A STUDY OF RUTHENIUM COMPLEXES CONTAINING CHELATING DITERTIARY PHOSPHINES

BY

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Mixed-valence complexes of ruthenium of general formula \( \text{Ru}_2\text{Cl}_5(P-P)_2 \), \( P-P = \text{chiraphos}, \text{norphos}, \text{dppp}, \text{dppb} \) or \( \text{diop} \), have been prepared by reaction of \( \text{RuCl}_3P_2(\text{DMA})_2 \), \( P = \text{PPh}_3 \) or \( \text{P}(\text{p-tolyl})_3 \), with one equivalent of the appropriate ditertiary phosphine. The solid state structure of the chiraphos derivative is shown to be a symmetrical triply chloro-bridged dimer by X-ray analysis. The extent of electron delocalisation in these mixed-valence complexes has been studied by means of their intervalence transfer bands in the near-infrared region. A low energy absorption is assigned to the dinuclear complex; however, additional absorptions at higher energy indicate more than one species is present in solution.

Investigations of the reaction of \( \text{Ru}_2\text{Cl}_5(\text{chiraphos})_2 \) with \( \text{H}_2 \) in DMA show this to be an autocatalytic reaction, but attempts to elucidate mechanistic details have been unsuccessful. The product generated \textit{in situ} by reaction with \( \text{H}_2 \) is the ionic species, \([\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^-\text{DMAH}^+\). The neutral complexes \([\text{RuCl}_2(P-P)]_2 \), \( P-P = \text{chiraphos}, \text{dppp}, \text{dppb} \), or \( \text{diop} \), are isolated via such an ionic complex, or alternatively by reaction in toluene in the presence of added base. N.m.r. studies show the neutral complexes to have structure I, but the complexes readily adopt a triply chloro-bridged structure (II) in the presence of coordinating solvents (S).
The complexes \([\text{RuCl}_2(P-P)]_2\), \(P-P = \text{chiraphos or diop}\), catalyse the asymmetric hydrogenation of prochiral alkenes. The nature of the phosphine and substrate are found to be significant in terms of the hydrogenation rate, \% e.e., and product configuration. Hydrogenation of (Z)-\(\alpha\)-acetamidocinnamic acid with 97\% e.e. has been achieved using the chiraphos derivative. An unusual increase in \% e.e. of the hydrogenated substrate with decreasing temperature is observed.

The reaction of \(\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})_2\), with \(\text{H}_2\) has been investigated. In DMA, in the presence of added base, a hydrido-complex is generated, but has not been isolated pure. The reaction of \(\text{I}\) with \(\text{H}_2\) in \(\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}\) produces the dinuclear complex, \(\text{Ru}_2\text{H}_2(\text{CO})\text{Cl}_2(\text{dppb})_2\) (III). This product is also
formed in the absence of \( \text{H}_2 \), and is thought to arise via base promoted decarbonylation of methanol.

Addition of norbornadiene (nbd) to \( \text{RuCl}_2 \) produces \( \text{RuCl}_2 \text{(nbd)} \text{(dppb)} \), which has been characterised by \( ^1\text{H} \)- and \( ^3\text{P} \)-n.m.r., and elemental and X-ray analysis. The reaction of this complex with \( \text{H}_2 \) is complicated by initial dissociation of the norbornadiene ligand. However, one of the minor products is thought to be \( \text{RuHCl(nbd)(dppb)} \), a stable hydrido-alkene complex, even in the presence of \( \text{H}_2 \).

Cationic complexes of ruthenium(II) have been prepared from \( \text{I} \) and \( \text{Ru}_2\text{Cl}_5 \text{(dppb)}_2 \) by halide abstraction using \( \text{AgPF}_6 \). These are the dinuclear complexes \( [\text{Ru}_2\text{Cl}_3 \text{(dppb)}_2 \text{(S)}_n]^+ \text{PF}_6^- \), \( n = 2 \), \( S = \text{acetonitrile} \) and \( n = 1 \), \( S = \text{acetone} \); and the mononuclear complexes \( [\text{RuCl(dppb)\text{(CH}_3\text{CN)}_3}]^+ \text{PF}_6^- \) and \( [\text{RuCl(dppb)(}^6\text{-toluene)}]^+ \text{PF}_6^- \).

The reaction of \( [\text{RuCl(dppb)\text{(CH}_3\text{CN)}_3}]^+ \text{PF}_6^- \) with \( \text{H}_2 \), results in reduction of the acetonitrile ligands to triethylamine. The catalytic properties of this complex have also been investigated for the hydrogenation of nitrile and imine substrates.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>angstrom(s)</td>
</tr>
<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere; 1 atm. = 760 mm Hg</td>
</tr>
<tr>
<td>C_eq</td>
<td>equivalent concentration</td>
</tr>
<tr>
<td>chiraphos</td>
<td>(2S,3S)-bis(diphenylphosphino)butane</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>d</td>
<td>day(s); doublet</td>
</tr>
<tr>
<td>diop</td>
<td>(2R,3R) or (2S,3S)-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N-dimethylacetamide, CH$_2$CO.N(CH$_3$)$_2$</td>
</tr>
<tr>
<td>DMA.HCl</td>
<td>N,N-dimethylacetamidehydrochloride</td>
</tr>
<tr>
<td>DMA.HBr</td>
<td>N,N-dimethylacetamidehydrobromide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulphoxide</td>
</tr>
<tr>
<td>dppb</td>
<td>1,4-bis(diphenylphosphino)butane</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dppp</td>
<td>1,3-bis(diphenylphosphino)propane</td>
</tr>
<tr>
<td>D_s</td>
<td>static dielectric constant</td>
</tr>
<tr>
<td>e.e.</td>
<td>enantiomeric excess</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz, cycles per second</td>
</tr>
<tr>
<td>i.r.</td>
<td>infrared</td>
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</table>
J     coupling constant, in Hz
k     rate constant
K     equilibrium constant
log    logarithm
m     medium
M     molar, moles per liter
mL    milliliter
m.p.  melting point
n     optical dielectric constant
nbd   norbornadiene
nm    nanometers
n.m.r. nuclear magnetic resonance
morphos (R,R)-(−)-2-exo-3-endobis(diphenylphosphino)-bicyclo[2.2.1]heptene
Ph    phenyl
P-P   chelating ditertiary phosphine
PPh₃   triphenylphosphine
ppm   parts per million
PS    Proton Sponge, 1,8-bis(dimethylamino)-naphthalene
PS.HCl Proton Sponge hydrochloride
P(p-tolyl)₃   tri(p-tolyl)phosphine
s     second(s); singlet; strong
S     solvent
t     time; triplet
TMS   tetramethylsilane
v:v   volume by volume
w     weak
X     anionic ligand
δ     chemical shift in ppm downfield from standard
Δ     difference
Δν₁/₂ bandwidth at half intensity
ε     molar extinction coefficient, M⁻¹ cm⁻¹
λ     wavelength, nm
<table>
<thead>
<tr>
<th>Symbols</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>wavelength of maximum absorbance, nm</td>
</tr>
<tr>
<td>$\lambda_{\text{o}}$</td>
<td>limiting ionic conductance</td>
</tr>
<tr>
<td>$\Lambda_{\text{e}}$</td>
<td>equivalent molar conductivity, ohm$^{-1}$ cm$^2$ mole$^{-1}$</td>
</tr>
<tr>
<td>$\Lambda_{\text{o}}$</td>
<td>equivalent conductance at infinite dilution, ohm$^{-1}$ cm$^2$ mole$^{-1}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>magnetic susceptibility, BM</td>
</tr>
<tr>
<td>$\nu$</td>
<td>frequency, cm$^{-1}$</td>
</tr>
<tr>
<td>$\nu_{\text{max}}$</td>
<td>frequency of maximum absorbance, cm$^{-1}$</td>
</tr>
<tr>
<td>$[\cdot]$</td>
<td>concentration</td>
</tr>
<tr>
<td>${^{1}\text{H}}$</td>
<td>broadband proton decoupled</td>
</tr>
</tbody>
</table>

### Phosphines

- Bppfa: bisphenylphosphineferrocenylamine
- CAMP: $p$-anisylmethylphenylphosphine
- DiCAMP: 1,2-bis($p$-anisylcyclohexylphosphino)ethane
- DiPAMP: 1,2-bis($p$-anisylphenylphosphino)ethane
- diphos: 1,2-bis(diphenylphosphino)ethane (dppe)
- MPPP: methylphenylpropylphosphine
- NMPPP: neomenthyldiphenylphosphine
- PAMP: $p$-anisylmethylphenylphosphine
- PCy$_3$: tricyclohexylphosphine
- Prophos: 1,2-bis(diphenylphosphino)propane
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I wish to thank Drs. S. J. Rettig and M. Ponnuswamy and Mr. S. Evans for crystal structure determinations, both successful and unsuccessful. The skillful technical assistance of the microanalyses, glass-blowing, n.m.r., electrical and mechanical services are gratefully acknowledged.

I am indebted to John Haynes for his diligence in proof-reading this manuscript.

Finally, I would like to dedicate this thesis to Kate and Paul, for their support, and for tolerating neglect and irascibility.
CHAPTER I

INTRODUCTION

1.1 General Introduction

The ability of transition metal complexes to catalyse processes such as hydrogenation, hydroformylation, hydrosilylation, hydrocyanation, epoxidation, and C-C bond formation is well established\(^1\). The use of homogeneous catalysts for such reactions is of interest since compared to the industrially prevalent heterogeneous systems they generally provide higher activity and specificity, and mechanistic details are generally attainable\(^2\). Perhaps the most important feature of homogeneous systems is that the properties of the catalyst may be changed by simply varying the ligands and reaction conditions to obtain optimum results. Such catalysts also allow, by incorporation of auxiliary chirality, the possibility of asymmetric synthesis in which enantiomeric products are produced in unequal amounts.

The use of optically active compounds for either biological or chemical synthetic purposes is often such that one particular enantiomer is required since specific activity is usually related to only one form. Isolation of a single form is usually brought about by using biochemical processes\(^3\) or by the costly process of resolution of a
racemic mixture. The use of homogeneous catalysts containing chiral ligands provides a viable alternative for producing specific compounds, and has been successfully applied for a variety of asymmetric transformations. For these catalysts to be successful it is necessary for the chiral complex to interact with a substrate by the so-called diastereotopic interaction, to generate diastereomeric transition states at the configuration determining step. The free energy difference between these transition states determines the product composition of a kinetically controlled asymmetric synthesis. A measure of the efficiency of a particular synthesis is the enantiomeric excess, which is defined as:

\[
\% \text{ enantiomeric excess (e.e.)} = \left| \% R - \% S \right| \tag{1.1}
\]

1.2 Asymmetric Hydrogenation of Prochiral Alkenes

Of particular relevance to the studies in this thesis is the asymmetric hydrogenation of prochiral alkenes in accordance with equation 1.2.

\[
\begin{align*}
\text{H}_2 &\quad \text{R}_1\text{R}_2\text{C}=\text{CHR}_3 &\rightarrow &\quad \text{R}_1\text{R}_2\text{C}^{\text{HCH}_2\text{R}_3}
\end{align*}
\tag{1.2}
\]

Transformations of this type have been studied extensively using chiral rhodium catalysts and, whilst a brief overview will be presented here, numerous comprehensive reviews have been published.

One of the first examples of asymmetric hydrogenation, but in the heterogeneous phase, was by Akabori et al. who hydrogenated various oxime and oxazolone derivatives using metallic palladium absorbed on silk. Due to the inherent difficulties with heterogeneous catalysts few
effective systems\textsuperscript{11,12} have been found. The use of soluble transition metal catalysts offers a more controlled system, and research in this field was initiated in 1968 with the preparation of chiral phosphines of the type, P*PhR\textsubscript{1}R\textsubscript{2}, which contain a chiral phosphorus atom.

Replacement of triphenylphosphine in Wilkinson's catalyst\textsuperscript{13}, RhCl(PPh\textsubscript{3})\textsubscript{3}, which is a catalyst precursor for the effective hydrogenation of alkenes, by chiral phosphines led to the hydrogenation of substituted styrenes with a low but significant % e.e.\textsuperscript{14}. This provided the impetus primarily for the development of other chiral phosphines; the first significant ones were NMDPP\textsuperscript{15}, a monodentate ligand containing a chiral carbon atom in the neomenthyl substituent, and DIOP\textsuperscript{16}, a bidentate ligand with chiral carbons in the bridging portion of the molecule. From these three basic types of chiral phosphine, the development has been prolific with variations in the groups on the phosphorus atoms, and in the nature of the skeleton which holds the two phosphorus atoms in the case of bidentate ligands, or both. In the space of 10 years over 130 different phosphines have been synthesised\textsuperscript{17} and, when incorporated into a rhodium catalyst, a wide spectrum of data (in terms of % e.e.) has resulted.

With the synthesis of new phosphines has come the need of new ways to generate the catalyst precursor compared to the original studies. Two basic routes have been employed: (a) generation \textit{in situ} by displacement of a coordinated diene in [RhCl(diene)]\textsubscript{2} with the appropriate amount of phosphine (L), and (b), more recently, isolation as [Rh(diene)L\textsubscript{2}]\textsuperscript{+}X\textsuperscript{-} by displacement of chloride by another anion.
such as PF$_6^-$, ClO$_4^-$ or BF$_4^-$. 

High stereoselectivity, with enantiomeric excesses in some cases of essentially 100%, has been obtained for the reduction of certain alkenes. A selection of the phosphine ligands used with Rh that show high asymmetric inductions and activities is given in Figure 1.1. Whilst correlations have been proposed$^7,27,28$ to explain how absolute configurations of a diphosphine and the reduced alkene are related, there is no simple explanation as to why one particular phosphine is more effective than another. This is perhaps best illustrated by the series:

\[
\begin{align*}
\text{Phosphine} & & \text{MPPP} & & \text{PAMP} & & \text{CAMP} & & \text{DiPAMP} & & \text{DiCAMP} \\
\% \text{ e.e.} & & 25\% & & 50-60\% & & 80-88\% & & 95\% & & 64\%
\end{align*}
\]

for the reduction of (Z)-α-acetamidocinnamic acid$^8,29$. Successive substitution of an o-methoxyphenyl and a cyclohexyl group for the isopropyl and phenyl groups of methylpropylphenylphosphine (MPPP) to produce PAMP and CAMP, respectively, results in a marked increase in enantiomeric excess. "Dimerisation" of PAMP to produce the more rigid DiPAMP results in an optimum structure yet DiCAMP, which might be expected to give equally good results, is in fact inferior. Bidentate phosphines are generally more efficient than the monodentate, since the latter have a certain amount of rotational freedom which permits a
Figure 1.1 Selected chiral phosphines for asymmetric catalysis.
variety of diastereotopic interactions upon alkene coordination. Ultimately it is the steric or polar constraints imposed by the molecular framework of the phosphine that determines the extent to which asymmetric induction takes place during catalysis.

In the process of producing a large number of chiral rhodium complexes a wide variety of prochiral alkenes have been reduced\textsuperscript{17}. The choice of alkene is an important factor, since unfortunately the substrate also contributes to the asymmetric induction. Prochiral alkenes can be divided into two broad classes. The first is comprised of the simple alkenes such as $\alpha$-ethylstyrene, for which enantiomeric excesses are invariably low. The second consists of substrates which have polar groups close to the double bond, such as the derivatives of $\alpha$-acylaminoacrylic acids:

\[
\begin{align*}
\text{R}^1\text{-CH} &= C \quad \text{COOR}^2 \\
\text{NH-CO-R}^3
\end{align*}
\]

X-ray analysis\textsuperscript{30} has shown that such groups provide a secondary interaction with the metal, and these types of alkenes are in general asymmetrically reduced more efficiently. Other alkenes in this class such as derivatives of itaconic acid, $\text{CH}_2=\text{C}($$\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$, however, tend to give lower enantiomeric excesses, which is believed\textsuperscript{31} to be a consequence of intermolecular $\text{H}$-bonding interactions that prevent chelation.

Of commercial importance\textsuperscript{32} is the reduction:
since the initially reduced product is readily transformed into the amino acid L-DOPA, a drug for treating Parkinson's disease. Other commercial processes utilising chiral rhodium complexes have been considered\(^4\), but only that for L-DOPA is in large scale production.

Whilst extensive qualitative synthetic studies have shown the potential and complexity of asymmetric hydrogenation, it is quantitative kinetic studies which have provided an understanding of the catalytic mechanism, and allowed for the design of better systems. The major contributions in this respect came from studies of the extremely effective chiraphos and DiPAMP (and nonchiral analogue diphos) complexes by Halpern's group\(^{35}\). Addition of \(\alpha\)-amino acid precursors to \([\text{Rh}(P-P)(\text{MeOH})_n]^+\) species, generated by the reduction of the diene precursor, results in the formation of two diastereomeric complexes which differ in the olefinic face coordinated, and which can be distinguished by \(^{31}\text{P}-\text{n.m.r.}\). It was originally thought\(^{34}\) that the stereoselectivity of the reduction was determined by the initial diasteromeric ratio. However, the chiraphos system with ethyl-(Z)-\(\alpha\)-acetamidocinnamate showed only one diastereomer to be present in solution and the X-ray analysis of the isolated product showed that the face of the alkene which is coordinated to the metal is not the one that is predominantly reduced\(^{35}\). Combined n.m.r. and kinetic studies led to the catalytic scheme in Figure 1.2 being proposed\(^{36}\).
Figure 1.2 Proposed scheme for the catalytic asymmetric hydrogenation of prochiral alkenes by rhodium catalysts.
The initial binding of the alkene to the catalyst to form the
diastereomeric complexes $A'$ and $A''$ is not the key step, but rather
their subsequent reactivity with $H_2$ that determines the
enantioselectivity. The X-ray analysis and $^{31}$P-n.m.r. data show that
$A'$ is the major initial adduct, but the greater reactivity of the minor
one leads to the R isomer as the principle product (e.e. = 95%). For
the $[\text{Rh}(\text{R,R-DiPAMP})]^+$-catalysed hydrogenation of methyl-($Z$)-$\alpha$-
acetamidocinnamate at 25°C the kinetic parameters $K_1 = 3.7 \times 10^4 \text{ M}^{-1}$,
$K_1'' = 3.3 \times 10^3 \text{ M}^{-1}$, $k_2 = 1.1 \text{ M}^{-1}\text{sec}^{-1}$ and $k_2'' = 6.4 \times 10^2 \text{ M}^{-1}\text{sec}^{-1}$
were obtained. The ca. 580 fold higher reactivity of $A''$ in this case
compensates for its lower concentration, and results in formation of the
S enantiomer in greater than 96% enantiomeric excess. This mechanism
also explains the observed dependence of optical yield with hydrogen
pressure. Increasing the hydrogen concentration increases the
rate-determining oxidative addition step ($k_2'$ and $k_2''$) until
eventually the stereochemistry of the reaction becomes solely determined
by the initial binding of substrate to catalyst. In the
$[\text{Rh}(\text{R,R-DiPAMP})]^+$-system this leads to increased proportions of the
R enantiomer.

By far the most extensive research in the field of asymmetric
hydrogenation has been directed towards rhodium systems containing
chiral phosphines. Hydrogenation by other chiral metal complexes to
date have shown low reactivity and/or specificity, and relatively few
examples are known. These include Ziegler-type catalysts involving
titanium-cyclopentadiene complexes$^{37}$, complex cobalt systems$^{38}$ which
catalyse the reduction of conjugated double bonds, and ruthenium complexes which are discussed in Section 4.1.

1.3 General Overview of Hydrogen Activation and the Homogeneous Hydrogenation of Alkenes

A key step in the hydrogenation of alkenes or other unsaturated substrates is the activation of hydrogen, although this is not the only prerequisite for the metal complex to be active. The uncatalysed addition of hydrogen to an alkene, whilst being thermodynamically favourable in the ground state is a symmetry forbidden process\(^{39}\). A transition metal complex can catalyse hydrogenation reactions by overcoming the net symmetry restrictions through a series of symmetry allowed reaction steps involving a metal hydride intermediate. Hydrogenation is accomplished by activation of both hydrogen and substrate, but the system must also be capable of transferring the hydrogen and releasing the reduced product. Effective hydrogenation catalysts are generally of the group VIII metals in low initial oxidation states (\(d^6-d^8\)). These are frequently coordinatively unsaturated thereby allowing sites for activation, and accommodating an increase in the formal oxidation state. Catalytic activity has been found for other transition metal complexes, notably those of Ti\(^{40}\), Zr\(^{41}\), and Nb\(^{42}\) which have \(d^2\) or \(d^3\) configurations.

Activation of hydrogen can occur in two basic ways depending largely on the metal complex used: (a) oxidative addition via a three-centre transition state that results in homolytic cleavage of the
H-H bond, and (b) heterolytic cleavage of the bond to form a hydride and proton.

(a) **Oxidative addition** \[ \text{ML}_n + H_2 \rightarrow \text{ML}_n H_2 \]

Considering a hydride ligand as a formally -1 unit, this mode of activation results in the formation of a dihydride (or polyhydride if hydride ligands are already present) with an increase in the oxidation state of the metal by two. The dihydride products formed have a cis geometry for the two hydrogens, although in principle a trans concerted addition is allowed. The reaction is often reversible, the forward reaction being promoted by low initial oxidation state, high metal basicity and coordinative unsaturation. For these reasons the reaction is commonly observed for square planar \( d^8 \) complexes which upon addition form the favoured octahedral \( d^6 \) configuration. Examples of this type of activation are:

\[
\begin{align*}
\text{RhCl(PCy}_3\text{)}_2 + H_2 & \rightarrow \text{RhH}_2\text{Cl(PCy}_3\text{)}_2 \\
\text{Ru(CO)}_2(\text{PPh}_3)_3 + H_2 & \rightarrow \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{PPh}_3 \\
\text{IrCl(PPPh}_3\text{)}_3 + H_2 & \rightarrow \text{IrH}_2\text{Cl(PPPh}_3\text{)}_3
\end{align*}
\]

The first two examples generate catalytically active dihydrides, the second proceeding with loss of a phosphine ligand, whilst the product of reaction 1.5 is inactive. The formation of inactive dihydride complexes is not unusual since, if the metal-hydride bonds are thermodynamically or kinetically too stable, hydrogen transfer to the alkene will not occur.
The general mechanism for alkene hydrogenation involving dihydride catalysts involves two possible routes depending on when the dihydride is formed (Scheme 1-1). Coordination of the alkene after oxidative addition of the H₂, followed by two consecutive hydrogen atom transfers, produces the saturated product, via the so-called "hydride" route. The alternative "unsaturate" route proceeds with coordination of the alkene followed by oxidative addition of H₂. Both routes generate the same dihydride-substrate intermediate, but generally the unsaturate route is less favoured since prior coordination of the substrate is expected to remove electron density from the metal making subsequent oxidative addition of H₂ less probable. In cases where the unsaturate route does occur, the substrate acts as a ligand in stabilising the subsequently formed metal hydride, as is generally thought to be the case in the asymmetric hydrogenation discussed previously (Section 1.2). Wilkinson's catalyst \(^{49}\), RhCl(PPh₃)₃,
which coordinates both alkene and hydrogen separately, has been shown to efficiently hydrogenate alkenes by both routes\textsuperscript{50,51}.

Whilst monomeric complexes generally give rise to dihydride species, differences are found for dimeric complexes. Equation 1.6 shows an oxidative addition of H\textsubscript{2} that results in a dimeric product

\[
[IrH(\mu-SBu\textsubscript{t})(CO)(PPh\textsubscript{3})]\textsubscript{2} \quad (1.6)
\]

with one hydrogen atom bound to each metal\textsuperscript{52}. The addition is thought to occur at one metal centre, followed by hydride migration from Ir(III) to Ir(I); the resulting formally Ir(II) atoms attain an 18-electron configuration through metal-metal bond formation. The related complexes

\[
[Ir(\mu-S)(CO)(dppm)]\textsubscript{2} \quad (53) \quad \text{and} \quad [RhCl(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2} \quad (54)
\]

also add H\textsubscript{2}, but in these cases migration does not occur and mixed-valence products with a dihydride on one metal centre are formed. Oxidative addition of hydrogen to pentacyanocobaltate(II) (equation 1.7) is unusual in that a monohydride is generated\textsuperscript{55}:

\[
2Co(CN)\textsubscript{5}\textsuperscript{3-} \quad \text{or} \quad Co\textsubscript{2}(CN)\textsubscript{10}\textsuperscript{6-} + H_2 \quad \rightarrow \quad 2CoH(CN)\textsubscript{5}\textsuperscript{3-} \quad (1.7)
\]

It is uncertain whether this reaction involves a direct termolecular step, H\textsubscript{2} addition to undetectable amounts of dimer, or by hydride abstraction from transient dihydrides. The hydrogenation of alkenes employing this catalyst is also unusual in that the saturated product is formed generally via binuclear reductive elimination from the reaction of a metal alkyl with a metal hydride complex\textsuperscript{56}. Hydrogen atom transfers
without coordination of the substrate have also been demonstrated for the pentacyanocobaltate(II) catalyst\(^{56}\), as well as for CoH(CO)\(_4\)\(^{57}\).

Whilst the hydride ligand has been considered as a -1 unit, the shortcomings in this description are apparent. Homolytic cleavage of \(\text{H}_2\) only becomes an oxidative addition when electrons are transferred from the metal to the hydrogen atoms. However, such cleavage may be formulated in three ways\(^ {58}\) depending on the metals involved (equations 1.8 a-c). The products differ only in the position of the electrons originally associated with the hydrogen atom. The detection of hydrogen atom transfers by HCo(CN)\(_5\)\(^{3-}\) in hydrogenation studies implies that the hydrogen is better pictured as a stabilised atom (equation 1.8a) rather than a hydride (equation 1.8c), at least in the transition state. Alternatively, addition of \(\text{H}_2\) to [Ir(cod)L\(_2\)]\(^+\) and [Ir(cod)\(_2\)]\(^+\) has been considered\(^ {59}\) to be reductive rather than oxidative in character (equation 1.8b).

(b) Heterolytic Cleavage \(\text{ML}_n + \text{H}_2 \rightleftharpoons \text{ML}_{n-1}^\text{H}^- + \text{H}^+ + \text{L}\)

This type of hydrogen activation involves a net substitution of a hydride for another ligand without changing the oxidation state of the metal. Usually the ligand substituted is a halide, such as shown\(^ {60}\) in equation 1.9, although the hydrogenolysis of metal-alkyl, aryl or allyl
bonds also generates monohydrides in formally analogous reactions. The reversible nature of these reactions is generally not observed if the released proton is stabilised by base, which can be either an initially coordinated ligand, the solvent, or an externally added base.

There are two plausible mechanisms for explaining the net heterolytic cleavage of hydrogen\textsuperscript{58}. The first involves oxidative addition of $H_2$ to form a dihydride, which subsequently breaks down via reductive elimination into the metal hydride and protonated anion:

\[
M - X + H_2 \rightarrow M - H + HX
\]  

(1.10)

Such a process seems reasonable for metals in low oxidation states such as Ru(II) (Equation 1.9), which could proceed via a seven coordinate Ru(IV) intermediate. For metals in higher oxidation states, e.g. Ru(III) and Rh(III), a different mechanism is invoked where overlap between a filled metal orbital with an empty hydrogen orbital results in a polarized $H_2$-metal intermediate:

\[
M - X + H_2 \rightarrow M - H + HX
\]  

(1.11)

Loss of the positively polarized end of the $H_2$ molecule to the
self-generated, or added base X, gives rise to the metal hydride.

As for the dihydride catalysts generated by oxidative addition, the complexes that heterolytically split hydrogen can hydrogenate alkenes by two routes as shown in Scheme 1-2. Formation of the monohydride prior to alkene activation is known as the hydride route, which is exhibited for example by trichlorostannate(II) complexes of Pt(II). Heterolytic cleavage of $H_2$ by a metal-alkene complex constitutes the unsaturation route, and has been substantiated for chlororuthenate(II) species.

![Scheme 1-2](image)

The interaction between hydrogen and transition metal complexes is clearly of importance for both stoichiometric and catalytic reactions. The literature dealing with this topic is extensive, but comprehensive reviews covering the literature to 1982 have been published.
1.4 **Scope of this Thesis**

Since the modification of Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, to include chiral phosphines, the employment of rhodium catalysts for the asymmetric hydrogenation of prochiral alkenes has been extensive (Section 1.2). Modification of other transition metal complexes which are known to be catalytically active, however, has been very limited. The main objective of the work for this thesis was to prepare a ruthenium-hydride complex containing a chiral bidentate phosphine, for the purpose of a detailed asymmetric hydrogenation study. Due to the high cost of chiral phosphines the work included the use of nonchiral ditertiary phosphines, and much of the general chemistry was performed on complexes containing these phosphines.

The very nature of known ruthenium hydride complexes precluded direct modification so it was necessary to generate them by alternative methods. The isolation of the mixed-valence complexes of general formula $\text{Ru}_2\text{Cl}_5(\text{P-P})_2$ ($\text{P-P} = \text{bidentate phosphine}$) was the first step (Chapter III). An X-ray study of the chiraphos derivative confirmed the structure in the solid state but the nature of these complexes in solution was strongly dependent on the solvent. This was monitored by changes in their near-infrared spectra. The reactions of these complexes with hydrogen generated ionic species in situ, and these reactions were investigated in an attempt to ascertain mechanistic details.

Chapter IV describes the neutral complexes, $[\text{RuCl}_2(\text{P-P})]_2$ isolated from the reduction of the mixed-valence complexes. Variable
temperature n.m.r. was primarily used to establish the nature of these complexes in solution. Complexes of this type had been previously detected spectroscopically, but these were the first examples of isolated complexes. In the case of the chiral phosphines (where P-P = chiraphos and diop), the complexes were tested as catalysts for asymmetric hydrogenation of prochiral alkenes.

Various routes were attempted in order to prepare a hydrido-complex (Chapter V). The generation of hydride species from \([\text{RuCl}_2(\text{dppb})]_2\) and \([\text{RuCl}_2(\text{nbd})(\text{dppb})]\) using \(\text{H}_2\) was observed. However, the only compound to be isolated and well characterised was \(\text{Ru}_2\text{H}_2\text{Cl}_2(\text{CO})(\text{dppb})_2\) for which molecular hydrogen was not necessary for synthesis.

Chapter VI deals with cationic complexes prepared by halide abstraction from \(\text{Ru}_2\text{Cl}_5(\text{dppb})_2\) and \([\text{RuCl}_2(\text{dppb})]_2\) using \(\text{AgPF}_6\). These were prepared as potential hydride precursors and consequently their reactions with hydrogen were studied.

Whilst the goal of isolating a hydrido-complex for a study of the asymmetric hydrogenation of prochiral alkenes was not achieved, the potential of ruthenium phosphine complexes for this purpose is demonstrated, and routes for generating hydrido-species are provided.
CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 Solvents

Spectroquality grade solvents were obtained from Aldrich, Eastman, Fisher, Mallinckrodt, B.D.H. or M.C.B. Chemical Co. Benzene, hexanes and toluene were distilled from sodium/benzophenone/2,5,8,11,14-pentaoxapentadecane (Aldrich) under one atmosphere of nitrogen. Distillation under nitrogen of acetone was from anhydrous K$_2$CO$_3$, of dichloromethane from P$_2$O$_5$, and of alcohols from the corresponding magnesium alkoxide. Acetonitrile and DMA were stirred over CaH$_2$ for 24 h prior to fractional distillation, which for DMA was under vacuum. After distillation both acetonitrile and DMA were stored under argon in the dark.

For spectrophotometric studies those solvents not distilled were dried by storing over molecular sieves (BDH type 5A).

Anhydrous diethyl ether was used without further purification.

2.1.2 Gases

Research grade hydrogen was obtained from Union Carbide Canada Ltd., and Matheson Gas Co., and was passed through an Engelhard Deoxo
catalytic purifier to remove trace oxygen. Purified argon and nitrogen were supplied by Union Carbide Canada Ltd., and Matheson Gas Co. or Canada Liquid Air Ltd. Lecture bottles of anhydrous hydrogen chloride and hydrogen bromide were obtained from Matheson Gas Co.

All gases, with the exception of hydrogen, were used without further purification.

2.1.3 Phosphines

Triphenylphosphine (Aldrich or Eastman Kodak Co.), tri(p-tolyl)phosphine, 1,2-diphenylphosphinoethane (dppe), 1,3-diphenylphosphinopropane (dppp), 1,4-diphenylphosphinobutane (dppb), (2S,3S)-bis(diphenylphosphino)butane (chiraphos), and (2R,3R)-(-)-2,3,0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((-)diop) (Strem) were used as supplied for synthesis. A literature method was used to prepare (R,R)-(-)-2-exo-3-endobis(diphenylphosphino)bicyclo[2.2.1]heptene (norphos).68

2.1.4 Alkene Substrates

Itaconic acid (methylenesuccinic acid) was supplied by Eastman Kodak Co., (Z)-α-acetamidocinnamic and α-acetamidoacrylic acids, and citraconic acid (methylnaleic acid) by Fluka Chemical Co., and acrylamide (propenamide) by K & K Laboratories Inc. These substrates were recrystallised from hot ethanol to yield colourless crystals, and their $^1$H-n.m.r. spectra recorded to confirm purity. Hex-1-ene and styrene were obtained from Aldrich, and were passed through an alumina
column prior to use.

Atropic acid (2-phenylpropenoic acid) was prepared as follows: 36 g (0.2 mol) of ethyl atropate (prepared according to Ames and Davy) was saponified by refluxing for 4 h with 30 g (0.74 mol) of NaOH in 250 mL water. The basic mixture was acidified and the atropic acid extracted with three 100 mL portions of diethyl ether. Evaporation of the solvent produced a white powder which was recrystallised from hot ethanol to yield 24 g (79% yield) of atropic acid: δ\text{DMSO} : 5.97 (doublet, 1H, -C=CH), 6.27 (doublet, 1H, -C=CH), 7.43 (5H, aromatic).

2.1.5 Other Materials

Norbornadiene (Eastman) was purified by passing through a column of alumina prior to use. Silver hexafluorophosphate (Alpha Inorganics) was stored in the dark in a desiccator under vacuum. Polyvinylpyridine was kindly supplied by Reilly International Chemicals Inc. Proton Sponge, 1,8-bis(dimethylamino)naphthalene (Aldrich), was purified by passing a petroleum ether (30°C-60°C) solution through an alumina column. Concentration of the solution yields proton sponge as a white solid.

2.1.6 DMA Salts

2.1.6.1 N,N-Dimethylacetamidehydrochloride, DMA.HCl

Anhydrous HCl was bubbled into DMA (30 mL) to produce a copious white precipitate. The mixture was filtered under argon, washed well with diethyl ether and vacuum dried. Recrystallisation from
acetone/diethyl ether afforded colourless, extremely hygroscopic crystals of DMA.HCl. Yield: 13.5 g (34%); \( \text{C}_4\text{H}_{10}\text{ClNO} \) requires C : 38.87, H : 8.10, N : 11.34%; found C : 38.8, H : 8.2, N : 11.3%, \( \delta_{\text{CDCl}} : 2.60 \text{ (s, 3H CH}_3\text{C-)}, 3.22 \text{ (s, 6H, (CH}_3\text{)_2N-)}, 15.60 \text{ (s, 1H, proton)}. \)

2.1.6.2 N,N-Dimethylacetamidehydrobromide, DMA.HBr

This was prepared in an analogous way to the preceding compound, but using anhydrous hydrogen bromide. Yield: 15.1 g (28%); \( \text{C}_4\text{H}_{10}\text{BrNO} \) requires C : 28.57, H : 5.95, N : 8.33%; found C : 28.6, H : 5.8, N : 8.5%; \( \delta_{\text{CDCl}} : 2.76 \text{ (s, 3H CH}_3\text{C-)}, 3.27 \text{ (s, 6H, (CH}_3\text{)_2N-)}, 14.8 \text{ (s, 1H, proton)}. \)

2.1.7 Ruthenium Compounds

The ruthenium was obtained as RuCl\(_3\).3H\(_2\)O which was supplied on loan from Johnson Matthey Ltd. The proportion of Ru varied from 39 to 42% depending on batch.

All reactions were carried out in deoxygenated solvents under an atmosphere of argon by employing Schlenk techniques unless specified otherwise.

Additional characterisation data are presented in the designated sections of the thesis.
2.1.7.1 *Trichlorobis(triphenylphosphine)(DMA)ruthenium(III).DMA solvate, RuCl$_3$(PPh$_3$)$_2$(DMA).DMA*

RuCl$_3$·3H$_2$O (2.0 g, 7.6 mmol) in 60 mL DMA was stirred for 24 h at room temperature with PPh$_3$ (4.0 g, 15.3 mmol). The green air-stable product was filtered, carefully washed with DMA, rinsed with hexanes and dried under vacuum. Yield: 4.6 g (66%); C$_{44}$H$_{48}$N$_2$O$_2$Cl$_5$P$_2$Ru requires C : 58.31, H : 5.30, N : 3.09, Cl : 11.76%; found C : 58.1, H : 5.3, N : 3.1, Cl : 11.8%; $\nu_{\text{max}}$: 1630 cm$^{-1}$ (uncoordinated DMA), 1590 cm$^{-1}$ (coordinated DMA).

2.1.7.2 *Trichlorobis(tri-p-tolylphosphine)(DMA)ruthenium(III).DMA solvate, RuCl$_3$(P(p-tolyl)$_3$)$_2$(DMA).DMA*

The synthesis was the same as described for the triphenylphosphine complex, but using a two fold excess of P(p-tolyl)$_3$ (4.7 g, 15.3 mmol). Yield 4.0 g (76%); C$_{50}$H$_{60}$N$_2$O$_2$Cl$_5$P$_2$Ru requires C : 60.64, H : 6.06, N : 2.83, Cl : 10.76%; found C : 60.5, H : 6.1, N : 2.9, Cl : 10.6%; $\nu_{\text{max}}$: 1638 cm$^{-1}$ (uncoordinated DMA), 1595 cm$^{-1}$ (coordinated DMA).

2.1.7.3 *Tri-μ-chloro-dichlorobis(bidentate phosphine)diruthenium(II,III), Ru$_2$Cl$_5$(P-P)$_2$, P-P = dppb or diop (Sections 3.2-3.5)*

A suspension of RuCl$_3$(PPh$_3$)$_2$(DMA).DMA (1 g, 1.1 mmol) and one equivalent of the appropriate bidentate phosphine was refluxed in 150 mL of hexanes under nitrogen for 24 h. The red-brown product was filtered, washed well with hexanes and vacuum dried. Recrystallisation
from CH$_2$Cl$_2$-diethyl ether gave air-stable red powders.

**P-P = dppb** : 0.47 g (1.1 mmol) of dppb used.

Yield: 0.49 g (72%); C$_{56}$H$_{56}$Cl$_5$P$_4$Ru$_2$ requires C : 54.57, H : 4.59, Cl : 14.38%; found C : 54.7, H : 4.6, Cl : 14.2%; $\nu_{\text{max}}$: 338 cm$^{-1}$ (Ru-Cl); m.p.: 198°C (dec.).

**P-P = diop** : 0.55 g (1.1 mmol) of diop used.

Yield: 0.50 g (66%); C$_{62}$H$_{64}$O$_4$Cl$_5$P$_4$Ru$_2$ requires C : 54.09, H : 4.65, Cl : 12.90%; found C : 53.9, H : 4.8, Cl : 12.8%; $\nu_{\text{max}}$: 340 cm$^{-1}$ (Ru-Cl); m.p.: 207°C (dec.).

### 2.1.7.4 Tri-$\mu$-chloro-dichlorobis(bidentate phosphine)diruthenium(II,III)

Ru$_2$Cl$_5$(P-P)$_2$, P-P = chiraphos, norphos, dppp (Sections 3.2-3.5)

The preparative procedure for these complexes is the same as for the dppb and diop analogues described in the preceding section, but using RuCl$_3$(P(p-tolyl)$_3$)$_2$(DMA).DMA (1.0 g, 1.0 mmol) and the appropriate bidentate phosphine.

**P-P = chiraphos** : 0.43 g (1.0 mmol) of chiraphos used.

Yield: 0.51 g (82%); C$_{56}$H$_{56}$Cl$_5$P$_4$Ru$_2$ requires C : 54.57, H : 4.59, Cl : 14.38%; found C : 54.7, H : 4.6, Cl : 14.2%; $\nu_{\text{max}}$: 340 cm$^{-1}$ (Ru-Cl); m.p.: 242°C (dec.).

**P-P = norphos** : 0.46 g (1.0 mmol) of norphos used.

Yield: 0.32 g (49%); C$_{62}$H$_{64}$O$_4$Cl$_5$P$_4$Ru$_2$ requires C : 57.08, H : 4.30, Cl : 13.62%; found C : 56.7, H : 4.5, Cl : 13.8%; $\nu_{\text{max}}$: 331 cm$^{-1}$ (Ru-Cl); m.p.: 262°C (dec.).
P-P = dppp: 0.41 g (1.0 mmol) of dppp used.

Yield: 0.26 g (43%); C_{34}H_{52}Cl_{15}P_{4}Ru_{2} requires C : 53.84, H : 4.32; Cl : 14.75%; found C : 53.7, H : 4.5, Cl : 14.6%; ν_{max} : 340 cm\(^{-1}\) (Ru-Cl); m.p.: 214°C (dec.).

2.1.7.5 Dichlorobis(bidentate phosphine)ruthenium(II) dimers,

\[ [\text{RuCl}_{2}(\text{P-P})]_2, \text{P-P} = \text{dppb, dppp (Sections 4.2 and 4.3)} \]

\[ \text{Ru}_{2}\text{Cl}_{5} (\text{P-P})_2, \text{P-P} = \text{dppb or dppp (1.0 g, 0.81 mmol) in DMA (30 mL) was stirred under H2 (1 atm.) for 16 h. The volume of the resulting brown solution was reduced to 5 mL, after which methanol (40 mL) was added, and the suspension stirred for 3 h. The resulting orange solid was filtered, washed with methanol and vacuum dried to give a brown solid. The solid obtained by this method occasionally contained nitrogen present as DMA impurity (by elemental analysis) which could be removed by recrystallisation from CH\(_2\)Cl\(_2\) - diethyl ether.} \]

P-P = dppb: Yield: 0.83 g (85%); C_{56}H_{56}Cl_{14}P_{4}Ru_{2}.H_{2}O requires C : 55.35, H : 4.78, Cl : 11.70%; found C : 55.4, H : 5.0, Cl : 11.5%

P-P = dppp: Yield: 0.39 g (40%); C_{54}H_{52}Cl_{14}P_{4}Ru_{2}.H_{2}O requires C : 54.64, H : 4.55, Cl : 11.97%; found C : 54.7, H : 4.8, Cl : 11.9%

The dppb complex was particularly hygroscopic and air-sensitive, readily turning green. A more stable form of this complex was obtained by dissolution in CH\(_2\)Cl\(_2\) (20 mL) to which an equal volume of acetone was added. Stirring the solution causes precipitation of an orange
solid which was filtered, washed with diethyl ether, and vacuum dried. The complex was identified as Ru$_2$Cl$_4$(dppb)$_2$(acetone).acetone.

Yield: 0.72 g (68%); C$_{62}$H$_{68}$Cl$_4$P$_2$Ru$_2$ requires C : 56.71, H : 5.18, O : 2.44, Cl : 10.82%; found C : 56.5, H : 5.1, O : 2.6, Cl : 10.6%; $\nu_{\text{max}}$: 1705 cm$^{-1}$ (uncoordinated acetone), 1645 cm$^{-1}$ (coordinated acetone).

2.1.7.6 Dichlorobis(bidentate phosphine)ruthenium(II) dimers, [RuCl$_2$(P-P)]$_2$, P-P = diop, chiraphos (Sections 4.2 and 4.3)

Polyvinylpyridine (3 g) was deoxygenated by pumping on the solid prior to addition of 60 mL of toluene, and then stirring the suspension under Ar and occasionally a partial vacuum at ca. 60°C for 0.5 h. This suspension was added to Ru$_2$Cl$_5$(P-P)$_2$, P-P = diop or chiraphos, and stirred under H$_2$ (1 atm.) for 24 h. Separation of the insoluble polymer by filtration left a brown solution which was reduced in volume to 10 mL. Hexanes were added, and the solution set aside to allow formation of an orange crystalline solid in the case of P-P = chiraphos, and a brown solid for the diop complex. The product was filtered, washed with hexanes and vacuum dried. The volume of filtrate was reduced and further precipitation induced by adding more hexanes.

P-P = diop: Yield: 0.79 g (81%); C$_{62}$H$_{64}$O$_4$Cl$_4$P$_2$Ru$_2$ requires C : 55.52, H : 4.78, Cl : 10.60%; found C : 55.7, H : 5.0, Cl : 10.8%

P-P = chiraphos: Yield: 0.76 g (78%); C$_{56}$H$_{56}$Cl$_4$P$_2$Ru$_2$ requires C : 56.19, H : 4.68, Cl : 11.87%; found C : 56.3, H : 4.8, Cl : 11.7%
The chiraphos complex was also obtained as an acetone adduct by concentration of the brown solution to 10 mL to which an equal volume of acetone was added. Precipitation with hexanes produced an orange solid identified as $\text{Ru}_2\text{Cl}_4(\text{chiraphos})_2(\text{acetone})$. Yield: 0.75 g (74%); $\text{C}_{59}\text{H}_{62}\text{OCl}_4\text{P}_4\text{Ru}_2$ requires C: 56.46, H: 4.94, O: 1.28, Cl: 11.32%, found C: 56.3, H: 4.9, O: 1.4, Cl: 11.3%; $v_{\text{max}}$: 1624 cm$^{-1}$ (coordinated acetone).

2.1.7.7 *Tri-μ-chlorobis[chloro(1,4-diphenylphosphinobutane)-
 ruthenium(II)] PSH*+, $[\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^*\text{PSH}^*$ (Section 3.7.4)

$\text{Ru}_2\text{Cl}_5(\text{dppb})_2$ (0.5 g, 0.4 mmol) and Proton Sponge (0.3 g, 1.4 mmol) were dissolved in toluene (60 mL), and stirred under $\text{H}_2$ (1 atm.) for 16 h. The brown solution was concentrated to 20 mL; this caused precipitation of an orange solid which was filtered, washed well with hexanes and vacuum dried. Yield: 0.43 g (73%); $\text{C}_{76}\text{H}_{75}\text{N}_2\text{Cl}_5\text{P}_4\text{Ru}_2$ requires C: 58.07, H: 5.18, N: 1.94, Cl: 12.27%; found C: 58.1, H: 5.4, N: 1.9, Cl: 12.1%; $^{31}\text{P}$-{1H}-n.m.r. (CD$_2$Cl$_2$, 30°C), s, 53.6 ppm.

2.1.7.8 *Di-μ-chloro-μ-hydrido-hydrido(carbonyl)bis(1,4-diphenyl-
 phosphinobutane)diruthenium(II), Ru$_4$H$_2$(CO)Cl$_2$(dppb)$_2$ (Section 5.3)

$\text{Ru}_4\text{Cl}_4$(dppb)$_2$(acetone).acetone (0.5 g, 0.38 mmol) and Proton Sponge (0.4 g, 1.9 mmol) were stirred under Ar in CH$_2$Cl$_2$ (30 mL) and MeOH (20 mL) for 24 h. The red solution was concentrated to 10 mL causing precipitation of an orange solid. The mixture was filtered and
the solid washed with hexanes (10 mL), and vacuum dried. The solid was extracted with diethyl ether (60 mL), and the filtrate concentrated to 20 mL. Precipitation with hexanes afforded red crystalline material or an orange powder; the solids were filtered, washed with hexanes and vacuum dried. The filtrate was concentrated and further precipitation induced by adding more hexanes. Yield: 0.19 g (43%);

C$_{57}$H$_{58}$OCl$_2$P$_4$Ru$_2$ requires C : 59.12, H : 5.01, O : 1.38%; found C : 59.2, H : 5.1, O : 1.6%; $\nu_{\text{max}}$ : 2030 cm$^{-1}$ (w, Ru-H) and 1953 cm$^{-1}$ (s, Ru-CO).

2.1.7.9 Dichloro(norbornadiene)(1,4-diphenylphosphinobutane)-ruthenium(II)

RuCl$_2$(dppb)(nbd) (Section 5.4)

Norbornadiene (4 mL, 39 mmol) was added to a suspension of Ru$_2$Cl$_4$(dppb)(acetone).acetone (1.0 g, 0.76 mmol) in benzene (50 mL). After 24 h, the volume of the resulting orange solution was reduced under vacuum to 20 mL and diethyl ether added. Slow precipitation afforded a brown crystalline material whilst trituration produced an orange powder; the solids were filtered, washed with diethyl ether, and vacuum dried. The product contained a molecule of benzene per two molecules of complex (evident in the X-ray crystal structure) which could not be completely removed even after drying at 100°C for 6 h under vacuum. Yield: 0.71 g (64%); C$_{35}$H$_{36}$Cl$_2$P$_2$Ru.0.5 C$_6$H$_6$ requires C : 62.55, H : 5.35, Cl : 9.74%; found C : 62.5, H : 5.4, Cl : 9.5%. 
2.1.7.10 **Trichloro(1,4-diphenylphosphinobutane)ruthenium(III) dimer**, 
\([\text{RuCl}_3\text{(dppb)}]_2\) (Section 3.6)

To \(\text{Ru}_2\text{Cl}_5\text{(dppb)}_2\) (1.0 g, 0.81 mmol) in \(\text{CH}_3\text{CN}\) (60 mL) was added \(\text{AgPF}_6\) (0.103 g, 0.41 mmol) in \(\text{CH}_3\text{CN}\) (10 mL), and the solution stirred for 0.5 h. The pale red solution was filtered through Celite, and the filtrate evaporated to a red oil. Addition of \(\text{C}_6\text{H}_6\) (50 mL) and rapid stirring for 16 h cause precipitation of a pale red solid. The mixture was filtered, and the solid washed with \(\text{C}_6\text{H}_6\) to yield a yellow solid (identified as \([\text{Ru}_2\text{Cl}_3\text{(dppb)}_2(\text{CH}_3\text{CN})_2]^+\text{PF}_6^-\), see next section). The filtrate and washings were combined, concentrated to 10 mL, and hexanes (40 mL) added to cause precipitation of a red-brown solid. This was filtered, washed well with hexanes and vacuum dried. The product was recrystallised from \(\text{CH}_2\text{Cl}_2/\text{hexanes}\) to give a maroon compound. Yield: 0.18 g (35%); \(\text{C}_{56}\text{H}_{56}\text{Cl}_6\text{P}_4\text{Ru}_2\) requires C : 53.00, H : 4.42, Cl : 16.8%; found C : 52.9, H : 4.51 Cl : 16.6%; \(\nu_{\text{max}}\) : 352 cm\(^{-1}\) (Ru-Cl); m.p.: 238°C (dec.).

2.1.7.11 **Tri-\(\mu\)-chlorobis[acetonitrile(1,4-diphenylphosphinobutane)-
ruthenium(II)] Hexafluorophosphate**, \([\text{Ru}_2\text{Cl}_3\text{(dppb)}_2(\text{CH}_3\text{CN})_2]^+\text{PF}_6^-\) (Section 6.2.1.1)

The complex is isolated from the reaction of \(\text{Ru}_2\text{Cl}_5\text{(dppb)}_2\) and \(\text{AgPF}_6\) in \(\text{CH}_3\text{CN}\), as described in the previous section. The benzene-insoluble yellow solid was recrystallised from \(\text{CH}_2\text{Cl}_2/\text{hexanes}\) to yield a bright yellow compound identified as \([\text{Ru}_2\text{Cl}_3\text{(dppb)}_2(\text{CH}_3\text{CN})_2]^+\text{PF}_6^-\). Yield: 0.39 g (70%).
C₆₀H₆₂N₂Cl₃F₅P₅Ru₂ requires C : 51.89, H : 4.47, N : 2.02, Cl : 7.68%; found C : 52.1, H : 4.5, N : 2.0, Cl : 7.7%; νₘₐₓ : 2315 and 2280 cm⁻¹ (coordinated CH₃CN), 840 and 568 cm⁻¹ (non-coordinated PF₆⁻).

2.1.7.12 Tris(acetonitrile)chloro(1,4-diphenylphosphinobutane)ruthenium(II) Hexafluorophosphate, [RuCl(dppb)(CH₃CN)]⁺ PF₆⁻ (Section 6.2.2.1)

To Ru₂Cl₄(dppb)₂(acetone).acetone (1.0 g, 0.76 mmol) dissolved in CH₃CN (50 mL) was added AgPF₆ (0.385 g, 1.52 mmol) in CH₃CN (10 mL). The solution was stirred for 0.5 h, filtered through Celite, and the filtrate concentrated to 10 mL. Addition of diethyl ether (40 mL) with rapid stirring precipitates a pale yellow product which was filtered, washed with diethyl ether and vacuum dried. Recrystallisation from CH₂Cl₂/diethyl ether gave a yellow crystalline product. Yield: 0.93 g (72%); C₃₄H₃₇N₃Cl₆F₅P₃Ru.H₂O requires C : 48.08, H : 4.60, N : 4.95, Cl : 4.18%; found C : 48.4, H : 4.5, N : 4.9%, Cl : 4.0%; νₘₐₓ : 2268 cm⁻¹ (coordinated CH₃CN), 840 and 572 cm⁻¹ (non-coordinated PF₆⁻) and 285 cm⁻¹ (Ru-Cl)

2.1.7.13 (Acetone)tri-μ-chlorobis[(1,4-diphenylphosphinobutane) ruthenium (II)] Hexafluorophosphate, [Ru₂Cl₃(dppb)₂(acetone)]⁺ PF₆⁻ (Section 6.2.1.2)

To Ru₂Cl₄(dppb)₂(acetone).acetone (1.0 g, 0.76 mmol) dissolved in CH₂Cl₂ (25 mL) and acetone (25 mL) was added AgPF₆
(0.194 g, 0.76 mmol) in acetone (10 mL). The solution was stirred at ca. 40°C for 2 h and then filtered through Celite. The filtrate was concentrated to 10 mL and diethyl ether (40 mL) added to bring about precipitation of an orange solid. The mixture was filtered and the solid washed with benzene (40 mL) and diethyl ether (30 mL). The solid was recrystallised from CH₂Cl₂/acetone (1:1, V:V) by slow precipitation with diethyl ether. Yield: 0.69 g (66%);

C₅₉H₆₂OCl₇F₆P₅Ru₂ requires C : 51.93, H : 4.55, Cl : 7.81%;
found C : 51.7, H : 4.5, Cl : 7.8%; νmax : 1670 cm⁻¹ (coordinated acetone), 848 and 570 cm⁻¹ (non-coordinated PF₆⁻).

2.1.7.14 Chloro(η⁶-toluene)(1,4-diphenylphosphinobutane)ruthenium (II) Hexafluorophosphate, [RuCl(dppb)(η⁶-toluene)]⁺ PF₆⁻ (Section 6.2.2.2)

To Ru₂Cl₄(dppb)₂(acetone).acetone (1.0 g, 0.76 mmol) partially dissolved in toluene (40 mL) and acetone (30 mL) was added AgPF₆ (0.385 g, 1.52 mmol) in acetone (10 mL). The solution was stirred at ca. 40°C for 2 h and then filtered through Celite. The filtrate was concentrated to 10 mL and diethyl ether (40 mL) added to bring about precipitation of a pale orange solid. The mixture was filtered and the solid washed with benzene (40 mL) and diethyl ether (30 mL). Slow recrystallisation from CH₂Cl₂/acetone (1:1, V:V) by precipitation with diethyl ether initially affords a yellow solid. Further work-up of the filtrate after separation of the yellow solid yields an orange product identified as [Ru₂Cl₃(dppb)₂(acetone)]⁺
PF$_6^−$. The yellow compound was recrystallised from acetone/diethyl ether to produce a dark yellow crystalline material. Yield: 0.47 g (40%); C$_{35}$H$_{36}$ClF$_3$Ru requires C : 52.53, H : 4.50, Cl : 4.55%; found C : 52.5, H : 4.7, Cl : 4.7%; $ν_{max}$: 840 and 568 cm$^{-1}$ (non-coordinated PF$_6^−$) and 302 cm$^{-1}$ (Ru-Cl).

2.1.7.15 Reaction between $[\text{RuCl(dppb)(CH}_3\text{CN)}_3]^+\text{PF}_6^−$ and H$_2$,
(Section 6.4)

A DMA solution (25 mL) of $[\text{RuCl(dppb)(CH}_3\text{CN)}_3]^+\text{PF}_6^−$ (0.5 g, 0.60 mmol) and Proton Sponge (0.3 g, 1.40 mmol) was stirred under 1 atm. H$_2$ for 2 d. The orange solution was filtered to remove an off-white material. The filtrate was evaporated under vacuum to an oil which was dissolved in acetone (20 mL) to produce an orange solution which slowly turned yellow. Addition of diethyl ether (40 mL) precipitated a yellow solid which was filtered, washed with diethyl ether and vacuum dried. Extraction of the yellow solid with CH$_2$Cl$_2$ (50 mL) yields a white insoluble material and a yellow solution. The mixture was filtered, the filtrate concentrated to 10 mL and diethyl ether added to induce precipitation of a yellow solid.

Characterisation of the initial off-white solid and final yellow solid is presented in Section 6.4. The white CH$_2$Cl$_2$-insoluble material was identified as PSH$^+\text{PF}_6^−$: C$_{14}$H$_{19}$N$_2$F$_6$P requires C : 46.67, H : 5.28, N : 7.77%; found C : 46.4, H : 5.2, N : 7.7%; $δ$(CH$_3$CN): 3.15 (s, 12H, -N-CH$_3$), 7.8 (m, 6H, aromatic), 18.70 (s 1H, proton).
2.2 Instrumentation

Infrared spectra were recorded on a Perkin Elmer 598 grating spectrophotometer or a Nicolet 5DX FT-IR instrument. Spectra were obtained as Nujol mulls between CsI plates, and calibrated with the 1601 cm\(^{-1}\) peak of polystyrene.

Near-infrared spectra were recorded on a Cary 17D spectrophotometer, and visible spectra were recorded on Perkin Elmer 553A or Cary 17D spectrophotometers. Anaerobic spectral cells, as shown schematically in Figure 2.1, with quartz cells of 1.0 and 0.1 cm path length were used, and were thermostated when necessary. In most cases the weighed sample was placed in the quartz cell whilst the solvent was deoxygenated by a freeze and thaw static vacuum technique in the sidearm flask prior to mixing.

Gas uptakes for stoichiometric, kinetic or hydrogenation purposes were measured on the constant pressure gas-uptake apparatus described elsewhere\(^70\). \(^71\)

\(^1\)H-n.m.r. spectra were recorded on Bruker WP80, Varian XL100 or Bruker WH400 spectrometers with tetramethylsilane (TMS) at 60.0 as standard. \(^31\)P\(^{\text{1H}}\)-n.m.r. spectra were recorded on Varian XL100 (40.5 MHz for \(^31\)P) or Bruker WP80 (32.4 MHz for \(^31\)P) spectrometers. The standard for \(^31\)P\(^{\text{1H}}\)-n.m.r. spectra was the signal for triphenylphosphine at -6 ppm, this being relative to 85% \(\text{H}_3\text{PO}_4\). Downfield shifts are taken as positive and are reported relative to 85% \(\text{H}_3\text{PO}_4\). All spectrometers were operated in the Fourier transform mode and were equipped with variable temperature attachments.
2.3 Isolation of Hydrogenated Alkene Products

For solid products resulting from the hydrogenation experiments, the solution mixture was evaporated to a viscous oil from which the
products were separated as follows (alkene substrates are listed):

(a) Itaconic, citraconic and atropic acids: The residue was dissolved in 25 mL of 5% NaOH solution, stirred briefly and filtered through Celite to give a colourless filtrate. The filtrate was acidified with 10% HCl and extracted twice with diethyl ether (25 mL). The ethereal extracts were dried with anhydrous MgSO₄, filtered and concentrated to afford the saturated acid.

(b) N-α-acetamido-acrylic and -cinnamic acids: The residue was dissolved in 20 mL of CH₂Cl₂ and stirred until an off-white compound separated. This was filtered and washed well with CH₂Cl₂ to give a pure white product. Further purification, if necessary, was by dissolution in water (5 mL) and extraction with 20 mL CHCl₃. The aqueous layer was then freeze-dried to recover the product.

(c) Acrylamide: The residue was heated to 100°C under vacuum when white crystals of propionamide sublimed.

The liquid products obtained from the hydrogenation of styrene and hex-1-ene were separated from the solution mixture by distillation.

The products so obtained were identified by their ¹H-n.m.r. spectra, and their % purity determined. For the hydrogenated prochiral alkenes, the products were used also for the determination of their optical rotation in the appropriate solvents (Section 4.4).

2.4 Optical Rotation Measurements

All optical rotation values were measured on a Perkin Elmer 141 polarimeter at room temperature using a one decimeter path length cell.
The rotations were measured at the sodium-D line (589 nm), and the specific rotation calculated using the equation:

\[ [\alpha]^T_D = \frac{100 \cdot \alpha}{l \cdot c} \]  \hspace{1cm} (2.1)

Where \([\alpha]^T_D\) = specific rotation at temperature T measured at the sodium-D line.

\[ \alpha = \text{observed optical rotation} \]
\[ l = \text{path length of cell in decimeters} \]
\[ c = \text{concentration of solution in g/100 mL solvent.} \]

The percentage enantiomeric excess (% e.e.) of the hydrogenated product was determined according to the equation:

\[ \text{% e.e.} = \frac{[\alpha]^T_D \text{ of sample}}{[\alpha]^T_D \text{ of pure enantiomer}} \times 100 \]  \hspace{1cm} (2.2)
CHAPTER III

A STUDY OF CHLORO-BRIDGED DIRUTHENIUM(II,III) COMPLEXES
CONTAINING CHELATING CHIRAL AND NONCHIRAL DITERTIARY
PHOSHINE LIGANDS

3.1 General Introduction

Studies on ruthenium complexes containing chelating diphosphine ligands were initiated by Chatt and Hayter\textsuperscript{72} with the synthesis of an extensive series of complexes of general formula $\text{RuX}_2(P-P)_2$ and $\text{RuXY}(P-P)_2$, where $X$ and $Y$ are anionic ligands such as halides, pseudohalides, hydrides, or $\sigma$-bonded alkyl and aryl groups, and $P-P$ represents a chelating diphosphine. Other workers utilising a variety of diphosphines have since prepared coordinatively unsaturated complexes,\textsuperscript{73,74} as well as carbonyl\textsuperscript{75-77} and nitrosyl derivatives\textsuperscript{77}.

Considering the extensive literature on the chemistry, properties\textsuperscript{78} and catalytic applications\textsuperscript{63} of tertiary phosphine complexes of ruthenium, it is surprising that the chemistry of analogous diphosphine complexes is relatively undeveloped. A possible explanation is the inherent stability associated with having two diphosphines per ruthenium, while coordinatively unsaturated complexes containing only one diphosphine have not been reported.
This chapter presents a study of mixed-valence complexes of general formula $\text{Ru}_2\text{Cl}_5(P-P)_2$, where $P-P$ represents the chiral diphosphines, chiraphos (I), norphos (II), and diop (III), and diphosphines of the type $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ where $n=4$ (dppb) and $n=3$ (dppp). A description of their preparation, characterisation, and reactions with hydrogen is presented. To prevent repetition in the ensuing text $P-P$ will represent all of the phosphines above unless specifically designated.

3.2 Preparation of Tri-$\mu$-chloro-dichlorobis(bidentate phosphine)-diruthenium(II, III), $\text{Ru}_2\text{Cl}_5(P-P)_2$

Several methods were tried in an attempt to produce a ruthenium complex containing only one chelating diphosphine. These included the reactions outlined in equations 3.1 - 3.5 (references referring to

\[
\begin{align*}
\text{RuCl}_3\times\text{H}_2\text{O} + P-P & \rightarrow \text{RuCl}_3(P-P) & (3.1) \\
\text{RuCl}_2(P-P)\text{PPh}_3 & + \text{HBF}_4 \rightarrow \text{RuCl}_2(P-P) + \text{HPPh}_3^+\text{BF}_4^- & (3.2) \\
[\text{RuCl}_2(\text{cod})] & + P-P \rightarrow \text{RuCl}_2(\text{cod})(P-P) & (3.3) \\
\text{RuCl}_2(\text{nbd})(p\text{-toluidine})_2 & + P-P \rightarrow \text{RuCl}_2(\text{nbd})(P-P) & (3.4) \\
\text{RuCl}_3(\text{PPh}_3)_2(\text{DMA})\times\text{DMA} + P-P & \rightarrow \text{RuCl}_3(P-P)(\text{DMA}) & (3.5)
\end{align*}
\]
literature methods used for the preparation of starting materials). The products given in these reaction schemes are those that were expected to be produced, but none of these complexes were successfully isolated. The reaction involving phosphine ligand exchange at Ru(III) (equation 3.5) did, however, produce binuclear complexes of general formula RU₂Cl₅(P-P)₂.

Refluxing RuCl₃(PPh₃)₂(DMA).DMA with one equivalent of either dppb or diop in hexanes under anaerobic conditions led to the exchange of the triphenylphosphine ligands by the bidentate phosphine. This exchange was accompanied by concomitant dimerisation and reduction to produce in high yield the insoluble complexes RU₂Cl₅(P-P)₂, where P-P = dppb or diop. The exchange was confirmed by isolating the free PPh₃ from the filtrate after removal of the insoluble red product. In both cases only PPh₃ was detected by $^1$H-n.m.r.

This preparative procedure was unsuccessful in the case of all other P-P ligands as evidenced by the $^1$H-n.m.r. of the free phosphine. However, using the tolylphosphine derivative, RuCl₃(P(p-tolyl)₃)₂(DMA).DMA as precursor, afforded the analogous RU₂Cl₅(P-P)₂ complexes for the remaining diphosphines with the exception of dppe. Full preparative details are given in sections 2.1.7.3 and 2.1.7.4

The method of ligand exchange has been used previously to prepare the series of complexes trans-RuHCl(P-P)₂, where P-P = dppm, dppe, dppp, dppb, and diop, from RuHCl(PPh₃)₃.DMA; and the complexes Ru₂Cl₄(diop)₃ and RuCl₂(PPh₃)(diop) from RuCl₂(PPh₃)₃. These exchanges
result in incorporation of more than one diphosphine or one diphosphine with retention of a monodentate phosphine. To prepare mono(diphosphine) complexes therefore necessitated the choice of a more appropriate ruthenium precursor.

The choice of RuCl$_3$P$_2$(DMA).DMA, where P = PPh$_3$ or P(p-tolyl)$_3$, seemed appropriate in that due to the limited number of coordination sites available the exchange would simply produce RuCl$_3$(P-P)(DMA). The mixed-valence complexes Ru$_2$Cl$_5$(P-P)$_2$ were in fact the isolable products, and the nature of the exchange was determined by the monodentate phosphine. Both dppb and diop form seven-membered rings upon coordination and the size of this ring relative to those formed with the other diphosphines appears to enhance the displacement of PPh$_3$. In the case of dppp which forms a six-membered ring, chiraphos and norphos which form five-membered rings, the successful exchange with the tolylphosphine is presumably due to this monodentate phosphine being slightly more labile than PPh$_3$. Interestingly, the exchange is accompanied by reduction at the metal, presumably by the monodentate phosphine prior to dimer formation, although formation of a Ru$_2^{III,III}$ complex and subsequent one electron reduction cannot be ruled out. Reduction by phosphines is not uncommon; however, a co-reducing agent such as water is required in the formation of RuCl$_2$(PPh$_3$)$_3$. In the present synthesis, however, reduction ensues even under anaerobic conditions and in distilled solvent with the participation of the liberated phosphine. The $^{31}$P{$^1$H}-n.m.r. of the free phosphine does show the presence of
phosphine oxide in the ratio $1 \text{PO}(p\text{-tolyl})_3 : 6 \text{P}(p\text{-tolyl})_3$ which is close to that calculated (1:7) for the reduction of 50% of the Ru^{III}. A plausible mechanism to explain the formation of the complexes Ru$_2$Cl$_5$(P-P)$_2$ is shown in Scheme 3-I.

Support for the route involving reduction prior to "dimerisation" comes from the isolation of small amounts (<10% of the total yield) of Ru^{II} species. Work-up of the filtrate from the recrystallisation results in more of the original product contaminated with, in the case of P-P=chiraphos, yellow crystals of trans-RuCl$_2$(chiraphos)$_2$ and,
for P-P=dppb, green crystals of \([\text{RuCl}_2(\text{dppb})_{1.5}]_2\). These products were characterised by: X-ray analysis for the chiraphos complex, and by elemental analysis (C$_{84}$H$_{84}$Cl$_4$P$_6$Ru$_2$ requires C:62.15, H:5.18, Cl:8.73%; found C:61.9, H:5.0, Cl:8.5%) and visible spectrum for the known dppb complex\textsuperscript{73}.

The exchange of dppe with either of the RuCl$_2$(P$_3$DMA).DMA (P=PPH$_3$, P(p-tolyl)$_3$) precursors was unsuccessful, and the only product isolated in significant yield was \textit{trans}-RuCl$_2$(dppe)$_2$. The reason for this is not obvious since dppe is analogous to chiraphos and norphos in that a five-membered ring is formed upon coordination.

3.3 X-Ray Structure Determination of Tri-\(\mu\)-chloro-dichloro-bis(chiraphos)diruthenium(II,III), Ru$_2$Cl$_5$(chiraphos)$_2$

The complexes, Ru$_2$Cl$_5$(P-P)$_2$, after recrystallisation were usually obtained as red powders; the exception was the chiraphos derivative which invariably formed dark red crystals. A single crystal X-ray diffraction study carried out by S. J. Rettig of this department revealed the complex to be the highly symmetrical \(\mu_2\)-chloro-bridged complex shown in Figure 3.1. The coordination sphere about each ruthenium is octahedral, and the metal to ligand bond distances and angles at both centres are essentially identical (Table 3.1). Two of the bridging chloro-ligands (Cl(2) and Cl(3)) are \textit{trans}- to phosphorus atoms and have longer Ru-Cl distances (average 2.49Å) compared to those for the third bridging chloro-ligand (average 2.36Å) which is \textit{trans}- to the two terminal chloro-ligands, due to the stronger \textit{trans
Figure 3.1 An ORTEP diagram of the Ru$_2$Cl$_5$(chiraphos)$_2$ molecule.
Table 3.1

Selected Bond Lengths and Bond Angles for $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2^*$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length(Å)</th>
<th>Angle</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1) - Cl(1)</td>
<td>2.365(1)</td>
<td>Cl(1) - Ru(1) - Cl(2)</td>
<td>80.24 (5)</td>
</tr>
<tr>
<td>Ru(1) - Cl(2)</td>
<td>2.476(1)</td>
<td>Cl(1) - Ru(1) - Cl(3)</td>
<td>78.90 (5)</td>
</tr>
<tr>
<td>Ru(1) - Cl(3)</td>
<td>2.527(1)</td>
<td>Cl(1) - Ru(1) - Cl(4)</td>
<td>169.76 (5)</td>
</tr>
<tr>
<td>Ru(1) - Cl(4)</td>
<td>2.370(1)</td>
<td>Cl(1) - Ru(1) - P(1)</td>
<td>102.93 (5)</td>
</tr>
<tr>
<td>Ru(1) - P(1)</td>
<td>2.266(1)</td>
<td>Cl(1) - Ru(1) - P(2)</td>
<td>94.80 (5)</td>
</tr>
<tr>
<td>Ru(1) - P(2)</td>
<td>2.267(1)</td>
<td>Cl(2) - Ru(1) - Cl(3)</td>
<td>81.53 (5)</td>
</tr>
<tr>
<td>Ru(2) - Cl(1)</td>
<td>2.351(1)</td>
<td>Cl(2) - Ru(1) - Cl(4)</td>
<td>92.81 (5)</td>
</tr>
<tr>
<td>Ru(2) - Cl(2)</td>
<td>2.477(1)</td>
<td>Cl(2) - Ru(1) - P(1)</td>
<td>176.48 (5)</td>
</tr>
<tr>
<td>Ru(2) - Cl(3)</td>
<td>2.483(1)</td>
<td>Cl(2) - Ru(1) - P(2)</td>
<td>96.64 (5)</td>
</tr>
<tr>
<td>Ru(2) - Cl(5)</td>
<td>2.358(1)</td>
<td>Cl(3) - Ru(1) - Cl(4)</td>
<td>92.71 (6)</td>
</tr>
<tr>
<td>Ru(2) - P(3)</td>
<td>2.287(1)</td>
<td>Cl(3) - Ru(1) - P(1)</td>
<td>97.49 (5)</td>
</tr>
<tr>
<td>Ru(2) - P(4)</td>
<td>2.278(1)</td>
<td>Cl(3) - Ru(1) - P(2)</td>
<td>173.64 (5)</td>
</tr>
<tr>
<td>Ru(1) - Ru(2)</td>
<td>3.251(1)</td>
<td>Cl(4) - Ru(1) - P(1)</td>
<td>83.84 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl(4) - Ru(1) - P(2)</td>
<td>93.46 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1) - Ru(1) - P(2)</td>
<td>84.69 (5)</td>
</tr>
</tbody>
</table>

* According to numbering scheme in Figure 3.1.

Estimated standard deviations given in parentheses.
influence of the phosphine ligands. This shortening of the Ru-Cl(1) bond length results in a wider Ru-Cl(1)-Ru bond angle compared to the other two Ru-Cl-Ru angles. Two regular octahedra sharing one face have a bridging angle \( \phi \), where \( \phi \) is given by \( \cos(\phi/2) = \left(\frac{2}{3}\right)^{1/2} \) hence \( \phi = 70.5^\circ \). In this complex the average bridging angle is 83.4°, and hence the ruthenium atoms are further apart than they would be in a regular cofacial bioctahedron. The distance between the ruthenium centres (3.25Å) is well outside the range (2.28 - 2.95Å) usually found for a Ru-Ru bond\(^{83-89}\). The Ru-P lengths (average 2.28Å) are comparable to those found in ruthenium complexes containing tertiary phosphines\(^90\).

An analogous mixed-valence complex of ruthenium(II,III) containing monodentate phosphines has been reported previously. Nicholson\(^91\) isolated the complex \( \text{Ru}_2\text{Cl}_5(\text{P(n-butyl)}_3)\)\(^4\), from a concentrated ethanolic solution of \( \text{RuCl}_3 \) and tri-n-butylphosphine. The structure\(^92\) was elucidated as;

\[
\begin{array}{c}
\text{R}_3\text{P} \\
\text{R}_3\text{P} \\
\text{Cl} \\
\text{Ru} \\
\text{Cl} \\
\text{Cl} \\
\text{PR}_3 \\
\text{PR}_3
\end{array}
\]

Unlike the chiraphos complex, it is unsymmetrical in that one of the octahedra has been rotated by ±120° about the Ru-Ru vector. Even so, the two octahedra are very similar to one another, and as for the chiraphos complex it is not possible to assign formal valence states to the ruthenium atoms on a purely crystallographic basis.
3.4 Magnetic Susceptibility Measurements

The magnetic susceptibilities were determined by Evans' method. Methylene chloride solutions containing approximately 2% t-butanol were used at ambient temperatures. Values of $\mu_{\text{eff}}$ are given below and are consistent with one unpaired electron per molecule. Due to limited solubility of the dppb and dppp complexes, the paramagnetic shifts for these systems could not be measured accurately.

Solution $\mu_{\text{eff}}$, B.M.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$</td>
<td>1.95</td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_5(\text{norphos})_2$</td>
<td>2.01</td>
</tr>
<tr>
<td>$\text{Ru}_2\text{Cl}_5(\text{diop})_2$</td>
<td>1.78</td>
</tr>
</tbody>
</table>

3.5 Electronic Spectral Data

3.5.1 Near-Infrared Spectra

Intervalence charge transfer transitions are a characteristic feature of mixed-valence complexes, these transitions often occurring in the low energy near-infrared region of the spectrum. The spectra in this region for $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ in CDCl$_3$ and CCl$_4$ under anaerobic conditions are presented in Figure 3.2, and the inset shows the high energy absorption in CDCl$_3$ and DMA on an expanded scale. Unfortunately the complete absorption spectrum at longer wavelengths (>2600 nm) could not be studied because of the limitations of the spectrophotometer. Values of $\lambda_{\text{max}}$, $\nu_{\text{max}}$, $\epsilon$, and $\Delta\nu_{1/2}$ were obtained in a variety of solvents and the results are summarised in
Figure 3.2 Near-infrared spectra of $\text{Ru}_2\text{Cl}_5\text{(chiraphos)}_2$ in $\text{CDCl}_3$ and $\text{CCl}_4$.
Inset shows high energy absorption obtained in $\text{CHCl}_3$ and DMA.
Table 3.2. Spectra were mainly recorded using 0.1 cm matched cells, and deuterated solvents were used whenever possible to minimise the interference of solvent infrared overtone absorptions. The weaker absorption at ca. 1100 nm was studied independently so that more accurate data could be obtained; the shorter wavelength allowed for the use of non-deuterated solvents in matched 1.0 cm cells. The near-i.r. absorptions of Ru$_2$Cl$_5$(chiraphos)$_2$ in CDCl$_3$ obeyed Beer's law over the concentration range 1.5 x 10$^{-3}$ to 1.5 x 10$^{-2}$ M. The spectra in DMSO-d$_6$ and CD$_3$NO$_2$ were similar, but were found to decrease in intensity with time until there was no absorption in this region. The times taken for complete disappearance of the absorptions were approximately 1h and 5h for DMSO-d$_6$ and CD$_3$NO$_2$ solutions, respectively. In DMA there was a 10% decrease in the absorption at 2340 nm over 24h, whilst in CD$_2$CN there was no absorption observed, implying an instantaneous loss of absorption upon dissolution. The solid state spectrum measured after evaporation of the CD$_3$NO$_2$ solvent following complete loss of the near-i.r. absorption bands did not show regeneration of these absorptions. Evaporation of a CCl$_4$ solution produced solid whose spectrum was identical to that observed in solution, and redissolving the sample in CDCl$_3$ yielded the spectrum originally found in this solvent.

The CDCl$_3$ solution spectra for Ru$_2$Cl$_5$(P-P)$_2$, (P-P = norphos, dppp and dppb) are shown in Figure 3.3. The spectrum for the diop analogue is essentially identical to that found for the dppb complex. Whilst these complexes were not studied as extensively as the
Table 3.2  
Near-Infrared Spectral Data for Ru$_2$Cl$_2$(chiraphos)$_2$-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$(1/n^2-1/D)_{S}^a$</th>
<th>$\lambda_{\text{max}}$ (v$_{\text{max}}$) nm$\pm$10 (cm$^{-1}$)</th>
<th>$\varepsilon^b$ M$^{-1}$ cm$^{-1}$</th>
<th>$\Delta\nu_{1/2}$, cm$^{-1}$</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$NO$_2$</td>
<td>0.498</td>
<td>2340 (4270)</td>
<td>5530</td>
<td>1660</td>
<td>3140</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1150 (8700)</td>
<td>490</td>
<td>5030</td>
<td>4480</td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_6$O$_3$$^d$</td>
<td>0.481</td>
<td>2340 (4270)</td>
<td>5510</td>
<td>1650</td>
<td>3140</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1150 (8700)</td>
<td>530</td>
<td>3600</td>
<td>4480</td>
<td></td>
</tr>
<tr>
<td>DMA</td>
<td>0.457</td>
<td>2340 (4270)</td>
<td>5460</td>
<td>1650</td>
<td>3140</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120 (8930)</td>
<td>510</td>
<td>5380</td>
<td>4540</td>
<td></td>
</tr>
<tr>
<td>DMSO-$d_6$</td>
<td>0.438</td>
<td>2350 (4260)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1190 (8400)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>0.266</td>
<td>2350 (4260)</td>
<td>5540</td>
<td>1630</td>
<td>3140</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1090 (9170)</td>
<td>660</td>
<td>4410</td>
<td>4600</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>0.493</td>
<td>1150 (8700)</td>
<td>550</td>
<td>5180</td>
<td>4480</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0.381</td>
<td>980 (10200)</td>
<td>660</td>
<td>4410</td>
<td>4654</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_3$$^e$</td>
<td>0.027</td>
<td>2050 (4880)</td>
<td>1100</td>
<td></td>
<td>5120</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>880 (11360)</td>
<td>2060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl$_4$$^e$</td>
<td>0.018</td>
<td>2050 (4880)</td>
<td>1030</td>
<td></td>
<td>5120</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>880 (11360)</td>
<td>2170</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Values calculated using indices of refraction (n) and bulk dielectric constants (D$_S$) given in Ref. 94.
(b) Molar extinction coefficients in CD$_3$NO$_2$ and DMA calculated for initial absorbance observed. No value is given for DMSO-$d_6$ due to appreciable loss of absorption even for initial spectra.
(c) $\Delta\nu_{1/2}$ is the bandwidth at half-height. Determined by assuming a Gaussian band shape for the high energy slope, and calculated using equation 3.6 (see text).
(d) Propylene carbonate.
(e) Since the low energy absorption is so broad the values given for $\lambda_{\text{max}}$ are for a selected wavelength; value for $\Delta\nu_{1/2}$ could not be calculated accurately.
Figure 3.3 Near-infrared spectra of Ru$_2$Cl$_5$(P-P)$_2$, P-P=norphos, dppp and dppb in CDCl$_3$. 
chiraphos analogue, the spectra were recorded in other solvents and the
data are given in Table 3.3

The solid state spectra (KBr pellets) of the chiraphos and dppb
complexes showed the same absorptions at low energy as were found in
solution.

The reduction of DMA solutions of all the complexes with $H_2$ to
produce the Ru$_{II,II}^{II}$ congeners (see Section 3.7) resulted in a loss
of absorption in the near-i.r. region.

3.5.2 Visible Spectra

The visible spectra of the Ru$_2$Cl$_5$(P-P)$_2$ complexes are all
similar in DMA or CDCl$_3$, although some variations in intensities and
absorption positions are observed with changing phosphine, as shown in
Figure 3.4 for P-P = norphos, dppp and dppb. The spectrum for P-P =
diop is the same as that for the dppb complex. The drastic differences
in the near-i.r. observed for Ru$_2$Cl$_5$(chiraphos)$_2$ in toluene (or
CCl$_4$) compared to CDCl$_3$ are accompanied by only slight changes in
the visible region. The spectrum in toluene or CCl$_4$ resembles that of
the dppb analogue in CDCl$_3$ with a shoulder at 450 nm instead of a
maximum at 420 nm. The final spectra obtained in both DMSO-d$_6$ and
CD$_3$NO$_2$ are the same, but are substantially different from that
measured in CDCl$_3$ as is the spectrum in CH$_3$CN. The spectra of
Ru$_2$Cl$_5$(chiraphos)$_2$ in CDCl$_3$ and CCl$_4$ are presented in Figure
3.5, and those obtained in CD$_3$NO$_2$ and CH$_3$CN are presented in
Figure 3.6. Freshly prepared DMA solutions of Ru$_2$Cl$_5$(chiraphos)$_2$
Table 3.3
Near-Infrared Spectral Data for the Complexes Ru₂Cl₆(P-P)₂
Complexes a, P-P = dppb, diop, dppp or norphos

<table>
<thead>
<tr>
<th>P-P</th>
<th>Solvent</th>
<th>λ max (ν max)</th>
<th>ε</th>
<th>Δν/2, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>nm±10 (cm⁻¹)</td>
<td>M⁻¹ cm⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Obser.</td>
<td>Calc.</td>
<td></td>
</tr>
<tr>
<td>dppb</td>
<td>CDCl₃</td>
<td>2050 (4880)</td>
<td>1180</td>
<td>3040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>970 (10310)</td>
<td>890</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMA</td>
<td>2050 (4880)</td>
<td>850</td>
<td>3040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>970 (10310)</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCl₄</td>
<td>2050 (4880)</td>
<td>1290</td>
<td>3100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>970 (10310)</td>
<td>1080</td>
<td></td>
</tr>
<tr>
<td>diop</td>
<td>CDCl₃</td>
<td>2050 (4880)</td>
<td>1410</td>
<td>2940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950 (10530)</td>
<td>1030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMA</td>
<td>2050 (4880)</td>
<td>1140</td>
<td>2940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950 (10530)</td>
<td>784</td>
<td></td>
</tr>
<tr>
<td>dppp</td>
<td>CDCl₃</td>
<td>2060 (4850)</td>
<td>2070</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>960 (10420)</td>
<td>1590</td>
<td></td>
</tr>
<tr>
<td></td>
<td>norphos</td>
<td>2350 (4260)</td>
<td>3240</td>
<td>2220</td>
</tr>
<tr>
<td></td>
<td>CDCl₃</td>
<td>950 (10530)</td>
<td>2820</td>
<td>4390</td>
</tr>
</tbody>
</table>

(a) [RuII,III]²⁺ = 2.0 (± 0.2) x 10⁻³ M in each case except for P-P =
dppb in CCl₄: [RuII,III]²⁺ = 4.15 x 10⁻⁴ M, and P-P = dppp:
[RuII,III]²⁺ = 5.85 x 10⁻⁴ M.

(b) Extinction coefficient per [RuII,III]²⁺; due to broadness of
low energy band, the given values are calculated for a particular
wavelength.

(c) Calculated in accordance with equation 3.6, and assuming a
Guassian band shape for the high energy slope (see text).
Figure 3.4 Visible spectra of Ru₂Cl₅(P-P)₂, P-P=norphos, dppp and dppb in CDCl₃ ([Ru₂] = 2.0(±0.2) x 10⁻³ M).
Figure 3.5 Visible spectra of Ru$_2$Cl$_5$(chiraphos)$_2$ in CDCl$_3$ and CCl$_4$.

Figure 3.6 Visible spectra of Ru$_2$Cl$_5$(chiraphos)$_2$ in CD$_3$NO$_2$ and CH$_3$CN after complete loss of absorption in the near-infrared region.
obey Beer's law, but on standing slight changes in the spectra are observed. The dppb analogue does not obey Beer's law; the extinction coefficient for the absorption at 370 nm increases and those at 520 and 450 nm decrease with dilution.

3.5.3 Discussion of Electronic Spectral Data

Intervalance transfer (I.T.) bands of mixed-valence complexes result from the electron transfer process:

\[ \text{M} \rightleftarrows \text{M}^+ \]

where M is a metal centre, \( \text{M}^+ \) its one-electron oxidation product, and \( \rightleftarrows \) denotes bridging ligands. The extent of electron delocalisation between the metal centres contributes significantly to the ease of transfer, and therefore, has a strong influence on the physical properties of such complexes. Robin and Day\(^{95} \) have used the degree of delocalisation as a criterion for distinguishing three broad classes of mixed-valence binuclear complexes:

**Class I:** The interaction between M and \( \text{M}^+ \) centres is weak as a result of large intermetallic distances or very different metal coordination spheres. These factors produce a strongly localised system in which the complex exhibits properties observed for isolated mononuclear M and \( \text{M}^+ \) species. The I.T. bands are of high energy (u.v. region).

**Class II:** The metal ions have identical or near identical coordination environments, but have distinguishable valences due to only slight delocalisation. This results in properties which may not be
associated with the isolated units.

Class III-A: The interaction between the two centres is large and electron delocalisation is complete. The metal ions are indistinguishable and the complex shows only properties discernable for a \((\mathbf{M} \wedge \wedge \mathbf{M})^+\) unit. The I.T. band of such complexes is most often observed at low energy (near-i.r.).

The most extensive research in this field has been on ionic complexes of the type \([\text{Ru(NH}_3)_5]^2_L-L^5^+\) where \(L-L\) is a bridging group, and these systems have been reviewed along with other \(d^5-d^6\) species by Creutz\(^{96}\). Theoretical models\(^{97}\) describing the intervalence charge transfer process have also been developed. The treatment of Hush\(^{98}\) describes the characteristics of the Class II system where the absorption band represents the transition:

\[

This electron transfer transition occurs instantaneously on the vibrational time scale and results in the metal ions being in the equilibrium coordination spheres of the other oxidation state. Therefore, the energy between the ground and excited mixed-valence states, \(E_{op}\), is determined by the excess vibrational energy of the excited state over the ground state. For such a system Hush predicts that the bandwidth at half intensity, \(\Delta V_{1/2}\), is a function of the energy of the I.T. band, \(V_{\text{max}}\), where

\[
V_{\text{max}} = \frac{(\Delta V_{1/2})^2}{2310} \text{ cm}^{-1}
\]  

(3.6)
The energy of the I.T. band is also solvent dependent since both inner sphere and outer sphere (solvent) vibrational modes contribute to the excess vibrational energy of the I.T. excited state. This manifests itself as a linear relationship between $E_{\text{op}}$ and $(1/n^2 - 1/D_s)$ where $n$ and $D_s$ are the optical and static dielectric constants of the solvent, respectively. For a Class III-A system, in which the I.T. band represents an electronic transition between the ground and excited state molecular orbitals of the completely delocalised $(\text{M-M})^+$ complex, Hush's theories are not applicable.

The nature of the valence state in $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ is of fundamental importance as it is the representative member of a new class of $d^5-d^6$ mixed-valence dinuclear metal complexes. The high solubility of the complex also permits investigations in a wide variety of solvents.

The structure of $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ (Figure 3.1) shows that the ruthenium centres have very similar crystallographic environments which clearly rules out a Class I formulation. The slight inequivalence of the metal centres and lack of crystallographically imposed metal ion equivalence argues for the formulation of $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ as a Class II compound, although the inequivalence could result from solid state packing within the crystal. The properties of the complex in solution, however, are clearly dependent on the solvent and direct classification is not immediately obvious. Even so, the fact that the absorptions detected in the near-i.r. are not observed in either the $\text{Ru}_2^{\text{II,II}}$ or $\text{Ru}_2^{\text{III,III}}$ congeners (Section 3.6) shows that these
absorption bands result from intervalence transitions.

From Figure 3.4 it is apparent that Ru₂Cl₅(chiraphos)₂ can exist in two basic forms, that found in toluene or CCl₄ and that found in the other solvents used. The latter case will be considered first, in which the complex exhibits the main absorption at ca. 2340 nm and a less intense one at ca. 1100 nm. The properties of the band at ca. 2340 nm deviate considerably from those predicted by Hush for a Class II system. From equation 3.6 the calculated band width at half-height is 3140 cm⁻¹ which is very much larger than the observed value, assuming the curves to be Gaussian, of ca. 1650 cm⁻¹; also there is negligible variation in the energy of this band with changing solvent. These data suggest the alternative Class III-A formulation, in contradiction to the Class II based on the crystal structure. Assuming the crystal is representative of the complex it would appear that the slight differences observed between the ruthenium centres are a result of packing forces. A Class III-A formulation seems reasonable in view of the short metal-metal distance together with the participation of the bridging chloride 3p orbitals which could facilitate strong orbital interaction to produce a delocalised system.

The existence of a second I.T. band is unexpected although theoretically not impossible. For a Ru₂¹,III species, where both metals are in sites of octahedral symmetry, intervalence transfer occurs when a Ru(II)t₂g electron is transferred to a Ru(III)t₂g acceptor orbital. Transfer to a Ru(III)e g acceptor orbital would result in a second I.T. absorption, but of much higher energy. In the
present case, the second near-i.r. band probably arises from other species.

The I.T. band at ca. 1100 nm appears similar to that observed for a Class II system in that the exact position varies with solvent, but the required linear dependence of $\nu_{\text{max}}$ with $(1/n^2 - 1/D_s)$ is clearly not observed (Figure 3.7). Closer examination of the band shape shows it is not symmetrical, and since the band is sensitive to the change in solvent it appears to be composite in character. This conclusion is strengthened by the observed value of $\Delta\nu_{1/2}$ which in most cases is greater than that calculated by equation 3.6. A tentative explanation for this I.T. band is the presence of polynuclear mixed-valence species. This suggestion is supported by the observed irreversible disproportionation in CH$_2$CN, DMSO-$d_6$, CD$_3$NO$_2$ and to a certain extent DMA (Section 3.6) in accordance with the equation:

$$2 \text{Ru}_2\text{Cl}_5(\text{P-P})_2 \longrightarrow [\text{RuCl}_2(\text{P-P})]_2 + [\text{RuCl}_3(\text{P-P})]_2$$  \hspace{1cm} (3.7)

which results in complete loss of absorption in the near-i.r. Formation of the dimeric products requires invoking a tetranuclear intermediate species (Section 3.6) through which chloride ion and electron transfer occurs. If such a species was sufficiently long-lived, it would be expected to show only slight delocalisation due to the unsymmetrical nature of the terminal and bridging metal centres, thereby tending to a Class II system. Dissociation of any binuclear species to solvated monomers could generate trinuclear species such as $\text{Ru}_3\text{Cl}_8(\text{P-P})_3$ by complexation of a monomer with the original dimers. Such additional
species could explain the composite nature of the band at ca. 1100 nm.

In toluene or CCl₄, the near-i.r. spectrum of Ru₂Cl₅(chiraphos)₂ changes dramatically, and shows only a broad absorption at low energy and a single symmetrical band at 880 nm (Figure 3.2). That the principal low energy absorption observed previously is not present in toluene or CCl₄, which are non-polar and essentially non-solvating, reflects the need of a solvent sphere about this complex
to maintain a triply chloro-bridged binuclear structure. This was shown by evaporation of a CCl₄ solution to yield a solid-state spectrum the same as observed in solution, while addition of CDCl₃ to the solid produced the spectrum originally observed in this solvent. Since no such solvent sphere is available in toluene or CCl₄, the complex could undergo dimerisation to the tetranuclear species discussed previously, although some of the binuclear species must still remain in order to explain the broad unresolved band found at low energy. Since the absorption at 880 nm is symmetrical, the presence of only one polynuclear species is suggested.

The similarity between the near-i.r. and visible spectra of Ru₂Cl₅(chiraphos)₂ in toluene or CCl₄ and Ru₂Cl₅(dppb)₂ in all solvents used suggests that the same mixture of tetranuclear and binuclear species is present. The spectrum of the dppb derivative is invariant to solvent (CDCl₃, CCl₄ or DMA), which implies that formation of the tetranuclear species is determined by the larger ring size relative to chiraphos rather than by a solvent effect. Beer's law is not obeyed for Ru₂Cl₅(dppb)₂ in DMA, and so disproportionation in accordance with equation 3.2 is assumed. The behaviour of the Ru₂Cl₅(dppp)₂ system (Figure 3.3) appears to be intermediate between that of dppb and that of chiraphos, the system showing single, relatively intense absorptions at 2060 and 960 nm. The extremely low solubility of this complex prevents measurement of the near-i.r. spectra in other solvents.
Whilst the assignment of I.T. bands to polynuclear species is necessarily tentative until such species are isolated and characterised, there is a precedent for this in the literature. A limited study of a Cu$^{II}$-Cu$^{I}$-macrocyclic-ligand complex revealed two I.T. absorptions at 1725 and 1175 nm, the latter being solvent dependent. Evidence for possible formation of tetranuclear species from the dimer was obtained from the EPR spectrum of a frozen acetonitrile solution which showed additional absorptions assignable to such a species. The near-i.r. spectra of the polynuclear species $[(\text{NH}_3)_5\text{Ru}(\text{pz}-\text{Ru}(\text{NH}_3)_4)_n\text{pz}-\text{Ru}(\text{NH}_3)_5)]^{(2n+1)+}$, where pz = pyrazine and $n = 3-6$, reported by Taube's group show shifts to higher energy with increasing $n$. For the case of $n = 3$, the absorption is composite and sensitive to solvent, but no definite conclusions were drawn.

Mixed-valence complexes of chloro-bridged ruthenium complexes have been examined previously, but these were generated electrochemically in situ which restricts analysis. Johnson et al. generated $[(2,2'$-bipyridine)$_2\text{RuCl}]^{3+}$, but this decomposed readily and spectral data were not obtained. The most closely related systems to those studied here are the triply chloro-bridged diruthenium complexes of general type $[\text{L}_3-x\text{Cl}_x\text{RuCl}_y\text{RuCl}_y\text{L}_3-x-y]^2$ where, L is a soft neutral ligand and $Z = -1$ to +2. Of these, the symmetrical species $[\text{P}_3\text{RuCl}_3\text{RuP}_3]^2$, $P = \text{PET}_2\text{Ph}$, and $[\text{As}_2\text{ClRuCl}_2\text{RuClAs}_2]$, $\text{As} = \text{As(toly1)}_3$, were found to be delocalised systems. Their near-i.r. spectra in 0.5 M n-\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2 at 233 K reveal absorption maxima at 2230 ($\epsilon = 3750 \text{M}^{-1}\text{cm}^{-1}$) and 1695 nm ($\epsilon = 1700 \text{M}^{-1}\text{cm}^{-1}$) for the phosphine and
arsine species, respectively. These data are similar to those found here, at least for Ru$_2$Cl$_5$(chiraphos)$_2$ in polar solvents. The authors also note the existence of an additional band whose position appears to parallel the degree of interaction between the metal centres. No details were given, but this band could correspond to the absorption observed at higher energy in the present work.

3.6 **Disproportionation of Ru$_2$Cl$_5$(P-P)$_2$**

The loss of the absorption bands in the near-i.r. spectra of Ru$_2$Cl$_5$(P-P)$_2$ P-P = chiraphos or dppb, in CH$_3$CN, DMSO-d$_6$ and CD$_3$NO$_2$, and to a certain extent DMA (Section 3.5) implies that the mixed valence complexes undergo disproportionation in these solvents. The final visible spectrum obtained for Ru$_2$Cl$_5$(chiraphos)$_2$ was similar in both DMSO-d$_6$ and CD$_3$NO$_2$, but was markedly different to that obtained in CH$_3$CN (Figure 3.6). Similar solution behaviour was observed for the dppb analogue. The disproportionation of Ru$_2$Cl$_5$(chiraphos)$_2$ in DMSO solvent (Figure 3.8) proceeds with isosbestic points at 403 and 345 nm.

In addition to exhibiting different visible spectra, acetonitrile solutions of the dppb and chiraphos complexes gave molar conductivities of 112 ohm$^{-1}$cm$^2$mole$^{-1}$ ($2 \times 10^{-3}$ M solutions) whereas no conductance was observed in the other solvents. This value is typical of a uni-valent electrolyte; however, simple dissociation of a chloride ion can be ruled out since this would still result in a mixed-valence species which should exhibit an intervalence charge-transfer band.
Figure 3.8 Changes in visible spectrum with time for a DMSO solution of Ru₂Cl₅(chiraphos)₂.

In order to determine the species present in solution the metathesis reaction of Ru₂Cl₅(dppb)₂ and AgPF₆ (2:1 mole ratio) in CH₃CN was performed as described in Section 2.1.7.10.

Two complexes were isolated: [RuCl₃(dppb)]₂, a maroon solid which is assumed to be a Ru³⁺ dimer by analogy to [Ru₂Cl₃(P(n-butyl)₃)₂]₂ and in contrast to the green monomeric RuCl₃P₂(DMA).DMA, P = PPh₃ or P(p-tolyl)₃ complexes from which the mixed-valence complexes are initially prepared. The lack of coordinated solvent suggests a coordinatively saturated species.
(Structure 3-I). The second product is the dimeric 

\[
[Ru_2\text{Cl}_3(dppb)_2(CH_2\text{CN})_2]^+PF_6^-
\]

species for which characterisation and discussion is given in Section 6.2.1.1 and 6.3, respectively.

The visible spectra of isolated \([RuCl_3(dppb)]_2\) and \([Ru_2\text{Cl}_3(dppb)_2(CH_2\text{CN})_2]^+PF_6^-\) in acetonitrile are shown in Figure 3.9. Superposition of these spectra result in essentially an identical spectrum to that observed for Ru$_2$Cl$_5$(dppb)$_2$ in this solvent thereby suggesting that disproportionation of the latter to these complexes does occur. Neither of the isolated complexes exhibit absorptions in the near-i.r. as is to be expected for single valence complexes. Since Ru$_2$Cl$_5$(chiraphos)$_2$ in CH$_3$CN gives the same visible spectrum and conductivity it is assumed that this complex undergoes the same disproportionation although the products have not been isolated.

In DMSO-$d_6$ and CD$_2$NO$_2$ the loss of the near-i.r. absorptions for Ru$_2$Cl$_5$(P-P)$_2$ P-P = chiraphos and dppb are slower but still suggest that disproportionation also occurs in these solvents. However, the lack of conductivity and the difference in final spectra compared to
that observed in CH₃CN indicate that disproportionation is only to the neutral dimeric complexes. This is supported by the visible spectra of DMSO solutions of [RuCl₃(dppb)]₂ and [RuCl₂(dppb)]₂; the latter is isolated as described in Section 4.2. Superposition of these spectra gives the same spectrum as obtained for Ru₂Cl₅(dppb)₂ (Figure 3.10).

The formation of dimeric products from the disproportionation of Ru₂Cl₅(P-P)₂, P-P = chiraphos or dppb, can be explained by two mechanisms. The first involves dissociation of Ru₂Cl₅(P-P)₂ to
monomeric Ru$^{II}$ and Ru$^{III}$ complexes which then undergo dimerisation. The second involves initial dimerisation to generate a tetranuclear species which by unsymmetrical bridge-cleavage generates the dimeric products (Scheme 3-II). Whilst monomeric Ru$^{II}$ species are observed in acetonitrile (section 6.2.1.1), the presence of dimeric Ru$^{III}$ in this solvent and only dimers in the other solvents tend to support the second proposal. In CH$_3$CN the disproportionation of Ru$_2$Cl$_5$(P-P)$_2$ must be rapid as loss of absorption in the near-i.r. is instantaneous.
upon dissolution. In DMSO-d₆ and CD₃NO₂ the process is much slower (1 h and 5 h respectively) and, if the tetranuclear species is sufficiently long-lived, this could account for additional absorption(s) observed in the near-i.r. region (Section 3.5).

3.7 Activation of Molecular Hydrogen by the Ru₂Cl₅(P-P)₂ Complexes

3.7.1 Stoichiometry of the Reaction in DMA

The Ru₂Cl₅(P-P)₂ complexes in DMA readily absorb hydrogen at 20-30°C with an accompanying colour change from red to orange-brown. The final gas uptake corresponded to half a mole of H₂ per mole of complex in each case except for P-P norphos which at 50°C showed an additional slow uptake of two moles of H₂. For P-P = chiraphos the gas uptakes were sufficiently slow so that detailed kinetic plots could be obtained (Figure 3.1l). These show an induction period followed by a marked acceleration in rate; the induction was not due to slow dissolution of the complex because a homogeneous solution was obtained immediately. The reactions show features characteristic of an
Figure 3.11 Uptake plots for the reaction between Ru$_2$Cl$_5$(chiraphos)$_2$ and H$_2$ in DMA at 25°C. [Ru$_{II,III}$]$^x 10^3 = 10.00 (\nabla)$, 7.57 (●), 4.88 (■) and 3.00 M (◆) [H$_2$] = 0.88 x $10^{-3}$ M.

Inset shows log plot for data where [Ru$_{II,III}$]$^x 10^3 = 10.00 x 10^{-3}$ M.
autocatalytic reaction. For P-P = dppb or diop under similar conditions, the uptake was much more rapid and was complete within 500 seconds. The final stoichiometry is consistent with reduction of the mixed-valence complexes to a Ru$_{2}^{II,II}$ species (see also Section 3.7.3.2) as outlined in equation 3.8.

$$\text{Ru}_2\text{Cl}_5(P-P)_2 + 0.5\text{H}_2 \rightarrow \text{Ru}_2\text{Cl}_4(P-P)_2 + \text{H}^+ + \text{Cl}^- \quad (3.8)$$

The additional uptake of two moles of H$_2$ for P=P = norphos is presumably a result of the reduction of the carbon-carbon double bond in the phosphine ligand which has been observed previously.$^{24}$

The use of DMA, a polar aprotic solvent, promotes the reduction since in toluene negligible reaction occurs unless base is added (Section 3.7.4). The final orange-brown solutions were air-sensitive returning to their original red colour and then slowly turning green.

3.7.2 Spectral Studies

The gas uptakes for the reduction of Ru$_2$Cl$_5$(chiraphos)$_2$ in DMA were sufficiently slow to be measured accurately, but due to the small uptake involved, a more convenient method for studying the reaction kinetics employing smaller amounts of complex was visible spectroscopy. Upon reduction of Ru$_2$Cl$_5$(chiraphos)$_2$, new absorption maxima are observed at 456, 365(sh), and 300 nm, and the reaction proceeds with isosbestic points at 356 and 292 nm, as shown in Figure 3.12. Monitoring the changes in absorbance at a single wavelength results in
Figure 3.12 Changes in absorbance for the reaction of Ru$_2$Cl$_5$(chiraphos)$_2$ and H$_2$ in DMA at 25°C.
plots (Figure 3.13) which have a maximum slope at ca. half the total absorbance change. Differentiating the plots graphically gives rise to the curves shown in Figure 3.14 which are nearly symmetrical about the 50% reaction point, and are typical of an autocatalytic process\textsuperscript{104}.

An extensive study was carried out in which solutions were freshly prepared for each measurement. Dependences of the initial and maximum rates on [Ru\textsubscript{2}\textsuperscript{II,III}], [H\textsubscript{2}], [DMA.HCl] and temperature were determined. A mechanism to rationalise the kinetics has not been formulated, since it was later observed that an initially prepared stock solution of Ru\textsubscript{2}Cl\textsubscript{5}(chiraphos)\textsubscript{2} was not under equilibrium conditions. The initial and maximum rates measured under the same conditions increased markedly on storage of the solution, even in the dark. Whilst changes in rate were observed, the visible spectrum of the solution remained essentially unchanged with time (the monitoring of the near-i.r. region (Section 3.5.1) was carried out only in later work).

Although the "non-equilibration" data could not be readily analysed, points merit discussion. Our interest in the reduction of Ru\textsubscript{2}Cl\textsubscript{5}(P-P)\textsubscript{2} was in the autocatalytic nature of the reaction which is relatively uncommon in inorganic reactions involving gas molecules. An understanding of such autocatalytic behaviour could offer some insight into H\textsubscript{2} activation by hydrogenase systems which appear to operate via iron cluster species, and an analogy to an autocatalytic Ru\textsuperscript{IV}/Ru\textsuperscript{III}/H\textsubscript{2} system has been suggested\textsuperscript{107}. The catalytically active species in the autocatalytic Ru\textsubscript{2}Cl\textsubscript{5}(chiraphos) system is presumably a Ru(II) species whose concentration continually increases
Figure 3.13 Spectral changes at 530nm with time for the reaction of Ru$_2$Cl$_5$(chiraphos)$_2$ and H$_2$ in DMA at 25°C. Reaction monitored at 530nm $[\text{Ru}_2^{II,III}]$: (1) = 7.56 x 10$^{-4}$M, (2) = 4.24 x 10$^{-4}$M. $[\text{H}_2]$ = 1.76 x 10$^{-3}$M.

Figure 3.14 Plot of rate of change of absorbance with time against concentration of Ru$_2$Cl$_5$(chiraphos)$_2$. 
with reaction time. This is supported further by the observed increase in initial and maximum rates with storage time of DMA solution; this is a result of slow disproportionation (Section 3.5.6) which increases the initial concentration of $[\text{RuCl}_2(\text{P-P})]_2$. Greater initial disproportionation could be a factor in the much faster reductions found for $\text{Ru}_2\text{Cl}_5(\text{dppb})_2$ and the diop analogue.

The $\text{H}_2$-uptakes by $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ at the higher ruthenium concentration (Figure 3.11) are similar, qualitatively, to those found for the reduction of Ru(IV) by Ru(III) in HCl solutions, for which the mechanism outlined in equations 3.9 and 3.10 was proposed\textsuperscript{[106]}.

\begin{align*}
\text{Ru}^{\text{III}} + \text{H}_2 & \overset{k_1}{\iff} \text{Ru}^{\text{III}}\text{H}^- + \text{H}^+ \quad (3.9) \\
\text{Ru}^{\text{III}}\text{H}^- + 2\text{Ru}^{\text{IV}} & \overset{\text{fast}}{\longrightarrow} 3\text{Ru}^{\text{III}} + \text{H}^+ \quad (3.10)
\end{align*}

In the chiraphos system the required linear dependence of $\log[\text{Ru}^{\text{II}}]$ vs. time in analogy to this mechanism was not obtained (Figure 3.11). This is possibly due to inhibition of the rate, particularly at the later stages, because of formation of the less active $[\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^\text{H}^+$, a species that is known to be formed from $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$ in the presence of chloride (Section 3.7.3). This was demonstrated by monitoring the reduction of $\text{FeCl}_3$ by $\text{H}_2$ using a $\text{H}_2$-reduced solution of $\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2$. The reaction being catalysed is given in equation 3.11, and proceeds at 1 atm. $\text{H}_2$ and 25°C for ca. 4.5 turnovers before stopping. Whilst the
\[ 2\text{Fe}^{III} \text{Cl}_3 + \text{H}_2 \rightarrow 2\text{Fe}^{II} \text{Cl}_2 + 2\text{H}^+ + 2\text{Cl}^- \]  (3.11)

concentration of HCl is increasing continually, the ruthenium(II) concentration remains constant, and so the reaction proceeds until formation of the inactive ionic species is complete. In the presence of proton sponge (PS) the iron(III) reduction proceeds at a comparable rate for 7 turnovers when the formation of \([\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^-\text{PSH}^+\) is considered to prevent further reduction. In the presence of a 40-fold excess of DMA.HCl no reduction of FeCl$_3$ occurs.

At lower concentrations of the complex, the uptake plots for the H$_2$-reduction of Ru$_2$Cl$_5$(chiraphos)$_2$ show a definite step-wise behaviour (Figure 3.11), which indicates that two consecutive reactions are occurring. These could correspond to the reduction, by a Ru$^{II}$ species, of Ru$_2$Cl$_5$(chiraphos)$_2$, and also of Ru$_2$Cl$_6$(chiraphos)$_2$ formed from the disproportionation reaction (Section 3.6).

In view of the complex nature of Ru$_2$Cl$_5$(chiraphos)$_2$ in solution it is not surprising that the "non-equilibriated" kinetic data could not be analysed readily. However, the study does serve to point out that a reaction proceeding with isosbestic points in the visible spectral region is not necessarily a simple one.

3.7.3 Conductivity Measurements

The product isolated from the H$_2$-reduction of Ru$_2$Cl$_5$(chiraphos)$_2$ in DMA is the Ru$_2$Cl$_4$(chiraphos)$_2$ dimer given in equation 3.8 (Section 4.2); however, this was not the product generated in situ. DMA
solutions of the mixed-valence chiraphos complex are non-conducting, but on reduction conductance is observed, and the results of measurements obtained by successive dilution under an atmosphere of H₂ at 25°C are given in Table 3.4. The equivalent conductance $\Lambda_e$, varies linearly with the square-root of the equivalent concentration, assuming a 1:1 electrolyte (Figure 3.15), in accordance with the Onsager limiting law. The intercept which represents the equivalent conductance at infinite dilution, $\Lambda_0$, is 35.3 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\). In order to determine the nature of the species generated by the H₂-reduction, the conductivity of HCl and HBr was studied, since the limiting ionic equivalent conductivities of the proton and chloride ion in DMA had not been measured previously.

### 3.7.3.1 Conductivity Measurements on DMA.HCl and DMA.HBr

A convenient source of HCl and HBr for conductivity measurements were the DMA salts of these acids which were prepared as described in Section 2.1.6. Dilution conductivities were determined for both salts in DMA at 25°C under argon, and the results are given in Table 3.5. A plot of $\Lambda_e$ vs. $C_{eq}^{1/2}$ is linear for DMA.HBr, but shows marked curvature for DMA.HCl (Figure 3.16). The limiting conductance, $\Lambda_0$, for DMA.HBr is 65.4 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\). The Onsager limiting law applies only to strong electrolytes, and is clearly unsuitable for DMA.HCl so recourse was made to the Fouss-Shedlovsky treatment for weak electrolytes. The fundamental equation involved may be written as:
Table 3.4
Equivalent Conductivity of Ru$_2$Cl$_6$(chiraphos)$_2$ in DMA at 25° C

<table>
<thead>
<tr>
<th>[Ru$_2$] x 10$^4$, M</th>
<th>$\Lambda_e$, ohm$^{-1}$cm$^2$mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prior to reaction with hydrogen</td>
<td>11.42</td>
</tr>
<tr>
<td>After complete reaction with hydrogen$^a$</td>
<td>11.42</td>
</tr>
<tr>
<td></td>
<td>6.95</td>
</tr>
<tr>
<td></td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>1.69</td>
</tr>
</tbody>
</table>

$^a$) Measured under an atmosphere of hydrogen

Figure 3.15 Onsager plot for H$_2$-reduced Ru$_2$Cl$_6$(chiraphos)$_2$ in DMA at 25°C.
### Table 3.5

Dilution Conductivities of DMA.HCl and DMA.HBr in DMA at 25°C

<table>
<thead>
<tr>
<th>[DMA.HCl] x 10³, M</th>
<th>( \Lambda_e ) ohm⁻¹ cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.76</td>
<td>6.1</td>
</tr>
<tr>
<td>6.88</td>
<td>8.5</td>
</tr>
<tr>
<td>3.44</td>
<td>11.5</td>
</tr>
<tr>
<td>1.72</td>
<td>15.6</td>
</tr>
<tr>
<td>1.86</td>
<td>21.2</td>
</tr>
<tr>
<td>1.43</td>
<td>27.1</td>
</tr>
<tr>
<td>1.22</td>
<td>35.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[DMA.HBr] x 10³, M</th>
<th>( \Lambda_e ) ohm⁻¹ cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.92</td>
<td>41.1</td>
</tr>
<tr>
<td>9.54</td>
<td>42.5</td>
</tr>
<tr>
<td>7.63</td>
<td>45.4</td>
</tr>
<tr>
<td>6.11</td>
<td>47.1</td>
</tr>
<tr>
<td>3.11</td>
<td>52.2</td>
</tr>
<tr>
<td>1.55</td>
<td>56.1</td>
</tr>
<tr>
<td>1.78</td>
<td>58.9</td>
</tr>
</tbody>
</table>

Figure 3.16 Onsager plots for DMA.HCl and DMA.HBr in DMA at 25°C.
\[ SA = \Lambda_0 - \frac{CF^2 S^2 \Lambda^2}{K\Lambda_0} \]  

(3.12)

where \( S = \left( \frac{Z}{2} + \sqrt{1 + \left( \frac{Z}{2} \right)^2} \right)^2 \)

\[ Z = \alpha \sqrt{CA} / \Lambda_0^{3/2} \]

\( \alpha = \) Onsager coefficient

\( f = \) activity coefficient from \(-\log f = \beta \sqrt{C_i} \)

and \( K = \) dissociation constant.

Substitution of the experimental values and known constants into equation 3.12, and plotting \( SA \) vs. \( CF^2 S^2 \Lambda^2 \) gives a linear plot (Figure 3.17), where the value of the ordinate intercept corresponds to \( \Lambda_0 \) and the slope is equivalent to \(-1/K\Lambda_0 \). The limiting conductance for DMA.HCl is found to be 69.8 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\), and the dissociation constant is \(1.1 \times 10^{-4}\)M.

The limiting ionic conductance \( (\lambda_0^-) \) reported for the bromide ion\(^{110} \) in DMA at 25°C is 43.2 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\). Applying Kohlrausch's law of independent ionic mobilities, \( \Lambda_0 = \lambda_0^- + \lambda_0 \) (= 65.4 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\) for DMA.HBr), the value of the limiting conductance for the solvated proton is therefore 22.2 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\) and \( \lambda_0 \text{Cl}^- = 69.8 - 22.2 = 47.6 \) ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\).

3.7.3.2 Analysis of Conductivity Measurements on H\(_2\) Reduced Solutions of Ru\(_2\)Cl\(_5\) (chiraphos)\(_2\) in DMA

The marked differences between the plots of \( \Lambda_e \) vs. \( C_{eq}^{1/2} \) for the reduced solutions of Ru\(_2\)Cl\(_5\) (chiraphos)\(_2\) (Figure 3.15) and DMA.HCl (Figure 3.16) show that free HCl is not liberated as given in
Figure 3.17 Plot of $\Delta \Lambda$ against $\text{Cl}^2 \text{S}^2 \Delta^2$ in accordance with equation 3.12.

Equation 3.8. A feasible reaction still consistent with the stoichiometry is 3.13, where the chloride ion product shown in

$$\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2 + 0.5\text{H}_2 \rightarrow [\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^ - \text{H}^+ \quad (3.13)$$

equation 3.8 has added to the Ru$^{\text{II}}_2$ dimer product to give presumably a triply chloro-bridged anion with the solvated proton as the counter-ion (see below). Further support for this ionic product comes
from the calculated limiting conductance, which for [Ru₂Cl₅(chiraphos)₂]⁻ can be estimated from Stokes law:

\[ r_s = \frac{F^2}{6\pi\eta\lambda_o} \]  \hspace{1cm} (3.14)

in which \( F \) is the Faraday, \( N \) is Avogadro's number, \( \eta \) is the viscosity of the solvent (9.19 x 10⁻³ poise for DMA), and \( r_s \) is the Stokes radius of the anion. Assuming the anion to have the same crystallographic radius as that found for Ru₂Cl₅(chiraphos)₂ (7.14Å), the calculated \( \lambda_o \) is 12.4 ohm⁻¹ cm² mole⁻¹. Since \( \lambda_o H^+ \) is 22.2 ohm⁻¹ cm² mole⁻¹, the calculated value of \( \Lambda_o \) for the product of equation 3.15 is 34.6 ohm⁻¹ cm² mole⁻¹ which is in excellent agreement with the experimental value of 35.3 ohm⁻¹ cm² mole⁻¹.

More direct evidence for the nature of the anion comes from the \(^{31}P\{^1H\}- n.m.r. spectrum of the in situ product generated in DMA/toluene-d₈ (v:v = 1:1). The spectrum consists of an AB quartet (\( \delta_A = 88.26, \delta_B = 80.35 \) ppm, \( ^2J_{AB} = 36.8 \) Hz) from ambient temperature to -50°C. This is consistent with structure 3-II where the inequivalence of the phosphines is a result of the ligand being chiral.

[Chemical structure diagram]

3-II
(see Section 4.3.2). The spectrum of the analogous dppb complex under the same conditions exhibits only a singlet at 50.9 ppm.

The product was isolated as the protonated amide chloride salt by evaporation of the DMA under reduced pressure and addition of deoxygenated hexanes to the resulting oil; this produced an orange precipitate which was filtered, washed well with degassed hexanes and dried in vacuo. Analysis: \( (C_{60}H_{66}ClNO_PRu_0) \) requires C:54.61, H:5.01, N:1.06%; found C:55.19, H:4.98, N:0.96%. Addition of deoxygenated methanol to the oil, however, displaces the DMA.HCl and the neutral \( Ru_2Cl_4(\text{chiraphos})_2 \) complex can be isolated (Section 4.2).

### 3.7.4 Reaction of \( Ru_2Cl_5(P-P)_2 \) Complexes with \( H_2 \) in Toluene

The title complexes are unreactive towards hydrogen in toluene unless a base is present. This reaction was studied for \( Ru_2Cl_5(dppb)_2 \) using Proton Sponge, PS, as base. The gas uptake shows the reaction proceeds with absorption of 0.5 \( H_2:Ru_2^{II,III} \), and is accompanied by a colour change from red to orange-brown as found for the study in DMA in the absence of added base. The reaction is much slower, but is again consistent with reduction to a \( Ru_2^{II,II} \) species which is found to contain PS.HCl, and which can be isolated as described in Section 2.1.7.7. The product analyses for \( [Ru_2Cl_5(dppb)_2]^{-PSH}^+ \); the HCl produced in the reduction reacts with the base to produce PS.HCl which subsequently adds to the neutral dimer.

The variation of conductivity in DMA with concentration was determined at 25°C under argon (Table 3.6); this gives a linear Onsager
### Table 3.6

**Dilution Conductivities of \([\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{+}\text{PSH}^+\) in DMA at 25°C**

<table>
<thead>
<tr>
<th>([\text{Ru}_2]) (x 10^3, \text{M})</th>
<th>(\Lambda_e ) (\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.79</td>
<td>26.6</td>
</tr>
<tr>
<td>1.35</td>
<td>28.5</td>
</tr>
<tr>
<td>1.01</td>
<td>30.3</td>
</tr>
<tr>
<td>0.76</td>
<td>31.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>([\text{Ru}_2]) (x 10^3, \text{M})</th>
<th>(\Lambda_e ) (\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>32.0</td>
</tr>
<tr>
<td>0.43</td>
<td>33.1</td>
</tr>
<tr>
<td>0.32</td>
<td>33.8</td>
</tr>
<tr>
<td>0.16</td>
<td>35.4</td>
</tr>
</tbody>
</table>

---

**Figure 3.18** Onsager plot for \([\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{+}\text{PSH}^+\) in DMA at 25°C.
plot (Figure 3.18) from which the limiting conductance is 38.7 ohm$^{-1}$ cm$^2$ mole$^{-1}$ as compared to 35.3 ohm$^{-1}$ cm$^2$ mole$^{-1}$ found for $[\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^{-}\text{DMAH}^+$. Assuming $[\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{-}$ to have the same limiting ionic conductance as the chiraphos derivative (12.4 ohm$^{-1}$ cm$^2$ mole$^{-1}$), the limiting conductance for PSH$^+$ is 26.3 ohm$^{-1}$ cm$^2$ mole$^{-1}$. This value is somewhat greater than that found for the solvated proton in DMA (22.2 ohm$^{-1}$ cm$^2$ mole$^{-1}$), implying for the latter, perhaps, that the proton is bonded to more than one molecule of DMA which would result in a lower ionic mobility.

The $^{31}\text{P}^{1}\text{H}$-n.m.r. spectrum of $[\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{-}\text{PSH}^+$ in CD$_2$Cl$_2$ is a singlet (53.6 ppm) from ambient temperature to -70°C. This is consistent with the complex having the same structure (3-II) as found for the in situ generated $[\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{-}\text{DMAH}^+$ (previous section).
CHAPTER IV

SYNTHESIS AND CHARACTERISATION OF DIMERIC RUTHENIUM(II) COMPLEXES AND THEIR APPLICATION AS ASYMMETRIC HYDROGENATION CATALYSTS

4.1 Introduction

The use of rhodium phosphine complexes as asymmetric hydrogenation catalysts has been studied extensively, and with a number of phosphines it is possible to hydrogenate derivatives of α-acylaminoacrylic acids with >90% e.e (Section 1.1). Ideally, a catalyst for general chemical synthetic use should be able to asymmetrically hydrogenate any prochiral alkene, or selectively hydrogenate one diastereomer of a chiral alkene with high enantiomeric excess. Towards this goal, the development of highly enantioselective catalysts is preferred, rather than production of more chiral phosphines. This can be achieved either by using chiral ligands other than phosphines or by using catalysts which hydrogenate by different mechanisms, and which hopefully are more discriminatory. Research in these two areas has been limited, and to date, not too successful⁴.

In this laboratory, ruthenium complexes containing chiral phosphine and sulfoxides have been prepared and used as asymmetric hydrogenation catalysts. An exchange reaction using RuCl₂(PPh₃)₃
and the chiral phosphine diop produced Ru$_2$Cl$_4$(diop)$_3$, a complex containing a bridging diop ligand. This complex in DMA was found to absorb 1 or 2 moles of H$_2$ per dimer in the absence and presence of diop, respectively, in accordance with equations 4.1 and 4.2. The hydride product, 1, could be prepared independently by a

$$\text{Ru}_2\text{Cl}_4(\text{diop})_3 + H_2 \rightarrow \text{RuHCl(diope)}_2 + \text{RuCl}_2(\text{diop}) + \text{HCl} \quad (4.1)$$

$$\text{Ru}_2\text{Cl}_4(\text{diop})_3 + 2H_2 \rightarrow 2\text{RuHCl(diope)}_2 + 2\text{HCl} \quad (4.2)$$

phosphine exchange method from RuHCl(PPh$_3$)$_3$ and diop. Although 1 was originally thought to have the hydride cis to chloride, the crystal structure later showed it to be a trans configuration.

Analogues of 1 with the diphosphines dppm, dppe and dppp were catalytically inactive for hydrogenation, clearly implying that steric factors associated with the seven-membered ring of diop upon coordination were important.

The diop complexes hydrogenated under mild conditions a variety of prochiral alkenes with modest enantiomeric excesses (up to 59% e.e.) Hydrogenations using Ru$_2$Cl$_4$(diop)$_3$ were complicated by the presence of two ruthenium species (equation 4.1) which resulted in reduced products differing in e.e. from those found using RuHCl(diope)$_2$ alone. This suggested that RuCl$_2$(diope), a species that was not isolated, did contribute to the hydrogenation. Kinetic data for the hydrogenation of acrylamide and atropic acid catalysed by RuHCl(diope)$_2$ were consistent with the mechanism shown in equations 4.3 - 4.5.
The dissociation of a diop ligand in the first step is necessary for catalytic activity, but how this influences the extent of asymmetric induction is not obvious. In the present study the use of complexes containing one bidentate phosphine per ruthenium eliminates the need for ligand dissociation, and details of these asymmetric hydrogenation catalysts are given in this Chapter.

Ruthenium complexes containing chiral phosphines have also been used for a number of other asymmetric transformations. The cluster \( \text{Ru}_4\text{H}_4(\text{CO})_8(\text{diop})_2 \) has been used for the hydrogenation of prochiral substrates containing C=C, C=O or C=N- groups, using either \( \text{H}_2 \) or in some cases by hydrogen transfer from alcohols\(^{113}\). These types of reductions have also been studied by Ohkubo et al.\(^{114}\) using \( \text{Ru}_2\text{Cl}_4(\text{diop})_3 \). However in both these reports more vigorous conditions were required.

4.2 Synthesis of \([\text{RuCl}_2(\text{P-P})]_2\) Complexes

The reaction of the mixed-valence complexes \( \text{Ru}_2\text{Cl}_5(\text{P-P})_2 \), \( \text{P-P} = \text{chiraphos, dppp, dppb and diop} \), with \( \text{H}_2 \) in DMA generates the ionic species \([\text{Ru}_2\text{Cl}_5(\text{P-P})_2]^- \text{DMAH}^+ \) (Section 3.7) in accordance with equation 4.6. From this reaction the neutral species
\[
\text{Ru}_2\text{Cl}_5(\text{P-P})_2 + 0.5\text{H}_2 \overset{\text{DMA}}{\longrightarrow} [\text{Ru}_2\text{Cl}_5(\text{P-P})_2]^- \text{ DMAH}^+ \quad (4.6)
\]

[\text{RuCl}_2(\text{P-P})]_2 can be obtained by addition of methanol which causes displacement of DMA-HCl and precipitation of the product. In the case of P-P = diop or dppb, the [\text{RuCl}_2(\text{P-P})]_2 complexes have been observed spectroscopically (Section 4.3.1) by disproportionation of other complexes \textit{in situ}, but have not been isolated previously.

The preparation of the chiraphos and diop complexes were complicated by their high solubility in methanol, and necessitated the use of small quantities of solvent and cooling to bring about precipitation. The products so obtained are generally in relatively low yield (ca. 40%) and DMA impurity is present, as indicated by elemental analysis. For this reason an alternative procedure was devised. Since the use of Proton Sponge as added base in toluene generated an ionic species analogous to that formed in DMA (Section 3.7.4), the use of polyvinylpyridine seemed appropriate. This base is polymeric and remains so as the hydrochloride salt, thereby making addition to the [\text{RuCl}_2(\text{P-P})]_2 complexes improbable, and separation by filtration is easily accomplished. This method gave good yields of the desired diop and chiraphos complexes. Full preparative details are given in Sections 2.1.7.5 and 2.1.7.6, and their characterisation by \textsuperscript{31}\text{P}(\text{\textsuperscript{1}H})-n.m.r. is presented in the following section.

All of the complexes are hygroscopic and, with the exception of [\text{RuCl}_2(\text{chiraphos})]_2, are very air sensitive, turning green on
exposure to air. The molecular weight of the chiraphos complex was
determined by the Signer method\textsuperscript{115} to be 1100 which is in reasonable
agreement with that expected for a dimeric species (calc. 1196).

The chiraphos complex obeys Beer's law in DMA; however, the
visible spectrum is solvent dependent (Figure 4.1). Addition of one
equivalent of dppb to a DMA solution of the dppb analogue produces a
change in colour from brown to green. The visible spectrum of the
resulting solution (Figure 4.2) is the same as that previously reported
for $[\text{RuCl}_2(\text{dppb})_{1.5}]_2$\textsuperscript{73}. In the present study the formation of
this phosphine-bridged binuclear complex is in accordance with:

$$ [\text{RuCl}_2(\text{dppb})]_2 + \text{dppb} \rightarrow \begin{array}{c}
\begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{P} \\
\text{P} \\
\text{Cl} \\
\text{Cl} \\
\text{P} \\
\text{P}
\end{array}
\end{array} $$

More air stable forms of the $[\text{RuCl}_2(\text{P-P})]_2$ complexes could be
obtained by recrystallisation in the presence of a coordinating solvent
such as acetone. With P-P = dppb, the product so obtained has the
formula $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})_2(\text{acetone})$.acetone and shows i.r. stretches at
1645 and 1705 cm\textsuperscript{-1} which are assigned to coordinated and uncoordinated
acetone, respectively. For the P-P = chiraphos complex only coordinated
acetone was present as characterised by a single $\nu_{\text{acetone}}$ (1645
\text{cm}^{-1}) and by elemental analysis.
Figure 4.1 Visible spectra of \([\text{RuCl}_2(\text{chiraphos})]_2\) in CH\(_2\)Cl\(_2\), toluene and DMA.

Figure 4.2 Visible spectrum obtained upon addition of one equivalent of dppb to \([\text{RuCl}_2(\text{dppb})]_2\) in DMA.
4.3 $^{31}$P-$^1$H - N.m.r. Studies

4.3.1 Studies in Non-Coordinating Solvents

The $^{31}$P-$^1$H-n.m.r. spectra of the complexes $[\text{RuCl}_2(\text{P-P})]_2$, P-P = diop, dppb and dppp, in CD$_2$Cl$_2$ all consist of an AB pattern, centred at 48.6, 57.9 and 54.3 ppm respectively. The chemical shifts of these patterns vary slightly with temperature whilst the coupling remains constant (Table 4.1). The spectra of $[\text{RuCl}_2(\text{chiraphos})]_2$ in CD$_2$Cl$_2$ or toluene-$d_8$, however, show two independent AB systems at higher frequency of equal integrated intensity. These two systems have been designated AB and CD on the basis of chemical shift ($\delta_{\text{AB}} \approx 83$, $\delta_{\text{CD}} \approx 82$ ppm), although a definite assignment is not possible since the coupling constant is the same for each resonance ($^2J_{\text{PP}} = 39.1$ Hz). In addition, on standing the chiraphos complex in CD$_2$Cl$_2$ develops a singlet at 82 ppm, the intensity of which increases with time. The $^{31}$P-$^1$H-n.m.r. data for all of the complexes are presented in Table 4.1, and Figures 4.3 and 4.4 show the spectra for $[\text{RuCl}_2(\text{chiraphos})]_2$ in CD$_2$Cl$_2$ and toluene-$d_8$, respectively.

Whilst the spectra of the chiraphos complex and those of the diop, dppb, and dppp complexes show marked difference, all are consistent with a dimeric structure, since a monomeric RuCl$_2$(P-P) species would produce a singlet in the $^{31}$P-$^1$H-n.m.r. spectrum for either a tetrahedral or square-planar configuration. The observed resonance patterns are attributed to the complexes having a bridged structure with two square pyramids sharing a basal edge (structure 4-I), which is
Table 4.1

$^{31}$P{${}^1$H}-N.m.r. Data For [RuCl$_2$(P-P)]$_2$ Complexes$^a$

(i) [RuCl$_2$(dppb)]$_2$, CD$_2$Cl$_2$, $^2J_{AB} = 46.8$ Hz

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$P_A$</th>
<th>$P_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.0</td>
<td>53.7</td>
</tr>
<tr>
<td>-70</td>
<td>62.2</td>
<td>54.3</td>
</tr>
</tbody>
</table>

(ii) [RuCl$_2$(diop)]$_2$, CD$_2$Cl$_2$, $^2J_{AB} = 46.4$ Hz

<table>
<thead>
<tr>
<th>Temperature, °C</th>
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<th>$P_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>50.0</td>
<td>47.1</td>
</tr>
</tbody>
</table>

(iii) [RuCl$_2$(dppp)]$_2$, CD$_2$Cl$_2$, $^2J_{AB} = 57.4$ Hz

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$P_A$</th>
<th>$P_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>58.0</td>
<td>50.5</td>
</tr>
</tbody>
</table>

(iv) [RuCl$_2$(chiraphos)]$_2$, CD$_2$Cl$_2$, $^2J_{AB} = ^2J_{CD} = 39.1$ Hz

<table>
<thead>
<tr>
<th>Temperature, °C</th>
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(v) [RuCl$_2$(chiraphos)]$_2$, toluene-$_d_8$, $^2J_{AB} = ^2J_{CD} = 39.1$ Hz

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</table>

$^a$ Chemical shifts in ppm, relative to 85% H$_3$PO$_4$

$^b$ This singlet develops on standing and is absent in freshly prepared samples.
Figure 4.3 $^{31}\text{P}^{1\text{H}}$-N.m.r. spectra of [RuCl$_2$(chiraphos)]$_2$ in CD$_2$Cl$_2$ at 30°C and -50°C at 32.4 MHz.
Figure 4.4 $^{31}\text{P}^\text{1H}$-N.m.r. spectra of [RuCl$_2$(chiraphos)]$_2$ as a function of temperature in toluene-d$_8$ at 32.4 MHz.
analogous to that proposed for \([\text{RuCl}_2(\text{PPh}_3)_2]_2\). In such a structure for P-P = dppb or dppp, \(P_A(\text{Ru}^1)\) is equivalent to \(P_A(\text{Ru}^2)\), similarly for \(P_B\), but \(P_A\) is not equivalent to \(P_B\) and a single AB pattern results.

The two AB patterns observed for \([\text{RuCl}_2(\text{chiraphos})]_2\) are also consistent with a structure such as 4-I. Incorporation of chirality into the phosphine back-bone results in \(P_A(\text{Ru}^1)\) no longer being equivalent to \(P_A(\text{Ru}^2)\), and \(P_B(\text{Ru}^1)\) is inequivalent to \(P_B(\text{Ru}^2)\). In such a case a diastereotopic pair of inequivalent phosphines may generate two AB patterns in a 1:1 ratio, as observed. This explanation, however, requires the diastereomer of structure 4-I to have accidentally degenerate resonances or there to be rapid interconversion between the two. An alternative explanation is that the diastereotopic pair of phosphines on the two ruthenium centres are degenerate and the two AB patterns then arise from an inequivalence of the two diastereomers. In this case the diastereomers would have to be formed in equal proportions to explain the observed 1:1 integrated intensity ratio of the two patterns. Dimeric chloro-bridged ruthenium complexes have a propensity to form triply-bridged species (Section
4.3.2), and interconversion of diastereomers, via such an intermediate, is not unreasonable as shown in Scheme 4-I. A single species rather than two diastereomers is therefore considered to give rise to the observed two AB patterns.

Scheme 4-I

Surprisingly, the $^{31}$P-$^1$H-n.m.r. of $[\text{RuCl}_2(\text{diop})]_2$ is a single AB pattern although diop is chiral and the complex would be expected to exhibit a $^{31}$P spectrum similar to that of the chiraphos derivative. Diop gives rise to a larger ring size upon coordination, and is somewhat more flexible than the rigid chiraphos ligand; so possibly slight fluctuation of the phosphine removes any inequivalence or alternatively they are simply coincidentally degenerate.

The generation of a singlet at 81 ppm in the spectrum of $[\text{RuCl}_2(\text{chiraphos})]_2$ in CD$_2$Cl$_2$ on standing is not readily explained. A singlet has been observed previously for $[\text{RuCl}_2(\text{PPh}_3)_2]_2$ but only in polar, coordinating solvents such as DMA, and has been assigned to a solvated monomer$^{116}$. Since this singlet constitutes a principal resonance in the spectra of the
chiraphos complex in CD$_2$Cl$_2$-acetone as a result of the presence of the coordinating solvent (see next Section), it is possible that trace water generates a corresponding singlet in the CD$_2$Cl$_2$ solvent. The absence of the singlet in freshly prepared samples, which are prepared using dry glassware and solvents under anaerobic conditions suggests a possible slow leaching of water from the n.m.r. tube.

The $^{31}$P$^1$H-n.m.r. of [RuCl$_2$(diop)]$_2$ has been observed previously$^{79}$ in the spectrum of RuCl$_2$(diop)PPh$_3$ as a result of partial dissociation of triphenylphosphine in toluene (equation 4.8). In addition to the ABX pattern expected for the starting complex, an AB

$$\text{RuCl}_2(\text{diop})\text{PPh}_3 \rightarrow 1/2[\text{RuCl}_2(\text{diop})]_2 + \text{PPh}_3$$

(4.8)

pattern ($\delta_A = 51.5$, $\delta_B = 49.2$ ppm, $J_{AB} = 50$Hz) of integrated intensity twice that of the free ligand signal was observed. During an analogous study on the RuCl$_2$(dppb)PPh$_3$ complex Jung et al.$^{117}$ have reported recently the n.m.r. parameters for the dppb complex ($\delta_A = 62.6$, $\delta_B = 54.4$ ppm, $J_{AB} = 47$Hz) which, as for the diop complex, are in good agreement with those obtained in the present study with the isolated complexes.

Finally, the variation in chemical shifts for coordinated diphosphines of varying ring size is not unusual$^{118, 199}$, and invariably the five membered chelates of diphos-type ligands, as in chiraphos, exhibit the largest $^{31}$P-n.m.r. coordination chemical shifts. This phenomenon is usually considered$^{119}$ to be due to a large
deshielding contribution arising from strain in the five-membered ring although the situation appears more complex in that the coordination shift for four-membered chelates is not as large.

4.3.2 Studies in Coordinating Solvents

The visible spectrum of [RuCl₂(chiraphos)]₂ in solution (Figure 4.1) shows marked differences when either toluene, DMA or acetone are used as solvents. In all solvents the complex is believed to be dimeric, but in the case of DMA or acetone, solvent interaction is invoked to explain the spectral differences and the isolation of complexes containing coordinated solvent (Section 4.2). In order to ascertain the nature of this interaction the ³¹P{¹H}-n.m.r. spectra of DMA and acetone solutions were obtained.

The addition of acetone to a freshly prepared CD₂Cl₂ solution of [RuCl₂(chiraphos)]₂ (which exhibits no singlet at 81 ppm) produces a time-invariant spectrum consisting of a single AB pattern, δₐ₉ = 83.4 ppm, ²Jₚₚ = 37.8 Hz and a singlet at 80.9 ppm of equal integrated intensity ratio. Cooling the solution diminishes the proportion of the singlet and a second AB pattern (designated CD, δ₇ = 82.8 ppm, ²Jₚₚ = 34.2 Hz) becomes apparent of intensity less than the original AB pattern which remains essentially unchanged (Figure 4.5). At -90°C the two AB patterns are clearly resolved in essentially a 1:1 ratio, with the singlet still present at ca. 5% integrated intensity. The same spectra are obtained using isolated Ru₂Cl₄(chiraphos)₂(acetone) in CD₂Cl₂-acetone, but in
Figure 4.5 $^{31}\text{P}^1\text{H}$-N.m.r. spectra of \([\text{RuCl}_2(\text{chiraphos})]_2\)
as a function of temperature in CD$_2$Cl$_2$-acetone at 32.4 MHz.

Continued on next page
CD$_2$Cl$_2$ alone the spectrum shows only two broad unresolved resonances centred at 63.3 and 72.4 ppm even to -60°C.

The $^{31}$P($^1$H)-n.m.r. spectrum of [RuCl$_2$(chiraphos)]$_2$ in toluene-d$_8$-DMA at various temperatures is shown in Figure 4.6. In this solvent mixture the major species is one containing two independent AB systems, assigned as AB and CD. At 30°C the high field resonances are coincidental, but on lowering the temperature the two patterns separate, due to different variations in chemical shifts with temperature until at -60°C, $\delta_{AB} = 82.9$ ppm, $J_{AB} = 36.6$ Hz and $\delta_{CD} = 80.7$ ppm, $J_{CD} = 34.1$ Hz. Clearly evident are resonances due to other species, the parameters for which cannot be readily elucidated. The n.m.r. parameters for the principle resonances of [RuCl$_2$(chiraphos)]$_2$ in toluene-d$_8$-DMA and CD$_2$Cl$_2$-acetone are given in Table 4.2.

In order to determine if any of the resonances for the chiraphos complex in either DMA or acetone are as a result of the ligand being chiral, the $^{31}$P($^1$H)-n.m.r. spectrum of Ru$_2$Cl$_4$(dppb)$_2$(acetone) in CD$_2$Cl$_2$-acetone was recorded (Figure 4.7). At ambient temperature the spectrum is unresolved, but at -40°C three AB patterns are observed, a lower field pattern centred at 57.9 ppm ($^2J_{pp} = 46.8$ Hz) and two higher field patterns ($\delta_{AB} = 50.9$, $^2J_{AB} = 44.8$ Hz and $\delta_{CD} = 49.0$ ppm, $^2J_{CD} = 39.2$ Hz) which are complicated in appearance because of their similar chemical shifts. On further cooling of the solution, the integrated intensity of the higher field resonances increase at the expense of those at lower field. The spectra for this
Figure 4.6 $^{31}\text{P}^{1\text{H}}$-N.m.r. spectra of $[\text{RuCl}_2(\text{chiraphos})]_2$ as a function of temperature in toluene-d$_6$-DMA at 40.5 MHz.

Continued on next page
Figure 4.6 continued

-40°

-60°

PA  PC  PB

90  80  70 ppm
Table 4.3

\[^3\text{P}({^1\text{H}})\text{-N.m.r. Data For } [\text{RuCl}_2(\text{chiraphos})]_2 \text{ in} \]
\[\text{CD}_2\text{Cl}_2-\text{Acetone and Toluene-d}_8\text{-DMA}^a\]

(i) \[\text{CD}_2\text{Cl}_2-\text{acetone (v/v = 3:1)}\]
\[^{2}J_{AB} = 37.8 \text{ Hz, } ^{2}J_{CD} = 34.2 \text{ Hz}\]

<table>
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<th>Temperature, °C</th>
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<td>76.4</td>
<td>80.6</td>
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</tbody>
</table>

(ii) \[\text{Toluene-d}_8\text{-DMA (v/v = 3:1)}\]
\[^{2}J_{AB} = 36.6 \text{ Hz, } ^{2}J_{CD} = 34.1 \text{ Hz}\]

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<th>P_B</th>
<th>P_C</th>
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\(^a\) Chemical shifts in ppm, relatively to 85\% H\textsubscript{3}PO\textsubscript{4}
Figure 4.7 $^{31}P\{^1H\}$-N.m.r. spectra of $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})$.acetone as a function of temperature in $\text{CD}_2\text{Cl}_2$-acetone at 40.5 MHz.
The addition of coordinating solvents to solutions of the $[\text{RuCl}_2(P-P)]_2$ complexes, $P-P =$ chiraphos and dppb, produces marked changes in the n.m.r. spectra and, for the chiraphos complex, different behaviour is observed in DMA to that in acetone solution. For all of the systems studied, the principle species produces two AB patterns suggesting that the complexes remain dimeric in the presence of these coordinating solvents. The spectra are most easily interpreted in terms of a triply chloro-bridged dimer in which the two ends of the unit are different because of coordination of the solvent (structure 4-II).

Table 4.3

$^{31}$P-$^1$H-n.m.r. Data For $[\text{RuCl}_2(\text{dppb})]_2$ in

\begin{align*}
\text{CD}_2\text{Cl}_2-\text{Acetone}^* \\
\text{CD}_2\text{Cl}_2-\text{acetone (v:v = 3:1)}
\end{align*}

$^2J_{AB} = 44.8$ Hz, $^2J_{CD} = 39.2$ Hz, $^2J_{EF} = 46.8$ Hz

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* Chemical shifts in ppm, relative to $85\% \text{H}_3\text{PO}_4$.  

-system are shown in Figure 4.7, and parameters are given in Table 4.3.
The differences in spectra for the three systems arises from different solute-solvent interactions. For $[\text{RuCl}_2(\text{chiraphos})]_2$ in CD$_2$Cl$_2$-acetone the spectrum at 30°C is a simple AB pattern ($J_{AB} = 37.8$ Hz) and a singlet. The AB pattern is assigned to the resonances of the (P-P)(Cl)RuCl$_3$ portion of the molecule, which is in a locked conformation (assuming the triple chloro-bridge does not undergo rearrangement) and remains so throughout the temperature range studied. Support for this locked conformation comes from the same coupling ($J_{pp} = 37.8$ Hz) found for $[\text{Ru}_2\text{Cl}_5(\text{chiraphos})_2]^-$ (Section 3.7.3), in which both ends of the dimer have this conformation. The singlet may be rationalised by invoking an equilibrium between free and coordinated solvent at Ru$^2$, the exchange being rapid on the n.m.r. time scale. Assuming that the solvent can coordinate at any of the three non-bridging sites, then this will result in a scrambling of the P$_C$ and P$_D$ phosphorus atoms and generation of a single resonance. Such a scrambling, however, will not effect the resonances of P$_A$ and P$_B$ since these are always diastereotopic as a result of the chirality in the back-bone. On cooling the solution, the intensity of the singlet
decreases, presumably because the equilibrium favours solvent coordination, and the thermodynamically more stable product is formed with the solvent occupying one particular site. Further cooling increases the proportion of the second AB pattern at the expense of the singlet due to the generation of the more rigid Cl₃Ru(S)(P-P) moiety. Since only one set of two AB patterns is observed, either one diastereomer is present or interconversion by exchange of terminal and bridging chlorides makes the diastereomers degenerate. This proposed explanation could be tested experimentally if the non-chiral analogue [RuCl₂(dppe)]₂ was prepared. In CD₂Cl₂-acetone this would be expected to exhibit two singlets in the ³¹P{¹H}-n.m.r. spectrum at ambient temperature, and on cooling produce the expected two AB patterns. However, the required precursor complex Ru₂Cl₅(dppe)₂ could not be prepared (Section 3.2).

Such a thermodynamic equilibrium also explains the observed two broad unresolved resonances for Ru₂Cl₄(chiraphos)₂(acetone) in CD₂Cl₂. In the absence of significant amounts of acetone the complex will revert principally to structure 4-I, and only a small proportion will be present as the triply chloro-bridged species. This is expected to produce an averaging of the resonances between these species, and presumably the signals could be resolved only at lower temperatures beyond the limitations imposed by the solvent.

Of particular interest was the interaction of [RuCl₂(chiraphos)]₂ with DMA. This should give information on species originally present in the hydrogenation studies in this solvent.
which are described in subsequent sections. Addition of DMA to a toluene-d$_8$ solution of the chiraphos complex generates the spectra shown in Figure 4.6. In this case the two AB patterns assigned to structure 4-II are evident at 30°C, suggesting that the coordination of DMA at least in toluene, is much stronger than coordination of acetone in CD$_2$Cl$_2$. On cooling the system, the almost coincidental higher field resonances shift to varying degrees and make the two AB patterns become clearly apparent. The resonances centred at $\delta \approx 81$ ppm, $^{2}J_{pp} = 34.1$ Hz, are assigned to the Cl$_2$Ru(S)(P-P) moiety since the coupling constant is essentially the same as that found when S = acetone (34.2 Hz). Also apparent in the spectra are several less intense resonances which cannot be readily assigned. Since DMA is a stronger donor than acetone the products may be now kinetically controlled, and whilst coordination of solvent at one site may be favoured, coordination at the two other sites will generate diastereomers which could give rise to the additional resonances. Alternatively, coordination at the two vacant sites of a doubly chloro-bridged complex is possible, and assignment of the resonances must await well-resolved spectra or isolation of the particular species.

The spectra of Ru$_2$Cl$_4$(dppb)$_2$(acetone).acetone in CD$_2$Cl$_2$-acetone (Figure 4.7) is also assigned to structure 4-II. However, another type of equilibrium must exist: at ambient temperatures the spectra are unresolved, but on cooling to -40°C three AB patterns are observed, the higher field pair being of equal integrated intensity. The lower field pattern ($\delta_{EF} = 57.9$ ppm,
$^{2}J_{EF} = 46.8$ Hz) is assigned to the doubly chloro-bridged structure observed in the absence of coordinating solvent ($\delta = 57.8$ ppm, $^{2}J_{pp} = 46.8$ Hz, Section 4.3.1). The higher field patterns assignable to the triply chloro-bridged species are not immediately obvious, since in both cases $\Delta \delta / J$ is small, causing the outer resonances to be of low intensity. The spectra are also complicated by the proximity of the two overlapping patterns ($\delta_{AB} = 50.9$, $\delta_{CD} = 49.0$ ppm). On further cooling the system, the proportion of the solvent-coordinated species increases with loss of the solvent-free complex. As with $[\text{RuCl}_{2}(\text{chiraphos})]_{2}$ in CD$_{2}$Cl$_{2}$-acetone, the binding of acetone to the dppb analogue cannot be strong. The system does differ though, in that the solvent exchange must be slow on the n.m.r. time scale because resonances of the individual species are observed.

The formation of triply chloro-bridged species has been observed previously in a number of triphenylphosphine complexes. The complexes of general formula, Ru$_2$Cl$_5$(L)(PPh$_3$)$_4$ where L = CO$^{121}$, CS$^{122}$, PF$_3$$^{123}$, N$_2$$^{124}$, DMA$^{67}$, and acetone$^{67}$ have been isolated or generated in situ. In each case two AB patterns are observed, one having relatively constant $^3P(\text{H})$-n.m.r. parameters ($\delta_{AB} \approx 48$ ppm, $^{2}J_{pp} = 36-38$ Hz) which is assigned to the Cl$_3$RuCl(PPh$_3$)$_2$ portion of the molecule. In none of these examples is a clearly defined dynamic equilibrium observed as found in the present study. For the complexes containing the $\pi$-acids (L = CO, CS, PF$_3$) this seems reasonable, in that these ligands will not readily dissociate. For L = DMA or acetone, the spectra are strongly
temperature dependent, and at ambient temperature the greater fluctionality of the monodentate relative to bidentate phosphines presumably inhibits observation of any equilibria.

Whilst complexes of the type $P_2(L)ClRuCl_2RuCl(L)P_2$ are known ($L = CO^{121}, CS^{122}$), there appears to be a greater propensity for dimeric ruthenium chloro-complexes to form triply chloro-bridged species containing one $L$. This is evident in the present study from the $^{31}P{^1H}$-n.m.r. spectra obtained in the presence of coordinating solvents and DMA.HCl, (generated in situ, Section 3.6), and is supported by isolation of complexes containing a single coordinated solvent molecule, as characterised by elemental analysis and infrared spectroscopy.

4.4 Asymmetric Hydrogenation of Prochiral Alkenes

A study of the hydrogenation of various prochiral alkenes using the complexes $[RuCl_2(diop)]_2$ and $[RuCl_2(chiraphos)]_2$ was undertaken to determine their potential as catalysts or catalyst precursors.

All experiments were performed on a constant pressure gas-uptake apparatus. In a typical experiment ca. 0.2 g of substrate was dissolved in DMA (5 mL) and the solution deoxygenated prior to addition of $H_2$ and complex. The study was limited to those substrates which were readily available, and whose reduced form had a known specific rotation (Figure 4.8) from which the enantiomeric excesses were calculated. For each experiment there was a 200-fold excess of substrate per ruthenium
Itaconic Acid

\[
\text{H}_2\text{C} = \text{C} - \text{CH}_2\text{CO}_2\text{H} + \text{H}_2 \rightarrow \text{R}(+) - \text{and} \text{S}(-)-\text{2-methylsuccinic acid}
\]

\[
\left[ \alpha \right]^{25}_D = \pm 17.09^\circ \text{ (c10.5, C}_2\text{H}_5\text{OH})^{125}
\]

Citraconic Acid

\[
\text{HO}_2\text{C} = \text{C} - \text{CH}_3 + \text{H}_2 \rightarrow \text{R}(+) - \text{and} \text{S}(-)-\text{2-methylsuccinic acid}
\]

\[
\left[ \alpha \right]^{25}_D = \pm 17.09^\circ \text{ (c10.5, C}_2\text{H}_5\text{OH})^{125}
\]

Atropic Acid

\[
\text{H}_2\text{C} = \text{C} - \text{C}_6\text{H}_5 + \text{H}_2 \rightarrow \text{R}(-) - \text{and} \text{S}(+)-\text{2-phenylpropanoic acid}
\]

\[
\left[ \alpha \right]^{25}_D = \pm 76.1^\circ \text{ (c8.06, CHCl}_3)\]

\[
\alpha\text{-Acetamidoacrylic Acid}
\]

\[
\text{H}_2\text{C} = \text{C} - \text{NHCOCH}_3 + \text{H}_2 \rightarrow \text{N}-\text{Acetyl} -[\text{R}(+) \text{ or S}(-)]\text{-alanine}
\]

\[
\left[ \alpha \right]^{25}_D = \pm 66.5^\circ \text{ (c2, H}_2\text{O})^{127}
\]

\[
\text{C}_6\text{H}_5\text{C} = \text{C} - \text{NHCOCH}_3 + \text{H}_2 \rightarrow \text{N}-\text{Acetyl} -[\text{R}(-) \text{ or S}(+)]\text{-phenylalanine}
\]

\[
\left[ \alpha \right]^{25}_D = \pm 46.5^\circ \text{ (c1, C}_2\text{H}_5\text{OH})^{128}
\]

\[
(Z)-\alpha\text{-Acetamidocinnamic Acid}
\]

Figure 4.8 Prochiral alkenes used in hydrogenation studies and their reduced form. The specific rotations given are those reported for the pure enantiomer.
dimer. The uptakes showed an induction period of up to 500 s before linear rates were attained and reduction was generally monitored until the reaction was complete. Isolation and characterisation of the reduced product were as described in Section 2.3.

The results of hydrogenation studies at various temperatures using \([\text{RuCl}_2(\text{diop})]_2\) are given in Table 4.4, whilst those for the chiraphos analogue are in Table 4.5. The time taken for complete hydrogenation varied considerably, but in general the chiraphos complex was more efficient. For both complexes the reduction of the tri-substituted alkenes, citraconic and \((Z)-\alpha\text{-acetamidocinnamic acids, was much slower compared to the other alkenes which are all terminal, presumably because of steric effects. Examination of the product configuration results yields no obvious overall correlation between product and ligand configurations. The \((R,R)\)-diop complex, except in the case of \(N\)-acetamidoacrylic acid gives reduced products of the opposite \((S)\)-configuration, whilst for the chiraphos complex there is no such trend. The variation in \(\%\) e.e with the substrate also offers little information as to the nature of the catalyst-substrate interaction for either complex or for a comparison of the two. The diop complex is more effective for those alkenes containing only acid groups, but is essentially non-discriminatory towards the acetamido-acrylic and -cinnamic acids. Hydrogenation, utilising the chiraphos complex, shows similar trends except for the marked asymmetric reduction of \((Z)-\alpha\text{-acetamidocinnamic acid which at } 30^\circ\text{ yields essentially one enantiomer. Another feature of this latter case is the dramatic}
Table 4.4

Asymmetric Hydrogenation of Unsaturated Substrates
Using $[\text{RuCl}_2((R,R)-\text{diop})]_2$ \(^{a}\)

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<tr>
<th>Substrate</th>
<th>Temp., °C</th>
<th>% e.e.</th>
<th>Prod. Config.</th>
<th>Approx. total reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Itaconic Acid</td>
<td>30</td>
<td>56</td>
<td>S</td>
<td>3d</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>53</td>
<td>S</td>
<td>12h</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>51</td>
<td>S</td>
<td>5h</td>
</tr>
<tr>
<td>Itaconic Acid(^b)</td>
<td>50</td>
<td>38</td>
<td>S</td>
<td>7d</td>
</tr>
<tr>
<td>Citraconic Acid(^c)</td>
<td>70</td>
<td>43</td>
<td>S</td>
<td>2d</td>
</tr>
<tr>
<td>Atropic Acid</td>
<td>50</td>
<td>32</td>
<td>S</td>
<td>15h</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>25</td>
<td>S</td>
<td>6h</td>
</tr>
<tr>
<td>$\alpha$-Acetamidoacrylic</td>
<td>50</td>
<td>3</td>
<td>R</td>
<td>8d</td>
</tr>
<tr>
<td>Acid</td>
<td>70</td>
<td>2</td>
<td>R</td>
<td>3d</td>
</tr>
<tr>
<td>(Z)-$\alpha$-Acetamidocinnamic</td>
<td>50</td>
<td>2</td>
<td>S</td>
<td>16d</td>
</tr>
<tr>
<td>Acid</td>
<td>70</td>
<td>0</td>
<td></td>
<td>5d</td>
</tr>
</tbody>
</table>

\(^a\) $[\text{Ru}_2] = 1.00 \times 10^{-3} \text{M}, \ [\text{alkene}] = 2.00 \times 10^{-1} \text{M}, 760 \text{ mm H}_2$.

\(^b\) Ru$_2$Cl$_5((R,R)$-diop)$_2$ as catalyst.

\(^c\) 70% completion.
Table 4.5

Asymmetric Hydrogenation of Unsaturated Substrates

Using $[\text{RuCl}_2((S,S)-\text{chiraphos})]_2$ \(^a\)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp., °C</th>
<th>% e.e, Config.</th>
<th>Prod.</th>
<th>Approx. total reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Itaconic Acid</td>
<td>50</td>
<td>39 R</td>
<td></td>
<td>3.5h</td>
</tr>
<tr>
<td></td>
<td>50(^b)</td>
<td>40 R</td>
<td></td>
<td>3.5h</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>35 R</td>
<td></td>
<td>45 min.</td>
</tr>
<tr>
<td>Citraconic Acid</td>
<td>70</td>
<td>15 R</td>
<td></td>
<td>18h</td>
</tr>
<tr>
<td>Atropic Acid</td>
<td>50</td>
<td>12 S</td>
<td></td>
<td>21h</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>10 S</td>
<td></td>
<td>5h</td>
</tr>
<tr>
<td>$\alpha$-Acetamidoacrylic</td>
<td>50</td>
<td>4 S</td>
<td></td>
<td>24h</td>
</tr>
<tr>
<td>Acid</td>
<td>70</td>
<td>5 S</td>
<td></td>
<td>6h</td>
</tr>
<tr>
<td>(Z)-$\alpha$-Acetamidocinnamic Acid</td>
<td>30</td>
<td>97 S</td>
<td></td>
<td>24h</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>63 S</td>
<td></td>
<td>5h</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>19 S</td>
<td></td>
<td>1.5h</td>
</tr>
</tbody>
</table>

\(^a\) $[\text{Ru}_2] = 1.00 (± 0.03) \times 10^{-3} \text{M}, [\text{alkene}] = 2.00 (± 0.15) \times 10^{-1} \text{M}, 760\text{mm H}_2$.

\(^b\) Test for reproducibility.
increase in % e.e. with a lowering of the temperature, a feature that is common to reductions of all alkenes catalysed by both complexes, but unfortunately not to the same extent.

Reduction of itaconic acid with the diop mixed-valence complex, \( \text{Ru}_2\text{Cl}_5(\text{diop})_2 \), proceeds at a much slower rate and with a lower asymmetric induction than with the dimeric ruthenium (II) complex under the same conditions.

The main purpose of this hydrogenation study was to determine if the complexes \([\text{RuCl}_2(\text{P-P})]_2\), \( \text{P-P} = \text{chiraphos or diop} \), were suitable for asymmetric hydrogenation. Of importance though is the nature of the catalytically active species (dimeric, monomeric, hydride or alkene complex ?). In order to investigate this, the reactivity of the chiraphos complex was studied with: substrate alone, and with \( \text{H}_2 \) alone. Addition of up to a 200-fold excess of \((Z)-\alpha\)-acetamidocinnamic acid to DMA solutions of the complex in the absence of \( \text{H}_2 \) produced no changes in the visible spectra suggesting no binding of substrate. In the absence of substrate a \( 3.0 \times 10^{-3} \) M DMA solution of \([\text{RuCl}_2(\text{chiraphos})]_2 \) at 50°C, gave a \( \text{H}_2 \) uptake corresponding to \( 1.0\text{Ru}_2:0.20\text{H}_2 \) after 150s. In the presence of Proton Sponge at the same conditions the uptake increased to \( 1.0\text{Ru}_2:1.57\text{H}_2 \). That the reaction with \( \text{H}_2 \) is base-promoted, suggests the formation of a ruthenium-hydride species via reductive elimination of HCl, rather than formation of a neutral or ionic dihydride. The time taken for \( \text{H}_2 \)-uptake in the absence of substrate is comparable to the induction period observed in the catalytic hydrogenation studies, hence initial
formation of an active hydrido-species appears probable (see also Section 5.2).

4.4.1 Discussion

The hydrogenation of prochiral alkenes utilising $[\text{RuCl}_2(\text{chiraphos})]_2$ or the diop analogue as catalyst precursors proceeds in relatively mild conditions. The wide variation in rates, product configuration, and % e.e. indicate that both the nature of the chiral phosphine ligand and substrate are significant factors in the overall process. Speculation as to the nature of the substrate-catalyst interaction in order to explain these large variations, for example by applying Knowles' empirical quadrant rule, is tempting. However, without a better understanding of the catalytically active species and mechanistic details, such speculation is not appropriate. Instead, a comparison with the data obtained by other workers using other catalysts will be presented.

Of particular relevance are the data obtained previously using the complexes $\text{RuHCl(diop)}_2$ and $\text{Ru}_2\text{Cl}_4(\text{diop})_3$ (Section 4.1). Table 4.6 gives the data for these complexes at 60°C and those obtained in this study at 50°C. The observed differences in product configuration must simply be as a result of using phosphine ligands of opposite configuration. Since $\text{Ru}_2\text{Cl}_4(\text{diop})_3$ reacts with $\text{H}_2$ to generate $\text{RuHCl(diop)}_2$ and $[\text{RuCl}_2(\text{diop})]_2$ (equation 4.1), any differences between the bridged-diop complex and that of the isolated hydride must be attributed to $[\text{RuCl}_2(\text{diop})]_2$. The higher % e.e. found for the
Table 4.6
Hydrogenation of Prochiral Alkenes by Ruthenium-Diop Complexes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>RuHCl((+diop)_2</th>
<th>Ru_2Cl_4((+diop)_3</th>
<th>[RuCl_2((-diop)]_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prod. %e.e.</td>
<td>Prod. %e.e.</td>
<td>Prod. %e.e.</td>
</tr>
<tr>
<td>Atropic Acid</td>
<td>R(-) 27</td>
<td>R(-) 40</td>
<td>S(+) 32</td>
</tr>
<tr>
<td>Itaconic Acid</td>
<td>R(+) 23</td>
<td>R(+) 38</td>
<td>S(-) 53</td>
</tr>
<tr>
<td>α-Acetamidoacrylic</td>
<td>S(-) 59</td>
<td></td>
<td>R(+) 3</td>
</tr>
<tr>
<td>Acid</td>
<td>0</td>
<td></td>
<td>S(-) 43</td>
</tr>
<tr>
<td>Citraconic Acid</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hydrogenation of atropic and itaconic acids, using Ru_2Cl_4(dio)_{3} relative to the hydride complex, is consistent with the higher enantioselectivity obtained using the [RuCl_2(dio)]_{2} complex. The reason for the large difference (and apparent inconsistency) in the data for the other two prochiral alkenes is not obvious. For RuHCl(dio)_2 to become catalytically active the complex must undergo initial dissociation of a dio ligand \(^{111}\) (equation 4.3). Since the use of the "dio-deficient" species should eliminate the need for such a dissociation step it was hoped that this would increase the enantioselectivity. For the reduction of itaconic acid the asymmetric induction is significantly better (Table 4.6), but for atropic acid only
a marginal increase in e.e. is found between these two complexes.

The initial dissociation of a phosphine ligand from RuHCl(diop)$_2$ as a prerequisite step for catalytic activity restricts the type of disphosphine that can be used. For P-P = dppm, dppe, and dppp, which are less bulky than diop, ligand dissociation presumably does not occur, as the corresponding Ru hydrides are catalytically inactive for hydrogenation$^{79}$. The use of the [RuCl$_2$(P-P)]$_2$ complexes as catalyst precursors provides a viable alternative for the incorporation of any diphosphine with presumably a good chance of some activity. This is exemplified by the chiraphos system: the RuHCl(chiraphos)$_2$ complex would be expected to be catalytically inactive by analogy to the corresponding dppe complex, whilst [RuCl$_2$(chiraphos)]$_2$ has been shown to be active.

With the notable exception of the $\alpha$-acetamido-acrylic and -cinnamic acids, the hydrogenation of the other prochiral alkenes using [RuCl$_2$(chiraphos)]$_2$ produces only modest enantiomeric excesses (Table 4.5). The hydrogenation of (Z)-$\alpha$-acetamidocinnamic acid at 30°C with 97% e.e. is in sharp contrast to the hydrogenation of $\alpha$-acetamidoacrylic acid which proceeds essentially with no enantioselectivity. The most obvious explanation lies in the presence of the bulky phenyl group. This may play a role in the step at which asymmetric induction takes place; an interaction of the phenyl group with the rigid array of phenyl groups of the phosphine would result in the favoured formation of one diastereomer. The absence of such a bulky substituent on the alkene, as in $\alpha$-acetamidoacrylic acid, clearly
generates "equivalent" diastereomers at the asymmetric induction step. The hydrogenation of (Z)-α-acetamidocinnamic acid compares favourably with that found using [Rh((S,S)-chiraphos)]$^+$ (89% e.e. (R) in ethanol) but a product of opposite configuration is generated; this implies a substantially different mechanism for chiral recognition. For the hydrogenation of α-acetamidoacrylic acid, however the substrate-catalyst interaction is non-discriminatory which is in sharp contrast to the rhodium system$^{18}$ for this substrate (91% e.e. in ethanol).

Of particular interest is the observed increase in % e.e with decreasing temperature for essentially all substrates and both [RuCl$_2$(P-P)]$_2$ complexes. For the rhodium-catalysed hydrogenation (Section 1.2) the enantioselectivity arises from the greater reactivity of the minor diastereomeric catalyst-substrate adduct towards H$_2$ rather than the initial proportions of the diastereomers. The proposed mechanism$^{33}$ predicts that lowering the temperature will reduce the rate of interconversion of the diastereomeric adducts as this has a higher activation enthalpy than the subsequent reaction with H$_2$. Since it is the interconversion of adducts which determines the enantioselectivity of the reaction, a reduction of the interconversion rate leads to a reduction in % e.e. This has been observed in some rhodium-catalysed systems$^{129, 130}$, and in one case the optical yield increased from 0 to 60% e.e. in going from 0° to 100°C$^{130}$. For the ruthenium-catalysed hydrogenations in the present study the opposite phenomenon is observed; this is particularly dramatic for the
hydrogenation of (Z)-α-acetamidocinnamic acid by the chiraphos complex which shows a decrease from 97 to 19\% e.e. in going from 30° to 70°C. This suggests that either the major diastereomer at the asymmetric induction step has the greater reactivity or, a restriction of motion of the coordinated substrate occurs with lowering the temperature.

The hydrogenation of itaconic acid using Ru$_2$Cl$_5$(diop)$_2$ as catalyst precursor proceeds at a slower rate and gives a lower e.e. relative to [RuCl$_2$(diop)$_2$]$_2$ (Table 4.4). The reduction in rate is presumably due to the formation of inactive [Ru$_2$Cl$_5$(diop)$_2$]$^-$ DMAH$^+$ (Section 3.7) formed by addition of the HCl generated in the reduction of the mixed-valence complex to the active catalyst precursor. How formation of the anion affects the enantioselectivity is not clear; however, the hydrogenation involving [RuCl$_2$(P-P)$_2$]$_2$ requires initial generation of the hydrido-species and therefore simultaneous generation of HCl. Addition of generated HCl to the starting complex also generates some [Ru$_2$Cl$_5$(P-P)$_2$]$^-$ (Section 5.2) and this should also affect the rate and optical yield. Consequently the full potential of the 1:1 Ru:(P-P) catalytic systems has not been realised. The use of an isolated hydrido-species is expected to give improved results, and would be invaluable in attempts to elucidate mechanistic details.
CHAPTER V

GENERATION OF RUTHENIUM HYDRIDE COMPLEXES

5.1 Introduction

The preparation of transition metal hydride complexes has been accomplished by a number of methods: using molecular H₂, oxidative addition of HX, protonation, hydrogen transfer from alcohols, BH₄⁻ or AlH₄⁻ (and their derivatives), reducing agents (i.e. hydrazine, formic acid, alkali metals), and intramolecular hydrogen transfer from organic ligands. The method used obviously depends on the nature of the starting compound and the stability of the products. In this laboratory H₂ is most frequently used, as this reagent is most likely to generate the hydride species present in catalytic hydrogenations that utilise H₂ gas as the source of hydrogen.

The generation of hydrido-phosphine complexes of ruthenium using H₂ is usually from a halide precursor and, since such a reaction generates HX (Section 1.3), a base is commonly required, as exemplified by equations (5.1) and (5.2), where P is a monodentate phosphine:

\[
\text{RuCl}_2\text{P}_3 + \text{H}_2 \xrightarrow{\text{NET}_3} \text{RuHClP}_3 + \text{Et}_2\text{NH}^+\text{Cl}^- \quad (5.1)
\]

\[
2\text{RuCl}_2\text{P}_2 + 4\text{H}_2 \xrightarrow{\text{PS}} [\text{RuH}_2\text{ClP}_2]_2 + 4\text{PS}^+\text{Cl}^- \quad (5.2)
\]
The choice of base is important: for example, if reaction 5.2 is carried out in the absence of Proton Sponge (PS), and a weakly basic solvent (DMA) is used, the reduction proceeds only to \([RuCl_2P_2]_2\). Triethylamine \((pK_a = 10.6)\) readily promotes hydride formation; however, complications can arise through coordination and/or dehydrogenation of this strong base. The use of Proton Sponge is favoured, since it is a sufficiently strong base \((pK_a = 11.3)\), and is generally thought to be unable to coordinate because of steric hindrance about the nitrogen atom.

In the present study, the isolation of a hydride complex was primarily of interest in order to determine the active species present in, and mechanistic details of, the alkene hydrogenations (Section 4.4). Attempts to generate hydrido-species directly from the mixed-valence complexes \(Ru_2Cl_5(P-P)_2\) were unsuccessful in DMA or in toluene with added Proton Sponge (Section 3.7). In both cases reduction occurs, but the apparent high affinity of the product for Cl\(^-\) leads to generation of \([Ru_2Cl_5(P-P)_2]^{-}BH^+\) (B = DMA or PS). Alternative routes were therefore necessary, and this chapter describes the generation of three hydride complexes.

5.2 Reaction of \(Ru_2Cl_4(dppb)_2(\text{acetone})\).acetone (1) with \(H_2\) in DMA

The \(H_2\)-uptake (at 1 atm.) of a DMA solution of 1 at 30° C in the presence of Proton Sponge corresponded to 1.0 \(Ru_2\): 1.6 \(H_2\) over 1 h. This fractional uptake is inconsistent with the complete formation
of any simple hydrido-complex. The reaction was therefore performed on a preparative scale in an attempt to isolate and characterise the hydride product. A DMA solution (40 mL) of 1 (1.0 g, 0.76 mmol) and Proton Sponge (0.6 g, 2.8 mmol) was stirred under 1 atm. H₂ at ambient temperature for 16 h. The resulting red solution was concentrated to a viscous oil to which C₆H₆ (40 mL) was added with stirring to cause dissolution. The solution was filtered through Celite, and concentrated to ca. 20 mL. Three successive slow precipitations by addition of hexanes and further concentration afford ca. 0.6 g of an orange complex identified as [Ru₂Cl₅(dppb)₂]⁻PSH⁻ [³¹P(^1H)-n.m.r., (CD₂Cl₂) s, 54.6 ppm, and elemental analysis, (Section 2.1.7.7)]. The filtrate left after removal of this product was evaporated to dryness and taken up in C₆H₆ (5 mL). To the red solution was added diethyl ether to bring about precipitation of an orange-brown product (50 mg).

The ³¹P(^1H)-n.m.r. spectrum (CDCl₂, -95°C) of this final product (Figure 5.1) clearly shows the presence of more than one phosphorus-containing species of which only [Ru₂Cl₅(dppb)₂]⁻PSH⁻ is obviously assignable. However, the ^1H-n.m.r (CD₂Cl₂, ambient temperature) does show broad hydride resonances at -17.65 δ (t, J = 32 Hz) and -21.90 δ (t, J = 32 Hz) in an approximate 1:1 ratio. The reaction of 1 with H₂ does, therefore, generate hydride species but these have not yet been isolated or characterised. Some points concerning the isolation of [Ru₂Cl₅(dppb)₂]⁻PSH⁻ merit
Figure 5.1 $^{31}\text{P}^{(1)\text{H}}$-N.m.r. spectrum (CD$_2$Cl$_2$, -95°C) of the final product obtained from the reaction of Eu$_2$Cl$_4$(dppb)$_2$(acetone).acetone with H$_2$.

The reaction of the triphenylphosphine analogue of $[\text{RuCl}_2(\text{dppb})]_2$, in the presence of added base has been shown$^{67}$ to give a H$_2$-uptake stoichiometry consistent with:

$$[\text{RuCl}_2(\text{PPh}_3)_2]_2 + 3\text{H}_2 \xrightarrow{\text{base}} [\text{RuH}_2\text{Cl(PPh}_3)_2]_2 + 2\text{HCl} \quad (5.3)$$

The hydride product, although not isolated by this route, was characterised ($^{31}\text{P}^{(1)\text{H}}$-n.m.r. and visible spectra) by comparison
with an authentic sample. At the onset of the present study it was hoped that the bidentate phosphine analogues would undergo a corresponding reaction. The low H₂ stoichiometry and isolation of [Ru₂Cl₅(dppb)₂]⁻PSH⁺ clearly show, however, that this is not the case. The generation of a hydrido-species from H₂ results presumably in simultaneous generation of HCl, but unlike the PPh₃ analogue, the high chloride affinity of the starting material results in the formation of the ionic complex which is unreactive towards H₂. Addition of chloride to [RuCl₂(PPh₃)₂]₂ in the absence of H₂ also results in formation of a pentachloro diruthenium anion; however, this must be more reactive than the dppb analogue. The high solubility of [Ru₂Cl₅(dppb)₂]⁻PSH⁺ in benzene suggests a non-dissociated structure which is unfortunate, since easier separation of this species would probably mitigate isolation of the hydride complex.

5.3 Formation of Di-µ-chloro-µ-hydrido-hydrido-(carbonyl)-bi(dppb)diruthenium(II), Ru₂H₂(CO)Cl₂(dppb)₂, 2

5.3.1 Preparation

The H₂-reduction of Ru₂Cl₅(dppb)₂ in DMA generates in situ the ionic complex, [Ru₂Cl₅(dppb)₂]⁻DMAH⁺ (Section 3.7.3.2). Addition of methanol causes displacement of DMA.HCl and the neutral complex, [RuCl₂(dppb)]₂ can be isolated (Section 4.2). Since attempts to generate a hydrido-complex from Ru₂Cl₄(dppb)₂(acetone).acetone, 1, led to the formation of large
proportions of \([\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^-\text{PSH}^+\) (previous Section), the use of methanol as solvent to displace the PS.HCl, and promote the reaction with \(\text{H}_2\) seemed feasible. The insolubility of the starting complex in methanol necessitated the use of a second solvent. The solvent chosen was \(\text{CH}_2\text{Cl}_2\) since \(\text{I}\) is very soluble in this, and also it was hoped that after reaction with \(\text{H}_2\), concentration of the solution would first remove the \(\text{CH}_2\text{Cl}_2\) and cause precipitation of the product, whilst the PS.HCl generated and excess Proton Sponge would be soluble in the methanol.

From the reaction of \(\text{I}\) with \(\text{H}_2\) in the presence of Proton Sponge in \(\text{CH}_2\text{Cl}_2/\text{MeOH}\) (1:1 by volume) the complex \(\text{Ru}_2\text{H}_2(\text{CO})\text{Cl}_2(\text{dppb})_2\), \(\text{2}\), was isolated and characterised (next Section). The isolation was somewhat fortuitous in that addition of diethyl ether to wash the product initially obtained, caused dissolution of the hydrido-carbonyl complex and facilitated easy separation from the diethyl ether-insoluble material which remains uncharacterised.

To confirm the assignment of a weak absorption in the infrared spectrum of \(\text{2}\) to \(\nu_{\text{Ru-H}}\) the reaction was repeated using \(\text{D}_2\). Of interest, the product obtained, gave the same infrared spectrum, and more importantly, the \(^1\text{H}-\text{n.m.r.}\) spectrum showed the same hydride resonances in the correct integrated ratio as found for the \(\text{H}_2\)-generated product. This strongly suggested that \(\text{H}_2\) was not involved in the formation of \(\text{2}\), and this was then confirmed by isolation when the reaction was performed under argon. Details of the preparation of \(\text{2}\) are given in Section 2.1.7.8.
5.3.2 Characterisation

The Ru$_2$H$_2$(CO)Cl$_2$(dppb)$_2$ complex (2) in CD$_2$Cl$_2$ at ambient temperature exhibits two high-field resonances in the $^1$H-n.m.r. spectrum (Figure 5.2). These hydride resonances are a triplet (-19.816, J = 30 Hz), and a doublet of triplets of doublets (-9.49 $\delta$, J = 83, 15, 8 Hz). The hydride resonances have an integration ratio of 1:1, and their combined integration is 1/20th of that for the phenyl resonances of the dppb ligand. Phosphorus decoupling resulted in collapse of the hydride resonances to two singlets.

The $^{31}$P{$^1$H}-n.m.r. spectrum of 2 (CD$_2$Cl$_2$, 30°C) is shown in Figure 5.3. The complex exhibits four discrete resonances (assigned on the basis of chemical shift) at 68.2 (P(1)), 58.0 (P(2)), 46.4 (P(3)) and 17.0 (P(4)) ppm in the intensity ratio 1:1:1:1. Of these, the deceptively simple triplet (P(2)) appears to arise from coupling to all other phosphorus atoms, the couplings being unresolved as they are comparable to the line-widths of the signals. P(1) is only coupled to P(2), whereas P(3) and P(4) couple to one another as well as to P(2). The simulated spectrum is shown in Figure 5.4. The $^{31}$P{$^1$H}-n.m.r. spectrum of 2 was identical in DMA, C$_6$D$_6$, and in CD$_2$Cl$_2$ at -30°C. Attempts to selectively decouple the proton resonances of the dppb ligand were unsuccessful.

The infrared spectrum of 2 shows absorptions at 2030 (w, terminal Ru-H) and 1953 cm$^{-1}$ (s, terminal CO), and no absorptions attributable to a terminal Ru-Cl stretch.
5.3.3 Discussion

The isolation of $\text{Ru}_2\text{H}_2(\text{CO})\text{Cl}_2(\text{dppb})_2$, 2, from just stirring $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})\cdot\text{acetone}$ in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ at room temperature was unexpected. The formation of 2 under argon, as well as in the presence of $\text{H}_2$ or $\text{D}_2$, strongly suggests that methanol is acting as a reducing agent and a source of CO. The stoichiometry shown in equation 5.4 shows perhaps the simplest possibility; the decarbonylation reaction will be discussed in further detail at the end of this section.

$$\text{Ru}_2\text{Cl}_4(\text{dppb})_2 + \text{CH}_3\text{OH} \xrightarrow{\text{PS}} \text{Ru}_2\text{H}_2(\text{CO})\text{Cl}_2(\text{dppb})_2 + 2\text{HCl} \quad (5.4)$$

To rationalise the available spectroscopic data, structure 5-I is proposed for 2, in which the geometry about each ruthenium atom is pseudo-octahedral. The labelling scheme for the phosphorus atoms is
Figure 5.3 \(^{31}\text{P}^\text{(1H)}\)-N.m.r. spectrum of Ru\(_2\)H\(_2\)(CO)Cl\(_2\)(dppb)\(_2\) in CD\(_2\)Cl\(_2\) at ambient temperature at 32.4 MHz.

Figure 5.4 Simulated \(^{31}\text{P}^\text{(1H)}\)-n.m.r. spectrum of Ru\(_2\)H\(_2\)(CO)Cl\(_2\)(dppb)\(_2\).
based on the chemical shift data presented in Section 5.3.2.

The triplet observed at high field in the $^1$H-n.m.r. spectrum of 2 can be assigned to the terminal hydride (H(1)), which is coupled equally to the two cis-phosphorus nuclei ($^2J_{PH} = 30$ Hz). The bridging hydride, however, is coupled to all four phosphorus atoms. The largest coupling ($^2J_{PH} = 83$ Hz) is within the range normally found for trans coupling constants in mononuclear complexes of ruthenium(II) (60 - 90 Hz)\textsuperscript{134}, and therefore arises from coupling to P(4). The additional smaller couplings are consistent with the remaining phosphorus atoms being cis, and it is not unreasonable that $^2J_{P(1)-H(2)} = ^2J_{P(2)-H(2)} = 15$ Hz and $^2J_{P(3)-H(2)} = 8$ Hz. The unobserved $J_{HH}$ coupling indicates that it is quite small which is not unusual for polyhydride complexes\textsuperscript{134}.

The $^{31}$P($^1$H)-n.m.r. spectrum observed for 2 is one of an increasing number found for polynuclear-ruthenium complexes\textsuperscript{67, 135}. The chemical shift of P(4), 17.0 ppm, is of much lower frequency than the others, which is consistent with the phosphorus being trans to a hydride. However, the P(4) resonance is not to such low field as is observed\textsuperscript{136} for phosphorus trans to a terminal hydride, and suggests
that a trans bridging hydride does not have such a marked effect on the chemical shift.

To explain the observed coupling phenomena it is assumed that all phosphorus atoms on the same ruthenium atom are coupled. Since no coupling is observed between P(1) and P(4), these must be on different ruthenium atoms. The observed $^{2}J_{P(1)-P(2)} = 44.1$ Hz necessitates P(1) and P(2) to be on the same ruthenium (Ru$^{1}$), which is not unreasonable considering their similar chemical shifts, and consequently P(3) and P(4) are assigned to atoms on Ru$^{2}$. Whether the positions of P(1) and P(2) are as shown in 5-I or are in the reversed form, cannot be determined, but is of significance in terms of the chemical shifts (68.2 vs. 58.0 ppm) and the transfer of coupling between the ruthenium centres to P(2) ($^{4}J_{P(4)-P(2)} = 39.7$ Hz and $^{4}J_{P(3)-P(2)} = 2.9$ Hz). The difference in chemical environments of P(1) and P(2) is expected to produce differences in chemical shift, but which arrangement produces the observed coupling is not obvious.

The transfer of coupling between ruthenium-ruthenium centres has been observed in compounds of the general types 5-II, which contain a Ru-Ru bond. The observed coupling constants ($^{3}J_{PP} = 82-189$ Hz)
appear to be a function of the Ru-X-Ru bridge angle, with $^3J_{PP}$ increasing from $X = \text{halo}$ to carboxylato to methoxo$^{137}$. These values are comparable to the $^2J_{PP}$ coupling constants found for mononuclear trans phosphorus atoms, which reflects the high degree of overlap of the Ru-Ru orbitals in P-Ru-Ru-P moieties$^{137}$. In the present study, the lack of a Ru-Ru bond (as evidenced by the complexes diamagnetic character) implies that a metal-metal bond is not a prerequisite for transfer of coupling, although some degree of overlap of the Ru orbitals is perhaps essential via the bridging hydride.

A $^{31}P\{^1H\}$-n.m.r. spectrum with the phosphine protons selectively decoupled was not obtained despite attempts at measurement; but this would confirm the assignments of P(3) and P(4). To unequivocally assign the positions of P(1) and P(2) requires theoretical considerations of $^4J_{PP}$ coupling.

As mentioned, the $^{31}P\{^1H\}$-n.m.r. spectrum observed for 2 has characteristics essentially the same as for two previously reported spectra of hydrido-phosphine complexes. Of these, the tetra-hydrido complex$^{67}$ [RuH$_2$Cl(P(p-tolyl)$_3$)$_2$]$_2$, 3, most closely resembles 2 in terms of proposed structures (5-III). The $^{31}P\{^1H\}$-n.m.r. spectrum of 3 in CD$_2$Cl$_2$ is only resolved at -95°C (Figure 5.5) indicating a low activation barrier for rearrangement by a proposed hydride scrambling$^{67}$. Each metal is formally Ru(III) and a Ru-Ru bond was proposed to explain the observed diamagnetism and transfer of coupling between ruthenium centres. The difference in structure proposed for 2 compared to that shown in 5-III, besides the change in
Figure 5.5 $^{31}P^1H$-N.m.r. spectrum of $[\text{Ru}_2\text{H}_2\text{Cl}(\text{P(\text{p-tolyl})}_2)]_2$ in CD$_2$Cl$_2$ at -95°C (from reference 67, reproduced with permission).
phosphine ligand, is replacement of the two terminal H(2) ligands by a carbonyl ligand. That the $^{31}\text{P}(^1\text{H})$-n.m.r. spectrum of 2 is resolved at ambient temperature indicates the absence of any facile rearrangement process, and a stable octahedral geometry about each ruthenium.

The other complex to exhibit similar $^{31}\text{P}(^1\text{H})$-n.m.r. characteristics is the tetranuclear species$^{135}$, 

$$\text{Ru}_4\text{H}_4(\text{OH})_2(\text{PPh}_2)_2(\text{CO})_2(\text{PPh}_3)_6(\text{Me}_2\text{CO})_2,$$

for which the spectrum has been simulated (Figure 5.6) using the parameters given in reference 135. The complex was prepared by refluxing RuHCl(PPh$_3$)$_3$ in acetone (< 1% H$_2$O added) with KOH. Based on a crystallographically determined molecular weight, elemental analysis, infrared, and $^1\text{H}$ and $^{31}\text{P}$-n.m.r. spectroscopy, the structures 5-V and 5-VI were proposed to account for ca. 90% of the data. The complex was shown to form by reaction of RuH$_2$(CO)(PPh$_3$)$_3$ and RuH(OH)(PPh$_3$)$_2$(acetone) with loss of benzene (g.l.c. detected) and PPh$_3$ ligands. These intermediates arose, respectively, from the base-catalysed decarbonylation of acetone and from the reaction of KOH with RuHCl(PPh$_3$)$_3$. A bridging diphenylphosphido group was invoked to rationalise the observed transfer of coupling in the tetranuclear species. Since the report of this complex, it has been observed that bridging organophosphido ligands in complexes containing metal-metal bonds exhibit large downfield shifts (100-250 ppm), whilst in complexes containing no metal-metal bond, the phosphido resonance is shifted upfield (ca. -100 ppm)$^{138}$. This suggests that in reference 135,
Figure 5.6 Simulated $^{31}\text{P}^1\text{H}$-n.m.r. spectrum of the tetranuclear species $\text{Ru}_4\text{H}_4(\text{PPh}_3)_6(\text{PPh}_2)_2(\text{OH})_2(\text{CO})_2(\text{acetone})_2$ using the parameters given in reference 135.
perhaps the assignment of a phosphorus labelled, P(2) (71.5 ppm), to a bridging diphenylphosphido ligand is in error, and that a structure akin to that proposed for 2 and 3 with bridging hydroxy-ligands is more reasonable.

Whilst the spectroscopic data for 2 appear consistent with structure 5-I, an important question is how this complex is generated from Ru₂Cl₄(dppb)₂(acetone).acetone. The formation of 2 in the absence of H₂ implies that methanol is acting as reducing agent and as a source of CO. However, involvement of acetone (present in the starting material 1) cannot be ruled out by analogy to the formation of the tetranuclear species in acetone.

The decarbonylation of methanol on metal surfaces is well documented, but few examples exist of base-unassisted decarbonylation of this alcohol by discrete metal complexes. For example, the RhCl(PPh₃)₃ complex which readily decarbonylates organic substrates, shows no tendency to decarbonylate methanol even at 80°C. Considerable interest in this field stems from possible mechanistic relationships to Fischer-Tropsch synthesis and the use of methanol as a hydrogen source in homogeneously catalysed hydrogenations.

The generation of ruthenium carbonyl and hydridocarbonyl complexes by the reaction of alcohols, especially ethanol and isopropanol, is common. The reactions usually require the use of alkoxide salts or their in situ generation by added base, as exemplified by:
In addition to the generation of carbonyl or hydridocarbonyl complexes, reactions of this type produce fragments arising from degradation of the alcohol (i.e. methane from ethanol\(^{144}\), equation 5.6).

An appealing possibility for the formation of \(2\) is the stoichiometry shown in reaction 5.4. A plausible mechanism is shown in Scheme 5-1, based on those previously postulated\(^{135,144,145}\) for alcohol decarbonylation, with the extra requirements that the dinuclearity of the complex is retained throughout, and no degraded fragments of methanol are produced. The proposed mechanism is admittedly speculative, but does serve to show the general intermediates typically involved in the decarbonylation of alcohols. The proposed\(^{135,144}\) initial step for decarbonylation in Ru systems is believed to be formation of a Ru-alkoxide species. In the previously cited examples (equations 5.5-5.7), this was via the alkoxide salt, but in the present study this could be promoted by abstraction of HCl by added Proton Sponge. The subsequent formation of a methanal adduct and formyl complex has been confirmed for the reaction of RuHCl(\(\text{PPh}_3\))\(_3\) with NaOMe by their independent generation or spectroscopic characterisation\(^{135}\).

A second possible mechanism for the formation of \(2\) involves the generation of mononuclear complexes and their subsequent recombination:
Scheme 5-1
Such a mechanism results in the generation of degraded alcohol fragments (CH₂O and H₂), and consequently could be supported by their detection.

5.4 Preparation of Dichloronorbornadiene(dppb)ruthenium(II).0.5C₆H₆, RuCl₂(nbd)(dppb).0.5C₆H₆, 4, and its reactivity with H₂.

In order to overcome the problem of addition of HCl, generated by reduction of Ru₂Cl₄(dppb)₂(acetone).acetone, to the complex itself (Section 5.2), the attempted use of a monomeric precursor seemed worthwhile. For this purpose RuCl₂(nbd)(dppb) was prepared because the dialkene was expected to stabilise the mononuclear fragment and yet could be easily removed by hydrogenation as norbornane, and then allow for subsequent formation of a hydrido-complex.

5.4.1 Preparation and Characterisation

Stirring a suspension of Ru₂Cl₄(dppb)₂(acetone).acetone with an excess of norbornadiene in benzene produces a brown solution. Concentration of this solution and precipitation with hexanes yields 4 as a yellow powder or brown crystalline material (Section 2.1.7.9). The use of benzene is important since if the reaction is performed in toluene a product of inferior analytical quality is obtained. This is
presumably because at the concentration stage the norbornadiene will be more readily removed than the toluene, and the excess of dialkene will no longer be maintained. Recrystallisation of the sample is also unsatisfactory, since from CH\textsubscript{2}Cl\textsubscript{2}/hexanes an orange product was obtained and identified as Ru\textsubscript{2}Cl\textsubscript{4}(dppb)\textsubscript{2}(elemental analysis).

The \textsuperscript{31}P{\textsuperscript{1}H}-n.m.r. spectrum of \textit{4} in CD\textsubscript{2}Cl\textsubscript{2} at ambient temperature exhibits a singlet at 17.0 ppm. The intensity of this signal then decreases with time and an AB quartet (P\textsubscript{A} = 62.8, P\textsubscript{B} = 53.5 ppm, J = 46.8 Hz), assignable to [RuCl\textsubscript{2}(dppb)\textsubscript{2}] (Section 4.2), becomes apparent. After 24 h the singlet constitutes ca. 40% of the integrated intensity. The \textsuperscript{1}H-n.m.r. spectrum of an "aged" CD\textsubscript{2}Cl\textsubscript{2} solution shows the presence of both coordinated (3.6 δ, (broad multiplet olefinic protons), and free (6.8 δ (t) olefinic protons) norbornadiene.

These findings are consistent with \textit{4} undergoing dissociation of the dialkene ligand in solution, equation 5.11. The monodentate

\[
\text{RuCl}_2(\text{nbd})(\text{dppb}) \rightarrow \frac{1}{2}[\text{RuCl}_2(\text{dppb})]_2 + \text{nbd} \tag{5.11}
\]

phosphine analogue of \textit{4}, RuCl\textsubscript{2}(nbd)(P(p-tolyl)\textsubscript{3})\textsubscript{2}, has been previously prepared\textsuperscript{67} (\textsuperscript{31}P{\textsuperscript{1}H}-n.m.r. (C\textsubscript{6}D\textsubscript{6}):20.6 ppm (s)), but is not reported to undergo dissociation.

In order to confirm that \textit{4} was a monomeric complex and not simply an alkene adduct of the dimeric starting compound, a single crystal X-ray diffraction study was carried out by S. Evans and M.
Ponnsuwamy of this department. The crystallographic analysis showed 4 to be a mononuclear-dialkene complex that crystallises with one molecule of benzene per two molecules of ruthenium complex. The complex has pseudo-octahedral geometry about the ruthenium(II) as shown in Figure 5.7. The chloro-ligands are slightly distorted from a trans configuration (Cl(1)-Ru-Cl(2) = 168.4°) which is possibly due to steric effects imposed by the dialkene. The norbornadiene moiety is bound through both double bonds, which are consequently lengthened (1.37(1)Å) compared to those in the free ligand (1.35Å)\(^{146}\) as a result of the participation of π-electrons in the bonding to the metal. The distances from ruthenium to the centre (CT) of the coordinated double bonds, [C(2)-C(3)] (CT(1)) and [C(5)-C(6)] (CT(2)), are 2.21 and 2.15Å, respectively. The angle CT(1)-Ru-CT(2) is 66.5°.

Table 5.1 lists selected bond lengths and angles.

A series of complexes analogous to 4 have been prepared using amines\(^{146}\) rather than phosphines. The crystal structure of RuCl\(_2\)(nbds)(piperidine)\(_2\) similarly has a distorted octahedral geometry with trans chloro-ligands. The distance from the metal to the centre of the double bonds in the piperidine complex is 2.07Å, and the angle subtended by the coordinated norbornadiene is 69.7°. For 4, the average distance is 2.18Å and the angle is 66.5°; this shows that the coordinated norbornadiene is less strongly bound, presumably because of the stronger trans effect of the phosphine compared to the piperidine ligand. This is reflected also to some extent in the length of the double bonds which are 0.02Å longer in the piperidine complex.
Figure 5.7 An ORTEP diagram of the RuCl$_2$(nbd)(dppb) molecule.
**Table 5.1**

Selected Bond Lengths and Bond Angles for RuCl₂(nbd)(dppb).0.5C₆H₆*

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length(Å)</th>
<th>Angle</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-Cl(1)</td>
<td>2.437 (1)</td>
<td>Cl₁(Ru-Cl₂)</td>
<td>168.37 (4)</td>
</tr>
<tr>
<td>Ru-Cl(2)</td>
<td>2.437 (1)</td>
<td>Cl₁(Ru-P₁)</td>
<td>87.32 (4)</td>
</tr>
<tr>
<td>Ru-P₁</td>
<td>2.399 (1)</td>
<td>Cl₁(Ru-P₂)</td>
<td>95.80 (4)</td>
</tr>
<tr>
<td>Ru-P₂</td>
<td>2.384 (1)</td>
<td>Cl₂(Ru-P₁)</td>
<td>81.86 (3)</td>
</tr>
<tr>
<td>Ru-C₂</td>
<td>2.322 (4)</td>
<td>Cl₂(Ru-P₂)</td>
<td>81.61 (3)</td>
</tr>
<tr>
<td>Ru-C₃</td>
<td>2.308 (4)</td>
<td>P₁(Ru-P₂)</td>
<td>98.16 (3)</td>
</tr>
<tr>
<td>Ru-C₅</td>
<td>2.254 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-C₆</td>
<td>2.252 (4)</td>
<td>[CT₁]-Ru-[CT₂]</td>
<td>66.50</td>
</tr>
<tr>
<td>Ru-[CT₁]</td>
<td>2.212</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-[CT₂]</td>
<td>2.146</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* According to numbering scheme in Figure 5.7. Estimated standard deviation given in parentheses. CT₁ and CT₂ refer to the centre of the coordinated double bonds [C₂-C₃] and [C₅-C₆] respectively.
relative to that found in 4 (1.39 Å vs. 1.37 Å).

5.4.2 Reaction with \( \text{H}_2 \)

The use of \( \text{RuCl}_2(\text{nbd})(\text{dppb}).0.5\text{C}_6\text{H}_6 \) 4 as a hydride precursor seemed appropriate, since the complex is mononuclear and it appeared feasible to remove the dialkene by reduction. However, the dissociation of 4 (equation 5.5) could clearly lead to complications in investigations of the reactivity with \( \text{H}_2 \), as \( \left[ \text{RuCl}_2(\text{dppb}) \right]_2 \) is known to react with \( \text{H}_2 \) (Section 5.2). In order to ascertain the extent to which the dissociation of 4 affects the reaction, the hydrogen uptake of a DMA solution of 4 at 50°C in the presence of Proton Sponge was monitored. The uptake corresponded to 1.7 \( \text{H}_2:1.0 \text{Ru} \) after 1.5 h, at which point the reaction was complete. This low stoichiometry implies that not all, if any, of the norbornadiene is being hydrogenated. Support for this comes from the attempted catalytic hydrogenation of norbornadiene using \( \text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})_2 \). This complex readily hydrogenates acrylamide, hex-1-ene, and styrene (Table 6.4, Section 6.4). Under the same conditions the hydrogenation of norbornadiene is much slower (max. rate = 1.4 \( \times 10^{-5} \) M s\(^{-1} \)) and stops after ca. 3 h with an uptake corresponding to the reduction of only 2.5% of the available substrate.

The inability to reduce norbornadiene suggests a catalytically inactive complex is being formed during reaction with \( \text{H}_2 \). The \( \text{H}_2 \)-reduction of 4 was attempted on a preparative scale in order to isolate any such complex. The preparative method was the same as used
for the reduction of Ru₂Cl₄(dpb)_2(acetone).acetone (Section 5.2) and, whilst a different hydride product was obtained (vide infra) the principle product (0.7 g) was [Ru₂Cl₂(dpbb)_2]⁻PSH⁺. The brown product (60 mg) obtained after separation of the ionic complex, was analytically impure but allowed for identification of a component. The principle resonance in the ³¹P⁻¹H⁻n.m.r. spectrum (C₆D₆, 30°C) of the minor impure product is a singlet (42.9 ppm), but there are also other unassignable resonances to lower field. However, the ¹H⁻n.m.r. spectrum shows broad resonances assigned to the olefinic protons of coordinated norbornadiene (3.96) and a hydride resonance (t, -9.68δ, J = 21 Hz).

To explain the available uptake and limited n.m.r. data it is proposed that one of the products of the reduction of 4 is RuHCl(nbd)(dpbb)(5-VII). Whilst such a conclusion must be tentative until

```
5-VII
```

the complex has been isolated pure, strong support comes from the n.m.r. data for the PPh₃ analogue.

Wilkinson and coworkers reported the preparation of RuHCl(nbd)(PPh₃)₂ by the interaction of RuHCl(PPh₃)₃ and norbornadiene. The complex was originally considered to be a mixture of
isomers because of the large number of resonances due to the dialkene. Other workers\textsuperscript{147} have since shown that only one isomer exists which has the structure on which the dppb analogue is based (5-VII). The \( ^{31}P\{^1H\}\text{-n.m.r.} \) spectrum of RuHCl(nbd)(PPh\(_3\))\(_2\) consisted of a singlet (40.6 ppm), whilst the \(^1\text{H}\text{-n.m.r.} \) spectrum exhibited a triplet (-8.88\(\delta\), \(^2J_{PH} = 24 \text{ Hz} \)) assigned to the hydride, and resonances at 3.45 and 3.63\(\delta\) due to the olefinic protons. The close similarity between the data for the dppb and PPh\(_3\) hydrido-complexes suggests analogous structures. It is noted\textsuperscript{67} that in the preparation of RuHCl(nbd)(PPh\(_3\))\(_2\) attempts to improve the yield by reducing the volume of the solution prior to precipitation of the product, or by scaling-up the reaction compared to the original reported preparation, gave impure products. Considering the procedure found necessary for isolating "RuHCl(nbd)(dppb)" it is perhaps not surprising that the \( ^{31}P\{^1H\}\text{-n.m.r.} \) spectrum shows additional resonances of unidentified species.

Of interest is how the hydrido-alkene complex is generated from 4. The monodentate phosphine analogue of 4, RuCl\(_2\)(nbd)(P(p-tolyl)\(_3\))\(_2\), is reported\textsuperscript{67} as being unreactive towards H\(_2\). If this is true for the dppb complex, hydride formation must arise from the [RuCl\(_2\)(dppb)]\(_2\) generated by dissociation (equation 5.5). The H\(_2\)-reduction of this dimer generates HCl which is trapped by the added Proton Sponge but adds to the starting complex to generate [Ru\(_2\)Cl\(_5\)(dppb)\(_2\)]''PSH\(^+\) (Section 5.2). The norbornadiene liberated from the dissociation apparently stabilises the hydride
intermediate to yield RuHCl(nbd)(dppb):

\[
\begin{align*}
\text{RuCl}_2(nbd)(dppb) & \rightarrow [\text{RuCl}_2(dppb)]_2 + \text{nbd} \\
\text{nbd} & \rightarrow \text{RuHCl}(dppb) \\
\text{RuHCl}(nbd)(dppb) & \rightarrow \text{[Ru}_2\text{Cl}_5(dppb)_2]^- \text{PSH}^+
\end{align*}
\]

The reported preparation of RuHCl(nbd)(PPh\textsubscript{3})\textsubscript{2} by phosphine-displacement from the hydrido-percursor complex RuHCl(PPh\textsubscript{3})\textsubscript{3} requires no hydrogen; however, the hydrido-dialkene complex does react with H\textsubscript{2} \textsuperscript{67}. In DMA the hydrogen-uptake corresponded to 2.5 H\textsubscript{2}:1.0 Ru, which is entirely consistent with the transformation:

\[
\text{RuHCl(nbd)(PPh}_3)_2 + 2.5\text{H}_2 \rightarrow 0.5 [\text{H}_2\text{RuCl(PPh}_3)_2]_2 + \text{norbornane} \quad (5.12)
\]

The reaction was also monitored \textsuperscript{67} by \textsuperscript{1}H- and \textsuperscript{31}P(\textsuperscript{1}H)-n.m.r. and revealed initial formation of RuHCl(PPh\textsubscript{3})\textsubscript{3} and subsequent slow generation of [H\textsubscript{2}RuCl(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2} and norbornane. After 2 d only the products of equation 5.12 were observed. The initial generation of the trisphosphine complex necessitates the concurrent formation of a phosphine-deficient complex, although no such species was detected. No mechanistic details were proposed for the reduction of the norbornadiene ligand; however, the involvement of the trisphosphine or phosphine
deficient complex cannot be ruled out.

In the present study, the generation of RuHCl(nbd)(dppb) in the presence of H₂ suggests that it is a more stable hydrido-dialkene complex, at least with respect to reaction with H₂, than the PPh₃ analogue. The bidentate phosphine is unlikely to undergo dissociation and consequently no phosphine-deficient or trisphosphine complexes will be generated. This suggests that reduction of the norbornadiene in the PPh₃ system perhaps arises from the initially formed intermediates, rather than from migration-insertion of alkene into the metal-hydride bond within the starting material RuHCl(nbd)(PPh₃)₂, followed by reaction with H₂.

Whilst the results in the present study suggest quite different reactivity with H₂ of the norbornadiene complexes containing bidentate compared to monodentate phosphines, a preparative route to produce analytically pure RuHCl(nbd)(dppb) is necessary to quantify such differences.
CATIONIC COMPLEXES OF RUTHENIUM(II)

6.1 Introduction

The application of neutral ruthenium-phosphine complexes as homogeneous hydrogenation catalysts is well documented, but only limited attention has been paid to ionic ruthenium complexes. A species that has been investigated is the anionic hydride complex

\[ [(\text{Ph}_3\text{P})_2\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{RuH}_2]^- \text{K}^+ \text{C}_{10}\text{H}_8\cdot(\text{Et}_2\text{O}) \]

which was prepared as a possible catalytic analogue of LiAlH_4 for the reduction of polar organic substrates. Indeed, this complex was found to hydrogenate ketones, esters, nitriles and polynuclear aromatics. Recent hydrogenation studies of this orthometalated complex have shown the presence of three anionic polyhydride complexes, although which one is relevant to the hydrogenation of polar substrates has not been determined. Cationic complexes generated in situ from the action of fluoroboric acid on ruthenium(II) carboxylato-triphenylphosphine complexes have also been found to hydrogenate alkenes. The active species in this case was initially thought to be \([\text{Ru}(\text{PPh}_3)_2]^2^+\), although later work suggested the presence of the cationic hydride complex \([\text{RuH}(\text{PPh}_3)_2]^+\).

A possible explanation for the limited attention is that few
general methods have been reported for the preparation of such ruthenium phosphine complexes. The anionic complex mentioned previously was prepared by the reduction of RuHCl(PPh$_2$)$_3$ with potassium-naphthalene at low temperatures, whilst the cationic complexes are most frequently prepared by hydride abstraction from either hydride- or allyl-complexes. The use of salts of non-coordinating anions for halide abstraction has been used to prepare complexes such as [Ru(cod)Cl(CH$_3$CN)$_2$]$^+$, the coordinated dialkene of which can be substituted by various ligands including phosphine.

In the present study, the isolation of ionic complexes as potential hydride precursors was of interest because of the difficulties encountered in the preparation of hydride complexes from the neutral ruthenium complexes (Chapter V). The study was limited to the generation of cationic complexes by halide abstraction from ruthenium complexes containing the dppb ligand. The preparation, characterisation of mono- and dinuclear complexes and their reactivity with hydrogen is discussed.

6.2 Results
6.2.1 Formation of Dinuclear Cationic Complexes

6.2.1.1 Tri-u-chlorobis(acetonitrile(1,4-diphenylphosphinobutane)) ruthenium(II) Hexafluorophosphate, [Ru$_2$Cl$_5$(dppb)$_2$(CH$_3$CN)$_2$]$^+$PF$_6^-$, 5

Acetonitrile solutions of Ru$_2$Cl$_5$(dppb)$_2$ were found to undergo disproportionation as monitored by loss of absorption in the near-infrared (Section 3.6). These solutions also gave molar
conductivities of 112 ohm$^{-1}$cm$^2$mole$^{-1}$ ([Ru$_{II}$] = 2 x 10$^{-3}$M) (see Section 6.3). Addition of AgPF$_6$ to acetonitrile solutions of Ru$_2$Cl$_5$(dppb)$_2$ (1:2 mole ratio) led to precipitation of AgCl and a change in colour of the solution from red to pink. From the solution the complexes [RuCl$_3$(dppb)]$_2$ and 5 were isolated (Sections 2.1.7.10 and 2.1.7.11). The isolated complexes suggested a disproportionation consistent with:

$$2 \text{Ru}_2\text{Cl}_5(\text{dppb})_2 \xrightarrow{\text{CH}_3\text{CN}} [\text{RuCl}_2(\text{dppb})]_2 + [\text{RuCl}_3(\text{dppb})]_2 \xrightarrow{\text{AgPF}_6} [\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{CH}_3\text{CN})_2]^+\text{PF}_6^- + \text{AgCl}$$ (6.1)

The elemental analysis of the yellow hexafluorophosphate salt is consistent with two acetonitrile molecules per complex. These are also evident in the solid state infrared spectrum as weak absorptions at 2315 and 2280 cm$^{-1}$. The infrared spectrum also shows absorptions characteristic of non-coordinated PF$_6^-$ at 840 and 568 cm$^{-1}$, and the absence of terminal Ru-Cl stretching in the 250-350 cm$^{-1}$ region. The $^{31}$P{$^1$H}-n.m.r. spectrum of 5 in CD$_2$Cl$_2$ consists of an AB quartet ($\delta_A = 49.6$, $\delta_B = 46.6$ ppm; $^2J_{AB} = 36.6$ Hz) and a septet due to the PF$_6^-$ anion ($\delta = -145.3$ ppm, $J = 710.4$ Hz). These data are consistent with 5 being a triply chloro-bridged species (Structure 6-I). The $^{31}$P{$^1$H}-n.m.r. spectrum in CD$_2$CN, however, consists of a

$$\text{PF}_6^- \quad \text{P-P = dppb}$$

$$\text{S = CH}_3\text{CN}$$

6-I
singlet ($\delta = 40.6 \text{ ppm}$) and a septet due to the PF$_6^-$ anion ($\delta = -146.1 \text{ ppm}$, $J = 708.0 \text{ Hz}$).

This difference between dichloromethane and acetonitrile solutions of 5 is also apparent in the visible spectra and conductivity measurements. The visible spectrum in CH$_2$Cl$_2$ shows an absorption maximum at 374 nm which shifts to 317 nm in CH$_3$CN with no loss of intensity ($\varepsilon = 2950 \text{ M}^{-1}\text{cm}^{-1}$) as shown in Figure 6.1. Dilution conductivity measurements in both solvents under argon at 25°C yield linear Onsager plots (Figure 6.2). The limiting conductance in

![Figure 6.1](image)

**Figure 6.1** Visible spectra of [Ru$_2$Cl$_3$(dppb)$_2$(CH$_3$CN)$_2$]$^+$PF$_6^-$ in CH$_2$Cl$_2$ and CH$_3$CN.
Figure 6.2 Onsager plots for $\left[ \text{Ru}_2\text{Cl}_3\text{(dppb)}_2\text{(CH}_3\text{CN)}_2 \right]^+\text{PF}_6^-$ in CH$_2$Cl$_2$ and CH$_3$CN at 25°C.
CH$_3$CN is 240.0 ohm$^{-1}$cm$^2$mole$^{-1}$ which is outside the range generally accepted for 1:1 electrolytes in this solvent (120-160 ohm$^{-1}$cm$^2$mole$^{-1}$), although examples of particularly high conductivities are known. The value found for $5$ in CH$_3$CN is also in marked contrast to that found in CH$_2$Cl$_2$ (59.3 ohm$^{-1}$cm$^2$mole$^{-1}$). In acetonitrile the high conductivity and the presence of only a singlet in the $^{31}$P$\{$H$\}$-n.m.r. suggest dissociation (equation 6.2); such a proposal is supported by isolation of the mononuclear PF$_6^-$ species (Section 6.2.2.1).

$$[\text{Ru}_2\text{Cl}_3\text{(dppb)}_2\text{S}_2]^+\text{PF}_6^- \xrightarrow{\text{S}} \text{[RuCl(dppb)S}_n^+\text{PF}_6^- + \text{[RuCl(dppb)S}_n^-\text{Cl}^-}$$

$5$  

S = CH$_3$CN

6.2.1.2 (Acetone)tri-$\mu$-chlorobis[1,4-diphenylphosphinobutane])ruthenium (II) Hexafluorophosphate, $[\text{Ru}_2\text{Cl}_3\text{(dppb)}_2\text{(acetone)}]^+\text{PF}_6^-$, 6

The complex $[\text{RuCl}_2\text{(dppb)}_2]$ in donor solvents, such as acetone, exists as a triply chloro-bridged species with one coordinated solvent molecule, 6-II, (Section 4.3.2). Due to the apparent stability of the triple chloro-bridge, abstraction of the terminal chloride appeared to be a potential route for the generation of dinuclear
cationic complexes. Reaction of this complex in either toluene- or(CH2Cl2)-acetone mixtures with one equivalent of AgPF6 slowly produces a brown solution with precipitation of AgCl. The pale orange product isolated from the solution gave an elemental analysis consistent with formulation [Ru2Cl2(dpb)2(acetone)]PF6+, 6 (Section 2.1.7.13).

The i.r. spectrum of 6 shows an absorption for coordinated acetone (1663 cm⁻¹), strong absorptions for non-coordinated PF6⁻ (840 and 568 cm⁻¹) and no absorption is assignable to a terminal chloride.

The principle resonances expected for the dinuclear cation in the 31P{¹H}-n.m.r. spectrum of 6 are unresolved in CD2Cl2 or CD2Cl2-acetone mixtures even at -70°C. The spectrum in CD2Cl2-acetone at -70°C (Figure 6.3) shows resonances centred at ca. 47.5 ppm with no discernable coupling constants, a singlet (15% of the integrated intensity of the low field resonances) at 32.8 ppm, and a septet (δ = -146.0 ppm, J = 710.5 Hz) due to the PF6⁻ anion. The singlet is assigned to a mononuclear species by analogy to the findings in CH2CN as solvent (previous Section) and, whilst the unresolved resonances are assigned to the dinuclear cation, the complexity suggests the presence of more than one species. A possible explanation is a rapid equilibrium between mono- and bis- solvated species:
A CH$_2$Cl$_2$ solution of 6 ([Ru$_2$] = 2 x 10$^{-3}$M) gave a conductance of 39.6 ohm$^{-1}$cm$^2$mole$^{-1}$, consistent with the presence of a 1:1 electrolyte.

6.2.2 Formation of Mononuclear Cationic Complexes

6.2.2.1 Tris(acetonitrile)chloro(1,4-diphenylphosphinobutane)ruthenium(II) Hexafluorophosphate, [RuCl(dppb)(CH$_3$CN)$_3$]$^+$ PF$_6^-$, 7

The solution properties of [Ru$_2$Cl$_3$(dppb)$_2$(CH$_3$CN)$_2$]$^+$ PF$_6^-$, 5, in acetonitrile suggest dissociation of the complex into mononuclear species (Section 6.2.1.1). This was supported by further
reaction of 5 with $\text{AgPF}_6$ (1:1 mole ratio) in $\text{CH}_3\text{CN}$, from which the pale yellow complex $[\text{RuCl(dppb})(\text{CH}_3\text{CN})_3]^+ \text{PF}_6^-$, 7, was isolated. This complex could be prepared more easily from $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})$. acetone, by metathesis, with two equivalents of $\text{AgPF}_6$ in $\text{CH}_3\text{CN}$ (Section 2.1.7.12).

The solid state i.r. spectrum shows absorptions for coordinated $\text{CH}_3\text{CN}$ (2268 cm$^{-1}$), non-coordinated $\text{PF}_6^-$ (840 and 572 cm$^{-1}$) and a terminal Ru-Cl stretch (285 cm$^{-1}$).

The principle resonances in the $^{31}\text{P}\{^1\text{H}\}$-n.m.r. spectrum of 7 at ambient temperature are a singlet ($\delta = 40.6$ ppm in $\text{CD}_3\text{CN}$; $\delta = 41.2$ ppm in $\text{CD}_2\text{Cl}_2$) and a high field septet attributed to the $\text{PF}_6^-$ anion. The singlet is consistent with the acetonitrile ligands being in a fac-arrangement (6-III):

![Diagram](image)

6-III

In addition, the $^{31}\text{P}\{^1\text{H}\}$-n.m.r. spectrum in $\text{CD}_2\text{Cl}_2$ shows an additional singlet at 38.7 ppm (5% integrated intensity), which is assigned to a five-coordinate species arising from dissociation of an acetonitrile ligand. Support for this proposal comes from the addition of $\text{CD}_3\text{CN}$ (ca. 10%) to the solution which causes this additional
singlet to disappear, and from the reactivity of \( \tilde{7} \) with \( \text{H}_2 \) (Section 6.4). The spectrum of \( \tilde{7} \) in CD\(_2\)CN also shows an AB quartet (\( \delta_A = 42.5, \delta_B = 35.7 \) ppm; \( ^2J_{AB} = 34.2 \) Hz) corresponding to ca. 15\% of the integrated intensity of the low field resonances. The quartet is attributed to an isomer of the complex with a mer-arrangement of the acetonitrile ligands in CH\(_2\)CN solution.

Dilution conductivity measurements on \( \tilde{7} \) in CH\(_2\)CN under argon yield a linear Onsager plot with a limiting conductance of 126.5 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) (Figure 6.4). The molar conductivity in CH\(_2\)Cl\(_2\) ([Ru] = 2 \times 10\(^{-3}\) M) was 19.8 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\).

![Onsager plot for [RuCl(dppb)(CH\(_2\)CN)\(_3\)]\(^{+}\)PF\(_6^–\) in CH\(_2\)CN at 25°C.](image-url)
Chloro(η⁶-toluene)(1,4-diphenylphosphinobutane)ruthenium(II) Hexafluorophosphate, [RuCl(dppb)(η⁶-toluene)]⁺PF₆⁻, S

The $^{31}$P($^1$H)-n.m.r. spectrum of $[\text{Ru}_2\text{Cl}_3\text{(dppb)}_2\text{(acetone)}]^{+}\text{PF}_6^-$ in CD$_2$Cl$_2$-acetone (Section 6.2.1.2) shows a singlet which is assigned to a mononuclear species that is presumably analogous to the acetonitrile complex 7 discussed previously. In an attempt to isolate the mononuclear acetone species the reaction of Ru₄Cl₄(dppb)₂(acetone).acetone with two equivalents of AgPF₆ in toluene-acetone mixture was carried out. The pale orange product eventually obtained appeared to be the same as when one equivalent of AgPF₆ was used. However, slow recrystallisation of this product from CH$_2$Cl$_2$-acetone by precipitation with diethyl ether initially afforded a bright yellow crystalline product. Addition of more diethyl ether to the filtrate resulted in precipitation of a pale orange product that was identified as $[\text{Ru}_2\text{Cl}_3\text{(dppb)}_2\text{(acetone)}]^{+}\text{PF}_6^-$ (i.r., $^{31}$P($^1$H)-n.m.r., and elemental analysis). The yellow product initially formed was characterised as $[\text{RuCl(dppb)(η⁶-toluene)}]^{+}\text{PF}_6^-$, S (Section 2.1.7.14).

The presence of a π-bonded phenyl ring is evident in the $^1$H-n.m.r. spectrum (Figure 6.5). The resonances due to the ortho-, meta-, and para-protons of the coordinated toluene are shifted to a higher field compared to free toluene, and are affected to varying degrees by the metal to give rise to separate signals. The spectra may be interpreted on a first-order basis with assignment of the resonances at 65.74(t), 4.95(d) and 4.34(t) ppm to the meta-, ortho- and
Figure 6.5 Low-field region of the $^1$H-n.m.r. spectrum of 
$[\text{RuCl(dppb)(n}^6\text{-toluene})]^+\text{PF}_6^-$ in CD$_2$Cl$_2$ at 400 MHz.

para-protons, respectively ($J_{om} = J_{pm} = 6$ Hz, $J_{op} = 0$ Hz). The 
relative intensity of the coordinated toluene is one quarter of that for 
the phenyl resonances of the phosphine which are at 67.3-7.7 ppm. The 
$^{31}$P{$^1$H}-n.m.r. spectrum of $\mathbf{8}$ in CD$_2$Cl$_2$ consists of a 
singlet at 31.9 ppm which is invariant to temperature to -60°C. These 
findings are consistent with $\mathbf{8}$ having a pseudotetrahedral geometry as 
shown in structure 6-IV.

The solid state i.r. spectrum of $\mathbf{8}$ shows a terminal Ru-Cl 
stretch (302 cm$^{-1}$), and non-coordinated PF$_6^-$ (640 and 568 cm$^{-1}$).
A dichloromethane solution ([Ru] = 2 x 10^{-3} M) of 8 has a conductance of 28.9 ohm^{-1} cm^{2} mole^{-1} which is consistent with the complex being a 1:1 electrolyte.

6.3 Discussion

The method of halide abstraction using sodium or silver salts of non-coordinating anions is frequently used to generate cationic transition metal complexes. In this laboratory, attempts to generate cationic complexes by this method from ruthenium phosphine complexes such as RuCl_{2}(PPh_{3})_{2}, produced silver-phosphine adducts as the only characterisable products. Since in the present study the starting compounds contain bidentate phosphines, which are less likely to undergo dissociation, the use of silver salts seemed feasible. Indeed, this method led to the isolation of complexes which may all be thought of as containing the 12-electron RuCl(dppb)^+ unit. In the dinuclear complexes [Ru_{2}Cl_{2}(dppb)_{2}(S)_{n}]^+, n = 2, S = acetonitrile (5); and n = 1, S = acetone (6), the 12-electron
moiety is stabilised by the "chelating-ligand" RuCl₂(dppb) and solvent, whilst in the mononuclear examples \([\text{RuCl(dppb)(CH}_3\text{CN)}]_3^+(7), \) and \([\text{RuCl(dppb)(η}^6\text{-toluene)}]_3^+(8),\) the 12-electron unit is stabilised by solvent alone. \(^{31}\text{P(}^1\text{H)}\)-n.m.r. and conductivity data for these complexes are listed in Tables 6.1 and 6.2, respectively.

The preparation of the dinuclear cations is by independent routes: 5 is prepared by anion exchange, whilst 6 is prepared by abstraction of a non-dissociated chloride ligand. Complexes of this type containing monodentate phosphines have been reported previously, but rather than solvent occupying the vacant coordination sites the strong π-acids CO and CS are present.

The dinuclear cations 5 and 6 exhibit quite different solution behaviour, although in CH₂Cl₂ both give molar conductivities which are consistent with the dinuclearity of the isolated complex. The \(^{31}\text{P(}^1\text{H)}\)-n.m.r. spectrum of 5 in CD₂Cl₂ shows that the acetonitrile remains coordinated to both metal centres thereby generating a single AB pattern. The spectra of 6 exhibit unresolved resonances in CD₂Cl₂ even in the presence of acetone and at low temperatures. The data are consistent with the inability of the \([(\text{dppb})\text{RuCl}_2\text{Ru(dppb)}]^+\) moiety to coordinate two acetone molecules in the solid state or in solution. The weaker interaction of acetone compared to acetonitrile with the cationic complex is, perhaps, unexpected considering the base parameters for these solvents (Table 6.3). The values for both solvents are similar yet clearly the...
### Table 6.1

$^{31}\text{P}^{1\text{H}}$-N.m.r. Data for Cationic Complexes

<table>
<thead>
<tr>
<th>Cation</th>
<th>Solvent</th>
<th>Resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{CH}_3\text{CN})_2]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>$\delta_A=49.6$, $\delta_B=46.6$ ppm, $^2J_{AB}=36.6$ Hz</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{acetone})]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>multiplets centred at 47.5 ppm</td>
</tr>
<tr>
<td>$\text{fac-}[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+$</td>
<td>CD$_3$CN</td>
<td>singlet:40.6 ppm</td>
</tr>
<tr>
<td>$\text{mer-}[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>singlet:41.2 ppm</td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_2]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>singlet:38.7 ppm</td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})({\eta}^6\text{-toluene})]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>singlet:31.9 ppm</td>
</tr>
</tbody>
</table>

### Table 6.2

Conductivity Data for Cationic Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$\Lambda_e$</th>
<th>$\Lambda_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{CH}_3\text{CN})_2]^+\text{PF}_6^-$</td>
<td>CH$_3$CN</td>
<td>240.0</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{acetone})]^+\text{PF}_6^-$</td>
<td>CH$_2$Cl$_2$</td>
<td>59.3</td>
<td></td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$</td>
<td>CH$_3$CN</td>
<td>39.6</td>
<td></td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})({\eta}^6\text{-toluene})]^+\text{PF}_6^-$</td>
<td>CH$_2$Cl$_2$</td>
<td>126.5</td>
<td></td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})({\eta}^6\text{-toluene})]^+\text{PF}_6^-$</td>
<td>CH$_2$Cl$_2$</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>$[\text{RuCl}(\text{dppb})({\eta}^6\text{-toluene})]^+\text{PF}_6^-$</td>
<td>CH$_2$Cl$_2$</td>
<td>28.9</td>
<td></td>
</tr>
</tbody>
</table>

(a) Values given are in ohm$^{-1}$cm$^2$mole$^{-1}$

(b) $[\text{Ru}_2] = [\text{Ru}] = 2 \times 10^{-3}$ M
Table 6.3  
Base Parameters for Acetone and Acetonitrile

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values for:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td>Donor number</td>
<td>17.0</td>
</tr>
<tr>
<td>Acceptor number</td>
<td>12.5</td>
</tr>
<tr>
<td>$C_B^b$</td>
<td>2.33</td>
</tr>
<tr>
<td>$E_B^b$</td>
<td>0.99</td>
</tr>
<tr>
<td>$C_B/E_B^b$</td>
<td>2.36</td>
</tr>
</tbody>
</table>


Coordinating ability towards Ru(II) in the present study is quite different. Whilst Gutmann's donor-acceptor model is perhaps ambiguous since the corresponding acid parameters of ruthenium(II) are not known, Drago's $C_B/E_B$ model still predicts that acetone should coordinate more strongly than CH$_2$CN. It is possible that the $E_B$ and $C_B$ values do not reflect the preferred coordination of nitrogen donor ligands to ruthenium or that the weaker binding of acetone simply arises from greater steric hindrance compared to CH$_2$CN.

This difference between acetone and acetonitrile also manifests
itself in their ability to stabilise mononuclear species. In CH$_3$CN, 5 readily undergoes dissociation to generate [RuCl(dppb)(CH$_3$CN)$_3$]$^+$ $X^-$, $X = \text{Cl or PF}_6^-$. This is evident by the high conductivity ($\Lambda_0 = 240 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) and the presence of only a singlet in the $^{31}$P{$^1$H}-n.m.r. spectrum. The $^{31}$P{$^1$H}-n.m.r. spectrum of 6 in CD$_2$Cl$_2$/acetone does show a singlet assigned to a mononuclear species; however, the complex still exists predominantly as a dinuclear species. The fact that 5 is generated from Ru$_2$Cl$_5$(dppb)$_2$ in CH$_3$CN (equation 6.1), in which 5 has been shown to exist as a mononuclear species, shows that coordination to the RuCl(dppb)$^+$ moiety of the "chelating" RuCl$_2$(dppb) ligand is thermodynamically more stable than coordination of three acetonitrile ligands.

The dissociation of 5 was confirmed by isolation of [RuCl(dppb)(CH$_3$CN)$_3$]$^+$ PF$_6^-$, 7, by reaction of 5 with one equivalent of AgPF$_6$. The main resonance observed in the $^{31}$P{$^1$H}-n.m.r. spectrum of 5 in CD$_2$Cl$_2$ or CD$_3$CN is a singlet which suggests that the complex adopts a fac-configuration. The acetonitrile ligands are labile, as evidenced by an additional singlet observed in CD$_2$Cl$_2$, which is assigned to a five coordinate [RuCl(dppb)(CH$_3$CN)$_2$]$^+$ species; and by the ability to undergo rearrangement to the mer-configuration that probably is responsible for the AB quartet observed in CD$_3$CN.

Monodentate phosphine analogues ($P = \text{PPh}_3, \text{PMePh}_2$ and PMe$_2$Ph) have been prepared previously$^{153}$, equation 6.3; however, no spectroscopic data were provided for comparison with the data obtained in the present study.
The conductivity data obtained for 7 in CH$_3$CN are also quantitatively consistent with those found for 5. The limiting conductance of 7 is 126.5 ohm$^{-1}$cm$^2$ mole$^{-1}$ and, since $\lambda_0$PF$_6^-$ = 102.8 ohm$^{-1}$cm$^2$ mole$^{-1}$, the limiting conductance for the cationic mononuclear species is 23.7 ohm$^{-1}$cm$^2$ mole$^{-1}$. Using the limiting conductance of Cl$^-$ (91.6 ohm$^{-1}$cm$^2$ mole$^{-1}$), the value expected for dissociation of 5 in accordance with equation 6.2 is therefore $((2 \times 23.7) + 102.8 + 91.6) = 241.8$ ohm$^{-1}$cm$^2$ mole$^{-1}$ which is in excellent agreement with that found (240.0 ohm$^{-1}$cm$^2$ mole$^{-1}$).

The molar conductivity for the mixed-valence complex, Ru$_2$Cl$_5$(dppb)$_2$, (Section 6.2.1.1) is also consistent with that found for 7. In acetonitrile, the initial disproportionation of Ru$_2$Cl$_5$(dppb)$_2$ (equation 6.4) generates the dimeric Ru(II) complex which is expected to undergo subsequent chloride dissociations (equation 6.5) in a manner analogous to that found for the PF$_6^-$ salts in acetonitrile.

$$2\text{Ru}_2\text{Cl}_5(\text{dppb})_2 \xrightarrow{S} \text{[RuCl}_2(\text{dppb})]_2 + \text{[RuCl}_3(\text{dppb})]_2 \quad (6.4)$$

$$S = \text{CH}_3\text{CN}$$

$$\text{[RuCl}_2(\text{dppb})]_2 \rightarrow \text{[Ru}_2\text{Cl}_3(\text{dppb})_2\text{S}_2]^+\text{Cl}^- \rightarrow 2\text{[RuCl(dppb)S}_3]^+\text{Cl}^- \quad (6.5)$$
Since the concentration of the final mononuclear product is the same as the initial $^{\text{II,III}}\text{Ru}_2$ complex, the measured conductance for
\[ [\text{RuCl(dppb)}(\text{CH}_3\text{CN})_3]^+\text{Cl}^- \quad ([\text{Ru}] = 2 \times 10^{-5}\text{M}, \Lambda_e = 112 \text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}) \] compares favourably with that found for the analogous $\text{PF}_6^-$ salt, $\text{7}$.

The molar conductivity of $\text{7}$ in $\text{CH}_2\text{Cl}_2$ (19.8 ohm$^{-1}$cm$^2$mole$^{-1}$) is surprisingly lower than that expected for the dinuclear acetonitrile complex (5) at the same concentration (from Figure 6.2; $\Lambda_e = 45.5$ ohm$^{-1}$cm$^2$mole$^{-1}$). This is also apparent from the conductivity of the dinuclear acetone complex (6) which has a higher value (39.6 ohm$^{-1}$cm$^2$mole$^{-1}$) compared to the mononuclear toluene complex (8) (28.9 ohm$^{-1}$cm$^2$mole$^{-1}$). The solvent chosen for conductivity measurements should have a high dielectric constant and good solvating properties. Dichloromethane does not fit either of these criteria, but was used since it was the only solvent in which the complexes 5 - 8 readily dissolved. Whilst the values obtained are in the same range found for other 1:1 electrolytes$^{121,122}$, the unusually low conductivity for mononuclear complexes presumably arises from the low dielectric constant of the solvent.

The dissociation of $[\text{Ru}_2\text{Cl}_3(\text{dppb})(\text{acetone})]^+\text{PF}_6^-$ (6) in a manner analogous to the acetonitrile complex (5) is evidenced by the singlet (32.8 ppm) in the $^{31}\text{P}-\text{n.m.r.}$. The attempted isolation of the mononuclear acetone complex via reaction of $\text{Ru}_2\text{Cl}_4(\text{dppb})(\text{acetone})\text{.acetone}$ with 2 equivalents of $\text{AgPF}_6$ in a toluene-acetone solvent mixture was unsuccessful, and led to the isolation of the mononuclear complex $[\text{RuCl(dppb)}(\eta^6\text{-toluene})]^+\text{PF}_6^-$ (8).
Toluene was used simply to aid dissolution of the starting material, but clearly was more effective at stabilising the RuCl(dppb)\(^+\) unit rather than three acetone molecules. In retrospect, this perhaps is not surprising since the 12-electron unit is isoelectronic with Cr(CO)\(_3\) which readily coordinates six-electron donors to form stable 18-electron systems\(^{158}\).

The presence of coordinated toluene is unequivocally confirmed by the proton resonances between \(\delta 4.34 - 5.74\) ppm (Figure 6.5). The shift to higher field of these resonances relative to free toluene is thought\(^{159}\) to arise from the following effects: withdrawal of \(\pi\)-electron density from the aromatic ring by the metal, quenching of ring currents by interaction with the metal, and by magnetic anisotropy of the rest of the metal complex. Hydrido-monodentate phosphine analogues of 8 have been prepared for a series of arenes\(^{160}\), including PPh\(_3\) itself\(^{161}\). The complex \([\text{RuH}(\eta^6\text{-toluene})(\text{PPh}_3)_2]^+\text{BF}_4^-\) was prepared by hydride abstraction from \([\text{RuH}_2(\text{PPh}_3)_4]\) in the presence of toluene. This complex shows resonances for the coordinated phenyl at \(\delta 4.6, 5.3\) and \(6.4\) ppm for the ortho-, meta-, and para-protons, respectively. Complex 8 exhibits similar chemical shifts for the ortho- (\(\delta 4.95\) ppm) and meta- (\(\delta 5.74\) ppm) protons, but the para-proton is shifted to even higher field (\(\delta 4.34\) ppm). The para-proton must eclipse either the bridging portion of bidentate phosphine or the chloride ligand depending on the orientation of the phenyl ring (Structure 6-IV), and this could cause shielding of the proton resulting in a subsequent upfield shift.
The isolation of 8 was unexpected but is of interest as it shows the ability of the RuCl(dppb)$^+$ moiety to form $\pi$-arene complexes, and to separate the resonances of the ortho-, meta-, and para-protons. The development of such $\pi$-arene complexes is therefore potentially useful as n.m.r. shift reagents for aromatic rings; as at present, only cyclodextrins$^{162}$ and the ruthenium complexes$^{160}$ mentioned previously are effective. Although unproven, the complex $[\text{RuCl(dppb)}(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$ should be an ideal in-situ shift reagent as the lability of the acetonitrile ligands will allow easy coordination of an aromatic ring.

6.4 Reaction of Cationic Complexes with Hydrogen

The primary reason for the generation of the cationic complexes discussed above was as hydride precursors, and as potential hydrogenation catalysts. In order to determine if the cationic complexes were catalytically active a brief study of alkene hydrogenation using $[\text{Ru}_2\text{Cl}_3(\text{dppb})_2(\text{acetone})]^+\text{PF}_6^-$ (6) and $[\text{RuCl(dppb)}(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$ (7) was undertaken. The neutral complex $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone}).\text{acetone (1)}$ was also used as a catalyst for comparison. Table 6.4 lists the maximum rates observed, and the time taken for reduction of 50% of the substrate ($T_{1/2}$).

The data in Table 6.4 show that the cationic complexes are capable of hydrogenating alkenes, but exhibit quite different reactivity. The acetonitrile complex is generally less reactive, and shows discrimination towards the substrates. The differences in rate
Table 6.4
Hydrogenation of Alkenes by Neutral and Cationic Complexes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst (6)</th>
<th>Max. Rate</th>
<th>$T_{1/2}$</th>
<th>Max. Rate</th>
<th>$T_{1/2}$</th>
<th>Max. Rate</th>
<th>$T_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>($x10^4,Ms^{-1}$)</td>
<td>(s)</td>
<td>($x10^4,Ms^{-1}$)</td>
<td>(s)</td>
<td>($x10^4,Ms^{-1}$)</td>
<td>(s)</td>
</tr>
<tr>
<td>Hex-1-ene</td>
<td>(6)</td>
<td>7.4</td>
<td>310</td>
<td>0.8</td>
<td>2300</td>
<td>4.9</td>
<td>480</td>
</tr>
<tr>
<td>Styrene</td>
<td>(7)</td>
<td>2.7</td>
<td>730</td>
<td>2.4</td>
<td>750</td>
<td>3.0</td>
<td>600</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>(1)</td>
<td>2.6</td>
<td>790</td>
<td>0.1</td>
<td>13000</td>
<td>1.3</td>
<td>820</td>
</tr>
</tbody>
</table>

(a) $[6] = [7] = [1] = 2 \times 10^{-3}M$, [alkene] = 0.4 M, 1 atm.H$_2$, DMA, 50°C for hydrogenation catalysed by 7 are presumably because of the different electronic and steric contributions of the substrate. The rates observed for 6 are particularly high, and are comparable to those found for the neutral complex 1; the similar reactivity pattern perhaps suggests an active species common to both.

In the absence of substrate, 6 and 7 were found to react with H$_2$. The H$_2$-uptake at 50°C for a DMA solution of 6 in the presence of added base (Proton Sponge) corresponded to 1.0 Ru$_2$:1.35 H$_2$, the value being inconsistent with generation of any simple hydrido-complex. Since 6 undergoes dissociation in the presence of acetone to mononuclear species ($^{31}$P($^1$H)-n.m.r. evidence, Section 6.2.1.2), analogous behaviour seems likely in DMA (equation 6.6). The
observed stoichiometry with H₂ could result from reaction of the mono-

\[ [\text{Ru}_2 \text{Cl}_3(\text{dppb})_2(\text{acetone})]^+ \rightarrow 2[\text{RuCl(dppb)S}_n]^+ + \text{Cl}^- \] (6.6)

or dinuclear species or both. The isolation of the active species was
not attempted due to anticipated difficulties in separating the mixture of products.

The H₂-uptake for 7 in the absence of substrate, using the
same conditions as for 6, corresponded to 6.85 moles H₂ per mole of complex. The uptake-plot (Figure 6.6) shows an inflexion corresponding
to ca. 1 equivalent of hydrogen. This is followed by uptake of 5.85
moles H₂ per Ru which is quantitatively consistent with reduction of
the nitrile group of the acetonitrile ligands:

\[ [\text{RuCl(dppb)(CH}_3\text{CH})_3]^+PF_6^- + 7H_2 \rightarrow [\text{RuH(dppb)}(\text{C}_2\text{H}_5\text{NH}_2)_3]^+PF_6^- + \text{HCl} \] (6.7)

The coordination of ethylamine is necessary to account for the observed
stoichiometry: since ethylamine is a gas, if it were liberated from the
reduction the net uptake would only correspond to 4 moles of gas per
mole of 7.

In an attempt to confirm the reaction proposed in equation 6.7,
the hydrogenation was conducted on a preparative scale (Section
2.1.7.15). After reaction with H₂ for 2 d the DMA solution
precipitated an off-white solid. This was insoluble in most organic
solvents which precluded recrystallisation and n.m.r. studies. The
Figure 6.6 Uptake plot for the reaction of \([\text{RuCl(dppb)(CH}_3\text{CN)}_2]^{+}\text{PF}_6^-\) with H\textsubscript{2} in DMA at 50°C.
infrared spectrum of the solid shows medium absorptions at 3300, 3221, 3191 and 3144 cm\(^{-1}\) (coordinated amine), and a strong absorption at 1997 cm\(^{-1}\) (hydride). The elemental analysis found (C : 58.4, H : 6.6, N : 4.3\%) is very close to that expected for RuHCl(dppb)(C\(_2\)H\(_5\)NH\(_2\))\(_2\) (C : 58.76, H : 6.58, N : 4.28\%). The unexpected loss of PF\(_6^-\) (i.r. evidence) suggested that anion exchange between the product and the HCl generated by reduction had occurred. This was confirmed by the eventual isolation of a white solid coproduct identified by elemental analysis, i.r. and \(^1\)H-n.m.r. as PSH\(^+\)PF\(_6^-\) (PS = Proton Sponge). The product left after separation of the PSH\(^+\)PF\(_6^-\) was a yellow compound, which exhibited a weak absorption at 3300 cm\(^{-1}\) (v\(_{\text{NH}}\)), and absorptions due to non-coordinated PF\(_6^-\) in the infrared spectrum. The \(^1\)H-n.m.r. spectrum exhibited no hydride resonance, whilst the \(^{31}\)P{\(^1\)H}-n.m.r. spectrum (Figure 6.7) shows that more than one species is present. Attempts to separate these species have been unsuccessful, but the lack of hydride and amine absorptions suggests these are decomposition products resulting from the anion-exchange or work-up procedure.

The H\(_2\)-uptake for \(\mathbf{T}\) is consistent with the stoichiometric reduction of three acetonitrile ligands. To further confirm that reduction of -C≡N was occurring, the reaction of \(\mathbf{T}\) with H\(_2\) in the presence of CH\(_3\)CN was investigated. Direct addition of \(\mathbf{T}\) to DMA/CH\(_3\)CN solution (9:1, v:v) gave no H\(_2\)-uptake; however, injection of 10 µL (0.2 M) of CH\(_3\)CN to a DMA solution (10 mL) of \(\mathbf{T}\) which had already undergone some reaction with H\(_2\) gave the uptake plot shown in
Figure 6.7 $^{31}$P($^1$H)-N.m.r. spectrum of final yellow compound obtained from reaction of $[\text{RuCl(dppb)(CH}_2\text{CN)}_3]^+\text{PF}_6^-$ with $\text{H}_2$.

Figure 6.8. The uptake prior to addition of CH$_3$CN is the same as observed for the stoichiometry determination. After injection, the rate of hydrogenation falls-off markedly, but after 4 d the total uptake corresponds to 9.6 H$_2$:1.0 Ru at which point the monitoring was stopped.

The hydrogenation of nitriles presumably proceeds via imine intermediates; this was tested for, by the reaction of 7 with H$_2$ in the presence of N-(2-phenylpropylidene)-2-propyl-amine, C$_6$H$_5$CH(CH$_3$)C=N-CH(CH$_3$)$_2$, (prepared according to James and Young$^{163}$). In this reaction the imine was initially present in a 170-fold excess, and the temperature increased to 65°C in order to
Figure 6.8 $\mathrm{H}_2$-Uptake plot for $[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$ with addition of $\text{CH}_3\text{CN}$.

increase the rate. After 50 h, the $\mathrm{H}_2$-uptake corresponded to 50 turnovers at which point the monitoring was stopped (Figure 6.9).

6.4.1 Discussion

The additional $\mathrm{H}_2$-uptake obtained upon injection of $\text{CH}_3\text{CN}$ compared to the uptake in its absence is very small but significant. The fact that there is additional uptake supports the proposal that reduction of $\text{CH}_3\text{CN}$ is occurring.
The lack of $\mathrm{H}_2$-uptake when $7$ is added directly to a DMA/CH$_3$CN solution indicates that initial loss of a coordinated acetonitrile ligand is necessary for catalytic activity. The $^{31}\mathrm{P}^{-1}\mathrm{H}$-n.m.r. spectrum of $7$ in CD$_2$Cl$_2$ shows a singlet (38.7 ppm) which was assigned to a 5-coordinate species since addition of CH$_3$CN caused this resonance to disappear. This is consistent with the uptake data, since generation of a vacant site for $\mathrm{H}_2$-coordination would be necessary for initial hydride generation (equations 6.8 and
6.9); in the presence of CH$_3$CN the dissociation would not be favoured.

\[ \text{[RuCl(dppb)(CH}_3\text{CN)}_3]^+PF_6^- \rightarrow \text{[RuCl(dppb)(CH}_3\text{CN)}_2]^+PF_6^- + \text{CH}_3\text{CN} \] (6.8)

\[ \text{[RuCl(dppb)(CH}_3\text{CN)}_2]^+PF_6^- \text{H}_2 \rightarrow \text{[RuH(dppb)(CH}_3\text{CN)}_2]^+PF_6^- + \text{HCl} \] (6.9)

The inflexion step observed in the H$_2$-uptake of 7, corresponding to ca. 1 equivalent of H$_2$, is consistent with formation of a hydrido-acetonitrile complex. This is probably the initially active species, but subsequent reduction of the acetonitrile generates presumably mono-, bis-, and tris-ethylamine complexes which must also be active. The addition of CH$_3$CN after 2-5 h is therefore to a solution containing an active species, and subsequent reduction occurs. For the tris-ethylamine complex to be active, it has to undergo dissociation to allow for coordination of the nitrile. The additional uptake obtained when CH$_3$CN is added is very slow, and suggests that dissociation of an ethylamine ligand is not favoured.

The reduction of nitriles to amines has been accomplished by a number of transition metal complexes$^{63}$. Ruthenium complexes that catalyse this process include$^{164}$ RuCl$_2$(PPh$_3$)$_2$, RuHCl(CO)(PPh$_3$)$_3$, Ru$_2$(PMePH$_2$)$_4$ and RuHCl(CO)(PPh$_3$)$_3$, but forcing condition are required (10-120 atm. H$_2$, 20-130°C). Cenini et al.$^{165}$ have studied some catalytic properties of amine complexes derived from RuCl$_2$(PPh$_3$)$_3$. Unlike the present study, however, their investigations have been directed towards the reverse reaction,
oxidation of amines to nitriles, and under mild conditions (1 atm. O₂, 80°C) have successfully converted benzylamine to benzonitrile.

Complex 7 is also capable of reducing other unsaturated substrates. The reduction of simple alkenes and the imine, N-(2-phenylpropylidene)-2-propyl-amine, proceed at significantly faster rates compared to the reduction of acetonitrile. The increased rates suggest that these substrates are capable of displacing the coordinated CH₃CN, and thereby prevent formation of less-active ethylamine species. The reduction of the imine to N-(2-phenylpropyl)-N-(2-propyl)amine is also expected to lead to the formation of Ru-amine complexes, but since the amine is bulky, it is likely to bind considerably weaker than ethylamine. This is consistent with the high turnover and measured rate, although the observed fall-off in rate with time indicate formation of less-active species. In order to determine if the less-active species arise from the reduced imine or from ethylamine, it will be necessary to prepare a complex analogous to 7 but with non-reducible solvent ligands.

The reduction of imines is a relatively undeveloped field compared to the reduction of other unsaturated substrates. Catalysts capable of imine-reduction include phosphine complexes of Rh⁶⁶-⁷¹, Os⁶⁹ and Ru⁶⁹, Rh(pyridine)₃Cl₃ ¹⁷², and Fe(CO)₅ ¹⁷³. Of particular interest would be the use of a chiral phosphine in the present study as to date only modest enantiomeric excesses have been obtained for the asymmetric reduction of prochiral imines¹⁷⁰,¹⁷¹.
CHAPTER VII

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The aim of the work described in this thesis was to develop synthetic routes for the preparation of ruthenium complexes containing one ditertiary phosphine ligand per metal centre. Incorporation of a chiral ditertiary phosphine ligand, would then allow these complexes to be tested as potential asymmetric hydrogenation catalysts. Due to the high cost of chiral phosphines most of the investigations in the present study were limited to nonchiral phosphines, in particular dppb. Several important findings are summarised below, together with some suggestions for future work.

The mixed-valence complexes, $\text{Ru}_2\text{Cl}_5(P-P)_2$, $P-P =$ chiraphos, norphos, dppp, diop, or dppb were synthesised by phosphine exchange from a mononuclear Ru(III) starting compound in hexanes:

$$\text{RuCl}_3(P)_2 + P-P \rightarrow 0.5 \text{Ru}_2\text{Cl}_5(P-P)_2$$

$P=\text{PPH}_3$ or $\text{P(p-toly)}_3$

The phosphine exchange was dependent on the monodentate phosphine precursor, and appears to have limited application as attempts to prepare the mixed-valence dppe analogue were unsuccessful using either
the \( \text{PPh}_3 \) or \( \text{P(p-tolyl)}_3 \) complex. Hexanes were chosen as solvent as the ruthenium complexes are insoluble throughout the reaction whilst the phosphines (either added or liberated) are soluble, thereby facilitating easier separation. The use of a higher boiling point solvent (i.e. octane), or a solvent in which the ruthenium complexes are slightly soluble (i.e. benzene), might improve the phosphine exchange to include all bidentate phosphines, and eliminate the need for different monodentate phosphine precursor complexes.

A single crystal X-ray determination of \( \text{Ru}_2\text{Cl}_5(\text{chiraphos})_2 \) showed the complex to be triply chloro-bridged, with the desired one ditertiary phosphine per ruthenium (structure 7.1). The structure for the \( \text{P-P = norphos, dppb, diop or dppb analogues} \) are believed to be the same, but this has not been proven unambiguously.

The solution properties of the \( \text{Ru}_2\text{Cl}_5(\text{P-P})_2 \) complexes were most conveniently studied by examination of the intervalence charge transfer transitions in the near-infrared spectra. The chiraphos derivative exhibits strong solvent dependencies with absorptions due to at least two species. For example, in \( \text{CDCl}_3 \) the principle absorption is at low energy (ca. 2350 nm), and is assigned to the complex having
the same structure in solution as in the solid state. In CCl₄ the low
energy absorption is broad and unresolved, but there is a more intense
absorption at 880 nm. The tentative assignment of the high energy
absorption to a tetranuclear species needs substantiating if the
solution properties of Ru₂Cl₅(chiraphos)₂ are to be fully
understood.

The intervalence charge transfer transitions for the other
phosphine analogues were not so extensively studied. Preliminary
investigations, however, show these to exhibit unique near-infrared
spectra compared to the chiraphos complex in the same solvent.

The reaction of the Ru₂Cl₅(P-P)₂ complexes with H₂ in DMA
generated in situ ionic diruthenium(II) complexes:

\[
\text{Ru}_2\text{Cl}_5(P-P)_2 + 0.5 \text{H}_2 \rightarrow \left[\text{Ru}_2\text{Cl}_5(P-P)_2\right]^+ \text{DMAH}^+ \quad (7.2)
\]

The reduction was found to be autocatalytic, but attempts to ascertain
mechanistic details by kinetic measurements of the H₂-uptake, or
changes in visible spectrum were unsuccessful. This is presumably due
to the presence of more than one species (near-i.r. evidence), which was
not determined until later.

From the ionic product generated in situ (equation 7.2) the
neutral complexes, [RuCl₂(P-P)]₂, were isolated by addition of
methanol to displace the HCl generated by reduction. For P-P =
chiraphos or diop, the complexes were more conveniently prepared by
reduction in toluene in the presence of added based, polyvinylpyridine.
The [RuCl$_2$(P-P)]$_2$ complexes in non-coordinating solvents, all exhibit 31P{$^1$H}-n.m.r. spectra consistent with the dimeric formulation:

In the presence of coordinating solvents (acetone or DMA), [RuCl$_2$(chiraphos)]$_2$ and the dppb analogue were shown by 31P{$^1$H}-n.m.r. to adopt a triply chloro-bridged structure with coordination of one solvent molecule:

DMA solutions of [RuCl$_2$(P-P)]$_2$, P-P = chiraphos or diop catalysed the asymmetric hydrogenation of prochiral alkenes. The rate of hydrogenation, product configuration, and % e.e. varied considerably, with the nature of the chiral phosphine, and of the substrate, being significant factors in the overall process. The most notable result was an observed hydrogenation of (Z)-α-acetamidocinnamic acid with 97% e.e. using the chiraphos complex. Steric factors arising from the bulky phenyl group on this substrate appear important, and could be easily...
substantiated by hydrogenating other substituted α-aminoacrylic acids.

The hydrogenation study also showed the % e.e. to increase with lowering the temperature for essentially all the substrates used, and for both complexes. In order to explain the unusual temperature dependence, and the efficient hydrogenation of (Z)-α-acetamidocinnamic acid it will be necessary to obtain mechanistic details. This might be achieved by using the [RuCl₂(P-P)]₂ complexes, but ideally the active hydrido-species should be isolated, and used for n.m.r. and kinetic studies of the hydrogenation process.

Attempts to isolate such a hydrido-species from [RuCl₂(P-P)]₂ were unsuccessful. The reaction of DMA solutions of the dppb complex with H₂ in the presence of Proton Sponge did generate a hydride complex (¹H-n.m.r. evidence), although the principle product isolated was [Ru₂Cl₅(dppb)₂]⁻PSH⁺. This ionic product is formed by addition of the HCl (as PSH⁺Cl⁻), generated by reduction, to the starting complex. An improved preparative procedure is clearly required if the hydride complex is to be isolated pure. This might be achieved using a different base, such as NEt₃. Protonation of NEt₃ generates a smaller cation which might not stabilise [Ru₂Cl₅(dppb)₂]⁻ to the same extent as PSH⁺, thereby inhibiting anion formation. Alternatively the use of LiAlH₄ or its derivatives would eliminate the need for HCl removal.

Further attempts to generate a hydrido-complex led to the preparation and characterisation of RuCl₂(nbd)(dppb), and a brief investigation of the reaction with H₂. A single crystal X-ray
determination showed the complex to be mononuclear with coordinated
dialkene, but in solution the complex was found to undergo dissociation:

\[
\text{RuCl}_2(\text{nbd})(\text{dppb}) \rightarrow 0.5 \left[\text{RuCl}_2(\text{P-P})\right]_2 + \text{nbd} \quad (7.3)
\]

The reaction with H\textsubscript{2} in the presence of Proton Sponge generated a
hydride complex (n.m.r. evidence) which is thought to be
RuHCl(\text{nbd})(\text{dppb}), but again the major product of the reaction was
\([\text{Ru}_2\text{Cl}_5(\text{dppb})_2]^{+}\text{PSH}^{\text{+}}\). The formation of a hydrido-alkene
complex in the presence H\textsubscript{2} is unexpected, and merits further
investigation. The isolation of RuHCl(\text{nbd})(\text{dppb}) in high yield could
possibly be achieved by reducing RuCl\textsubscript{2}(\text{nbd})(\text{dppb}) in the presence of
excess norbornadiene, or by using a different base. An alternative
route via addition of norbornadiene to an isolated hydrido-complex is
the most attractive; however, this requires a suitable method for
generation of a precursor hydride complex (vide supra).

The isolation of RuH\textsubscript{2}(\text{CO})Cl\textsubscript{2}(\text{dppb})\textsubscript{2} by stirring a
CH\textsubscript{2}Cl\textsubscript{2}/MeOH solution of Ru\textsubscript{2}Cl\textsubscript{4}(\text{dppb})\textsubscript{2}(acetone).acetone with
Proton Sponge, was unexpected. The product is thought to form by
successive hydrogen atom transfers from a Ru-methoxide intermediate,
although mechanistic details are needed. Whilst not related to the
hydrogenation studies previously discussed, the catalytic properties of
Ru\textsubscript{2}H\textsubscript{2}(\text{CO})Cl\textsubscript{2}(\text{dppb})\textsubscript{2} should be examined. Assuming the complex
to be kinetically active, application as a transfer hydrogenation
catalyst using methanol or higher alcohols appears feasible.
The reaction of $\text{Ru}_2\text{Cl}_5(\text{dppb})_2$ and $\text{Ru}_2\text{Cl}_4(\text{dppb})_2(\text{acetone})$ with the appropriate amount of $\text{AgPF}_6$ produces mono- and dinuclear cationic complexes. Of these the complex $[\text{RuCl}(\eta^6\text{-toluene})(\text{dppb})]^+\text{PF}_6^-$ is particularly interesting due to the presence of coordinated toluene. The $^1\text{H-n.m.r.}$ of this complex exhibits a separation and upfield shift of the ortho-, meta-, and para-protons of the coordinated toluene relative to free toluene. The development of such $\pi$-arene complexes is therefore potentially useful as n.m.r. shift reagents for aromatic rings. The procedure for isolation of this $\pi$-arene complex negates general application, but using $[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$ as an in situ reagent seems feasible. The acetonitrile ligands of this complex are labile ($^{31}\text{P}\{^1\text{H}\}$-n.m.r. evidence), and should be easily displaced by an arene ligand.

The $[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+\text{PF}_6^-$ complex is also of interest for its apparent ability to hydrogenate nitrile and imine substrates. In the absence of substrate the complex reacts with hydrogen with a stoichiometry of 1.0 Ru:6.85 $\text{H}_2$. This is consistent with reduction of the acetonitrile ligands to ethylamine:

$$[\text{RuCl}(\text{dppb})(\text{CH}_3\text{CN})_3]^+\text{PF}_6^- \xrightarrow{7\text{H}_2} [\text{RuCl}(\text{dppb})(\text{C}_2\text{H}_5\text{NH}_2)_3]^+\text{PF}_6^- \quad (7.4)$$

The proposed product was not isolated due to complications arising from anion exchange, and an alternative procedure is necessary.
The catalytic reduction of the acetonitrile and imine were shown to occur by $H_2$-uptake beyond that found for the complex in the absence of substrate. The reduction of acetonitrile is extremely slow. This is thought to be due to the trisethylamine complex (equation 7.4) having to undergo ligand dissociation in order to further reduce acetonitrile. As the hydrogenation proceeds the concentration of ethylamine increases, and therefore the dissociation of ethylamine ligand will be less favoured. A physical means of removing the ethylamine is required, possibly by conducting the reduction in acidic media, although this might inhibit initial hydride formation.

The reduction of the imine using $[\text{RuCl(dppb)(CH}_2\text{CN})_3]^{+}\text{PF}_6^-$ was considerably faster than that found for the reduction of acetonitrile. The presence of reducible acetonitrile ligand clearly complicates the study. In order to investigate the imine hydrogenation successfully, it will be necessary to have a non-reducible labile ligand for the $\text{RuCl(dppb)}^+$ moiety. If such a catalytic system can be developed, the incorporation of a chiral phosphine will allow for the asymmetric hydrogenation of prochiral imines.
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