2 Reactions of $[\text{Ru}(L^1)(L^2)(\text{dmpe})_2]$  
($L^1 = \text{Cl}; L^2 = \text{Cl, H}$)

2.1 Introduction

Alkylphosphine ligands are strongly electron donating $\sigma$-donor ligands,\(^1\) and are stronger $\sigma$- and $\pi$-donors than their arylphosphine counterparts.\(^2\,^3\) This is manifest in the stronger activation of $N_2$ by depe as compared to dppe in complexes of the type $[\text{M}(N_2)_2(P-P)_2]$ ($\text{M} = \text{W, Mo};$ $P-P = \text{depe or dppe}$) or $[\text{Fe}(N_2)(P-P)_2]$.\(^3\,^4\) Alkylphosphine ligands frequently allow coordinatively unsaturated electron-rich complexes to be isolated,\(^5\) which are good targets for dinitrogen coordination in the absence of competing ligands or donor solvents.\(^6\,^7\) Despite these advantages, chelating alkylphosphine ligands have been investigated less than their chelating arylphosphine counterparts.\(^1\)

Dinitrogen complexes of iron(II) with a bis diphosphine ligand set are relatively common. $\text{trans-[FeHCl(depe)}_2]$, reacts with $\text{Na(BPh}_4)$ in acetone under $N_2$ to yield $\text{trans-[FeH(N}_2)(\text{depe)}_2](\text{BPh}_4)$,\(^8\) and $\text{trans-[FeH(N}_2)(\text{dppe)}_2]^+$ can be prepared by reaction of the five-coordinate species $\text{trans-[FeH(dppe)}_2]^+$ with $N_2$ in tetrahydrofuran.\(^3\) Similar complexes, such as $\text{[FeH}_2(N_2)(\text{PEtPh)}_2]$\(^9\) $\text{[FeH(N}_2}\{\text{P(}CH_2CH_2\text{PPh)}_2]\}^+$,\(^10\) $\text{[FeH(N}_2}\{\text{N(}CH_2CH_2\text{PPh)}_2\}^+$\(^10\) and $\text{[FeH(N}_2}\{(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\}_2\}]^+$\(^11\) have also been described.
Analogous dinitrogen complexes in which the hydride ligand is replaced by a chloride are less common, however, those which exist can be prepared quite simply. The green complex $[\text{FeCl}_2\text{(dmpe)}_2]$ dissolves in tetrahydrofuran under $N_2$, to give a green solution, yet in alcohol solvent the colour of the dissolved species ranges from orange to purple, depending upon its concentration. The addition of Na(BPh$_4$) to such a solution under $N_2$ gives a red crystalline solid, $\text{trans-}[\text{FeCl}(N_2)(\text{dmpe})_2]\text{(BPh}_4)$, with a strong $\nu_{\text{NN}}$ evident at 2105 cm$^{-1}$ in the infrared spectrum. When the analogous reaction is attempted with $[\text{FeCl}_2\text{(depe)}_2]$, dinitrogen coordination is similarly observed and an orange crystalline solid can be isolated by the addition of Na(BPh$_4$), but the nitrogen content varies from preparation to preparation and is always less than 1:1, despite the presence of a strong $\nu_{\text{NN}}$ absorption at 2081 cm$^{-1}$. Attempts at preparing $[\text{FeCl}(N_2)(\text{dmpe})_2]^+$ by reaction of $[\text{FeCl}_2\text{(dmpe)}_2]$ with either Ag(BF$_4$) or Tl(BF$_4$) in tetrahydrofuran or toluene under $N_2$ have been unsuccessful, thus highlighting the importance of solvent choice.

The complexes $\text{trans-}[\text{FeCl}_2\text{(dmpe)}_2]$ and $\text{trans-}[\text{FeCl}(H)(\text{dmpe})_2]$ will also react directly with ammonia or hydrazine (Scheme 2.1), both of which are ligands that are of interest within the area of nitrogen fixation chemistry.
The N$_2$ ligands in ruthenium complexes are somewhat more stable than those found in analogous Fe$^{II}$ derivatives,\textsuperscript{16,17} and as such, mono- and dinuclear ruthenium N$_2$ species have been the focus of research for those attempting to model iron-dinitrogen interactions and stabilise reactive intermediates.\textsuperscript{17} However, despite the stability of the ruthenium-dinitrogen bond and the long history of ruthenium dinitrogen complexes, relatively few classes of ruthenium dinitrogen complexes are known.

In this work, attention was focussed on the preparation of chloro-dinitrogen bis diphosphine complexes in place of the more commonly reported hydrido-dinitrogen complexes on the basis that the
presence of a chloride ligand *trans* to the coordinated dinitrogen will serve to ‘activate’ the NN bond to a greater extent than a *trans* hydride ligand owing to the fully occupied orbitals of the chloride ligand repelling the metal d$_\pi$ electrons, thus placing greater d$_\pi^*$ electron density on the N$_2$ ligand.$^{18}$

### 2.2 X-ray crystal structure of *trans*-[*RuCl$_2$(dmpe)$_2$*]

[*RuCl$_2$(dmpe)$_2$*] was selected as the starting material for most reactions in this work due to a number of favourable properties. Abstraction of a chloride ligand from [*RuCl$_2$(dmpe)$_2$*] leaves a chloride within the inner coordination sphere, both *cis*$^{19}$ and *trans*$_{20}$ isomers are readily prepared in high yield and high isomeric purity, and the analogous iron complex *trans*-[*FeCl$_2$(dmpe)$_2$*] facilely reacts with dinitrogen in ethanol to form *trans*-[*FeCl(N$_2$)(dmpe)$_2$]*Cl$^{12,13}$

*Trans*-[*RuCl$_2$(dmpe)$_2$*] was synthesised by heating at reflux a solution of RuCl$_3$.xH$_2$O with an excess of *bis*(dimethylphosphino)ethane in aqueous ethanol. Large yellow crystals of *trans*-[*RuCl$_2$(dmpe)$_2$*] were formed by slow evaporation of a benzene solution, and an X-ray crystal structure analysis was undertaken as it has not been reported in the literature and also for comparison with subsequent complexes reported in this work.

The asymmetric unit contains halves of two crystallographically independent complex molecules located on inversion centres, and two
complex molecules on general sites. An ORTEP depiction of one of the molecules situated on an inversion centre is provided in Figure 2.1.

Figure 2.1 – ORTEP diagram of one \( \text{trans-}[\text{RuCl}_2(\text{dmpe})_2] \) molecule in the unit cell at 50% displacement ellipsoids

Table 2.1 – Selected bond lengths and angles in \( \text{trans-}[\text{RuCl}_2(\text{dmpe})_2] \)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-P(2)</td>
<td>2.3186(6)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.3234(7)</td>
</tr>
</tbody>
</table>
The geometry about the ruthenium metal is slightly distorted from octahedral due to a chelate bite angle of 83.83(2)° imposed by the bidentate phosphine ligand, whilst the angle between adjacent phosphorus atoms of unique dmpe ligands is larger than 90° (96.17(2)°). The Ru-P bond lengths differ marginally from each other at 2.3186(6) and 2.3234(7) Å.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)-Ru(1)-Cl(1)'</td>
<td>180</td>
<td>P(1)-Ru(1)-P(1)'</td>
<td>180</td>
</tr>
<tr>
<td>Cl(1)-Ru(1)-P(1)</td>
<td>89.642(18)</td>
<td>P(1)-Ru(1)-P(2)'</td>
<td>96.17(2)</td>
</tr>
<tr>
<td>Cl(1)-Ru(1)-P(1)'</td>
<td>90.358(18)</td>
<td>P(1)-Ru(1)-P(2)</td>
<td>83.83(2)</td>
</tr>
<tr>
<td>Cl(1)-Ru(1)-P(2)</td>
<td>86.483(18)</td>
<td>P(2)-Ru(1)-P(2)'</td>
<td>180</td>
</tr>
<tr>
<td>Cl(1)-Ru(1)-P(2)'</td>
<td>93.517(18)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3 Direct reactions of trans-[RuCl$_2$(dmpe)$_2$]

No reaction of trans-[RuCl$_2$(dmpe)$_2$] with dinitrogen (atmospheric pressure), hydrazine or ammonia in ethanolic solution was observed after one week, nor were any changes observed on heating the samples or after the addition of sodium tetraphenylborate. This is in direct contrast to the Fe analogue which reacts readily with such N-donors (Section 2.1) and could be due to the less labile chloride ligand in the ruthenium complex.
2.4 Direct reactions with trans-[RuCl(H)(dmpe)$_2$]

No reaction of trans-[RuCl(H)(dmpe)$_2$] with dinitrogen (atmospheric pressure), hydrazine or ammonia in tetrahydrofuran or ethanol was observed after one week or with heating. This again contrasts with the chemistry of [FeCl$_2$(dmpe)$_2$] and further confirms that the chloride ligand is strongly bound to ruthenium.

2.5 Reaction of trans-[RuCl$_2$(dmpe)$_2$] with chloride abstraction agents

The only literature example of a ruthenium bis-diphosphine dinitrogen complex with a coordinated chloride ligand is the complex trans-[RuCl(N$_2$)(R,R-CHIRAPHOS)$_2$]$^+$, which is formed by the abstraction of a chloride ligand from trans-[RuCl$_2$(R,R-CHIRAPHOS)$_2$] using silver triflate in dichloromethane.$^{21}$ This agrees with the generally observed trend for halo-ruthenium complexes in which halide abstraction typically requires a stronger agent than Na$^+$ salts, usually Ag$^+$ or Tl$^+$ derivatives.$^7,22$ Thus, an approach to dinitrogen complexes of the form [RuCl(N$_2$)(P-P)$_2$]$^+$ (P-P = dmpe, depe) involving the abstraction of a single chloride from [RuCl$_2$(P-P)$_2$] with appropriate chloride scavengers was devised.
2.5.1 **Treatment of trans-[RuCl₂(dmpe)₂] with Ag(OTf) in dichloromethane**

Treatment of the yellow complex trans-[RuCl₂(dmpe)₂] with Ag(OTf) in dichloromethane under a dinitrogen atmosphere resulted not in the anticipated abstraction of chloride, but in oxidation of the ruthenium centre to ruthenium(III) and precipitation of metallic silver (Scheme 2.2).

\[
\begin{align*}
\text{Cl}_2\text{RuCl}_2\text{P}_2\text{P}_2\text{P}_2\text{Cl}_2\text{RuCl}_2\text{P}_2\text{P}_2\text{P}_2\text{Cl}_2 & \quad + \quad \text{Ag(OTf)} \\
& \quad \xrightarrow{\text{N}_2} \\
\text{Cl}_2\text{Ru}^{\text{III}}\text{Cl}_2\text{P}_2\text{P}_2\text{P}_2\text{Cl}_2\text{RuCl}_2\text{P}_2\text{P}_2\text{P}_2\text{Cl}_2 & \quad + \quad \text{Ag(s)}
\end{align*}
\]

Scheme 2.2

The paramagnetic complex trans-[RuCl₂(dmpe)₂](OTf) has an intense blue colour that is characteristic of ruthenium(III), and the \(^1\text{H}\) NMR spectrum reveals the methyl and ethylene resonances that have been paramagnetically shifted 18 ppm upfield to \(-17.32\) and \(-14.13\) ppm respectively (Figure 2.2). The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum exhibits no observable resonances, which is due to the close proximity of the phosphorus atoms to the paramagnetic centre. The complex could be readily crystallised from dichloromethane upon the addition of diethyl ether to give an analytically pure sample in 89% yield.
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Figure 2.2 – $^1\text{H}^{(31}\text{P})$ NMR spectrum ($d_8$-thf, 400 MHz) of trans-
$[\text{RuCl}_2(\text{dmpe})_2](\text{OTf})$, displaying paramagnetically shifted methyl (●) and
ethylene (◊) proton resonances

The X-ray crystal structure analysis reveals an asymmetric unit containing a trans-$[\text{RuCl}_2(\text{dmpe})_2]^+$ molecule and a triflate counter-ion, with the ruthenium atom being centred on an inversion site and the counter-ion residing on a mirror plane. Due to the inversion centre, there are only three unique ruthenium-ligand bonds. An ORTEP depiction of the molecule is presented in Figure 2.3, and pertinent bond lengths and angles are summarised in Table 2.2.
Figure 2.3 – ORTEP diagram of trans-\([\text{RuCl}_2(\text{dmpe})_2]\)(OTf) shown with 50% displacement ellipsoids

Table 2.2 – Selected bond lengths and angles in trans-\([\text{RuCl}_2(\text{dmpe})_2]\)(OTf)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th></th>
<th>Bond angles (°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-Cl(1)</td>
<td>2.3382(6)</td>
<td>Cl(1)-Ru(1)-Cl(1)'</td>
<td>180</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.3803(6)</td>
<td>P(1)-Ru(1)-P(1)'</td>
<td>180</td>
</tr>
<tr>
<td>Ru(1)-P(2)</td>
<td>2.3915(6)</td>
<td>Cl(1)-Ru(1)-P(1)</td>
<td>92.308(16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1)-Ru(1)-P(2)'</td>
<td>97.60(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl(1)-Ru(1)-P(1)'</td>
<td>87.692(16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1)-Ru(1)-P(2)</td>
<td>82.40(2)</td>
</tr>
</tbody>
</table>
The geometry about the central ruthenium is essentially unchanged compared to the Ru(II) starting material (Section 2.2). However, the ruthenium-chloride bond lengths are shorter by 0.1052 Å, providing further confirmation of the trivalent state of the metal. A corresponding increase of 0.0649 Å was observed in the average ruthenium-phosphine bond lengths.

The chemistry of trans-\([\text{RuCl}_2(\text{dmpe})_2](\text{OTf})\) will be elaborated upon in Section 2.7.

### 2.5.2 Treatment of trans-\([\text{RuCl}_2(\text{dmpe})_2]\) with TMS(OTf) in toluene

Attempts to achieve chloride abstraction with trimethylsilyl (TMS) triflate in toluene also resulted in ruthenium oxidation to give trans \([\text{RuCl}_2(\text{dmpe})_2](\text{OTf})\), though in a slightly reduced yield of 65%. Such oxidation presumably occurs via a one electron transfer from ruthenium to TMS(OTf) to form the radical species TMS\(^\cdot\), which, in the absence of suitable reactants, would then dimerise to give hexamethyldisilane (Scheme 2.3). Since no attempts were undertaken to identify any such species, the exact mechanism of this process remains unknown.
2.5.3 Treatment of trans-[RuCl$_2$(dmpe)$_2$] with Tl(OTf) in tetrahydrofuran

Thallium salts have frequently been employed in place of silver reagents when less oxidising conditions are needed.$^{24}$ The use of thallium triflate in place of silver triflate thus reduces the possibility of oxidising the ruthenium(II) centre to ruthenium(III).

Reaction of trans-[RuCl$_2$(dmpe)$_2$] with thallium triflate in tetrahydrofuran heated at reflux resulted in the precipitation of a white solid and the formation of a solution that changed colour between yellow and green depending upon the temperature of the solution and the length of time under N$_2$. At ambient temperature, the $^{31}$P{$^1$H} NMR spectrum of the isolated product reveals no observable signal other than a trace of residual trans-[RuCl$_2$(dmpe)$_2$], but cooling the sample down to 180 K results in the observation of a large single resonance at 41.1 ppm (Figure 2.4).
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Reactions of $[\text{Ru}(L^1)(L^2)(\text{dmpe})_2]$  

180 K

210 K

240 K

270 K

300 K

330 K

PPM 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31

**Figure 2.4 – Variable temperature $^{31}\text{P}^{(1}\text{H})$ NMR spectra ($d_8$-thf, 162 MHz) of $^{"\text{trans-}[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl(OTf)}"}$ ($\diamond$). Residual starting material (●).**

The chemical shift of $\delta_p$ 41.1 ppm is uncorrected for chemical shift drift with changing temperature, as all spectra were referenced to ambient temperature trimethylphosphite.

Analysis of the complex by IR spectroscopy reveals only CH and fingerprint stretches, whilst MALDI-MS exhibits predominantly the fragment ion $[\text{RuCl}(\text{dmpe})_2]^+$. Slow recrystallisation from acetone with pentane resulted in the formation of red crystals, that upon dissolution in tetrahydrofuran gave a yellow solution, spectroscopically identical to the initial reaction.
mixture. An X-ray crystal structure analysis identified the product as the mixed Ru/Tl species shown in Figure 2.5.

Figure 2.5 – Approximate repeating unit in a crystal of "trans-\([\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl(OTf)}\)". showing the tetrahedral arrangement of trans-\([\text{RuCl}_2(\text{dmpe})_2]\) molecules around each thallium atom. Hydrogen atoms, counter-ions and incorporated solvent molecules removed for clarity.
The structure consists of \textit{trans}-[RuCl\textsubscript{2}(dmpe)\textsubscript{2}] molecules tetrahedrally arranged around each thallium atom, with short contacts evident between the central thallium and the adjacent four chlorine atoms (average 3.02 Å). Each [RuCl\textsubscript{2}(dmpe)\textsubscript{2}] molecule interacts with a thallium atom at both chloride ligands, thus the structure may alternatively be considered to consist of staggered chains of \{[RuCl\textsubscript{2}(dmpe)\textsubscript{2}]Tl\}_n that are linked by \textit{trans}-[RuCl\textsubscript{2}(dmpe)\textsubscript{2}] bridges in three dimensions (Figure 2.6). Also incorporated into the unit cell are triflate counter-ions and solvent of crystallisation (acetone), both of which lie between the \{[RuCl\textsubscript{2}(dmpe)\textsubscript{2}]Tl\}_n chains.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_6.png}
\caption{Selected atoms in an isolated slice through the crystal of "\textit{trans}-[RuCl\textsubscript{2}(dmpe)\textsubscript{2}]\cdot\text{OTf}". Each thallium atom is further linked to [RuCl\textsubscript{2}(dmpe)\textsubscript{2}] either above or below the plane. Hydrogen atoms, counter-ions and incorporated solvent molecules removed for clarity.}
\end{figure}
In solution, this complex may be thought of as either trans-[RuCl(ClTl)(dmpe)$_2$](OTf) with thallium chloride occupying the vacant ruthenium coordination site, or as trans-[RuCl$_2$(dmpe)$_2$]·Tl(OTf), where thallium triflate is interacting with the ruthenium-chloride bond. Whichever view is chosen, the interaction with the thallium, whilst weak enough to remain fluxional on the NMR time scale at temperatures above 180 K, remains sufficient to prevent coordination of dinitrogen under one atm pressure. This chemistry is reminiscent of the behaviour observed during the reaction of trans-[RuCl$_2$(dppen)$_2$] (dppen = (Ph$_2$P)$_2$CCH$_2$) with silver triflate or silver tetrafluoroborate at ambient temperature in 1,2-dichloroethane (dce), in which an observable colour change (evident without precipitation) was attributed to the formation of the non-fluxional trans complex [RuCl(dppen)$_2$($\mu$-Cl)Ag]X (X = BF$_4$ or OTf).$^{25}$

Structures containing thallium or thallium chloride bridges are not unknown in the literature. The ambient temperature reaction of [RuCl(dcypb)($\mu$-Cl)$_3$Ru(dcypb)(N$_2$)] (dcypb = 1,4-bis(dicyclohexylphosphino)butane) with Tl(OC$_6$F$_5$) and excess tert-butylacetylene yielded Tl[\{Ru(C≡C'Bu)(dcypb)\}_2($\mu$-Cl)$_3$] as a minor by-product,$^{26}$ where, in the solid state, the [Ru($\mu$-Cl)$_3$Ru] sub-unit contains a thallium atom covalently bonded to two of the bridging chloride atoms (Figure 2.7). A similar coordination environment has also been reported for [Ru(dppe)$_2$($\mu$-F)$_2$](Tl)(PF$_6$)$_2$.}$^{27}$
Figure 2.7 – ORTEP diagram of Tl\{Ru(CCtBu)(dcypb)}_2(u-Cl)_3, containing a bridging TlCl_2 moiety (figure reproduced from Fogg et. al.\textsuperscript{26})

A more comparable example is the complex (P\textsubscript{2})PdCl\textsubscript{2}·Tl(OTf) (P\textsubscript{2} = \textit{o}-dimethyl-\textit{bis}(diphenylphosphino)tetrathiafulvalene) (Figure 2.8), which was formed by an attempted abstraction of chloride from (P\textsubscript{2})PdCl\textsubscript{2} with thallium triflate.\textsuperscript{28} Rather than effecting chloride abstraction, the thallium atom of Tl(OTf) bridged two Pd-Cl moieties to form a Pd-Cl-Tl-Cl-Pd unit. An identical complex geometry was obtained for the platinum analogue.\textsuperscript{28}
Another relevant example is the reaction of \([\text{RuCl}_2(\text{PPh}_3)([9]\text{aneS}_3)])\), ([9]aneS = 1,4,7-trithiacyclononane) with Tl(PF$_6$) in dichloromethane to form the tetranuclear hetero-cluster species \([\text{TlCl}_2\text{Ru(PPh}_3)([9]\text{aneS}_3)]_2(\text{PF}_6)_2\) (Figure 2.9), which incorporates a \([\text{RuCl}_2\text{Tl}_2\text{Cl}_2\text{Ru}]\) ladder. Two octahedral \([\text{RuCl}_2(\text{PPh}_3)([9]\text{aneS}_3)])\) units are bridged via coordinated Cl$^-$ ligands to two Tl$^+$ ions, giving two $\mu^2$-Cl and two $\mu^3$-Cl bridges, with the two halves of the cation being related by an inversion centre. In a similar manner to the palladium complex reported above, such a structure may also be written as a thallium adduct of the form \([\text{RuCl}_2(\text{PPh}_3)([9]\text{aneS}_3)]\cdot\text{Tl(PF}_6)\). It was reported that dissolution of this complex in acetone resulted in precipitation of TlCl and subsequent formation of the chloro-bridged dimer \([\{\text{RuCl(PPh}_3)([9]\text{aneS}_3)\}_2]\cdot(\text{PF}_6)_2\).
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**Figure 2.9 – ORTEP diagram of [TlCl\textsubscript{2}Ru(PPh\textsubscript{3})([9]aneS\textsubscript{3})]_2(PF\textsubscript{6})_2** (figure reproduced from Schröder et al.\textsuperscript{29})

The complex trans-[RuCl\textsubscript{2}(dmpe)]\cdot Tl(OTf) reacted with both ammonia and hydrazine by displacement of the thallium chloride, forming complexes of the type trans-[RuCl(L)(dmpe)](OTf) (L = NH\textsubscript{3}, H\textsubscript{2}NNH\textsubscript{2}) (Scheme 2.4).

![Scheme 2.4](image)

Both complexes are yellow and have \textsuperscript{31}P chemical shifts which are very similar to that of trans-[RuCl\textsubscript{2}(dmpe)]\textsubscript{2}. This somewhat hinders unambiguous identification, however IR spectra of the isolated complexes clearly show NH stretches. \textsuperscript{15}N-\textsuperscript{1}H HSQC spectroscopy of the
ammonia complex reveals an N-H correlation at $\delta_N = -35$, $\delta_H = 2.54$ ppm. In comparison, the iron-ammonia complex trans-[FeH(NH$_3$)(dmpe)$_2$](BPh$_4$) displays a $^{15}$N resonance at −50.4 ppm with a $^1$H correlation at −0.09 ppm.$^{30}$

2.5.4 Treatment of trans-[RuCl$_2$(dmpe)$_2$]·Tl(OTf) with sodium borate salts

Anion exchange on the complex trans-[RuCl$_2$(dmpe)$_2$]·Tl(OTf) with either sodium tetraphenylborate or tetrafluoroborate in methanol resulted in formation of multiple uncharacterised species, as observed by $^{31}$P{$^1$H} NMR spectroscopy. The crude material isolated displays a low-intensity absorbance in the IR spectrum at 2139 cm$^{-1}$, suggesting that at least one of the multiple species formed contains a coordinated dinitrogen molecule.

2.5.5 Treatment of trans-[RuCl$_2$(dmpe)$_2$]·Tl(OTf) with Na(BArF$_{24}$)

The anion tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (BArF$_{24}$) is a highly soluble, non-coordinating counter-ion which, unlike tetraphenylborate, is durable against acid and oxidants.$^{31}$ Furthermore, in contrast to tetrafluoroborate, tetraphenylborate, and hexafluorophosphate, BArF$_{24}$ is non-reactive even with strongly electrophilic complexes.$^{32}$
Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate was prepared via magnesium-bromine exchange between isopropylmagnesium chloride and 1-bromo-3,5-bis(trifluoromethyl)benzene, followed by reaction with sodium tetrafluoroborate (Scheme 2.5).\(^{33}\)

![Scheme 2.5](image)

In contrast to anion exchange with tetraphenyl- or tetrafluoroborate, treatment of a methanolic solution of trans-[RuCl\(_2\) (dmpe)\(_2\)]·Tl(OTf) with Na(BArF\(_{24}\)) gave a single product. The solution remained yellow throughout and the \(^{31}\)P\(\text{{}^1H}\) NMR chemical shift of the product (39.0 ppm) is close to that of trans-[RuCl\(_2\) (dmpe)\(_2\)]. Nevertheless, MALDI-MS (Figure 2.10) reveals a strong parent ion at \(m/z\) 465 with an isotopic distribution consistent with [RuCl(N\(_2\))(dmpe)\(_2\)]\(^+\), and IR spectroscopy reveals a distinctive \(\nu_{NN}\) signal at 2012 cm\(^{-1}\), thus the product is assigned as trans-[RuCl(N\(_2\))(dmpe)\(_2\)](BArF\(_{24}\)) (Scheme 2.6).
The IR stretch of 2012 cm\(^{-1}\) is some 17 cm\(^{-1}\) more ‘activated’ than the lowest reported \(\nu_{NN}\) for a ruthenium complex in the literature (2029 cm\(^{-1}\) for \([\{\text{RuCl}(\text{NNNN})\}_2(\mu-\text{N}_2)\}]\),\(^{34}\) which reflects the electron-releasing nature of the complex.
2.5.6 Treatment of trans-[RuCl₂(dmpe)₂] with Na(BArF₂₄)

Direct chloride abstraction from trans-[RuCl₂(dmpe)₂] using Na(BArF₂₄) was also attempted under a dinitrogen atmosphere. Stirring a solution of trans-[RuCl₂(dmpe)₂] and Na(BArF₂₄) in methanol at ambient temperature for 12 hours resulted in no detectable reaction. Likewise, heating the solution at reflux for 12 hours resulted in no obvious changes (either visually or by NMR spectra), however after removal of the solvent, the yellow solid slowly turned green under an atmosphere of N₂. ³¹P{¹H} NMR spectroscopy of the sample reveals the presence of an unsymmetrical cis complex as the major reaction product (43%), with a significant proportion (31%) of a symmetrical cis complex (Figure 2.11). The two trans species at δP 34.7 and 34.6 ppm occur as 8 and 6% of the total reaction products respectively.

The IR spectrum clearly reveals two absorbances in the νNN frequency region at 2011 and 1964 cm⁻¹, however neither is of sufficient intensity to belong to the major complex. MALDI-MS only contains an ion at m/z 465 attributable to [RuCl(dmpe)₂]⁺, and Raman spectroscopy was unsuccessful due to sample decomposition under laser, as was typical of strongly coloured complexes prepared in this work (Chapter 7, Section 7.1).

The weak IR absorbance at 1964 cm⁻¹ occurs at a frequency more commonly associated with ruthenium-carbonyl complexes, and thus the minor trans species with the resonance at δP 34.6 ppm could feasibly be
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*trans*- [Ru(H)(CO)(dmpe)₂]⁺, as observed in Section 2.5.11, whilst the resonance at δₚ 34.7 ppm and the IR absorbance at 2011 cm⁻¹ are consistent with the formation of *trans*- [RuCl(N₂)(dmpe)₂]⁺ (Section 2.5.5).

The symmetrical *cis* complex formed in significant yield appears to be *cis*- [RuCl₂(dmpe)₂] on the basis of ³¹P{¹H} NMR chemical shifts (Chapter 7, Section 7.3.9).

The major *cis* unsymmetrical product is one of the few such dmpe complexes which remained non-fluxional on the NMR timescale at ambient temperature, indicating a reasonable degree of bond stability. With no Raman data available, the lack of an IR active dinitrogen stretch may lend consideration to a dinitrogen-bridged structure, however the ³¹P{¹H} chemical shifts of the *cis* unsymmetrical product are not in agreement with such a structure (Section 2.6.2), and the identity of the major species formed is not known.
Figure 2.11 – $^{31}$P($^1$H) NMR spectrum ($d_8$-thf, 162 MHz) of the reaction mixture of trans-[RuCl$_2$(dmpe)$_2$] + Na(BArF$_{24}$). ◊ – cis unsymmetrical; ● – cis-[RuCl$_2$(dmpe)$_2$]; * – trans-[RuCl($N_2$)(dmpe)$_2$](BArF$_{24}$); ■ – trans-[Ru(H)(CO)(dmpe)$_2$](BArF$_{24}$)

Scheme 2.7

It is of interest to note is that the trans dichloride starting material affords mostly cis products (cis-[RuCl$_2$(dmpe)$_2$] and the unknown unsymmetrical cis complex), however, such transformations have been noted before. The treatment of trans-[RuCl$_2$(dppen)$_2$] with two equivalents of Ag(OTf) in dichloroethane results in the formation of
cis-[Ru(OTf)$_2$(dppen)$_2$] and analogous transformations also occur for trans-[RuCl$_2$(P-P)$_2$] (P-P = dppm, dppe, dppen, dppa).$^{35}$

The most likely explanation for the observed isomerisation is that the semi-stable five-coordinate species [RuCl(dmpe)$_2$]$^+$, formed by abstraction of a chloride from trans-[RuCl$_2$(dmpe)$_2$], adopts a geometry in which ligand addition preferentially occurs cis to the chloride ligand due to steric protection of the trans face of the complex. This is a particular influence on the formation of cis-[RuCl$_2$(dmpe)$_2$], which is thermodynamically less stable than the trans isomer, yet is formed kinetically through the re-addition of chloride from dissolved NaCl (Scheme 2.8).

![Scheme 2.8](image)

### 2.5.7 Treatment of trans-[RuCl$_2$(dmpe)$_2$] with Ag(OTf) in methanol

It has long been established that solvent effects can modify the oxidative potential of many reagents.$^{36}$ Thus by suitable solvent choice, the propensity of the ruthenium(II) centre to undergo oxidation to
ruthenium(III) can be minimised. Methanol, in addition to reducing the oxidative power of many reagents,\textsuperscript{36} has a higher dielectric constant and polarity than both dichloromethane and tetrahydrofuran. These properties make methanol well suited to ion solvation,\textsuperscript{37} thereby increasing the likelihood of chloride abstraction from ruthenium. It has also been noted that the acid character of methanol can cause the solvent itself to act as a chloride-ion abstractor,\textsuperscript{12} and there is precedence for dinitrogen coordination to occur via loss of a chloride ion in methanol in situations where direct chloride abstraction using silver or thallium salts in tetrahydrofuran or toluene were unsuccessful.\textsuperscript{12}

The reaction of trans-\([\text{RuCl}_3(\text{dmpe})_2]\) with silver triflate in methanol resulted in the formation of a light blue solution and a white precipitate. Unlike the reaction in dichloromethane (Section 2.5.1), there are no paramagnetically shifted \(1^H\) alkyl resonances in the proton NMR spectrum in the region surrounding \(-16\) ppm, which rules out the formation of \([\text{Ru}^{\text{III}}\text{Cl}_2(\text{dmpe})_2](\text{OTf})\). \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy reveals the formation of two species, both of which are fluxional on the NMR timescale. The major species is a \(cis\) unsymmetrical complex, the \(^{31}\text{P}\) resonances of which are broad at ambient temperature. Variable temperature NMR spectroscopy reveals that these resonances continue to sharpen as the temperature is decreased to \(208\) K (Figure 2.12). Also present is an extremely fluxional \(trans\) complex, which only becomes visible at \(208\) K, as a broad resonance at \(\delta_{p} 39.4\) ppm which sharpened considerably at \(178\) K. The very similar \(^{31}\text{P}\) chemical shift (54.1 and
53.5 ppm) of the equatorial phosphine atoms of the cis complex suggests similar equatorial coordination environments for each.

![Variable temperature $^{31}$P($^1$H) NMR spectra](image)

Figure 2.12 – Variable temperature $^{31}$P($^1$H) NMR spectra ($d_8$-thf, 202 MHz) of the reaction mixture of trans-[RuCl$_2$(dmpe)$_2$] + Ag(OTf). ○ – cis-[RuCl(OTf)(dmpe)$_2$]; ● – trans-[RuCl(OTf)(dmpe)$_2$]

The IR spectrum displays no signals that could be interpreted as dinitrogen stretches, and Raman spectroscopy of the coloured solid was unsuccessful due to sample decomposition under laser.

MALDI-MS reveals the fragments [RuCl(dmpe)$_2$]$^+$ and, to a lesser extent, [Ru(OTf)(dmpe)$_2$]$^+$, which taken together with the NMR data may allow assignment of the products as a mixture of cis- and
trans-[RuCl(OTf)(dmpe)$_2$] (Scheme 2.9). However, subsequent reactions that did not involve triflate- or silver-containing reagents (Section 2.6.3) produce spectroscopically (NMR, IR) identical products, suggesting that the coordination site vacated by the abstracted chloride either remains vacant in solution or only weakly coordinates solvent (methanol; tetrahydrofuran). Nevertheless, microanalysis results are consistent with a formulation as [RuCl(OTf)(dmpe)$_2$], although whether the triflate is coordinated or not is not known.

![Scheme 2.9](image_url)

### 2.5.8 Treatment of trans-[RuCl$_2$(dmpe)$_2$] with TMS(OTf) in methanol

The reaction of trans-[RuCl$_2$(dmpe)$_2$] with TMS(OTf) in methanol in place of toluene generates an extremely fluxional trans complex that is barely observable via $^{31}$P{$^1$H} NMR spectra until the temperature is lowered to 198 K (Figure 2.13).
In the solid state IR spectrum, the complex displays a fingerprint region that closely resembles that of the species isolated from the reaction between \( \text{trans-}[\text{RuCl}_2(\text{dmpe})_2] \) and \( \text{Ag(OTf)} \) in methanol (Section 2.5.7). Such data leads to the identification of the complex as \( \text{trans-}[\text{RuCl(OTf)(dmpe)}_2] \) (Scheme 2.10), which conforms with the expected reduced oxidative potential of chloride abstraction agents when in methanol.

![Scheme 2.10](image-url)
Abstraction of a chloride from trans-[RuCl₂(dmpe)₂] using silver and trimethylsilyl triflate salts is obviously successful when performed in a suitable solvent such as methanol, yet in both cases the triflate anion coordinates in preference to dinitrogen. Consequently, it seems that the use of less coordinating anions is required. Similar results regarding preferential anion coordination have been previously described. For example, Higgins et al.³⁸ reported that, whilst treatment of Ru(II)-phosphine complexes with Ag(I) or Tl(I) salts of non-coordinating anions often results in the coordination of solvent to Ru(II) or the formation of Ru-Cl-M adducts,²⁶,²⁹,³⁹ treatment of trans-[RuCl₂(P-P)₂] (P-P = dppen, dppm, dppe) with two equivalents of Ag(OTf) in dichloroethane gave cis-[Ru(OTf)₂(P-P)₂].³⁵

2.5.9 Treatment of trans-[RuCl₂(dmpe)₂] with Tl(BArF₂₄) in methanol

Generation of a range of M(I) salts is rather facile for thallium(I) due to the availability of Tl₂CO₃ as a starting material. Treating Tl₂CO₃ with an appropriate acid produces the desired thallium salt, along with carbon dioxide and water as the only side-products. By choosing an appropriate solvent (such as acetonitrile), the thallium salt can be crystallised from solution in high yield and purity. Tl(BArF₂₄) is obtainable in this manner as the BArF₂₄ anion forms a stable acid salt, [H(OEt)₂]⁺(BArF₂₄), unlike the tetraphenylborate anion which is slowly degraded by the acid to form
As the BArF$_{24}^-$ anion is essentially non-coordinating, it was proposed that by utilising Tl(BArF$_{24}^-$) in methanol as the chloride abstraction agent oxidation of the ruthenium centre would be avoided whilst and metal-anion interactions minimised, providing optimal conditions for dinitrogen coordination.

Stirring a solution of trans-[RuCl$_2$(dmpe)$_2$] and Tl(BArF$_{24}^-$) in methanol under an atmosphere of dinitrogen at 40°C for 14 hours resulted in the precipitation of a fine white solid, tentatively identified as TlCl, and an intense light green solution. Filtering the solution through celite and removal of the solvent in vacuo resulted in a light green solid, which, upon washing with a small portion of benzene, afforded an air-sensitive yellow powder.

The resulting trans complex is fluxional in $d_8$-thf, with a $^{31}$P{$_1^1$H} NMR resonance that remain somewhat broadened at 198 K (Figure 2.14). The IR spectrum contains no absorbances indicative of dinitrogen coordination and, whilst the Raman spectrum displays a weak signal at 2263 cm$^{-1}$, this signal is not of sufficient intensity to be assigned as a part of the major complex.
Multiple MALDI-MS almost invariably feature only a single ion envelope, consistent with \([\text{RuCl(dmpe)}_2]^+\). Taken together, the data suggests a coordinatively unsaturated complex of the form \(\text{trans-}[\text{RuCl(dmpe)}_2]\text{(BArF}_{24}\text{)}\) (Scheme 2.11), although the \(\text{BArF}_{24}\) anion or solvent may interact with the vacant coordination site. Such a structure is unknown for ruthenium complexes containing sterically unhindered diphosphine ligands, however the complex \([\text{FeCl(dmpe)}_3]\text{(BPh}_4\text{)}\) is known, as is the monodentate phosphine complex \(\text{trans-}[\text{RuCl(PMe}_3\text{)}_4]\text{(BF}_4\text{)}\) and five-coordinate ruthenium complexes with bulkier aromatic diphosphine ligands are readily isolatable.
2.5.10 Treatment of \( \text{trans-}[\text{RuCl}_2(\text{dmpe})_2] \) with \( \text{Tl(BF}_4 \) in methanol

Replacing \( \text{Tl(BArF}_{24} \) with \( \text{Tl(BF}_4 \) in the reaction with \( \text{trans-}[\text{RuCl}_3(\text{dmpe})_3] \) resulted in similar behaviour, generating a \( \text{trans} \) species which is extremely fluxional on the NMR timescale (Figure 2.15).

![NMR spectra](image)

**Figure 2.15** - Variable temperature \( {^3P\{^1H\}} \) NMR spectra (\( d_8\)-thf, 202 MHz) of the reaction mixture of \( \text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Tl(BF}_4 \). ◊ - \( \text{trans-}[\text{RuCl(BF}_4 \) (dmpe)_2]}

One slight difference is the apparent increase in ionic nature, and thus insolubility, of the complex \( \text{trans-}[\text{RuCl(dmpe)}_2](\text{BF}_4 \) with respect to \( \text{trans-}[\text{RuCl(dmpe)}_2](\text{BArF}_{24} \), as filtering a methanolic solution of the
complex through celite resulted in significant product loss. Such a result is easily explained when considering the lipophilic nature of the BArF$_{24}$ anion and its ability to solubilise ionic complexes in organic solvents.$^{11}$

MALDI-MS spectra show strong ion envelopes at $m/z$ 522 and 568 (Figure 2.16), both of which contain chloride as determined by isotopic analysis and best fit a formula of the form [RuCl(dmpe)$_2$ + organic fragment]$^+$, as additional chloride or thallium atoms would distort the isotopic distribution. Whilst the ion envelope at $m/z$ 522 is tantalisingly close in mass to that expected for [RuCl(BF$_4$)(dmpe)$_2$]$^+$ ($m/z$ 524) the isotopic distribution precludes such an assignment.

![Figure 2.16 – MALDI-MS of the product from the reaction of trans-[RuCl(dmpe)$_2$] with Tl(BF$_4$) in methanol](image)

2.5.11 Treatment of trans-[RuCl$_2$(dmpe)$_2$] with Na(BPh$_4$)

under 140 psi N$_2$

Coordination of dinitrogen to ruthenium is hampered by competition for vacant coordination sites by numerous other potential ligands, including
solvent molecules and counter-ions. Dinitrogen coordination is further discouraged by the low solubility of dinitrogen in most organic solvents. One potential method of minimising both of these difficulties is to use pressures of dinitrogen that are much greater than atmospheric, effectively increasing the concentration of dinitrogen in solution.

Reaction between $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2]$ and Na(BPh$_4$) in either methanol or tetrahydrofuran at 150°C and 140 psi dinitrogen resulted in formation of a colourless solution containing two new $\text{trans}$ species as determined via $^{31}\text{P}$$\{^{1}\text{H}\}$ NMR (Figure 2.17).

![Figure 2.17 – $^{31}\text{P}$$\{^{1}\text{H}\}$ NMR spectrum (d$_8$-thf, 162 MHz) of the high N$_2$-pressure reaction of $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2]$ + Na(BPh$_4$). ◊ – $\text{trans-}[\text{RuCl(CO)(dmpe)}_2]^{+}$; ● – $\text{trans-}[\text{Ru(H)(CO)(dmpe)}_2]^{+}$](image-url)

These two complexes give rise to strong absorptions in the IR spectrum at 1957 and 1936 cm$^{-1}$, whilst MALDI-MS reveal ion fragments that suggest formulation as $[\text{Ru(H)(CO)(dmpe)}_2]^{+}$, and $[\text{RuCl(CO)(dmpe)}_2]^{+}$, with the presence of a metal hydride being verified by a resonance at $-9.48$ ppm in the $^{1}\text{H}$$\{^{31}\text{P}\}$ NMR spectrum. Thus, despite CO not being one of the reagents, the products of the reaction are
trans-[RuCl(CO)(dmpe)]_2^+ and trans-[Ru(H)(CO)(dmpe)]_2^+ (Scheme 2.12). The complexes are assigned as carbonyls rather than dinitrogen-containing structures due to the presence of characteristic and strong $\nu_{\text{CO}}$ stretching frequencies in the IR region, the higher of which matches that of the previously reported hydride complex. Furthermore, the $^{13}\text{C}$\{1H, $^{31}$P\} NMR spectrum confirms the presence of carbonyl ligands with resonances at 197.9 and 199.1 ppm that are attributable to the coordinated carbonyl groups.

![Scheme 2.12](image)

The presence of a chloride ligand trans to the coordinated carbon monoxide is predicted to ‘activate’ the CO bond to a greater extent than a trans hydride ligand owing to the fully occupied orbitals of the chloride ligand repelling the metal d$\pi$ electrons, thus placing greater d$\pi$ electron density on the CO ligand. Therefore, the resonance at $\delta_{\text{C}}$ 197.9 ppm is proposed to be that of trans-[RuCl(CO)(dmpe)]_2^+, whilst the resonance at $\delta_{\text{C}}$ 199.1 ppm belongs to trans-[Ru(H)(CO)(dmpe)]_2^+. The greater CO activation displayed by the chloride complex compared with the hydride analogue is affirmed by its lower CO stretching frequency in the IR spectrum of said complex. This difference between chloride and hydride complexes is a pertinent factor in the choice of [RuCl(N$_2$)(P-P)$_2$]$^+$
complexes as synthetic targets in this work, as isoelectronic dinitrogen is similarly expected to be additionally activated by the presence of a trans chloride ligand.

Good quality colourless crystals of trans-[RuCl(CO)(dmpe)$_2$]$^+$ were formed upon slow heptane vapour diffusion into dichloromethane solution. Preliminary X-ray crystal structure analysis reveals a monoclinic unit cell containing four repeating units consisting of trans-[RuCl(CO)(dmpe)$_2$]$^+$, a chloride counter-ion and a lattice water molecule. An ORTEP depiction of the molecule is provided in Figure 2.18, with selected bond lengths and angles presented in Table 2.3.
Figure 2.18 – ORTEP diagram of \textit{trans}-[RuCl(CO)(dmpe)$_2$](Cl) at 50% displacement ellipsoids

Table 2.3 – Selected bond lengths and angles in \textit{trans}-[RuCl(CO)(dmpe)$_2$](Cl)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-Cl(1)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
</tr>
<tr>
<td>Ru(1)-P(2)</td>
</tr>
<tr>
<td>Ru(1)-P(3)</td>
</tr>
<tr>
<td>Ru(1)-P(4)</td>
</tr>
<tr>
<td>Ru(1)-C(13)</td>
</tr>
<tr>
<td>C(13)-O(1)</td>
</tr>
</tbody>
</table>
The central ruthenium dmpe chloride moiety is only slightly distorted from octahedral, and the metal-ligand bond lengths are marginally longer (Ru-P$_{av}$ = 2.358) than those observed in [RuCl$_2$(dmpe)$_2$] (Ru-P$_{av}$ = 2.321, Section 2.2). The C-O bond length of 1.140 Å is not statistically different from that observed in trans-[RuCl(CO)(dppe)$_2$](BF$_4$) (1.172(24) Å), despite the weakly activated ν$_{CO}$ (1973 cm$^{-1}$) evident in the IR spectrum for this arylphosphine complex.$^{43}$

Overall, the reaction between trans-[RuCl$_2$(dmpe)$_2$] and Na(BPh$_4$) under such driving conditions (150°C, 140 psi N$_2$) is something of an anomaly. Not only has dinitrogen failed to coordinate, but carbon monoxide has been formed and coordinated in its stead – this behaviour is observed in both methanol and in tetrahydrofuran and these solvents must be the source of CO. Additionally, Na(BPh$_4$) does not appear to play a stoichiometric role in the reaction.

Reaction of metal-halide complexes with alcohol to afford hydride, carbonyl, or hydride-carbonyl species is well known. The ruthenium(II) chloride complex [Ru$_2$Cl$_3$(PEt$_3$Ph)$_6$]Cl reacts with potassium hydroxide in ethanol heated at reflux to form [Ru(H)Cl(CO)(PEt$_3$Ph)$_3$],$^{44}$ whilst the
base-free reaction between $[\text{RuCl}_3(\text{NH}_4)_2]$ and excess triphenylphosphine in either 2-methoxyethanol or ethylene glycol heated at reflux generates $[\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$. Indeed, the general syntheses of a number of phosphine ligand complexes containing hydride and carbonyl ligands is facilitated by the abstraction of such ligands from alcohol.

### 2.6 Reactions of cis-$[\text{RuCl}_2(\text{dmpe})_2]$)

The *cis* configuration of any ruthenium(II) diphosphine complex has a number of different properties when compared to the *trans* analogue. Physical attributes such as dipole moment and steric interaction within the molecule and with incoming ligands differ, as do electronic effects arising from both metal orbital symmetry and the *trans* effect/influence of the donor ligands. Furthermore the structural differences between *cis* and *trans* geometries may affect the availability of particular insertion/elimination pathways, influencing the likelihood of oxidative addition or reductive elimination. Indeed, it has been reported that when compared with their *trans* counterparts, *cis* complexes of the form $cis-[\text{MCl}_2(\text{P-P})_2]$ are significantly more reactive towards chloride substitution; thus chloride abstraction from $cis-[\text{RuCl}_2(\text{dmpe})_2]$ was also attempted.
2.6.1 Treatment of cis-\([\text{RuCl}_2(\text{dmpe})_2]\) with TMS(OTf) in methanol

Cis-\([\text{RuCl}_2(\text{dmpe})_2]\) is readily prepared in good yield and high isomeric purity by reacting neat bis-dimethylphosphinoethane with tri-\(\mu\)-chloro-hexakis(dimethylphenylphosphine)diruthenium(II) chloride,\(^1\) itself readily prepared from ruthenium trichloride and dimethylphenylphosphine.\(^5\) Thus both the synthesis of cis- and trans-\([\text{RuCl}_2(\text{dmpe})_2]\) have \(\text{RuCl}_2.x\text{H}_2\text{O}\) as their ultimate starting material.

The reaction of cis-\([\text{RuCl}_2(\text{dmpe})_2]\) with TMS(OTf) in methanol generates a fluxional unsymmetrical cis complex with equatorial phosphine groups that exhibit near-coincident resonances in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum, and a minor amount of an extremely fluxional trans complex (Figure 2.19). Both of these species appear to be identical to the products formed in the reaction between trans-\([\text{RuCl}_2(\text{dmpe})_2]\) and Ag(OTf) in methanol (Section 2.5.7).
IR spectra contain no observable dinitrogen stretches and attempted Raman spectroscopy was unsuccessful due to the strongly coloured nature of the sample. MALDI-MS contains fragments that are assignable as $[\text{RuCl(dmpe)}_2]^+$ ($m/z$ 437), $[\text{RuCl(N}_2\text{)(dmpe)}_2]^+$ ($m/z$ 465) and $[\text{Ru(OTf)(dmpe)}_2]^+$ ($m/z$ 596). On the basis of the NMR data and the IR spectrum the most likely identity of the major product is cis-$[\text{RuCl(OTf)(dmpe)}_2]$ (Scheme 2.13).
2.6.2 Treatment of cis-[RuCl₂(dmpe)₂] with Tl(BArF₂₄) in methanol

Reaction of cis-[RuCl₂(dmpe)₂] with Tl(BArF₂₄) in methanol resulted in very rapid formation of a white precipitate and a very pale yellow solution. Filtering the solution through celite and removal of the solvent in vacuo resulted in isolation of an off-white coloured solid. ³¹P{¹H} NMR spectroscopy of the crude mixture reveals the presence of at least two major species, the dominant of which is a cis unsymmetrical complex which is not fluxional on the NMR timescale (Figure 2.20). Also present is a slightly fluxional symmetrical cis complex with very similar chemical shifts to the unsymmetrical product, and trans-[RuCl₂(dmpe)₂], either residual as a minor component of the starting material or formed through Na(BArF₂₄)-assisted isomerisation of cis-[RuCl₂(dmpe)₂].

![Figure 2.20 – Variable temperature ³¹P{¹H} NMR spectra (d₈-thf, 202 MHz) of the reaction mixture of cis-[RuCl₂(dmpe)₂] + Tl(BArF₂₄).](image)

◊ – cis-[{RuCl(dmpe)₂}(μ-N₂)](BArF₂₄)₂; ● – unknown cis symmetrical;
* – trans-[RuCl₂(dmpe)₂]
MALDI-MS reveals only \([\text{RuCl(dmpe)}_2]^+\), yet the Raman spectrum exhibits a clear symmetrical dinitrogen stretch at 2284 cm\(^{-1}\). No dinitrogen stretches are visible in the IR spectra. The combination of the rapid reaction time, non-fluxionality of the product, and the clear \(\nu_{NN}\) that is evident in the Raman spectrum support formulation of the complex as \([\text{cis-}\{\text{RuCl(dmpe)}_2\}_2(N_2)](\text{BArF}_{24})_2\) (Scheme 2.14).

![Scheme 2.14](image)

Note that the energy of the dinitrogen stretching observed in the Raman spectrum is unusually unactivated in energy, being some 134 cm\(^{-1}\) higher than the highest reported ruthenium bridging \(\nu_{NN}\) in the literature (2150 cm\(^{-1}\) for \(\{|\{(\text{PMe}_3)_3(\text{H})(\text{SiMe}_3)\text{Ru}\}_2(\mu-N_2)\}_2\}\))\(^{51}\) and 64 cm\(^{-1}\) higher than the highest reported ruthenium terminal \(\nu_{NN}\) (2220 cm\(^{-1}\) for \(\text{cis-}[\text{Ru(en)}_2(N_2)_2](\text{BPh}_4)\))\(^{52}\). To some extent this can be explained by observing that the coordinated dinitrogen must lie \textit{trans} to a phosphine group. Alkylphosphine ligands are significant \(\pi\)-acceptors and compete for the metal \(d_π\) retrodonation, which would otherwise lead to increased electron density in the \(\pi^*\) orbitals of the \(\text{N≡N}\) bond, thereby they decrease the observed activation of the \(\text{NN}\) bond.
2.6.3 Treatment of cis-\([\text{RuCl}_2(\text{dmpe})_2]\) with Tl(BF\(_4\)) in methanol

Reaction of cis-\([\text{RuCl}_2(\text{dmpe})_2]\) with Tl(BF\(_4\)) in methanol did not visually proceed at room temperature, however heating of the solution at reflux produced a white precipitate and a yellow solution that turned green upon filtering through celite. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the isolated material remains fluxional at temperatures above 198 K and reveals two major complexes: one unsymmetrical cis complex with equatorial phosphine resonances which are almost identical, and a symmetrical cis complex in which the equatorial phosphine resonances are broader and less resolved than the axial phosphine groups (Figure 2.21). Also present is an extremely fluxional minor trans complex that only becomes observable at 198 K. No dinitrogen stretches are observable by IR or Raman spectroscopy, whilst the MALDI-MS spectrum contains only the stable \([\text{RuCl}(\text{dmpe})_2]\)\(^+\) fragment.
The unsymmetrical complex appears at similar chemical shifts to the product of the reaction between \( \text{cis-}[\text{RuCl}_2(\text{dmpe})_2] \) and TMS(OTf) (Section 2.6.1), and is tentatively assigned as \( \text{cis-}[\text{RuCl}(\text{BF}_4)(\text{dmpe})_2] \). However, such similar spectra from solutions containing different coordinating anions may suggest that the true product instead has a vacant coordination site or a coordinating solvent molecule (\( \text{i.e.}, d_8\)-thf). The symmetrical \( \text{cis} \) complex is most likely a thallium-stabilised ruthenium-chloride dimer of the form \( \text{cis-}[\{\text{Ru(dmpe)}_2\}_2(\mu\text{-Cl})_2](\text{BF}_4)_2\cdot\text{Tl(Cl)} \) (Scheme 2.15), similar to that observed for \( [\text{RuCl}_2(\text{depe})_2] \) (Chapter 3, Section 3.1.3).
2.7  Reactions of trans-\([\text{RuCl}_2(\text{dmpe})_2](\text{OTf})\)

The chemical reactivity of trans-\([\text{RuCl}_2(\text{dmpe})_2](\text{OTf})\) displays a high degree of uniformity, with reactions dominated by the propensity of the ruthenium(III) centre to reduce to ruthenium(II) with phosphine and chloride bonds remaining intact. In addition to undergoing reduction with common reducing agents such as Na/Hg amalgam, magnesium turnings and zinc dust, trans-\([\text{RuCl}_2(\text{dmpe})_2](\text{OTf})\) is reduced to trans-\([\text{RuCl}_2(\text{dmpe})_2]\) with sodium borohydride, alcohols (more rapidly with methanol than ethanol), and hydrazine. Reduction with all reagents other than alcohol and magnesium turnings proceeds rapidly, reaching completion from within seconds to a few minutes. The reaction is easily observable due to the distinct and intense colours of the two ruthenium oxidation states.

Reduction with hydrazine is particularly disappointing in view of the ultimate goals of dinitrogen reduction. Proton NMR spectrum of the reaction mixture reveal only resonances associated with \([\text{RuCl}_2(\text{dmpe})_2]\) plus a broad resonance at 6.8 ppm, which could plausibly be assigned as
triflic acid, broadened due to the acidic, fluxional nature of the species. Therefore, not only is there no evidence of nitrogen coordination to the metal centre, but the dinitrogen-reduction intermediate (hydrazine) is oxidised stoichiometrically to form dinitrogen (Scheme 2.16).

\[
2 [\text{RuCl}_2(\text{dmpe})_2](\text{OTf}) + \text{H}_2\text{NNH}_2 \rightarrow 2 [\text{RuCl}_2(\text{dmpe})_2] + 2 \text{HOTf} + \text{N}_2 + \text{H}_2
\]

Scheme 2.16

2.8 Conclusions

Out of all the attempted reactions of cis- and trans-[RuCl₂(dmpe)$_2$] undertaken in this work, the only reactions which unequivocally led to the formation of dinitrogen-containing complexes were the reactions of cis-[RuCl₂(dmpe)$_2$] with Tl(BArF$_{24}$) (Section 2.6.2), and trans-[RuCl₂(dmpe)$_2$]·Tl(OTf) with Na(BArF$_{24}$) (Section 2.5.5). The reaction of cis-[RuCl₂(dmpe)$_2$] with Tl(BArF$_{24}$) led to the formation of cis-[[RuCl(dmpe)$_2$]$_2$(µ-N$_2$)](BArF$_{24}$)$_2$, which is directly analogous, both in form and in synthesis, to cis-[[RuCl(depe)$_2$]$_2$(µ-N$_2$)](BArF$_{24}$)$_2$ (Chapter 3, Section 3.2.2). Whilst a bridging dinitrogen coordination mode is expected to lead to a decrease in the observed $\nu_{\text{NN}}$ (cf. Chapter 1, Section 1.2.6), cis-[[RuCl(dmpe)$_2$]$_2$(µ-N$_2$)](BArF$_{24}$)$_2$ gives rise to an unactivated $\nu_{\text{NN}}$ of 2284 cm$^{-1}$ in the IR spectrum. Trans-[RuCl(N$_2$)(dmpe)$_2$](BArF$_{24}$), formed from the reaction of
trans-[RuCl₂(dmpe)₂]·Tl(OTf) with Na(BArF₂₄), whilst containing the same ligand set and anion, displays an activated $\nu_{NN}$ of 2012 cm$^{-1}$, which is the lowest reported $\nu_{NN}$ for a ruthenium complex. This difference highlights the significant influence of geometry in the activation of coordinated dinitrogen.

In addition to affecting the degree of activation, molecular geometry also influences the propensity of dinitrogen coordination. This is evident from the reaction of cis-[RuCl₂(dmpe)₂] with Tl(BArF₂₄), which resulted in coordination of dinitrogen, whilst the analogous reaction of trans-[RuCl₂(dmpe)₂] led to formation of the stable five-coordinate complex, trans-[RuCl(dmpe)₂](BArF₂₄).

As shown in the formation of trans-[RuCl₂(dmpe)₂]·Tl(OTf) (Section 2.5.3), the initial ruthenium-chloride bonds are surprisingly stable, enough so that the reaction of trans-[RuCl₂(dmpe)₂] with Na(BArF₂₄) in methanol (Section 2.5.6) resulted, in part, in the re-coordination of chloride post chloride abstraction to form cis-[RuCl₂(dmpe)₂]. Thus the first barrier is the removal of chloride not only from the complex, but from the system.

The oxidation of [RuCl₂(dmpe)₂] via treatment with triflate salts of silver(I) (Section 2.5.1) and trimethylsilane (Section 2.5.2) in non-polar solvents (dichloromethane, toluene) reflects upon the differences observed between alkyl- and arylphosphine ligands; the more electron-rich nature of alkylphosphine complexes increases the sensitivity to
oxidation. Contrastingly, the same reactions carried out in methanol (Sections 2.5.7 and 2.5.8) result in successful chloride abstraction, however, the triflate anion coordinates in preference to dinitrogen. Thus two further barriers to dinitrogen complex formation are noted: the ability of coordinative anions to prevent dinitrogen coordination, and the careful choice of solvent required to endue metal precursors with the reactivity desired.

The unexpected formation of trans-[Ru(H)(CO)(dmpe)$_2$][Cl] and trans-[RuCl(CO)(dmpe)$_2$][Cl] from the reaction of trans-[RuCl$_2$(dmpe)$_2$] with Na(BPh$_4$) at 140°C under 140 psi N$_2$ in both tetrahydrofuran and methanol (Section 2.5.11) highlights a fourth barrier, namely, that the chosen solvent may not be an innocent bystander and may react with the potentially unstable intermediates formed by chloride abstraction under the conditions used.

Even when not directly reacting, the presence of solvent may be sufficient to prevent N$_2$ coordination. This is seen in reactions such as that between trans-[RuCl$_2$(dmpe)$_2$] and Na(BArF$_{24}$) in methanol (Section 2.5.6) where visual and spectroscopic change occurred only after removal of the solvent, despite no spectroscopic evidence of solvent coordination.

Finally, despite the lack of competitor ligands – anion, solvent, or otherwise – the reaction between trans-[RuCl$_2$(dmpe)$_2$] and Tl(BArF$_{24}$)
(Section 2.5.9) results in the formation of the stable five-coordinate complex \(\text{trans-}[\text{RuCl(dmpe)}_2](\text{BArF}_2^+)\) instead of coordinating dinitrogen, thus even under optimal conditions for potential dinitrogen coordination, subtle thermodynamic influences outside direct control can make or break the likelihood of isolating a desired dinitrogen adduct.

Overall, the reactions attempted in this chapter indicate that dinitrogen coordination will only occur if all other potential products are less favourable, which, whilst obvious, appears to be a deceptively simple endeavour. Careful choice of solvent, chloride abstraction agent and anion are all required to achieve the goal of dinitrogen coordination to the electron rich core \([\text{RuCl(dmpe)}_2]^+\).
Chapter 2  Reactions of [Ru(L¹)(L²)(dmpe)]

References


Chapter 2  Reactions of \([\text{Ru}(L^1)(L^2)(\text{dmpe})_2]\)


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Chapter 2

Reactions of [Ru(L¹)(L²)(dmpe)]


53. This work.