, [\text{DMA-HCl}] = 0.0085 \text{M}, H_2\) uptake = 0.35 \times 10^{-5} \text{moles } H_2). With the addition of a 2:1 mole excess of "proton sponge" \(R\) the trimer reacted with further hydrogen at 70°C to a total extent of ≈20% to produce an orange solution.

8.3. U.V./Visible Spectral Observations on [\(RuCl_2(\text{MBMSO})_2\)]

The trimeric compound in DMA at 70°C under Ar gave a u.v./visible spectrum which showed a very slight spectral change with time, the majority of the change occurring within the first 1000 sec after dissolution, (fig. 8.1.). Addition of MBMSO (3:1 mole excess) resulted in no change to the final yellow solution. Addition of a 200-fold excess of acrylamide to the catalyst solution at 70°C resulted in small spectral changes in the 320 - 350 nm region, (fig. 8.2.). A freshly prepared solution of the complex, (ca. 0.003 M), 0.6 M acrylamide in DMA at 70°C and under 1 atm \(H_2\), gave similar spectral changes to those solutions without hydrogen.

† The concentrations of Ru(II) are expressed in terms of monomer concentrations.
Figure 8.1. U.v./visible spectral changes of $[\text{RuCl}_2(\text{MBMSO})_2]_3$, 8 in DMA at 70°C; $[\text{Ru}]_T = 0.0032 \text{M}$ as monomer, pAr = 620mm; time after solution attained; 1) 150 sec, 2) 1,100 sec.
Figure 8.2. Effect of added acryl on the spectrum of $\text{8}_-$ in DMA at 70°C;

$[\text{Ru}]_T = 0.0036 \text{M}$ as monomer, $[\text{acryl}] = 0.63 \text{M}$, $p\text{Ar} = 620 \text{mm}$;

1) spectrum of $\text{8}_-$, 2) spectrum with acryl added, 3) 1,000 after acryl added.
and after about the first 1500 sec of the catalytic hydrogenation the spectrum remained unchanged, (fig. 8.3.). The combined spectral data taken together with some kinetic data (see later) are consistent with the trimer dissociating to a slight extent, perhaps to monomers, (eqn. (8,1)), and the monomers reacting with acrylamide to form an olefin complex, (eqn. (8,2)).

$$[\text{RuCl}_2(\text{MBMSO})_2]_3 \rightleftharpoons K_D \quad 3\text{RuCl}_2(\text{MBMSO})_2(\text{DMA})_n \quad (8,1)$$

$$\text{RuCl}_2(\text{MBMSO})_2(\text{DMA})_n + \text{acrylamide} \rightleftharpoons K_1 \quad \text{RuCl}_2(\text{MBMSO})_2(\text{acryl})(\text{DMA})_n \quad (8,2)$$

8.4. **Catalytic Hydrogenation of Acrylamide**

Catalytic solutions were prepared by the sidearm bucket addition method described in Chapter II. The hydrogen uptake plots were generally recorded from the initial point of solution to ca. 6,000 sec. The uptake plots had an initial "autocatalytic type" non-linear region, the rate increasing to a constant value for a long period, (fig. 8.4.). For the same solutions but with added proton sponge \( R \), (0.056 M), the initial non-linear region lasted approximately twice as long. The constant rate of uptake lasted until approximately 60% reduction of the substrate had occurred, when the rate began to drop; the total uptake corresponded to total reduction of the substrate with no metal visible at this stage. The linear rates of uptake were measured graphically from ca. 1000 to 6000 sec. The rate dependencies on catalyst, hydrogen, substrate, added acid, added
Figure 8.3. Effect of added acryl and H₂ on the spectrum of 8 in DMA at 70°C; [Ru]₇ =0.0038M as monomer, [acryl] =0.05M, pH₂ =610mm; time after reactants combined; 1) 125 sec, 2) 1500 sec.
Figure 8.4. H₂ uptake plots for the reduction of acryl using DMA solutions of 8 at 70°C;

- [Ru]₀ =0.0020M as monomer, [acryl] =0.43M, pH₂ =685mm,
- [Ru]₀ =0.0068M as monomer, [acryl] =0.43M, pH₂ =685mm,
- [Ru]₀ =0.00113M as monomer, [acryl] =0.44M, pH₂ =585mm,
- [proton sponge] =0.056M
chlorides and added MBMSO ligand were studied by the variation of the concentration of one species while holding all other constant. In addition, the variation of rate with the concentration of catalyst, hydrogen, and substrate were studied at a constant added concentration of proton sponge \( R \). The summarized data are presented in Table 8.1.

8.4.1. Dependence on Acrylamide

Fig. 8.5., shows the linear plots of total experimental rate versus the concentration of acrylamide. The plot shows a first-order dependence on substrate but there is a non-zero intercept. A plot of \( \text{Rate}^{-1} \) vs \([\text{acryl}])^{-1}\) is a curve, showing that the dependence is not of the form \( k(\text{olefin})/(a+b(\text{olefin})) \), and that the intercept on the ordinate axis is real. If the non-zero intercept is subtracted from the total rate, the so-called unsaturate path rate curve is obtained, (the rationale behind this will be explained later in Section 8.5.). The slope of the lines is \( 4.82 \times 10^{-6} \text{s}^{-1} \) while the intercept is \( 1.79 \times 10^{-6} \text{Ms}^{-1} \). A similar plot, linear rate vs \([\text{acryl}]\), (fig. 8.6.), is constructed for experiments with added MBMSO (see Table 8.1.). The linear plot has a slope of \( 1.72 \times 10^{-6} \text{s}^{-1} \) and an intercept of \( 0.66 \times 10^{-6} \text{Ms}^{-1} \). The linearity implies again a first order dependence of rate on acrylamide. The intercept value is decreased from that for comparable experiments without added MBMSO. Fig. 8.7., shows the variation of rate with acrylamide for experiments with added proton sponge \( R \); it is not readily apparent whether the three data points represent a linear or curved plot. A curved plot implies a dependence on acrylamide between first and zero
Figure 8.5. Dependence of linear rate on [acryl]; [Ru]_T = 0.00675M as monomer, pH_2 = 686mm, ○ total rate, □ unsaturate rate
Figure 8.6. Dependence of linear rate on [acryl] with added MBMSO; [Ru] = 0.00234 M as monomer, pH = 586 mm, [MBMSO] = 0.0062 M,
- Total rate,  - unsaturate rate
Figure 8.7. Dependence of linear rate on [acryl] with added proton sponge; $[\text{Ru}] = 0.00114\text{M}$ as monomer, $\text{pH}_2 = 585\text{mm}$, $[\text{Proton sponge}] = 0.56\text{M}$.
### TABLE 8.1.

Linear hydrogenation rates for the reduction of acrylamide using $[\text{RuCl}_2(\text{MBMSO})_2]_3$ in DMA at 70°C

<table>
<thead>
<tr>
<th>[Ru$^{II}$]$^a$ x10$^3$</th>
<th>pH$_2$ mm</th>
<th>[H$_2$] x10$^3$</th>
<th>[acrylamide]</th>
<th>Linear Rate x10$^6$, Ms$^{-1}$ Total</th>
<th>Unsat. Path$^b$</th>
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<tr>
<td>6.74</td>
<td>685</td>
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<td>0.106</td>
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continued .........
TABLE 8.1. (cont'd)

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<td>14.84$k$</td>
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<td>0.435</td>
<td>18.18$k$</td>
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a Total amount of ruthenium expressed as the concentration of RuCl$_2$(MBMSO)$_2$ monomer.

b Unsaturate path contribution = total linear rate - olefin-independent linear rate, (see text).

c Added MBMSO; 0.0008M; 0.0012M; 0.0027M; 0.006M

g Added LiCl, 0.010M

h Added DMAHCl, 0.066M; 0.320M

i Added "proton sponge R", 0.026M; 0.056M
order, while a linear plot implies again a first order dependence. A linear plot would have a slope of $2.55 \times 10^{-5}$ s$^{-1}$ and an intercept of $3.66 \times 10^{-6}$ Ms$^{-1}$.

8.4.2. Dependence on Hydrogen

Plots of total linear rate against the concentration of hydrogen are shown in figs. 8.8., and 8.9., the latter for experiments with added proton sponge $R$. Both plots are linear and pass through the origin, indicating a first order rate dependence on hydrogen. Without added proton sponge $R$, the slope is $2.07 \times 10^{-3}$ s$^{-1}$, and for the unsaturate path, $1.20 \times 10^{-3}$ s$^{-1}$. The latter slope is obtained by subtracting the intercept value of fig. 8.6., and correcting for the hydrogen concentration, assuming the intercept is linearly proportional to $[H_2]$, (see Section 8.5.). With added proton sponge $R$, the total rate slope is $8.03 \times 10^{-3}$ s$^{-1}$.

8.4.3. Dependence on Catalyst Concentration

Figs. 8.10., and 8.12., show plots of total linear rate vs the total monomer catalyst concentration. Both curves are fitted to a rate = $a[Ru^{II}]_T^n$ curve, where $n = 0.28$ without proton sponge $R$, and 0.42 with; the latter case has less data points. These data suggest a one-third order dependence of rate on $[Ru^{II}]_T$. This is confirmed by plotting the total linear rate vs the total monomer catalyst concentration to the one-third order. The results are shown in figs. 8.11., and 8.13. The linear plots have slopes of $2.17 \times 10^{-5}$ M$^3$ s$^{-1}$ and $1.22 \times 10^{-5}$ M$^3$ s$^{-1}$ for the total and unsaturate paths, respectively, without added proton sponge $R$.,
Figure 8.8. Dependence of total linear rate on $[H_2]$; $[Ru]_T = 0.00675\text{M}$ as monomer, $[\text{acryl}] = 0.43\text{M}$

Figure 8.9. Dependence of linear rate on $[H_2]$ with added proton sponge$^R$; $[Ru]_T = 0.00116\text{M}$ as monomer, $[\text{acryl}] = 0.44\text{M}$, $[\text{proton sponge}] = 0.056\text{M}$
Figure 8.10. Dependence of total linear rate on $[\text{Ru}^{II}]_T$; pH$_2$ = 685 mm, [acryl] = 0.43 M

Figure 8.11. Dependence of total linear rate on $[\text{Ru}^{II}]_T^{1/3}$; pH$_2$ = 685 mm, [acryl] = 0.43 M
Figure 8.12. Dependence of linear rate on [Ru$^{II}$]$^T$ with added proton sponge$^R$; pH$_2$ =585mm, [acryl] =0.43M, [proton sponge] =0.056M

Figure 8.13. Dependence of linear rate on [Ru$^{II}$]$^{1/3}_T$ with added proton sponge$^R$; pH$_2$ =585mm, [acryl] =0.43M, [proton sponge] =0.056M
and $1.40 \times 10^{-4} \text{ M}^2 \text{s}^{-1}$ and $1.05 \times 10^{-4} \text{ M}^2 \text{s}^{-1}$, respectively, with added proton sponge $^R$. (The unsaturate path slopes are obtained by the same method as described previously (Section 8.4.2.), assuming the intercept is proportional to $[\text{Ru}^{\text{II}}]^3_T$, (see Section 8.5.).)

8.4.4. Dependence on Added MBMSO Ligand

Figs. 8.14. and 8.15., are plots of total linear rate and reciprocal total linear rate, respectively, against the concentration of added MBMSO. Fig. 8.16., shows the reciprocal linear rate vs the cube-root of the concentration of added MBMSO. The experiments were studied in the absence of proton sponge $^R$. Fig. 8.14., shows a definite inverse dependence of rate on the concentration of added MBMSO; the reciprocal plots, however, do not yield good linear relationships.

8.4.5. Dependence on Added Chloride

Addition of upto 0.01 M lithium chloride to a catalyst solution, (see Table 8.I.), had no significant effect on the uptake plot.

8.4.6. Dependence on Added Acid

Acid was added to the catalytic solutions as the HCl adduct of DMA. With 0.066 M DMA·HCl no observable effect on the uptake curve was detected. Further addition to 0.32 M acid at the conditions listed, (see Table 8.I.), resulted in an increase in total rate from $6.24 \times 10^{-6} \text{ Ms}^{-1}$ to $1.13 \times 10^{-5} \text{ Ms}^{-1}$. 
Figure 8.14. Dependence of total linear rate on [MBMSO]; [Ru]_T = 0.00235 M as monomer, pH_2 = 585 mm, [acryl] = 0.43 M.

Figure 8.15. Dependence of (total linear rate)^{-1} on [MBMSO]; [Ru]_T = 0.00235 M as monomer, pH_2 = 585 mm, [acryl] = 0.43 M.
Figure 8.16. Dependence of \((\text{total linear rate})^{-1}\) on \([\text{MBMSO}]^{1/3}; [\text{Ru}]_T = 0.00235\, \text{M as monomer}, \text{pH}_2 = 585\, \text{mm}, [\text{acryl}] = 0.43\, \text{M}\)
8.5. Discussion of Kinetic Results

As stated previously (Chapter VI, Section 6.5), the activation of molecular hydrogen and olefin can occur via either an unsaturate path or a hydride path, or possibly via both paths. The spectral data show some interaction of acrylamide with the trimer, suggesting a possible unsaturate pathway; while an observed reaction of \( \text{H}_2 \) (gas-uptake) with the starting catalyst likewise suggests a possible hydride pathway. The hydride pathway could occur with the formation of either a di- or monohydride, for example as in eqns. (8,3) and (8,4), written for an octahedral Ru(II) monomeric species.

\[
\text{RuCl}_2(\text{MBMSO})_2(\text{DMA})_n + \text{H}_2 \rightleftharpoons \text{H}_2\text{RuCl}_2(\text{MBMSO})_2 + n\text{DMA} \quad (8,3)
\]

\[
\text{RuCl}_2(\text{MBMSO})_2(\text{DMA})_n + \text{H}_2 \rightleftharpoons \text{HRuCl}(\text{MBMSO})_2(\text{DMA})_n + \text{HCl} \quad (8,4)
\]

The non-variance of the \( \text{H}_2 \)-uptake in the absence and presence of excess \( \text{HCl} \) favours the former, (see Section 8.2.). The formation of a ruthenium(IV) dihydride by oxidative addition to ruthenium(II) is well known \(^{106}\), and as written would be expected to show no significant dependence on added acid or chloride. The formation of a monohydride by the heterolytic cleavage of hydrogen and loss of \( \text{HCl} \) is also well known \(^{15,89-93}\); and this process should be inversely dependent on acid, although not necessarily chloride dependent. Proton sponge \(^R\) should aid a reaction such as (8,4)\(^{15}\). If either reactions (8,3) or (8,4) are rate determining steps and are followed in a catalytic pathway by faster reaction steps, then neither reaction
necessarily leads to an observable inverse acid dependence.

The non-linear induction period suggests the build up of active catalyst by trimer dissociation. The extension of this period in the presence of proton sponge \(^R\), together with enhanced activity, could imply more trimer dissociation due to equilibrium (8,4). The inverse dependence on added MBMSO suggests a) the possible loss of sulphoxide ligand prior to or during the rate determining step or b) co-ordination of sulphoxide to form a less active catalyst. These data combined suggest two plausible mechanisms for the hydrogenation of acrylamide without proton sponge \(^R\); after a steady concentration of catalyst species has been set up, Schemes 8-A, and 8-B could be operative.

\[
\begin{align*}
(I) & \quad [\text{Ru}^{II} \text{Cl}_2 \text{S}_2]_3 \xrightleftharpoons[K_D]{\text{K}_{D}} 3\text{Ru}^{II} \text{Cl}_2 \text{S}_2 \\
(II) & \quad \text{Ru}^{II} \text{Cl}_2 \text{S}_2 + \text{H}_2 \xrightarrow[k_1]{\text{slow}} \text{H}_2 \text{Ru}^{IV} \text{Cl}_2 \text{S} + \text{S} \\
(III) & \quad \text{fast} \xrightarrow[\text{K}_3]{\text{K}_3, \text{olefin}} \text{fast} \xrightarrow[k_2]{\text{olefin}} \\
(IV) & \quad \text{RuCl}_2 \text{S}_2 \text{olefin} + \text{H}_2 \xrightarrow[k_4]{\text{slow}} \text{HRuCl}_2 \text{S}_{\text{alkyl}} \xrightarrow[k_5]{\text{fast}} \text{RuCl}_2 \text{S} + \text{sat. product} \\
(V) & \quad \text{fast} \xrightarrow[k_6]{\text{S}} \\
(II) & \quad \text{Scheme 8-A}
\end{align*}
\]

(solvent molecules omitted; \(S = \text{MBMSO}\))
In Scheme 8-A the trimer (I) dissociates to monomers, (II), which react with either hydrogen or olefin to form the dihydride (III) or olefin complex (IV), respectively. The oxidative addition step to form (III) is considered rate determining.

Reaction of olefin with (III) in a fast step produces, presumably via a dihydrido-olefin complex, a hydrido-alkyl complex (II). Oxidative addition of hydrogen to the olefin complex (IV) is also considered a rate determining step, and forms via a dihydride-olefin complex the hydrido-alkyl (V). Saturated product is formed by reductive elimination from (V) in a fast step and the catalyst (II) is reformed by co-ordination of sulphoxide.
Scheme 8-B is similar to 8-A except that the slow steps are reaction of \( \text{H}_2 \) with (II) and (IV) by heterolytic cleavage to form the monohydride (III) and alkyl complex (V), respectively, plus HCl. This reaction can proceed by either direct substitution (hydride for chloride), or by oxidative addition of \( \text{H}_2 \) followed by reductive elimination of HCl. Insertion of olefin into the hydride bond of (III) in a fast step produces the alkyl complex (V). Rapid protonolysis of (V) with HCl yields the saturated product and regenerates the catalyst species (II). In Scheme 8-B as written, MBMSO is not dissociated although it is in Scheme 8-A.

When a steady concentration of species (I-IV) is reached (in the linear uptake region), the rate expression for both mechanisms is given by:

\[
\text{Rate} = R = \frac{d[H_2]}{dt} = k_4[\text{IV}][\text{H}_2] + k_1[\text{II}][\text{H}_2] = k^{1/3}k_3k_4[I][H_2][\text{olefin}] + k^{1/3}k_1[I][H_2] \quad (8,5)
\]

If the concentration of species (II - IV) is much smaller than that of (I) then; \([I] = [\text{Ru}^{II}]_T\) and \([\text{olefin}] = [\text{olefin}]_T\) (where the subscript T refers to total concentration), and eqn. (8,6) becomes:

\[
R = k^{1/3}k_3k_4[\text{Ru}^{II}]_T[H_2][\text{olefin}]_T + k^{1/3}k_1[\text{Ru}^{II}]_T[H_2] \quad (8,7)
\]

Eqn. (8,7) has the experimentally observed first order dependence on hydrogen and total olefin and the cube-root dependence on total trimer concentration. Rate expression (8,7) has an olefin-independent path, (I \( \rightarrow \) II \( \rightarrow \) III \( \rightarrow \) V), whose contribution to the total rate can be evaluated by
extrapolating the experimental rate vs [acryl] curve to zero [acryl], (fig. 8.5.). This olefin-independent hydrogen reduction of acrylamide arises from the rate determining step occurring prior to olefin coordination. Subtracting the olefin-independent (or hydride) path rate, eqn. (8,7), from the total rate gives the unsaturate path rate.

The rate dependence plots yield values for $K_D^{\frac{1}{2}}K_S^{1/2}k_4$ and $K_D^{1/2}k_1$. The value of $K_D^{\frac{1}{2}}K_S^{1/2}k_4$ is found from the slope of the rate vs [acryl] plot, and the value of $K_D^{1/2}k_1$ from this plot's positive intercept. With this value for $K_D^{1/2}k_1$, values for $K_D^{\frac{1}{2}}K_S^{1/2}k_4$ are calculated from the rate vs $[H_2]$ and $[Ru^{II}]^{1/2}$ plots. These values are tabulated in Table 8.II. The values are consistent which adds credence to the proposed mechanistic schemes.

The decision as to which mechanistic scheme, 8-A, or 8-B is more correct is not trivial. Both schemes as written should be independent of added acid or MBMSO, since reaction steps, where either is formed, are rate determining and have no reverse contributions. With Scheme 8-A, addition of MBMSO could decrease the reaction rate of the unsaturate path by interfering with oxidative addition of hydrogen to (IV); oxidative addition to form a seven-co-ordinate species could be less easy than addition to form a six-co-ordinate species. Inhibition of the olefin-independent, hydride pathway with the addition of MBMSO could arise if oxidative addition of $H_2$ involves a prior dissociation of sulfoxide; the addition of MBMSO could reverse this dissociation equilibrium. Experimental data in the presence of added sulfoxide show a decreased total rate and a decreased olefin-independent rate, while still retaining a first-order rate dependence on olefin substrate, (fig. 8.6.). The
TABLE 8.II.
Values of $K_D^{1/3} K_3 k_4$ and $K_D^{1/3} k_1$ for the hydrogenation of acrylamide using $[\text{RuCl}_2(\text{MBMSO})_2]_3$ in DMA at 70°C

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<th>$\frac{1}{3} K_D^{1/3} K_3 k_4$</th>
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<tr>
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</tr>
<tr>
<td>III</td>
<td>0.014</td>
<td>0.0046</td>
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\(^a\)Plot of Rate versus: I) [acrylamide]; II) $[H_2]$; III) $[\text{Ru}^{II}]_T^{1/3}$. 
decrease in both rates is by a factor of about one-third implying that added sulfoxide affects both pathways approximately equally. These data suggest that perhaps an additional MBMSO ligand co-ordinates to the active catalyst species (II) to form a less active species such as RuCl$_2$S$_3$(DMA)$_n$; however, no evidence for such a species was found from spectral data, (Section 8.3.), nor from the synthetic reaction, (Chapter VII). Scheme 8-B, as written, has no MBMSO dependence; however, as stated earlier, addition of MBMSO could by further co-ordination decrease the amount of active bis-sulfoxide catalysts (II), and hence decrease both the unsaturate and hydride path rates. A rate lowering with added MBMSO could occur if formation of the monohydride intermediate in the reaction of IV with H$_2$ proceeds via oxidative addition to form a seven-co-ordinate species which then dissociates sulfoxide to become six-co-ordinate; this then reductively eliminates HCl and undergoes insertion of olefin into the metal-hydride bond to form (V). This rate lowering will only occur for the unsaturate path since a seven-co-ordinate species is not present in the hydride path.

With Scheme 8-B, addition of proton sponge $^R$, should result in an overall rate lowering by impeding the final protonolysis step, while experimentally the opposite is observed, a large rate enhancement. The MBMSO and proton sponge $^R$ dependencies, as well as the acid independent reaction of trimer with H$_2$, strongly favour Scheme 8-A involving activation of H$_2$ by oxidative addition to give a dihydride. The experimentally observed doubling of rate with added 0.32 M DMA·HCl is probably not significant. Variations in H$_2$ solubility could well explain such
small changes. The possibility of the production of more active anionic species such as $[\text{RuCl}_3S_n\text{(DMA)}]^{-}$ was not investigated in any detail although added chloride to 0.01 M had no effect on the observed hydrogenation rates.

The catalytic scheme that is operating in the presence of proton sponge $^R$ is not clear. The overall rate dependencies are similar to those found in the absence of proton sponge $^R$, although the olefin dependence is somewhat ambiguous. Scheme 8-A has no obvious base dependence, while in (8-B) formation of monohydride species would be promoted but the final protonolysis impeded. The earlier presented uptake data for the reaction of 8 with $H_2$ could be accounted for by base-promoted formation of hydrido species containing no chlorides, for example eqn. (8,4) followed by:

\[
\begin{align*}
\text{HRu}^{\text{II}}\text{ClS}_2 + H_2 & \iff [\text{H}_3\text{Ru}^{\text{IV}}\text{ClS}_2] \iff \text{H}_2\text{Ru}^{\text{II}}\text{S}_2 + \text{HCl} \quad (8,8) \\
\text{H}_2\text{Ru}^{\text{II}}\text{S}_2 + H_2 & \iff \text{H}_4\text{Ru}^{\text{IV}}\text{S}_2 \quad (8,9)
\end{align*}
\]

These processes involve both a net heterolytic cleavage of $H_2$ to form a dihydride species, and then oxidative addition of $H_2$ to form a tetrahydrido complex. Reduction of an olefin co-ordinated to such hydrides could give the saturated product through hydride-transfer and reductive elimination. Proton sponge $^R$ could enhance formation of dihydride (III), (eqn. (8,8)). A $\text{H}_4\text{Ru(PPh}_3)_3$ complex has been synthesized by reaction of $\text{RuCl}_2(P\text{Ph}_3)_3$ with $H_2$ in the presence of added triethylamine base $^{107}$, presumably via reactions (8,4), (8,8), and (8,9), and such processes have been postulated by Strathdee and Given $^{108}$ to account for a rapid $H_2$-$D_2$ exchange reaction in the presence of benzene solutions of $\text{RuHCl(PPh}_3)_3$. 

8.6. Discussion

The mechanism proposed in Scheme 8-A, is basically similar to that proposed for the RhCl(PPh$_3$)$_3$ system by Wilkinson$^{106}$ and for Ru(I) systems by James and Hui$^{24}$. The olefin-independent hydride path can be expanded from that previously postulated to that shown below:

$$
\text{Ru}^{II}Cl_2S_2 \overset{k_1}{\text{fast}} \text{Ru}^{II}Cl_2S + S \overset{k_2}{\text{slow}} H_2 \text{Ru}^{IV}Cl_2S
$$

(8,10)

$$
H_2\text{Ru}^{IV}Cl_2S + \text{olefin} \overset{k_2}{\text{fast}} H_2\text{Ru}^{IV}Cl_2S(\text{olefin})
$$

(8,11)

$$
H_2\text{Ru}^{IV}Cl_2S(\text{olefin}) \overset{k_3}{\text{fast}} H\text{Ru}^{IV}Cl_2S(\text{alkyl})
$$

(8,12)

(solvent molecules omitted)

For the $d^8$Rh(I) and $d^7$Ru(I) systems mentioned above, the rate determining step was written as involving the reaction of olefin with the dihydride rather than formation of the dihydride. With the present Ru(II) system the change in rate determining step could result from the more difficult oxidative addition of $H_2$ to a $d^6$ system. Eqn. (8,10) involves loss of sulphoxide and the reaction of a monosulphoxide complex with $H_2$ to form a hydride having an accessible co-ordination site for the olefin; this dissociation can account in part for the observed inverse rate dependence on sulphoxide. Eqn. (8,11) involves formation of the dihydride-olefin complex, and eqn. (8,12), insertion of the olefin into the metal-hydride bond; both are fast steps, in comparison to $k_1$. 
The unsaturate path is shown in more detail below:

\[
\text{Ru}^{II}\text{Cl}_2\text{S}_2 + \text{olefin} \xrightarrow{k_3^{\text{fast}}} \text{Ru}^{II}\text{Cl}_2\text{S}_2(\text{olefin}) \quad (8,13)
\]

\[
\text{Ru}^{II}\text{Cl}_2\text{S}_2(\text{olefin}) \xrightarrow{k_4^{\text{fast}}} \text{Ru}^{II}\text{Cl}_2\text{S}(\text{olefin}) + \text{S} \quad (8,14)
\]

\[
\text{Ru}^{II}\text{Cl}_2\text{S}(\text{olefin}) + \text{H}_2 \xrightarrow{k_4^{\text{slow}}} \text{H}_2\text{Ru}^{IV}\text{Cl}_2\text{S}(\text{olefin}) \quad (8,15)
\]

\[
\text{H}_2\text{Ru}^{IV}\text{Cl}_2\text{S}(\text{olefin}) \xrightarrow{k_4^{\text{fast}}} \text{HRu}^{IV}\text{Cl}_2\text{S}(\text{alkyl}) \quad (8,16)
\]

The slow step is reaction (8,15), again oxidative addition of \( \text{H}_2 \) to a \( d^6 \) metal species to form a six-co-ordinate dihydride complex. The prior dissociation of sulphoxide, (eqn. (8,14)), could be partly responsible for the observed inverse added MBMSO dependence. Seven-co-ordinate hydride species do exist, for example \( \text{H}_4\text{Ru}(\text{PPh}_3)_3^{107} \), but here four of the ligands are small. James and Ng propose such an oxidative addition of \( \text{H}_2 \) to an olefin complex, as the rate determining step for a number of Rh(I) systems, including some with sulphide ligands, and certain of the RhClP\(_3\) systems may operate via this same unsaturate route\(^{106}\).

The last steps of mechanism 8-A involve reductive elimination of saturated product and reformation of the catalyst by co-ordination of sulphoxide:

\[
\text{HRu}^{IV}\text{Cl}_2\text{S} \text{alkyl} \xrightarrow{k_5^{\text{fast}}} \text{Ru}^{II}\text{Cl}_2\text{S} + \text{Sat. product} \quad (8,17)
\]

\[
\text{Ru}^{II}\text{Cl}_2\text{S} + \text{S} \xrightarrow{k_6^{\text{fast}}} \text{Ru}^{II}\text{Cl}_2\text{S}_2 \quad (8,18)
\]
Experiments have shown for the Ru(I) system and the Rh(I) system that the two hydride ligands of the $\text{H}_2\text{M}$ (olefin) complexes are transferred consecutively$^{110}$.  

8.6.1. **Comparison of the $[\text{RuCl}_2(\text{MBMSO})_2]_3$ System with that of $[\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]$**

At first glance close similarity might have been expected between the hydrogenation catalysis by the $[\text{RuCl}_3(\text{DMSO})_3]^{-}$ anion and the $\text{RuCl}_2(\text{MBMSO})_2$ monomer by virtue of their related ligands and their same initial ruthenium oxidation state. The marked differences, (type of $\text{H}_2$ activation, lack of an unsaturate path for the anion system, and type of final step which is protonolysis for the anion system and hydride ligand transfer for the trimer system) possibly stem from the number and type of co-ordinated sulphonyl oxide ligands. The initial catalyst species in the former system is six-co-ordinate, while in the latter it is four co-ordinate, neglecting solvent molecules. Initial oxidative addition of $\text{H}_2$ and olefin complexation to the four co-ordinate species seems intuitively more likely than to the co-ordinatively saturated six-co-ordinate species. For example, for oxidative addition the latter would require the loss of two co-ordinated ligands or else formation of an eight co-ordinate species. The larger number of chloride ligands of $\text{RuCl}_3(\text{DMSO})_3^{-}$ could favour heterolytic cleavage of $\text{H}_2$ and loss of $\text{HCl}$.

Both systems feature an olefin-independent path, which results from a rate determining reaction with $\text{H}_2$ followed by a fast olefin complexation and hydride ion transfer.
The mechanistic scheme proposed for \([\text{RuCl}_2(\text{MBMSO})_2]_3\), (8-A), is a precedent in that the system features as an initial reaction oxidative addition of \(\text{H}_2\) to form a dihydride species; the \(\text{HRuClP}_3\) catalysed systems are believed to involve oxidative addition of \(\text{H}_2\) to an intermediate metal-alkyl complex as the rate determining step. The \([\text{RuCl}_3(\text{DMSO})_3]^-\) anion system is similar to the aqueous chlororuthenate(II) systems of Halpern et al.\(^{13}\), which feature olefin co-ordination, followed by hydrogen activation by heterolytic cleavage of \(\text{H}_2\) and protonolysis of the resulting metal-alkyl complex.
CHAPTER IX

ASYMMETRIC HYDROGENATION OF OLEFINIC SUBSTRATES USING
DICHLOROBIS[(S,R,S,S)-2-METHYLBUTYL METHYL SULPHOXIDE]-
RUTHENIUM(II) COMPLEXES

9.1. Introduction

As mentioned earlier, homogeneous catalytic asymmetric hydrogenation with complexes containing chiral phosphine ligands is well known. The title catalyst is the first example of such hydrogenation using complexes containing chiral sulphoxide ligands. The enantiomeric excesses are modest in comparison to the phosphine systems but are nonetheless significant.

The similarity of the two catalysts, ether-solvated complex 7 and the trimeric complex 8 was pointed out in Chapter VII. The kinetics and mechanism of hydrogenation of acrylamide using 8 were presented in Chapter VIII. It seems highly likely that both catalysts 7 and 8 will hydrogenate the pro-chiral substrate olefins by the same mechanism, which presumably will be similar to that by which 8 reduces acrylamide.

9.2. Asymmetric Hydrogenation Results

Many hydrogenation experiments were conducted in DMA with ether-solvated 7 or trimeric 8, as catalysts. The substrate concentrations and hydrogen pressures were varied as were the reaction times.
Several olefin substrates could not be reduced over a reasonable time period (several days) at high pressure (1300 psi $H_2$). These included $\alpha$- and $\beta$-methylcinnamic acid (I) and (II), citraconic (III) and mesaconic acid (IV), (fig. 9.1.). No metal was produced in these experiments.

Itaconic acid (V) and 2-acetamidoacrylic acid (VI) were hydrogenated to $\alpha$-methylsuccinic acids (VII) and N-acetyllalanines (VIII), respectively, (fig. 9.1.), under homogeneous conditions with no production of metal.

Atropic acid (IX) was hydrogenated to 2-phenyl-propanoic acids (X) at 1 atm $H_2$ and 60°C in DMA, but metal formed rapidly during the reaction, (fig. 9.1.); in any case, the acid products had no optical rotation.

There are only a limited number and type of olefinic substrates that are available to be hydrogenated to products whose specific rotation of their R and S isomers is known. The useful olefins are mainly substituted mono- or dicarboxylic acids. In Table 9.1., are listed the results of asymmetric hydrogenation experiments, completed with I) ether-solvated RuCl$_2$(MBMSO)$_2$, complex 7, and II) trimeric 8, [RuCl$_2$(MBMSO)$_2$]$_3$. It can be seen that the largest enantiomeric excesses occur for itaconic acid at lower hydrogen pressure. Both catalysts appear to be similarly effective for stereoselective hydrogenation.

9.3. Discussion

A common feature of the four olefinic substrates that could not be reduced to any extent is their bulkiness. $\alpha$- and $\beta$-methylcinnamic, citraconic, and mesaconic acids are tri-substituted olefins with bulky substituents at the double bond. The large size likely results in poor co-ordination to the ruthenium(II) catalysts and hence ineffective
Figure 9.1. Prochiral olefin substrates and their hydrogenation products.
TABLE 9.1.

Results of asymmetric hydrogenations in DMA\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Ru\textsuperscript{II}]/\text{T}</th>
<th>Substrate</th>
<th>[Substrate]</th>
<th>T\textdegree C</th>
<th>pH\textsubscript{2} (psi)</th>
<th>% Reaction</th>
<th>t(hr.)</th>
<th>e.e.\textsuperscript{d} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I\textsuperscript{b}</td>
<td>0.018</td>
<td>2-acetamido acrylic acid</td>
<td>0.45</td>
<td>60</td>
<td>1500</td>
<td>100</td>
<td>240</td>
<td>1.5\textsuperscript{e} (R)</td>
</tr>
<tr>
<td></td>
<td>0.014</td>
<td></td>
<td>0.31</td>
<td>42</td>
<td>45</td>
<td>87</td>
<td>170</td>
<td>0.45\textsuperscript{e} (S)</td>
</tr>
<tr>
<td></td>
<td>0.021</td>
<td>itaconic acid</td>
<td>0.44</td>
<td>60</td>
<td>1300</td>
<td>74</td>
<td>68</td>
<td>4.3\textsuperscript{e} (R)</td>
</tr>
<tr>
<td></td>
<td>0.014</td>
<td></td>
<td>1.00</td>
<td>42</td>
<td>49</td>
<td>37</td>
<td>240</td>
<td>12.1\textsuperscript{e} (R)</td>
</tr>
<tr>
<td>II\textsuperscript{c}</td>
<td>0.018</td>
<td></td>
<td>1.35</td>
<td>40</td>
<td>44</td>
<td>53</td>
<td>240</td>
<td>14.8\textsuperscript{e} (R)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 5 ml. solution
\textsuperscript{b} Concentration as monomer M.W. = 542 g/mole including diethyl ether.
\textsuperscript{c} Concentration as monomer.
\textsuperscript{d} Predominant enantiomer in parentheses.
\textsuperscript{e} Enantiomeric excesses determined from the specific rotation of the sample; based on the maximum [\alpha]\textsubscript{D}\textsuperscript{1} of the pure chiral acid; (S)-N-acetyllalamine, [\alpha]\textsubscript{D}\textsuperscript{26} = -66.5\textdegree; C\textsubscript{2}, H\textsubscript{2}O\textsuperscript{111}, (R)-\textalpha-methyl\textalpha-

\textsuperscript{f} Enantiomeric excess determined with chiral shift reagent on the dimethyl ester of the product.
hydrogenation. Itaconic acid and 2-acetamidoacrylic acid, on the other hand, are both terminal olefins. The result is perhaps less steric interference to co-ordination and the availability of reduction pathways. Atropic acid appears to be a special case since it was the only substrate system that produced metal under the hydrogenation conditions. Formation of metal could result from destabilization of a hydrido-olefin complex with tendency to give metal formation, (eg., $\text{H}_2\text{Ru}^{IV}(\text{olefin}) \longrightarrow \text{Ru}^0 + 2\text{H}^+ + \text{olefin}$). This destabilization could be enhanced by either large $\sigma$-electron donation to the metal from the olefin, or small $\pi$ back-donation from the metal to the olefin. Atropic acid has an aromatic substituent which is capable of donating or withdrawing electron density to or from the metal-centre. The non-production of metal in the $\alpha$- and $\beta$-methylcinnamic acid system is perhaps indicative of the lack of formation of hydrido-olefin complexes in these cases.

9.3.1. Mechanistic Considerations Based on the Acrylamide Hydrogenation Catalysed by $[\text{RuCl}_2(\text{MBMO})_2]_3$

The catalyst and substrate concentrations employed for the previous kinetic study on acrylamide hydrogenation (Chapter VIII), overlap with those used for the present asymmetric reductions. The pressures employed in the latter are however ca. 3 or 100 times those used for the former. The use of acid substrates should have little effect on the basic mechanism of Scheme (8-A), (see Section 8.5., Chapter VIII). Both the olefin-independent hydride and olefin-dependent unsaturate paths involve complexation of the olefin and hydrogen to form a dihydrido-olefin complex, followed by hydrogen transfer to form the products. Complexation by
itaconic acid and 2-acetomidoacrylic acid is not limited to co-ordination through the double bond. It is possible that co-ordination by way of the carboxylic acid anion oxygen to the metal could occur. Hydrogen bonding is also possible between the non-ionized acid protons of the substrate or the proton of the amido NH group and the sulphoxide oxygen. Olefin movement could be restricted by electronic repulsion between a negatively charged carboxylic acid group, and the electron-rich sulphoxide oxygen.

In short then, there are many ways that the olefins could co-ordinate and lock themselves into position on the catalyst so that the addition of hydrogen to the double bond is stereospecific. Restricted rotation of the olefin about the metal-olefin bond can also arise from steric interaction of the bulky olefin substituents with the catalyst sulphoxide ligands. This cannot be the sole reason for stereoselective hydrogenation as both hydrogenation pathways likely involve species with only one co-ordinated sulphoxide.

Restricted rotation of the olefin alone will not result in high stereoselectivity, since it is also important which face of the olefin is presented to the catalyst for the hydrogen transfer steps. Indeed, the asymmetric process is probably a combination of all the above factors, electronic and steric. The fact that high $H_2$ pressures are required for effective reduction of the acid substrates compared to the $<1$ atm hydrogenation of acrylamide offers indirect support that addition of $H_2$ is involved in the rate determining step. Furthermore, the major pathway at higher olefin concentrations appear to be oxidative addition of $H_2$ to a Ru$^{II}$ (olefin) moiety, (cf. Scheme 8-A, Section 8.5. Chapter VIII). The
olefinic acid substrates when co-ordinated to the Ru$^{II}$ may well act as stronger $\pi$-acids than acrylamide; this would increase the promotion energy for the $H_2$ oxidative addition, and lead to the requirement of more severe conditions, such as higher $H_2$ pressures.

Each of the mechanistic steps, olefin co-ordination, hydrogen co-ordination, and hydrogen transfer, are likely concerned in the overall process leading to an enantiomer excess in the product. In both pathways the olefin and hydrogen activation steps govern which hydride-olefin complex is in excess, depending on the free energies of formation ($\Delta G^0$) and activation ($\Delta G^\dagger$) of these complexes; the $\Delta G$'s are of course related to the equilibrium constants $K_1^\prime$, $K_3^\prime$ and $K_4^\prime$, and the $\Delta G^\dagger$ activation energies to the rate constants, $k_1^\prime$, $k_2^\prime$, and $k_4^\prime$, eqns. (8,10) - (8,16).

The amount of each hydrido-alkyl complex formed in the first hydride transfer step is dependent upon the activation energies for the processes, and hence upon the rate constants, $k_2^\prime$ and $k_4^\prime$, and $k_4^\prime$, eqns. (8,12), (8,15), and (8,16). Reductive elimination of saturated product is the last governing factor on enantiomeric product distribution. The activation energies and hence $k_5^\prime$'s for production of each enantiomer controls this product distribution. For the fast steps governed by the different $k_2$'s and $k_5$'s, the extent of enantiomer ratio enhancement should be relatively small since these are fast steps. The slow steps, represented by the $k_1$'s and $k_4$'s could have a larger bearing on the overall stereo-selectivity of the hydrogenation. The order of fast and slow steps in the reduction mechanism could have a major influence on the overall enantiomeric excess. The hydride path involves a fast step for olefin co-ordination and hydride transfer; the unsaturate route involves an equilibrium.
governing olefin co-ordination and a slow step for oxidative addition. The result could be less stereoselectivity for the hydride path relative to the unsaturate path. The effect of severe conditions, (for example high pressure), could be the removal of differentiation between stereoselective pathways. Higher pressure could cause the $\Delta G^\circ$'s or $\Delta G^\ddagger$'s of a reaction step to become similar and make that step less stereoselective. Higher pressures could as well invert the relative orders of $\Delta G^\circ$'s or $\Delta G^\ddagger$'s of a reaction step, thus favouring a different product isomer. The effect of pressure on the catalytic system is large, with stereoselectivity reduced at higher pressures with itaconic acid, and the predominant enantiomer produced reversed at high pressures with 2-acetamidoacrylic acid (Table 9.I.).

Reasons for the low stereoselectivity for the reduction of 2-acetamidoacrylic acid are not obvious. In comparison to itaconic acid, the carboxyl or carboxylate group is not as far removed from the double bond as is one such group of itaconic acid. Co-ordination of the carboxylate anion oxygen to ruthenium or H-bonding of the carboxyl proton to a sulfoxide oxygen, or even a chloride ligand may not occur as with itaconic acid. Such reasoning, however, is in contradiction to the published work of Knowles et al.\textsuperscript{6}, who feel that for their Rh(I) phosphine systems with 2-acetamidoacrylic acid, co-ordination of the carboxylate anion oxygen to metal occurs as well as H-bonding of the N-H proton to an appropriate ligand atom; however, some very recent data by this group indicates the H-bonding hypothesis may not be correct\textsuperscript{114}.

The general low stereoselectivity for catalyst 8 could result
from one or both of two reasons; a) the presence of the olefin-independent path where olefin co-ordination and hydride transfer is fast and perhaps low in stereoselectivity, and b) the nature of the chiral MBMSO ligand which is a mixture of two diasteromers. A catalyst prepared from only one diastereomer may have a higher stereoselectivity for hydrogenation.
CHAPTER X

POLYMERIC CHLOROSULPHOXIDE COMPLEXES OF RUTHENIUM(II):
TRIMERIC DICHLOROBIS[(R)-(+)-METHYL P-TOLYL SULPHOXIDE]
RUTHENIUM(II) AND POLYMERIC DICHLOROBIS[METHYL PHENYL
SULPHOXIDE]RUTHENIUM(II)

10.1. Introduction

This chapter presents studies on two more polymeric ruthenium(II) compounds. The first member of this series, [RuCl\(_2\)(MBMSO)\(_2\)]\(_n\), was presented earlier, (Chapter VII). Trimeric [RuCl\(_2\)(MPTSO)\(_2\)]\(_3\), 10, contains sulphoxide ligands with completely chiral sulphur centres; to our knowledge this is the first ruthenium(II) complex of this type. Complex 10 catalytically hydrogenates olefinic substrates, for example acrylamide, atropic and itaconic acids, in DMA at 60°C under 1 atm of hydrogen; however, olefinic reduction occurs concomitant with the formation of ruthenium metal. The complex also reacts with carbon monoxide (1 atm) at 60°C in toluene.

Compound 6, [RuCl\(_2\)(MPSO)\(_2\)]\(_n\), has limited solubility in all solvents and hence has no observed hydrogenation properties.

10.2. Trimeric Dichlorobis[(R)-(+)-methyl p-tolyl sulphoxide]ruthenium(II), 10

This compound was prepared by the addition of (R)-(+)methyl p-tolyl
sulphoxide to a methanolic "blue solution" using a mole ratio of sulphoxide to Ru(II) of 2:1. The reaction residue, after filtering and removal of methanol by pumping, was dissolved in either chloroform or benzene and filtered. The product was precipitated from chloroform with diethyl ether or freeze-dried from benzene. The solid product could not be successfully recrystallized from various solvent systems, for example, CHCl₃-diethyl ether; only oils resulted. Solutions of compound 10 turned green in air over a few days, and on analogy to \[\text{RuCl}_2(\text{MBMSO})_2\]₃ probably contains ruthenium(III) species.

A degree of association of 2.8, (M.W. = 1358 g/mole) was obtained in benzene via freezing point depression, implying a trimer in the solid state. A measured $\nu^{22}_{\text{eff}}$ of 0.67 ± 0.15 B.M. per trimer, (Guoy Method), is consistent with a diamagnetic ruthenium(II) complex probably containing some paramagnetic ruthenium(III) impurities, (see Section 7.3., Chapter VII). The conductivity in DMA ($\Lambda^{22} = 4.6 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}$) indicates essentially a neutral complex. Complex 10 has similar solubility characteristics to \[\text{RuCl}_2(\text{MBMSO})_2\]₃.

10.2.1. I.r. Spectrum

A strong broad band centred at 1110 cm⁻¹ is indicative of S-bonded sulfoxide and is assigned to $\nu$(SO); $\nu$(SO) for the free ligand is at 1055 cm⁻¹. The presence of bands due to O-bonded sulfoxide in the region 900 to 980 cm⁻¹ is equivocal, since this region is complicated by strong bands present in the complex and free ligand at 950 and 975 cm⁻¹. In the far i.r. a medium, broad band centred at 325 cm⁻¹ is tentatively assigned to terminal Ru-Cl stretches.
10.2.2. **H n.m.r. Spectrum**

The n.m.r. spectrum of 10 in CDCl₃ consists of three rather broad resonances. At δ2.04 - 2.58 are resonances due to protons of the p-tolyl methyl group. From δ3.34 - 3.96 are resonances due to the sulphoxide methyl protons of S-bonded sulphoxide. From δ6.44 - 7.90 are resonances due to the aromatic protons. The free ligand has resonances at δ2.45, 2.74, and 7.46, due to the para-methyl, sulphoxide methyl, and aromatic protons, respectively. No definite resonances due to sulphoxide methyl protons of O-bonded sulphoxide are observed; however, there is low intensity broad absorbance between δ2.58 and 3.34 which complicates this detection. A ratio of intensities of the S-bonded region to this broad low intensity region indicates that little if any O-bonded sulphoxide is present.

The broadness of the peaks could be due to the many different chemical environments in the trimer, coupled with restricted ligand motion; the presence of paramagnetic impurity could be a problem, although the solution for n.m.r. study was prepared under Ar.

10.2.3. **Discussion**

Compound 10 appears to be similar to complex 8; both are neutral mainly S-co-ordinated, presumably chloride. bridged trimeric solids. The possible structures for this trimer are similar to those

† See also Chapter II, (fig. 2.10.).
suggested for compound 8, (see Section 7.3.3., Chapter VII). The difference in size between the two sulphoxides of compounds 8 and 10 (a sec-butyl group as compared to a para-tolyl group), apparently causes no changes in co-ordination or in the degree of monomer association.

10.3. The Reaction of Compound 10 with Carbon Monoxide

Complex 10 reacts with CO (1 atm) in toluene at 50°C. The total uptake ratio of CO to Ru is 2:1. I.r. spectra of the reaction solution, and the reaction residue after the toluene was pumped off and either dissolved in CCl₄ or neat, were recorded, (Table 10.1). A poorly resolved far i.r. resulted in no useful data from this region.

A solid product could not be isolated from the reaction residual oil either by precipitation with ether or crystallization from pet. ether (30-60°)-diethyl ether solvent.

10.3.1. Discussion

The similarity between compound 10 and 8 is again apparent with the formation of an apparent dichlorodicarbonylbis(sulphoxide)ruthenium(II) complex. The empirical formula is assigned from the CO uptake data and comparison with the CO derivatives of complex 8. No microanalytical data were collected on the product oil to confirm the formula.

Here again the product formed from the CO-reaction is an apparent cis-carbonyl isomer, although a small third ν(CO) band is present as a shoulder of the band at 2060 cm⁻¹. This could be due to the presence of a small amount of another cis- or even trans-carbonyl isomer. The
TABLE 10.I.

I.r. spectral data for carbonyl derivatives of \([\text{RuCl}_2(\text{MPTSO})_2]^3\)

<table>
<thead>
<tr>
<th></th>
<th>(v(\text{CO})^a)</th>
<th>(v(\text{SO})^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I)(^b)</td>
<td>2137s, 2080sh, 2060</td>
<td>-</td>
</tr>
<tr>
<td>II)(^c)</td>
<td>2137s, 2080sh, 2060</td>
<td>-</td>
</tr>
<tr>
<td>III)(^d)</td>
<td>2138s, 2068br</td>
<td>1100br</td>
</tr>
</tbody>
</table>

\(^a\) In cm\(^{-1}\).
\(^b\) Reaction mixture; toluene solvent in NaCl cells.
\(^c\) Reaction residue in CCl\(_4\) after the toluene was removed; in NaCl cells.
\(^d\) Reaction residue after the toluene was removed; between CsI plates.

s = sharp, sh = shoulder, br = broad
product again features the very high $\nu$(CO) band; the present band is higher than that found for the carbonyl derivatives of trimer 8, ($\nu$(CO) = 2130 cm$^{-1}$). Inspection of the $\nu$(SO) band illustrates the difference between this product and that from 8. Whereas the present product with a higher $\nu$(SO) has S-co-ordination, the product from 8 has O-co-ordination. In view of the arguments raised for the CO derivatives of 8, (see Section 7.4.1., Chapter VII), it would appear that if methyl p-tolyl sulphoxide was a stronger $\pi$-acid than triphenyl phosphine then the high $\nu$(CO) could be rationalized.

A fuller characterization of the carbonyl product must await further work.

10.4. **Catalytic Hydrogenation with Compound 10**

It was hoped that stereoselective hydrogenation of olefins would be attained using a complex such as 10 containing a pure chiral sulphur centre. However, with all olefinic substrates tested, acrylamide, itaconic and atropic acids, the hydrogenations were accompanied by the production of ruthenium metal. Experiments were done at high and low hydrogen pressures, (ca. 1800 and 14 psi), at 60°C in DMA with similar results. Complete hydrogenation of the olefinic substrates occurred; presumably heterogeneously catalysed by metal, but with no observable stereoselectivity.

Catalyst 10 in the presence of 1 atm H$_2$ at 60°C in DMA, for the same reaction time as used in the substrate experiments, did not
produce any metal. This suggests that any ruthenium hydride species produced were stable towards reduction to metal. The reduction of the ruthenium(II) sulphoxide catalyst must then occur by way of a reaction with hydrogen and olefin to produce an unstable hydrido-olefin complex which subsequently decomposes to metal; similar conclusions were drawn for the $[\text{RuCl}_2(\text{MBMSO})_3]$-atropic acid systems. The combination of poor $\pi$-electron acceptor ability of the co-ordinated olefin substrate with insufficient $\pi$-acceptor strength of the sulphoxide, or strong $\sigma$ donation of the olefin and of the sulphoxide, could lead to a high electron density on the Ru(II) with the subsequent reduction of the hydrido-olefin complex to metal. Available evidence, namely the lack of formation of metal with the $[\text{RuCl}_2(\text{MBMSO})_3]$-acrylamide system under similar reaction conditions, suggests that methyl p-tolyl sulphoxide is a weaker $\pi$-acid, or stronger $\sigma$-donor than 2-methylbutyl methyl sulphoxide. Data on phosphines however, suggest that triphenylphosphine is perhaps a poorer $\sigma$-donor than trialkyl phosphines. These data tend to suggest that the difference in the two sulphoxides is perhaps a $\pi$-effect.

10.5. Polymeric Dichlorobis(methyl phenyl sulphoxide)ruthenium(II), 6

Compound 6 was prepared from a methanolic "blue solution" by the addition of racemic methyl phenyl sulphoxide in a mole ratio of sulphoxide:ruthenium = 3:1. During the course of the reaction, a red solution precipitated a gold coloured solid in 63% yield. Recrystallization attempts failed due to limited solubility; the compound is very slightly soluble in acetone, $\text{CH}_2\text{Cl}_2$, EtOH, and DMA. Elemental analysis confirmed
the product to be the title compound. Determination of the magnetic moment of \( \text{6} \) by the Faraday method showed it to be diamagnetic or feebly paramagnetic. The measured \( X_M^{\text{corr.}} \) was \((76 \pm 9) \times 10^{-6}\) c.g.s. per monomer resulting in a \( \mu_{\text{eff}}^{22} \) which is negative or 0.42 B.M.

10.5.1. I.r. Spectrum

The i.r. spectrum contains a strong, fairly broad band centred at 1130 cm\(^{-1}\) assigned to \( v(SO) \) (S-bonded); the free sulphoxide \( v(SO) \) is at 1045 cm\(^{-1}\). A band due to \( v(SO) \) (O-bonded) is not observed, although again this region of the spectrum, 900 - 980 cm\(^{-1}\) is complicated by a strong ligand band at 960 cm\(^{-1}\). In the far i.r. a medium intensity band at 330 cm\(^{-1}\) is assigned to the terminal metal-chloride stretching mode.

10.5.2. Discussion

Compound \( \text{6} \) is similar to complexes \( \text{8} \) and \( \text{10} \). The striking difference between \( \text{6} \) and the other two compounds is its solubility. The low solubility could be due to a large aggregation size, although it is not readily apparent why a trimer is not formed. The lack of an alkyl substituent on the phenyl ring might perhaps lower its solubility relative to compound \( \text{10} \), as perhaps would alignment of the phenyl rings by restricting solvation.

The steric problems in forming tris- or tetrakis-sulphoxide complexes is again present with methyl phenyl sulphotide since the bis substituted complex is formed in the reaction mixture in the presence of an excess of sulphoxide ligand. Hydrogenation properties of this compound were not explored due to its low solubility.
CHAPTER XI

DICHLORO-DIOS AND -DDIOS COMPLEXES OF RUTHENIUM(II)

11.1. Introduction

Several research groups, including those of Knowles et al.\textsuperscript{6}, Kagan and Dang\textsuperscript{98}, and Cullen et al.\textsuperscript{111}, have had good success with stereo-selective hydrogenation of olefins using rhodium(I) complexes containing the chiral bidentate phosphine ligand, Diop. Very recently, similar good results were reported for such hydrogenation using ruthenium(II)-Diop catalysts\textsuperscript{28}.

It was decided in this laboratory that a sulphoxide analogue of this ligand could be made, along with corresponding ruthenium(II) complexes. The resulting compounds were indeed found to be stereoselective homogeneous hydrogenation catalysts for a number of olefin substrate systems, although the level of stereoselectivity attained is generally considerably less than that found for the Rh(I)- or Ru(II)-Diop systems reported above; however, this itself is of interest. Studies on the corresponding rhodium sulphoxide systems are currently being carried out in this laboratory\textsuperscript{115}.

This chapter discusses the characterization of stereoselective homogeneous hydrogenation catalysts containing the Dios ligand and/or DDios ligand; RuCl\textsubscript{2}(DDios)\textsubscript{2}·2H\textsubscript{2}O, RuCl\textsubscript{2}(Dios)(DDios), and RuCl\textsubscript{2}(DDios)(DMSO)(MeOH). The stereoselective hydrogenation studies with these catalysts are presented in the next chapter.
11.2. **Dichlorobis(DDios) ruthenium(II)dihydrate, 11**

Compound 11 was prepared from a methanolic "blue solution" via preparative route 1 (Chapter IV), or by sulphoxide exchange in methanol of Dios with RuCl$_2$(DMSO)$_4$, preparative route 3, (Chapter IV).

From the "blue solution" a light green solid initially precipitated during the reaction, and on cooling a yellow solid precipitated. Dissolution of both solids in water and precipitation with acetone yielded a yellow solid. The exchange reaction yielded a yellow solid. I.r. and n.m.r. spectral data showed all the above products to be similar in composition. Elemental analysis of the product from the "blue solution" confirmed the composition of the products as 11. Conductivity in DMA ($\lambda^{22} = 7.6 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}$), showed compound 11 to be essentially non-ionic. The compound is soluble in H$_2$O, slightly soluble in DMA, very slightly soluble in alcohols, and insoluble in acetone.

11.2.1. **I.r. Spectrum**

The i.r. spectrum of 11 contains a strong band at 1095 cm$^{-1}$ due to the SO stretching mode of S-bonded sulphoxide. No definite band can be assigned to O-bonded sulphoxide; however, there is an absorbance at 970 cm$^{-1}$ which on comparison with previous sulphoxide complexes is possibly due to a methyl rocking mode. A strong broad absorbance centred at 3370 cm$^{-1}$ together with a medium, broad absorbance centred at 1630 cm$^{-1}$ indicates the presence of H$_2$O. A definite $\nu$(OH) band for the diol cannot be assigned, but this band would be expected to occur in the 3400 cm$^{-1}$ region. Bands due to $\nu$(Ru-Cl) cannot be assigned due to a poorly resolved far i.r. region.
11.2.2. $^1$H n.m.r. Spectra

Compound 11 in $d_6$-DMSO and in $D_2O$ has similar n.m.r. spectra. Both have closely spaced narrow resonance peaks in the region of $\delta 3.25 - 3.70$ and broader absorbance in the region $\delta 3.70 - 4.30$. In $d_6$-DMSO there is an additional small peak at $\delta 3.10$ which is not present in the $D_2O$ spectrum. Further, a narrow resonance at $\delta 3.25$ is present in the former spectrum which decreases in height with the addition of molecular sieve 5A. These data suggest this peak is due to water. The narrow resonances in the $\delta 3.25 - 3.70$ region are due to the methylene and methyl protons of the S-bonded DDios ligand. The broad absorbances from $\delta 3.70 - 4.30$ are due to the methine and hydroxyl protons.

The small peak at $\delta 3.10$ is thought to be due to methylene or methyl protons of S-bonded sulphoxide of a different structural isomer not found in $D_2O$. No resonance absorption due to O-bonded or free sulphoxide are present in the region $\delta 2.00 - 3.00$. There is also an absence of peaks in the region $\delta 1.00 - 2.00$ where, in comparison to the free Dios ligand, the isopropylidene methyl protons of a co-ordinated Dios would be expected to resonate.

11.2.3. Discussion

Spectral and elemental analytical data together indicate compound 11 contains, $H_2O$ and DDios ligand ie., Dios ligand that had the

† See also Chapter II, (fig. 2.9.).
isopropylidene group cleaved to give the diol, DDios. Acetal groups are extremely susceptible to cleavage by dilute acid in the presence of water; cleavage of Dios results in DDios plus acetone, (eqn. 11,1).

\[
\text{Dios} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{DDios} + (\text{CH}_3)_2\text{CO} 
\]

(11,1)

The "blue solution" reaction mixture contains HCl produced from the \( \text{H}_2 \) reduction of ruthenium trichloride trihydrate, while the source of protons in the exchange reaction is not obvious. It is possible that the methanol is itself acidic enough to cleave the acetal or contains some acid impurity. The three required water molecules, (two \( \text{H}_2\text{O} \) are associated with compound 11 and one \( \text{H}_2\text{O} \) is required for cleavage of the acetal), are supplied from the ruthenium trichloride trihydrate or from the hygroscopic Dios ligand which has at least one molecule of water associated with it, (see Section 2.8.4.7viii). With complex 11 the two water molecules could be hydrogen-bonded to the alcohol groups rather than just present as molecules of solvation. Compound 11 is unique among sulfoxide complexes in that it has four S-co-ordinated sulfoxide moieties; this contrasts with \( \text{RuCl}_2(\text{DMSO})_4 \) where one DMSO ligand is O-bonded. These data suggest that the O-bonded DMSO results from steric interactions. The DDios ligand is fairly flexible with considerable distance between the two sulphur atoms. This presumably allows two such ligands to co-ordinate to ruthenium(II) through their sulphur atoms with much less steric interaction than four DMSO ligands with their sterically interacting methyl groups.
The limited spectral data available do not allow assignment of the structure of product 11. It is possible that the product as isolated is a mixture of isomers with trans- or cis-chlorides, as well as isomers containing different diastereomers of the sulphoxide ligand.

11.3. Dichloro(Dios)(DDios)ruthenium(II), 12

Compound 12 was prepared by the method described in preparative route 3 (Chapter IV), by exchange of Dios with RuCl₂(DMSO)₄ in CHCl₃. The two reagents were allowed to react with refluxing for 120 hr, at which time no further colour changes had occurred. After removal of CHCl₃ the oily residue was dissolved in acetone and the resultant solution filtered; this operation separated out any unreacted RuCl₂(DMSO)₄ which is insoluble in this solvent. Slow addition of diethyl ether precipitated the yellow product. Dissolution in acetone and precipitation were repeated to purify the product. Attempts at crystallization of the product from either CHCl₃-ether or acetone-ether solvent systems resulted in only precipitates. Conductivity in water, (\( \Lambda^{22} = 2.6 \text{ cm}^2\text{ ohm}^{-1}\text{mol}^{-1} \)) showed product 12 to be a neutral complex. Exposure of this solution to air gave green solutions which could possibly contain ruthenium(III) species.

Complex 12 is soluble in polar and halogenated solvents, and insoluble in ether and alkanes.

11.3.1. I.r. Spectrum

The i.r. spectrum of 12 contains a strong band at 1100 cm⁻¹, corresponding to \( v(\text{SO}) \), S-bonded, and a medium strength band at 932 cm⁻¹, which
could be \( v(\text{O}) \), O-bonded. Bands at 3500 and 1065 cm\(^{-1}\) are due to \( v(\text{OH}) \) and tentatively \( v(\text{CO}) \) of the diol, respectively; assignment of the C-O stretching mode is difficult, as this region of the spectra has other ligand bands. A medium strength doublet absorbance at 1104 and 1113 cm\(^{-1}\) is assigned to the C-H bending mode of a geminal dimethyl group\(^{117}\). The far i.r. region of the spectrum is not well resolved but an absorbance at 335 cm\(^{-1}\) is tentatively assigned to \( v(\text{Ru-Cl}) \).

11.3.2. \(^1\text{H n.m.r. Spectra}\)

The proton n.m.r. spectrum of \( \text{I}_2 \) in CDCl\(_3\) contains a singlet at \( \delta 1.42 \) due to the six equivalent isopropylidene methyl protons, and a singlet at \( \delta 2.58 \) due to the three equivalent protons of a methyl group \( \alpha \) to an unco-ordinated sulphur atom. Between \( \delta 2.61 - 2.90 \) are multiplet resonances due to the five protons of a methyl and a methylene group \( \alpha \) to an unco-ordinated or O-bonded sulphur atom. Between \( \delta 3.07 - 3.80 \), and \( \delta 3.90 - 4.70 \), are multiplet peaks due to the remaining protons of S-bonded Dios and DDios ligands. The integration ratios between the peaks due to the S-bonded, O-bonded, free sulphoxide methyl and methylene protons, and isopropylidene methyl protons, indicate that in CDCl\(_3\) three of the four sulphoxide moieties are S-bonded, and one O-bonded or unco-ordinated, and that the amount of Dios and DDios is equal. Compound \( \text{I}_2 \) in D\(_2\)O has essentially the same spectrum as in CDCl\(_3\), except there are two overlapping singlets at \( \delta 2.80 \) and 2.70 of approximately equal intensity due to the methylene and

\[^{\dagger}\text{See also Chapter II, (fig. 2.10.).}\]
methyl protons of one sulphur moiety which is in part O-bonded and uncoordinated.

Addition of 50% by volume of 38% DC1 in D₂O to the above solution rapidly (<2 min) results in a spectrum with no peak at δ1.42, and a singlet at δ2.05 attributed to acetone; these data show the cleavage by DC1 of the isopropylidene groups of co-ordinated Dios to form DDios and acetone.

11.3.3. Discussion

It is apparent that two Dios ligands cannot be chelated to a RuCl₂ moiety. Cleavage of one Dios to give DDios likely increases the flexibility, and decreases the size of the ligand, and this allows both ligands to co-ordinate. Even then, co-ordination through one sulphoxide oxygen atom appears necessary to decrease steric interactions.

The Dios ligand is more likely than DDios to alleviate steric interference by co-ordination through oxygen. A probable structure for compound 12 involves a bidentate DDios ligand chelated through sulphur atoms, with the Dios ligand co-ordinated through one sulphur and one oxygen atom.

Although the far i.r. spectrum has only one apparent ν(Ru-Cl) band, which suggests a trans-chloride octahedral structure, product 12 could be a cis-chloride isomer or a mixture of isomers, with the second cis ν(Ru-Cl) band unresolved.

Product 12 behaves like RuCl₂(DMSO)₄ in regard to the dissociation of O-bonded sulphoxide in chloroform and water; however, dissociation is not complete in water solution as shown by the n.m.r. spectra. A ready explanation
of this lies in the "chelate effect" reducing the effective lability of the "dangling O-atom".

The source of acid required to cleave the Dios ligand in the reaction solution is again not readily apparent. The chloroform could contain traces of HCl, since its commercial production from methane and Cl₂ produces HCl\(^{118}\). The water required for cleavage is supplied by the Dios ligand.

11.4. Dichloro(DDios)(DMSO)(MeOH)ruthenium(II), 13

Exchange of Dios with RuCl₂(DMSO)₄ in a 1:1 mole ratio in refluxing methanol resulted in the mixed sulphoxide complex, 13. The solid yellow product began precipitating from solution after 18 hr. Recrystallization from DMA affords the pure compound, as shown by elemental analysis, (see Chapter II).

Conductivity in DMA (\(\Lambda^{22} = 4.4 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1}\)) showed product 13 to be a neutral complex. Complex 13 is soluble in DMA and H₂O, and very slightly soluble in alcohols.

11.4.1. I.r. Spectrum

The i.r. spectrum of compound 13 contains a strong broad band centred at 3400 cm\(^{-1}\) assigned to the alcohol OH stretching mode. This band cannot be confused with \(\nu(\text{OH})(\text{H}_2\text{O})\) since the accompanying expected \(\text{H}_2\text{O}\) band at ca. 1600 cm\(^{-1}\) is not present. Strong bands at 1123, and 1100 cm\(^{-1}\) indicate S-bonded sulfoxide and are assigned to \(\nu(\text{SO})\). The
region 1000 to 1080 cm\textsuperscript{-1} has multiple adjacent absorbances and one sharp band at 1018 cm\textsuperscript{-1} which are presumably due to $\nu$(CO) for the three alcohol groups. Sharp absorbances are present in the region 900 - 980 cm\textsuperscript{-1}, but none can be definitely assigned to $\nu$(SO) (O-bond).

The far i.r. spectrum contains bands at 325 and 305 cm\textsuperscript{-1} which are tentatively assigned to $\nu$(Ru-Cl).

11.4.2. $^1$H n.m.r. Spectrum

The $^1$H n.m.r. spectrum of complex 13 in D\textsubscript{2}O consists in part of sharp closely spaced resonances (perhaps singlets). The peaks are at $\delta$3.52, 3.60, 3.63, and 3.75 and are due to the twelve methyl protons of S-bonded DDios and DMSO, the three methyl protons of methanol, and the four methylene protons of DDios. A pair of broad peaks between $\delta$3.9 - 4.1 and 4.2 - 4.4 are resonances of the methine protons of DDios, and three alcohol protons of DDios and methanol. Integration does not discern which protons are responsible for each of the broad peaks. An integration ratio of the sharp resonances to the broad resonances is about 4:1 confirming the peak assignments. No resonances due to O-bonded or free DMSO or DDios, ($\delta$2.0 - 3.0) are observed, nor are resonances due to isopropylidene methyl protons of Dios, (ca. $\delta$1.45). It seems likely that the observed n.m.r. spectrum in water is of RuCl$_2$(DDios)(DMSO)(H$_2$O) since methanol is a rather weak Lewis base and is labile to replacement by water\textsuperscript{77}.

\footnote{\textsuperscript{77} See also Chapter II for a Spectral Diagram, (fig. 2.9.).}
11.4.3. Discussion

The exchange of Dios with RuCl$_2$(DMSO)$_4$ in methanol gave the expected product in so far as the cleavage of Dios to DDios occurred. The reaction is similar to that which forms complex 11, except for the 1:1 mole ratio of Dios used. Considering the nature of complexes 11 and 12, this 1:1 reaction could be expected to produce RuCl$_2$(DDios)(DMSO)$_2$ or RuCl$_2$(DDios)(DMSO)(MeOH). The former product could have one O-bonded sulphur atom (possibly of a DMSO ligand) to limit unfavourable steric interaction. Formation of the co-ordinated methanol product is probably a result of the smaller size and higher concentration of the methanol ligand as compared to DMSO, and the limited solubility of the product in methanol.

Compounds containing co-ordinated methanol are known, in particular [Cr(MeOH)$_4$Cl$_2$]Cl$^{119}$, and [Ru$_5$(CO$_2$Me)$_6$(MeOH)$_3$]$^{99}$. The latter features i.r. bands at 3400 and 996 cm$^{-1}$, while compound 13 has a band at 3400 cm$^{-1}$, and a sharp band at 1018 cm$^{-1}$ which could be the υ(CO) band of co-ordinated methanol.

The far i.r. spectral data suggest a cis-chloride structure for complex 13, of which there are many isomers with, for example, methanol or DMSO or both ligands trans to chloride, or one of these trans to DDios. Product 13 as isolated could be a mixture of isomers, including some with different diastereomers of DDios.
CHAPTER XII
ASYMMETRIC CATALYTIC HYDROGENATION USING DIOS
AND DDIOS DICHLORO-COMPLEXES OF RUTHENIUM(II)

12.1. Introduction

As stated in Chapter XI the degree of stereoselectivity using the Dios/DDios ruthenium(II) catalysts is far below that found with compounds containing the Diop ligand. Nevertheless, higher stereoisolation is obtained than with the other Ru(II)-sulphoxide catalysts discussed in Chapter IX.

This chapter presents the results of some asymmetric hydrogenation experiments using the Dios/DDios complexes.

12.2. Asymmetric Hydrogenation Results

In DMA or water solution compound 11, RuCl₂(DDios)₂·2H₂O (0.01 M), under 1 atm hydrogen at 60°C with acrylamide (0.8 M) displayed no measurable hydrogen uptake. Addition of a two-fold excess of proton sponge R to the DMA catalyst solution resulted in an extremely slow hydrogen reaction. A chloride-free solution of a likely cationic catalyst formed from 11 (the chloride being removed by filtering after treatment with AgPF₆), with the same concentration of substrate and Ru and under the same relatively mild conditions as above, also reacted extremely slowly.
with hydrogen. Addition of a two-fold excess of proton sponge $^R$ to this solution resulted in a slightly faster hydrogen reaction. Catalyst 11 in DMA at 45 psi hydrogen with itaconic acid resulted in no measurable hydrogenation; however, at a much higher pressure of hydrogen using diethyl itaconate and proton sponge $^R$ 100% hydrogenation occurred, (see Table 12.I.).

Catalyst 12, RuCl$_2$(Dios)(DDios) (0.013 M), with itaconic acid (0.51 M) in DMA at 50°C under 1 atm H$_2$ gave a H$_2$ uptake plot similar to that of the [NH$_2$Me$_2$][RuCl$_3$(DMSO)$_2$]-acrylamide system, (fig. 6.4.), and had a linear uptake rate of 4.9 x 10$^{-7}$ Ms$^{-1}$. The same solution under a pressure of 3 atm H$_2$ at 55°C resulted in 49% hydrogenation after seven days and an enantiomeric excess = 25%, with the R enantiomer predominant. Catalyst 12 also asymmetrically hydrogenated atropic and 2-acetamidoacrylic acids, but with less stereoselectivity.

Catalyst 13, RuCl$_2$(DDios)(DMSO)(MeOH), under conditions similar to those used for 12, stereoselectively hydrogenated itaconic acid to give an enantiomeric excess = 5%, with the R enantiomer predominant. The details of the above asymmetric hydrogenations are summarized in Table 12.I., which shows that the most stereoselective hydrogenation catalyst is RuCl$_2$(Dios)(DDios) and that its asymmetric induction decreases with increasing temperature. All three catalysts give predominantly the R enantiomer of $\alpha$-methylsuccinic acid, as did the [RuCl$_2$(MBMSO)$_2$]$_3$ catalyst, (Chapter IX). The hydrogenation of the diethyl ester of itaconic acid was complete, but with the production of some metal at an undetermined step. The catalytic solutions containing 12 turned from yellow to orange
TABLE 12.I.
Asymmetric hydrogenation results using Dios and DDios ruthenium(II) catalysts in DMA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$[\text{Ru}^{II}]_T$</th>
<th>Substrate</th>
<th>$[\text{Substrate}]$</th>
<th>$\text{pH}_2$ psi</th>
<th>$T$ °C</th>
<th>$t$ hr.</th>
<th>% hydrogenation</th>
<th>ee $c$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.0074</td>
<td>Diethyl itaconate</td>
<td>0.49</td>
<td>1800</td>
<td>60</td>
<td>288</td>
<td>100</td>
<td>3.8(R)</td>
</tr>
<tr>
<td>I</td>
<td>0.015</td>
<td>Itaconic acid</td>
<td>1.81</td>
<td>45</td>
<td>42</td>
<td>144</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>II$^e$</td>
<td>0.013</td>
<td>Itaconic acid</td>
<td>0.51</td>
<td>44</td>
<td>55</td>
<td>168</td>
<td>49</td>
<td>25.2(R)</td>
</tr>
<tr>
<td>II$^f$</td>
<td>0.013</td>
<td>Itaconic acid</td>
<td>0.51</td>
<td>50</td>
<td>71</td>
<td>168</td>
<td>100</td>
<td>8.1(R)</td>
</tr>
<tr>
<td>II$^e$</td>
<td>0.016</td>
<td>Atropic acid</td>
<td>0.62</td>
<td>46</td>
<td>52</td>
<td>144</td>
<td>17</td>
<td>4.1(S)</td>
</tr>
<tr>
<td>II$^e$</td>
<td>0.016</td>
<td>2-acetamide-acrylic acid</td>
<td>0.45</td>
<td>47</td>
<td>55</td>
<td>240</td>
<td>62</td>
<td>7.2(S)</td>
</tr>
<tr>
<td>III</td>
<td>0.016</td>
<td>Itaconic acid</td>
<td>0.61</td>
<td>48</td>
<td>63</td>
<td>240</td>
<td>29</td>
<td>5.4(R)</td>
</tr>
</tbody>
</table>

$a$ 5-11 ml solutions. $b$ I) RuCl$_2$(D Dios)$_2$·2H$_2$O; (II) RuCl$_2$(Dios)(D Dios); (III) RuCl$_2$(DDios)(DMSO)(MeOH).
$\text{c}$ Predominant enantiomer in parenthesis. $d$ 0.0063M proton sponge $^R$ added; some metal present at the end of the reaction; $\alpha$-methyl succinic acid diethyl ester product hydrolyzed to the di-acid before enantiomeric excess determined. $e$ Initial yellow solutions became orange by the end of the reaction time. $f$ Initial yellow solution became red by the end of the reaction time with no metal produced. The enantiomeric excesses are based on the specific rotation of the chiral acid; (S)-N-acetylalanine, $\{[\alpha]_D^{26} = -66.5^\circ; C_2, H_2O\}^{111}$, (R)-$\alpha$-methylsuccinic acid, $\{[\alpha]_D^{20} = +17.09^\circ; C_{10}, \text{abs. EtOH}\}^{112}$, and (S)-2-phenylpropanoic acid, $\{[\alpha]_D^{25} = +76.1^\circ; C_8, \text{CHCl}_3\}^{112}$.
over the course of the reaction in the atropic and 2-acetamidoacrylic acid systems, and at complete hydrogenation of itaconic acid the solution was red with no metal produced. Qualitatively these solutions appear similar to those resulting from the reactions of \( \text{RuCl}_2(\text{DMSO})_4 \) and \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\) with hydrogen in the presence of proton sponge \( \text{R} \), (see Section 5.7.).

12.3. Discussion

Catalysts 11 - 13 are similar in composition to \( \text{RuCl}_2(\text{DMSO})_4 \), and indeed 12 exhibits similar hydrogen uptake curves to those found for the DMSO catalysts, \( \text{RuCl}_2(\text{DMSO})_4 \) and \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\). The necessity of adding proton sponge \( \text{R} \) to increase the hydrogenation rate of catalyst 11 suggests that the hydrogen is activated by a net heterolytic base-promoted reaction, and the systems summarized in Table 12.1. probably involve hydrogenation mechanisms similar to those invoked for the \( \text{RuCl}_3(\text{DMSO})_3^- \) anion and perhaps \( \text{RuCl}_2(\text{DMSO})_4 \), (Chapter VI). The higher pressures required to effect efficient catalysis using 11 - 13 suggests that activation of hydrogen is a rate determining step, as it is for the \([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\)-acrylamide system. Whether olefin is co-ordinated prior to or after this rate determining step cannot be ascertained without kinetic data. Catalyst 11 under high \( \text{H}_2 \) pressure fully hydrogenates diethyl itaconate with production of metal, and with low but significant stereoselectivity. These data suggest that formation of metal occurs after or during asymmetric hydrogenation with the homogeneous catalyst 11, although the possibility of asymmetric heterogeneous hydrogenation cannot
be entirely ruled out. Attempts to activate catalyst 11 in a cationic form by removal of the two chloride ligands essentially failed. This suggests that formation of a metal-hydride species by heterolytic cleavage of hydrogen is aided by the elimination of HCl; these data corroborate earlier data suggesting that the H₂ activation is rate determining. Catalyst 12 is a far more effective catalyst than 11, and at low pressure, (1 atm), is comparable in activity to [NH₂Me₂][RuCl₃(DMSO)₃].

The similarity in colour of the hydrogenation reaction solution (orange) and hydrogen uptake curves suggests a close similarity to the DMSO catalyst-system, i.e.; formation of a ruthenium(II)-hydride complex prior to olefin complexation. The increased effectiveness in rate of hydrogenation of this catalyst over 11 is probably due to the O-co-ordinated sulphoxide ligand which dissociates more easily than the fully S-bonded sulphoxide ligands of catalyst 11.

The stereoselectivity sequence 12 > 13 parallels the number of bulky chiral chelalate sulphoxide ligands.

With higher temperature the stereoselectivity of 12 is decreased. This could be due to greater ligand dissociation, and hence less stereoselective catalytic species present, or more freedom of movement of the co-ordinated olefin substrate.

The lower stereoselectivity of 12 for reduction of atropic and 2-acetamidoacrylic acids as compared to itaconic acid could result from differences in substrate bonding due to electronic effects of the substrate, as outlined previously for the [RuCl₂(MBMSO)]₃ systems, (Chapter IX). H-bonding involving one carboxyl group of itaconic acid and the OH group
of DDios could be important. It is not clear why 13, which has a labile methanol, gives much slower hydrogenation rates than 12.

A point that remains to be tested for is whether cleavage of the co-ordinated Dios occurs in the presence of the olefin substrates.
CHAPTER XIII
GENERAL CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE WORK

One of the most important findings of this work is the realization of asymmetric hydrogenation using Ru(II) complexes of chiral sulfoxides as catalysts. New sulfoxides with chirality in the associated alkyl groups were synthesized, for example, MBMSO, Dios, and BDios; Ru(II)-dichloro compounds were prepared from the first two, and asymmetric hydrogenation of itaconic, atropic and 2-acetamido-acrylic acids accomplished with these new compounds. The extent of asymmetric induction in the products was not large, for example, the \([\text{RuCl}_2(\text{MBMSO})_2]_3\)-itaconic acid system gave a typical enantiomeric excess of 15%, while for the \([\text{RuCl}_2(\text{Dios})(\text{DDios})]_3\)-itaconic acid system this value was 25%. Hydrogen pressures above 1 atm were required to effect asymmetric hydrogenation in a reasonable time period.

The whole area of asymmetric hydrogenation using Ru(II) sulfoxide catalysts is primed for future work. For example, isolation of chiral sulfoxides which are diastereometrically pure and the preparation of corresponding metal catalysts could well result in higher optical yields.

Another important area dealt with in this work involves the nature of DMSO bonding to Ru(II). The structure of a new complex, fac-\([\text{NH}_2\text{Me}_2][\text{RuCl}_3(\text{DMSO})_3]\), was determined by spectral means and confirmed by
crystallographic studies to have three S-bonded DMSO ligands. The literature confusion on the structure of RuCl$_2$(DMSO)$_4$ was alleviated by similar studies, and the complex found to be the cis-isomer with three S-bonded and one O-bonded DMSO, the latter being trans to a S-bonded DMSO.

The complex [NH$_2$Me$_2$][RuCl$_3$(Me$^n$prSO)$_3$] was prepared and spectral data demonstrated a structure analogous to the corresponding DMSO complex.

The complex RuBr$_2$(DMSO)$_4$ was also prepared and spectral data showed it to have three S-bonded and one O-bonded DMSO.

The major criterion for the presence of mixed or all S-bonded sulphoxides at Ru(II) appears to be a steric effect; although additional work involving more Ru(II) sulphoxide complexes should be carried out to categorically establish this.

The complexes [NH$_2$Me$_2$][RuCl$_3$(DMSO)$_3$] and RuCl$_2$(DMSO)$_4$ readily reacted with 1 atm H$_2$ in DMA at 60°C in the presence of proton sponge. The resulting hydride species exhibited very high $^1$H n.m.r. hydride chemical shifts. The isolation of these hydrides and a study of their possible catalytic properties is most certainly a topic for future consideration.

Based on kinetic and spectral studies a mechanism was formulated for the catalytic hydrogenation of acrylamide using the RuCl$_3$S$_3^-$ anion in DMA. The proposed mechanism is;
Activation of hydrogen is by two pathways, both involving net heterolytic fission. One such step and an olefin insertion step are considered rate determining, \((k_3\) and \(k_4\)).

The Dios group of catalysts appeared to hydrogenate by similar mechanisms.

The catalyst \([\text{RuCl}_2(\text{MBMSO})_2]\) is interesting because of its degree of association, although the catalytic activity results from a monomeric species formed by dissociation of the trimer. The kinetics of acrylamide hydrogenation using this catalyst led to the following mechanism:

\[
\begin{align*}
\text{Ru}^{II}\text{Cl}_2\text{S}_2^- + \text{H}_2 & \xrightleftharpoons[k_1]{k_-1} \text{HRu}^{II}\text{Cl}_2\text{S}_2^- + \text{HCl} \\
\text{HRu}^{II}\text{Cl}_2\text{S}_2^- + \text{olefin} & \xrightarrow{k_5} \text{Ru}^{II}\text{Cl}_2\text{S}_2\text{alkyl}^- \\
\text{Ru}^{II}\text{Cl}_2\text{S}_2^- + \text{Sat. Product} & \xrightarrow{k_6} \text{HCl}
\end{align*}
\]

Activation of hydrogen is by two pathways, both involving net heterolytic fission. One such step and an olefin insertion step are considered rate determining, \((k_3\) and \(k_4\)).

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\[
\begin{align*}
\text{Ru}^{II}\text{Cl}_2\text{S}_2^- + \text{H}_2 & \xrightarrow{k_1} \text{HRu}^{II}\text{Cl}_2\text{S}_2^- + \text{HCl} \\
\text{HRu}^{II}\text{Cl}_2\text{S}_2^- + \text{olefin} & \xrightarrow{k_5} \text{Ru}^{II}\text{Cl}_2\text{S}_2\text{alkyl}^- \\
\text{Ru}^{II}\text{Cl}_2\text{S}_2^- + \text{Sat. Product} & \xrightarrow{k_6} \text{HCl}
\end{align*}
\]

Activation of hydrogen is by two pathways, both involving net heterolytic fission. One such step and an olefin insertion step are considered rate determining, \((k_3\) and \(k_4\)).

The Dios group of catalysts appeared to hydrogenate by similar mechanisms.
The catalyst was far more active than the RuCl$_3$(DMSO)$_3^-$ anion catalyst. Rate determining hydrogen activation by two pathways appears to occur via oxidative addition to the Ru(II); olefin reduction via such ruthenium dihydrides has not previously been invoked.

Comparison of the catalytic properties of [RuCl$_2$(MBMSO)$_2$]$_3$ and [RuCl$_2$(MPTSO)$_2$]$_3$ suggests that differences in the relative π-acid strengths of the two sulphoxide ligands may be important (MBMSO > MPTSO), and further studies in this area seem worthwhile, for example, for comparison with triphenylphosphine, etc.

[RuCl$_2$(MBMSO)$_2$]$_3$ and RuCl$_2$(MPTSO)$_2$]$_3$ were found to react readily with CO to give dicarbonyl species, some of which have anomalously high ν(CO) bands. Further work in isolating and characterizing these carbonyl compounds would certainly be rewarding.

A general area worthy of effort involves supporting the sulphoxide catalysts on a polymer, which results in possible dual homogeneous/heterogeneous catalysts. Support of the asymmetric catalysts could be accomplished in a way similar to that used for phosphine-supported catalysts but using polymer-S-metal linkages rather than polymer-P-metal linkages.
REFERENCES


13) Reference 10, p. 78.


15) Ibid., pp. 82-83.

20) Reference 10, p. 43.
21) Ibid., p. 80.
22) Ibid., p. 402.
24) Ibid., pp. 95-96.
25) Ibid., pp. 204-219.


39) Ibid., p. C-221.


42) Ibid., p. C-559.


82) Ibid., ch. 5.
89) Reference 10, p. 85.
90) Ibid., p. 250.
91) Ibid., p. 330.
92) Ibid., p. 310.
96) Reference 10, p. 172.
106) Reference 10, pp. 204-206.
107) Ibid., p. 103.
110) Ibid., p. 214


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