Chapter 4  Reactions of \([\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2\)

4  Reactions of \([\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2\)

4.1  Introduction

The product formed from the reaction between \(\text{trans-}[\text{RuCl}_2(\text{depe})_2]\) with thallium triflate in tetrahydrofuran, on the basis of \(^{31}\text{P}\{^1\text{H}\}, \text{P}^{31}\text{P} \text{ EXSY NMR, and MALDI-TOF MS, is hypothesised to be} \) \(\text{cis-}\{[\text{Ru(depe)}_2]_2(\mu-\text{Cl})_2](\text{OTf})_2\} (\text{Chapter } 3, \text{ Section } 3.1.3). \) This compound is proposed to exist in solution as an equilibrium mixture between the dimer and a five-coordinate monomeric form, with a further equilibrium involving inner-sphere triflate coordination, as shown in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1 – Proposed equilibrium mixture of cis-\{[Ru(depe)_2]_2(\mu-Cl)_2](OTf)_2\}, cis-\{RuCl(depe)_2]\( \text{(OTf)} \) and cis-\{RuCl(OTf)(depe)_2\].**

A coordinatively malleable system such as this may be expected to readily react with a number of ligands (both neutral and anionic), herein is described an investigation into the coordination chemistry of this system. Notably, all of the coordination reactions explored proceeded with precipitation of a white solid, proposed to be a thallium salt (most...
likely thallium chloride), indicating that thallium (and presumably chloride as well) is still incorporated somewhere in the system. Given that thallium chloride is not soluble to any appreciable degree in organic solvents, the thallium in the system would plausibly be a component of the ruthenium dimer.

There is no spectroscopic evidence for thallium incorporation into the Ru(μ-Cl)₂Ru moiety, yet in NMR spectra the presence of thallium has been shown to stabilise the resonances assigned to the dimeric species when compared to samples prepared without it (for example, the product obtained from the reaction between trans-[RuCl₂(depe)] and TMS(OTf) in methanol, Chapter 3, Section 3.1.5). Thus, the most likely structure is one in which one or more thallium atoms ‘caps’ the chloride bridge. Possible structures are represented by a) and b) in Figure 4.2, each resembling complex Tl{Ru(C≡CtBu)(dcypb)}₂(μ-Cl)₃ that was discussed in Chapter 2 (Figure 2.6).¹ Arrangements for thallium incorporation that are analogous to c) and d) are also possible, but are ruled out in this case due to NMR symmetry requirements and/or the lack of incorporated thallium in the dimeric ruthenium complex observed via MALDI-MS ([Ru₂Cl₂(depe)]⁺).
4.2  Reactions with neutral ligands

4.2.1 Reaction with carbon monoxide

Exposing a sample of cis-\{Ru(depe)\}_2(\mu-Cl)_2(OTf)_2 in tetrahydrofuran to one atmosphere of CO resulted in rapid decolourisation of the solution and precipitation of a fine white solid (presumed to be thallium chloride). Spectroscopic analysis of the filtered solution revealed complete conversion to the new complex cis-\{RuCl(CO)(depe)\}_2(OTf). The complex displays a characteristic ν_{CO} at 1983 cm\(^{-1}\) in the infrared spectrum, which, whilst significantly lower than the value obtained for
free CO (2143 cm$^{-1}$),$^2$ is higher than that of similar ruthenium alkylphosphine carbonyl complexes (Table 4.1).

Table 4.1 – Infrared $\nu_{CO}$ absorptions for selected complexes of the type $[\text{Ru}(L)(CO)\text{(P+P)}_2]^{x+}$ ($L = \text{Cl, H}; \text{P+P} = \text{bidentate alkyl- or arylphosphine}; x = 0, 1$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{CO}$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$trans$-$<a href="%5Ctext%7BBF%7D_4">\text{RuCl(CO)(dppe)}_2</a>$</td>
<td>1973</td>
<td>$^3$</td>
</tr>
<tr>
<td>$trans$-$<a href="%5Ctext%7BBPh%7D_4">\text{RuCl(CO)(dcpe)}_2</a>$</td>
<td>1940</td>
<td>$^4$</td>
</tr>
<tr>
<td>$trans$-$[\text{Ru(CO)}_2]$</td>
<td>1945</td>
<td>$^5$</td>
</tr>
<tr>
<td>$trans$-$[\text{Ru(H)(CO)(dmpe)}_2]$(OH)</td>
<td>1950</td>
<td>$^6$</td>
</tr>
<tr>
<td>$trans$-$[\text{Ru(H)(CO)(dmpe)}_2]$(Cl)</td>
<td>1957</td>
<td>†</td>
</tr>
<tr>
<td>$trans$-$[\text{RuCl(CO)(dmpe)}_2]$(Cl)</td>
<td>1936</td>
<td>†</td>
</tr>
<tr>
<td>$trans$-$[\text{Ru(H)(CO)(depe)}_2]$(BPh$_4$)</td>
<td>1958</td>
<td>$^2$</td>
</tr>
<tr>
<td>$trans$-$[\text{RuCl(CO)(depe)}_2]$(OTf)</td>
<td>1938</td>
<td>†</td>
</tr>
<tr>
<td>$cis$-$[\text{RuCl(CO)(depe)}_2]$(OTf)</td>
<td>1983</td>
<td>†</td>
</tr>
</tbody>
</table>

† this work

The increase in $\nu_{CO}$ stretching frequency of $cis$-$[\text{RuCl(CO)(depe)}_2]$(OTf) in comparison with the literature complexes presumably arises due to the $cis$ geometry of this species. In the case of $cis$-$[\text{RuCl(CO)(depe)}_2]$(OTf), the carbonyl is $trans$ to a phosphine ligand, rather than a hydride, chloride or vacant orbital. Because alkyl phosphine ligands are effective $\pi$-acceptors, there is less electron density in the metal $d_\pi$ orbital which would usually retrodonate to the carbonyl. The decrease in the electron
density of the carbonyl $\pi^*$-orbital leads to a lesser degree of triple bond destabilisation, and hence a higher stretching frequency.

MALDI-MS gives a clear molecular ion at $m/z$ 577 which is in good agreement with the isotopic distribution calculated for $C_{21}H_{48}Cl_1O_1P_4Ru_1$ (Figure 4.3).

![Figure 4.3](image)

**Figure 4.3 – Comparison of experimental (MALDI-MS) and simulated ion envelopes of cis-\([\text{RuCl(CO)(depe)}_2]^+\)**

In the $^{13}C\{^{1}H, \, ^{31}P\}$ NMR spectrum of cis-\([\text{RuCl(CO)(depe)}_2](\text{OTf})\), the coordinated carbonyl gives rise to a resonance at 201.1 ppm, which can
be compared to the resonance at 197.9 ppm in the closely related complex \textit{trans}-[RuCl(CO)(dmpe)]$^+$ (Chapter 2, Section 2.5.11). Apparently, the chemical shift of the carbonyl ligand is insensitive to the \textit{cis} or \textit{trans} geometry that is adopted by the alkylphosphine complex, indicating that the electron density at the coordinated carbonyl carbon differs little between the \textit{cis} and \textit{trans} geometries, despite the significant change in $\nu_{\text{CO}}$ stretching frequency that is observed. This can be rationalised by the balance between ligand $\sigma$-donation and metal $\pi$-retrodonation, \textit{i.e.}, the stronger $\pi$-bond weakening that is associated with a lower $\nu_{\text{CO}}$ is offset by a reduction in ligand $\sigma^*$ electron density.$^7$\textsuperscript{,}$^8$ Thus, whilst there is a similar degree of electron density on the carbonyl carbon in both the \textit{cis} and \textit{trans} complexes, leading to similar $^{13}$C chemical shifts, the greater metal-carbonyl $\pi$-retrodonation in the \textit{trans} complex leads to a lowered $\nu_{\text{CO}}$.

Despite the carbonyl being coordinated \textit{trans} to a phosphine ligand, the complex was stable indefinitely under vacuum or N$_2$ atmosphere.

### 4.2.2 Reaction with acetonitrile

Addition of an excess of acetonitrile to a solution of \textit{cis}-[\{Ru(depe)$_2$\}$\mu$-Cl]$_2$(OTf)$_2$ resulted in precipitation of a white solid and formation of a light blue-green solution. The $^{31}$P{$^1$H} NMR revealed complete conversion of \textit{cis}-[\{Ru(depe)$_2$\}$\mu$-Cl]$_2$(OTf)$_2$ to the known complex \textit{cis}-[RuCl(NCMe)(depe)]$^+$, however, samples in solution
decomposed slowly such that after one month very little of the acetonitrile complex remained. As per literature reports, the complex does not give rise to an unambiguously identifiable ν_{CN} in the infrared spectrum, but a low-intensity signal at 2124 cm\(^{-1}\) could be due to the CN stretch. If this is indeed the case, the coordinated acetonitrile appears to be 'activated' relative to free acetonitrile (ν_{CN} = 2254 cm\(^{-1}\)),\(^{10}\) and is significantly lower in energy than in the related complexes cis-[RuCl(NCMe)(dppe)](PF\(_6\)) (2306 cm\(^{-1}\))\(^{11}\) and trans-[Ru(NCMe)\(_2\)(PPh\(_2\)C(Me)=C('Bu)O)]\(_2\)) (2267 cm\(^{-1}\))\(^{12}\), both of which possess ν_{CN} absorptions that are higher in energy than for free MeCN. Whether this is due to the electron-releasing nature of the depe ligand, or evidence that the IR signal is not due to coordinated acetonitrile is unclear.

The MALDI-MS does not contain a molecular ion, however, a small (ca. 26%) ion envelope corresponding to [Ru(NC)(depe)]\(^+\) (Figure 4.4) is detectable at m/z 540. That the only nitrile-containing ion is an acetonitrile fragmentation product containing the strong ligand CN\(^-\) is in agreement with the observed instability of the ruthenium-acetonitrile bond.
4.2.3 Reaction with tert-butyl isonitrile

As expected, tert-butyl isonitrile binds more effectively to the \([\text{RuCl(depe)}_2]\)^+ core than acetonitrile, with the reaction of cis-\([\text{Ru(depe)}_2(\mu-\text{Cl})_2](\text{OTf})_2\) with \(\text{tBuNC}\) yielding cis-\([\text{RuCl(CN'Bu)(depe)}_2](\text{OTf})\) as a light green solution that was indefinitely stable. The complex cis-\([\text{RuCl(CN'Bu)(depe)}_2](\text{OTf})\) displays a strong \(\nu_{\text{NC}}\) in the infrared region at 2139 cm\(^{-1}\), with low-intensity shoulders at 2169 and 2182 cm\(^{-1}\). The absorption at 2139 cm\(^{-1}\) is higher than is typically observed in complexes of the type
trans-$[\text{Ru}(\text{L})(\text{CN}^\text{'Bu})(\text{P}-\text{P})_2]^+$ (L = anionic ligand; P-P = bidentate alkyl- or aryl-phosphine), and is slightly higher than for the free isonitrile (Table 4.2). The $\nu_{\text{NC}}$ of cis-$[\text{RuCl}(\text{CN}^\text{'Bu})(\text{depe})_2](\text{OTf})$ is, however, lower in energy than that observed for the complex cis-$[\text{RuCl}(\text{CN}^\text{'Bu})(\text{dppm})_2](\text{PF}_6)$,\(^{13}\) which is in agreement with the increased electron-releasing nature of alkylphosphine complexes relative to their arylphosphine analogues and the decrease in $\pi$-retrodonation that occurs when a ligand is located trans to a phosphine ligand.

**Table 4.2 – Infrared $\nu_{\text{NC}}$ absorptions for selected complexes of the type $[\text{Ru(L)(CO)(P)}_2]^+$ (L = anionic ligand; P = alkyl- or aryl-phosphine)**

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu_{\text{NC}}$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free $^\text{'BuNC}$</td>
<td>2136</td>
<td>10</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BBPh%7D_4">\text{Ru(Tp)}(\text{CN}^\text{'Bu})(\text{PMe}^\text{iPr})_2</a>$</td>
<td>2124</td>
<td>14</td>
</tr>
<tr>
<td>trans-$<a href="%5Ctext%7BPF%7D_6">\text{Ru(CCPh)}(\text{CN}^\text{'Bu})(\text{dppe})_2</a>$</td>
<td>2124</td>
<td>15</td>
</tr>
<tr>
<td>trans-$<a href="%5Ctext%7BBPh%7D_4">\text{Ru(H)}(\text{CN}^\text{'Bu})(\text{depe})_2</a>$</td>
<td>2120</td>
<td>2</td>
</tr>
<tr>
<td>trans-$<a href="%5Ctext%7BPF%7D_6">\text{RuCl}(\text{CN}^\text{'Bu})(\text{dppm})_2</a>$</td>
<td>2127</td>
<td>13</td>
</tr>
<tr>
<td>cis-$<a href="%5Ctext%7BPF%7D_6">\text{RuCl}(\text{CN}^\text{'Bu})(\text{dppm})_2</a>$</td>
<td>2157</td>
<td>13</td>
</tr>
<tr>
<td>cis-$<a href="%5Ctext%7BOTf%7D">\text{RuCl}(\text{CN}^\text{'Bu})(\text{depe})_2</a>$</td>
<td>2139</td>
<td>†</td>
</tr>
</tbody>
</table>

† this work

Nuclear quadrupole coupling in uncoordinated isonitriles is very low, indicating a near zero electric field gradient about nitrogen, allowing the measurement of natural abundance $^{13}\text{C}$-$^{14}\text{N}$ spin-spin coupling.\(^{16}\) For free $^\text{'BuNC}$ these values are $^{1}J_{(\text{NC})} = 5.2$ and 3.9 Hz for the $\text{ipso}$ and isonitrile
carbons, respectively, which are typical of organic isonitrile molecules. In the $^{13}\text{C}\{^{1}\text{H},^{31}\text{P}\}$ NMR spectrum of $\text{cis-}[\text{RuCl(CN}^{t}\text{Bu)}(\text{depe})_{2}](\text{OTf})$, the resolution of this coupling is lost and the resonances due to these carbon atoms display a broadened appearance. The isonitrile carbon of $\text{cis-}[\text{RuCl(CN}^{t}\text{Bu)}(\text{depe})_{2}](\text{OTf})$ resonates at 149.4 ppm, which compares with 155.1 ppm for free $^{t}\text{BuNC}$, whilst the quaternary carbon resonance shifts downfield from 53.7 to 57.9 ppm upon isonitrile coordination.

In a similar fashion to that observed for $\text{cis-}[\text{RuCl(NCMe)}(\text{depe})_{2}](\text{OTf})$, the MALDI-MS of $\text{cis-}[\text{RuCl(CN}^{t}\text{Bu)}(\text{depe})_{2}](\text{OTf})$ contains ions arising from fragmentation of the coordinated isonitrile ligand. Unlike the acetonitrile complex, however, the molecular ion ($[\text{RuCl(CN}^{t}\text{Bu)}(\text{depe})_{2}]^{+}$) is clearly visible (Figure 4.5).
Interestingly, in addition to the fragmentation product formed through loss of tBu+ and Cl−, the ion [Ru(C)Cl(depe)2]+ is also present, presumably being formed via the loss of N− from the neutral (and thus unobserved) species [RuCl(NC)(depe)2].

Single crystals of [RuCl(CN′Bu)(depe)2](BPh4) suitable for X-ray analysis were formed by the addition of methanolic Na(BPh4) to a solution of cis-[RuCl(CN′Bu)(depe)2](OTf) in tetrahydrofuran. An ORTEP depiction of the molecular structure is provided in Figure 4.6, with selected
preliminary bond lengths and angles presented in Table 4.4. Surprisingly, X-ray analysis showed that the crystals were of trans-\(\text{[RuCl(CN'Bu)(depe)\textsubscript{2}](BPh}_4\text{)}\), revealing that a change in geometry had occurred preceding (or during) crystallisation. Such isomerisation has literature precedence, with the complex cis-\(\text{[RuCl(CN'Bu)(dppm)\textsubscript{2}](PF}_6\text{)}\) slowly isomerising to the trans form in dcm or toluene/acetone solutions, and indeed, this is the geometry in which it crystallises.\textsuperscript{13} Similarly, the complex cis-\(\text{[RuCl(NCMe)(dcpe)\textsubscript{2}](BPh}_4\text{)}\) is stable in dcm only at low temperature (\(-60^\circ\text{C}\)), quantitatively isomerising to the trans configuration at ambient temperature.\textsuperscript{17}
Figure 4.6 – ORTEP diagram of trans-[RuCl(′BuCN)(depe)₂](BPh₄) at 50% displacement ellipsoids. Counter-ion, hydrogen atoms and ethyl groups removed for clarity.

Table 4.3 – Selected preliminary bond lengths and angles in trans-[RuCl(′BuCN)(depe)₂](BPh₄)
Chapter 4  Reactions of \([\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2]\)

<table>
<thead>
<tr>
<th>Bond angles (°)</th>
<th>Ru(1)-P(4)</th>
<th>2.358</th>
<th>N(1)-C(2)</th>
<th>1.475</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Bond angles (°)</th>
<th>Ru(1)-P(4)</th>
<th>2.358</th>
<th>N(1)-C(2)</th>
<th>1.475</th>
</tr>
</thead>
</table>

The Ru-C bond length of 1.900 Å is similar to bond lengths found for other ruthenium-^tBuNC complexes in which the isonitrite ligand is located \(\text{trans}\) to an electron donor \((\text{O}^-, \text{Cl}^-, \text{etc})\), e.g. \(\text{cis-}[\text{Ru}(\text{acac})_2(\text{CN}^t\text{Bu})_2]\) \((1.910(6)\text{ Å})\) \(^1\text{8}\) \([\text{RuCl}_2(\text{P-O})(\kappa^1-\text{P-O})(\text{CN}^t\text{Bu})]\) \((1.918(3)\text{ Å}, \text{isonitrile} \text{trans to} \text{Cl})\) \(^1\text{9}\) and \(\text{trans}-[\text{RuCl}(\text{CN}^t\text{Bu})(\text{dppm})_2](\text{PF}_6)\) \((1.932(7)\text{ Å})\). \(^1\text{3}\) The C≡N and N-C bond lengths differ negligibly from those in other ruthenium isonitrile complexes.

### 4.2.4 Reaction with \(^{15}\text{N}\)-ammonia

Gaseous transfer of \(^{15}\text{N}\)-ammonia to a solution of \([\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2\) in tetrahydrofuran resulted in the immediate formation of the violet coloured complex \(\text{cis-}[\text{RuCl}(^{15}\text{NH}_3)(\text{depe})_2](\text{OTf})\) and concurrent precipitation of residual thallium chloride. The ammonia ligand was
relatively weakly coordinated, with MALDI-MS (in which sample preparation includes $\geq 30$ min at $10^{-8}$ torr) displaying a very weak molecular ion. Nevertheless, the complex withstood solvent evaporation \textit{in vacuo}, with solid samples displaying characteristic NH stretches in the infrared spectrum at \textit{ca.} 3316 cm$^{-1}$.

The coordinated ammonia has a $^{15}$N$\{^1$H$\}$ NMR resonance at $-29.3$ ppm (liquid ammonia scale), with a \textit{trans} phosphine coupling of 25.1 Hz. The NH$_3$ protons give rise to a weak and very broad signal at 0.38 ppm in the $^1$H$\{^{31}$P$\}$ NMR spectrum. In comparison, coordinated ammonia in the complex \textit{cis}-[FeCl(NH$_3$)(dmpe)$_2$](BPh$_4$) gives rise to a $^{15}$N NMR resonance at $-33.9$ ppm, whilst \textit{trans}-[Fe(H)(NH$_3$)(dmpe)$_2$](BPh$_4$) exhibits a $^{15}$N NMR resonance at $-50.4$ ppm.\textsuperscript{20} The similarity between the $^{15}$N chemical shifts of \textit{cis}-[RuCl($^{15}$NH$_3$)(depe)$_2$](OTf) and \textit{cis}-[FeCl(NH$_3$)(dmpe)$_2$](BPh$_4$) serves to further justify the use of ruthenium as an iron mimetic in dinitrogen chemistry.\textsuperscript{21-24}

\subsection*{4.2.5 Reaction with hydrazine}

The reaction of \textit{cis}-[\{Ru(depe)$_2$\}$_2$($\mu$-Cl)$_2$](OTf)$_2$ with anhydrous hydrazine in tetrahydrofuran initially resulted in a yellow solution that slowly darkened over time and began to precipitate an orange solid. $^{31}$P$\{^1$H$\}$ NMR spectroscopy of the solution revealed complete conversion of the starting material to a single product, with a spectrum that is, unsurprisingly, very similar to the ammonia complex, suggesting an
analogous structure for the hydrazine product. The $^1$H NMR spectrum exhibits an $\alpha$-NH$_2$ hydrazine resonance at 2.55 ppm with unresolved $^{31}$P coupling, whilst the terminal NH$_2$ protons resonate at 3.13 ppm and do not show any coupling to $^{31}$P, thus confirming the $\eta^1$-coordination mode of the hydrazine ligand. In comparison, the $\alpha$-NH$_2$ protons in the complex cis-$[\text{Ru}(\text{H})(\text{NH}_2\text{NH}_2)(\text{P(OEt})_3)](\text{BPh}_4)$ resonate at $\delta$ 3.14 ppm (NB: the $\beta$-NH$_2$ chemical shift is not reported),$^{25}$ whilst the complex trans-$[\text{Fe}(\text{H})(\text{NH}_2\text{NH}_2)(\text{dmpe})](\text{BPh}_4)$ exhibits resonances at 2.78 and 2.34 ppm corresponding to $\alpha$-NH$_2$ and $\beta$-NH$_2$, respectively.$^{20}$

Over time, the $^{31}$P-$^1$H NMR signals decrease with a concomitant increase in the amount of orange precipitate formed, perhaps due to oligomerisation. Polymerisation of metal-hydrazine complexes has been observed before,$^{26,27}$ however the solid species that eventually formed from the reaction of cis-$[\{\text{Ru(depe)}_2\}(_2\mu-\text{Cl})_2](\text{OTf})_2$ with hydrazine has not been identified.

### 4.2.6 Reaction with hydrogen

Exposing a sample of cis-$[\{\text{Ru(depe)}_2\}(_2\mu-\text{Cl})_2](\text{OTf})_2$ in tetrahydrofuran to one atmosphere of H$_2$ resulted in a rapid colour change from an inky dark green to a clear yellow with concomitant precipitation of thallium chloride. Spectroscopic analysis of the filtered solution revealed complete conversion to trans-$[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](\text{OTf})$, with NMR data that was in good agreement with that of the previously reported
complexes \( \text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)\text{(depe)}_2](\text{X}) \text{ (X = BF}_4\text{, PF}_6) \), which were formed by the addition of the corresponding acid to \( \text{trans-}[\text{RuCl}(\text{H})\text{(depe)}_2] \).\(^{11}\)

The dihydrogen complex gives rise to a singlet in the \(^{31}\text{P}\{^1\text{H}\} \text{ NMR spectrum at 54.0 ppm indicating a trans geometry, and a broad } ^1\text{H resonance at } -14.3 \text{ ppm which, at room temperature, displays unresolved } ^2J_{(\text{HP})} \text{ coupling. Application of a Gaussian multiplication window function (LB = } -15 \text{ Hz, GB = 0.15) resolves the multiplicity sufficiently to measure a } ^2J_{(\text{HP})} \text{ coupling constant of 7.5 Hz.} \)

Also present in the sample of \( \text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)\text{(depe)}_2](\text{OTf}) \) is a small amount (ca. 10\%) of \( \text{trans-}[\text{RuCl}(\text{H})\text{(depe)}_2](\text{OTf}) \), which exhibits a proton chemical shift at −11.4 ppm due to the hydride ligand and is presumably formed by heterolytic cleavage of the coordinated dihydrogen.

The identities of each of these species were confirmed by \(^1\text{H NMR } T_1 \) measurements (Figure 4.7 and Figure 4.8), with the species \( \text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)\text{(depe)}_2](\text{OTf}) \) having a \( T_1 \) minimum (\( T_{1\text{min}} \)) of 66.6 ms at 238 K and 500 MHz. Under these conditions, the resonance assigned as \( \text{trans-}[\text{RuCl}(\text{H})\text{(depe)}_2] \) has a \( T_1 \) value of over 500 ms. It is generally accepted that at 250 MHz, \( T_{1\text{min}} \) values greater than 150 ms indicate a hydridic species, whilst \( T_{1\text{min}} \) values shorter than 80 ms indicate \( \eta^2 \)-dihydrogen.\(^{28-31}\) Because \( T_1 \) values are proportional to field strength,\(^{29}\) these values correspond to 300 and 160 ms at the frequency (500 MHz) used. Thus, whilst the measured value of 66.6 ms is somewhat longer
than similar literature complexes (Table 4.4), indicating a greater degree of H-H separation than perhaps is the norm, it is still consistent with dihapto coordination.

The addition of a small quantity of MeOD resulted in deuterium uptake, with the resultant HD isotopomer having a $^{1}J_{\text{HD}}$ value of 25 Hz. This moderate coupling indicates a reasonable degree of H-D separation, but retention of the H-D bond (i.e., $\eta^2$ coordination), a point which is in agreement with the intermediate $T_1$ value discussed above.\textsuperscript{30,32}

### Table 4.4 – A comparison of dihydrogen $^1$H $T_1$ and $^{1}J_{\text{HD}}$ values in ruthenium dihydrogen complexes

<table>
<thead>
<tr>
<th>Species</th>
<th>$T_1$ (ms)</th>
<th>$^{1}J_{\text{HD}}$ (Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{<a href="BF_4">Ru(Cp)(\eta^2-H_2)(dippe)</a>}$</td>
<td>34\textsuperscript{a}</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>$\text{<a href="BF_4">Ru(Tp)(\eta^2-H_2)(PPh_3)</a>}$</td>
<td>19\textsuperscript{b}</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>$\text{trans-[RuH(\eta^2-H_2)(DuPHOS)]_2(PF_6)}$</td>
<td>9\textsuperscript{c}</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>$\text{trans-[Ru(H)(\eta^2-H_2)(dppe)]_2(BF_4)}$</td>
<td>20\textsuperscript{d}</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>$\text{trans-[RuCl(\eta^2-H_2)(dppe)]_2(OTf)}$</td>
<td>24\textsuperscript{e}</td>
<td>25.6</td>
<td>37</td>
</tr>
<tr>
<td>$\text{trans-[Ru(H)(\eta^2-H_2)(depe)]_2(BF_4)}$</td>
<td>16\textsuperscript{f}</td>
<td>32.3</td>
<td>36</td>
</tr>
<tr>
<td>$\text{trans-[RuCl(\eta^2-H_2)(depe)]_2(OTf)}$</td>
<td>67\textsuperscript{g}</td>
<td>25.3</td>
<td>†</td>
</tr>
</tbody>
</table>

Conditions: \(a - d_6\)-acetone, 400 MHz, 223 K; \(b - d_6\)-acetone, 400 MHz, 223 K; \(c - \text{CD}_2\text{Cl}_2\), 400 MHz, 213 K; \(d - d_6\)-acetone, 400 MHz, 230 K; \(e - \text{CD}_2\text{Cl}_2\), 400 MHz, 250 K; \(f - d_6\)-acetone, 400 MHz, 195 K; \(g - d_8\)-thf, 500 MHz, 238 K. † this work
Figure 4.7 – Stack plot of 1D $^1$H NMR traces ($d_8$-thf, 500 MHz, 238 K) extracted from a series of $T_1$ inversion-recovery experiments. Times at left show delay between spin inversion and recovery for each slice.
Chapter 4

Reactions of $\text{[Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2$

The dihydrogen ligand in $\text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](\text{OTf})$ is only weakly bound. Whilst stable under $\text{H}_2$ atmosphere indefinitely, samples exposed to vacuum or extended $\text{N}_2$ atmosphere lost $\text{H}_2$ to reform thallium-free $\text{cis-}[\{\text{Ru(depe)}_2\}_2(\mu-\text{Cl})_2](\text{OTf})_2$. Contrasting with the previously reported complexes $\text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](X)$ ($X = \text{BF}_4, \text{PF}_6$),\textsuperscript{11} the dihydrogen complex was reformed upon the addition of $\text{H}_2$. One possibility for the observed behavioural difference is the presence of the triflate anion, which is proposed to coordinate to $[\text{RuCl(depe)}_2]^+$ (Figure 4.1), stabilising what would otherwise be a very reactive species.

Figure 4.8 – Fitted $T_1$ relaxation curve of $\text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](\text{OTf})$ at 500 MHz and 238 K
4.2.7 Reaction with high pressure dinitrogen

Under conditions analogous to the high dinitrogen-pressure reaction between trans-[RuCl₂(dmpe)₃] and Na(BPh₄) (Chapter 3, Section 3.2.12), treatment of cis-[[Ru(depe)₂(µ-Cl)]₂(OTf)]₂ in tetrahydrofuran with 140 psi of dinitrogen in a steel pressure vessel at 150°C resulted in formation of a colourless solution, subsequently determined to contain the carbonyl complex trans-[RuCl(CO)(depe)₂](OTf).

The trans nature of the complex is deduced by the singlet in the $^{31}$P{$^1$H} NMR spectrum at 46.4 ppm, and unlike the carbonyl complexes formed from [RuCl₂(dmpe)₃] there is no evidence for the presence of any hydridic species.

The complex gives rise to a strong $\nu_{CO}$ in the infrared spectrum at 1938 cm$^{-1}$, some 44 cm$^{-1}$ lower in frequency than the previously isolated cis isomer (Section 4.2.1), and very similar to the dmpe analogue trans-[RuCl(CO)(dmpe)₂](Cl) (Chapter 2, Section 2.5.11), which has a $\nu_{CO}$ of 1936 cm$^{-1}$ (Table 4.1).

The lower energy of $\nu_{CO}$ for trans-[RuCl(CO)(depe)₂](OTf) compared with the cis analogue is consistent with the dπ competition that exists when the CO ligand is coordinated trans to a phosphine group, and, to a lesser extent, the dπ repulsion exerted by the chloride ligand, which increases...
retrodonation to the carbonyl ligand. Perhaps surprisingly, a trend appears to be emerging in which, for the dmpe analogues at least, the presence of a chloride ligand trans to the carbonyl provides greater CO activation than does reduction of the metal centre to ruthenium(0).

The MALDI-MS of trans-\([\text{RuCl(CO)(depe)}_2]\)(OTf) reveals a strong molecular ion at m/z 577 (Figure 4.9), which, unsurprisingly, is identical in appearance to the ion observed for the cis-isomer (Section 4.2.1).
4.2.8 Reactions with CO₂, H₂CCH₂, and N₂O

Reactions of cis-\{Ru(depe)₂\}_₂(\mu-Cl)_₂(OTf)_₂ with atmospheric pressures of carbon dioxide, ethylene, and nitrous oxide were also attempted. In all cases, no physical or spectroscopic changes were observed, indicating that the complex is unreactive towards these substrates.

4.3 Reactions with anionic ligands

4.3.1 Reaction with sodium tetraphenylborate

Reaction of cis-\{Ru(depe)₂\}_₂(\mu-Cl)_₂(OTf)_₂ with sodium tetraphenylborate affords a multitude of species (> 10) as observed by \(^{31}\text{P\{^1\text{H}\}}\) NMR spectroscopy, at least one of which gives rise to a dinitrogen stretch in the infrared spectrum at 2131 cm\(^{-1}\). MALDI-MS reveals that the Ru(\mu-Cl)₂Ru bridge is completely cleaved, with no evidence of [Ru₂Cl₂(depe)₂]\(^+\) or [RuCl₂(depe)₂]\(^+\) ion envelopes, whilst the only identifiable species is the [RuCl(depe)]\(^+\) ion envelope that is common to all reactions of cis-\{Ru(depe)₂\}_₂(\mu-Cl)_₂(OTf)_₂.

4.3.2 Reaction with sodium azide

Treating a solution of cis-\{Ru(depe)₂\}_₂(\mu-Cl)_₂(OTf)_₂ in tetrahydrofuran with solid sodium azide led to the formation of a white precipitate and a clear yellow solution that contained the three complexes.
Chapter 4  Reactions of [Ru\(_2\)Cl\(_2\)(depe)\(_4\)](OTf)\(_2\)

cis-[RuCl\((N_3)\)\(\)\(\)\(\)depe\(_2\)\(]\), cis-[RuCl(OTf)(depe)\(_2\)\(],\) and cis-[\{Ru(depe)\(_2\}\(\mu\-\)Cl\(_2\)]\(2^+\)
in a 2:2:1 ratio as determined by \(^{31}\)P\{\(^1\)H\} NMR spectroscopy.

The species cis-[RuCl\((N_3)\)\(\)\(\)\(\)depe\(_2\)\(]\) exhibits resonances at \(\delta_p\) 64.6 and 60.5 ppm that are attributed to the equatorial phosphorus atoms, whilst signals for the two axial phosphorus atoms are coincident (\(\delta_p\) 50.5 ppm). The complex shows the AMXY pattern expected for the two trans (axial) phosphine groups, however, the appearance of these resonances is significantly distorted due to the small chemical shift difference between the two strongly coupled atoms. Indeed, the tenting distortion is such that the outer four transitions of each multiplet lie below the noise floor of the spectrum, which prevented determination of the trans phosphine coupling constant.

MALDI-MS of the reaction mixture reveals only the coordinatively unsaturated fragment ion [RuCl\(\)\(\)\(\)depe\(_2\)]\(\)\(^+\), whilst infrared spectroscopy of the crude mixture reveals two strong \(\nu_{NN}\) absorptions at 2104 and 2043 cm\(^{-1}\). Ruthenium azide complexes are known to undergo redox decomposition to their dinitrogen analogues,\(^{38,39}\) therefore an assignment of the two stretches as belonging to Ru-N\(_2\) and Ru-N\(_3\) species, respectively, is a reasonable proposal. Such an assignment is in agreement with the generally observed trend for ruthenium azido-dinitrogen complexes of the type cis-[Ru(X)(Y)(LL)\(_2\)]\(^{1+}\) (X, Y = N\(_3\)\(^-\), N\(_2\); LL = en, 2 \times PMe\(_3\), depe; x = 0, 1, 2) (Table 4.5), in which complexed N\(_3\) \(\nu_{NN}\) stretches are typically observed some 60 cm\(^{-1}\) to
lower energy than that of the \( \text{N}_2 \) derivatives. Nevertheless, the evidence is insufficient to confirm that a dinitrogen complex is responsible for any of the observed resonances in the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum.

### Table 4.5 – A comparison of selected \( \nu_{\text{NN}} \) values in ruthenium azido/dinitrogen complexes of the type \( \text{cis-}[\text{Ru}(X)(Y)(LL)_2]^* \) (\( X, Y = \text{N}_3^-, \text{N}_2; \ LL = \text{en}, \ 2 \times \text{PMe}_3, \text{depe}; x = 0, 1, 2 \))

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu_{\text{N}_2} ) (cm(^{-1}))</th>
<th>( \nu_{\text{N}_3} ) (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cis-}[\text{Ru}(\text{N}_3)_2(\text{en})_2] )</td>
<td>–</td>
<td>2050</td>
<td>( ^{38} )</td>
</tr>
<tr>
<td>( \text{cis-}<a href="%5Ctext%7BPF%7D_6">\text{Ru}(\text{N}_3)(\text{N}_2)(\text{en})_2</a> )</td>
<td>2130</td>
<td>2050</td>
<td>( ^{38} )</td>
</tr>
<tr>
<td>( \text{cis-}<a href="%5Ctext%7BBPh%7D_4">\text{Ru}(\text{N}_2)_2(\text{en})_2</a>_2 )</td>
<td>2220, 2190</td>
<td>–</td>
<td>( ^{38} )</td>
</tr>
<tr>
<td>( \text{trans-}[\text{Ru}(\text{N}_3)_2(\text{PMe}_3)_4] )</td>
<td>–</td>
<td>2027</td>
<td>( ^{40} )</td>
</tr>
<tr>
<td>( \text{cis-[RuCl(N}_3)(\text{depe})_2]^+ )</td>
<td>–</td>
<td>2043</td>
<td>( ^{†} )</td>
</tr>
<tr>
<td>( \text{cis-[RuCl(N}_2)(\text{depe})_2]^+ )</td>
<td>2104</td>
<td>–</td>
<td>( ^{†} )</td>
</tr>
</tbody>
</table>

\( ^{†} \) this work

### 4.4 \( ^{31}\text{P}\{^1\text{H}\} \) simulation of unsymmetrical \( \text{cis-[RuXY(P-P)}_2 \) type complexes

A \( \text{cis} \) geometry of ruthenium \( \text{bis-diphosphine complexes results in either decidedly complex or deceptively simple }^{31}\text{P}\{^1\text{H}\} \) NMR spectra, depending upon whether the complex is unsymmetrically or symmetrically substituted. The spectral complexity of \( \text{cis-[RuXY(P-P)}_2 \) type compounds (\( \text{P-P} = \text{bidentate phosphine ligand} \) arises in part due to the inequivalence of every phosphine group, but also due to coupling
constants that are large compared to the chemical shift difference. For the cis ruthenium complexes of dmpe and depe presented in this work, the two phosphine groups trans to each other display couplings on the order of 240-310 Hz, whilst the observed chemical shift difference averages 800 Hz. The net effect is a deviation from first order behaviour, resulting in distortions in the intensities of the multiplets, particularly of the outer lines of the two trans phosphine splitting patterns, which further complicates the task of measuring accurate coupling constants. One method of dealing with this is to determine the coupling constants by simulation. Iterative algorithms such as those built into SpinWORKS 2.5.4 (© 1999-2006 Kirk Marat) allow for the coupling constants not only to be determined with greater accuracy than direct measurement, but also allows identification of each observed coupling.

Spectra were processed by applying a Gaussian Multiplication window function followed by Fourier transformation with a large number of data points (typically 256,000) to aid in resolution of densely populated regions of the spectral transitions, before iteratively refining the simulation until the root mean square (RMS) error ceased improving (typically ≤ 0.5 Hz RMS at 162 MHz). Phosphine labelling was consistent for all spectra, with the phosphine position trans to the coordinated chloride being labelled position A (Figure 4.10), although for some spectra the assignment of this position was not unambiguous. The remaining phosphine positions were determined via $^2J_{pp}$ measurements. A simulation example is presented in Figure 4.11.
Figure 4.10 – Phosphine labelling for simulated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of unsymmetrical cis complexes prepared in this work

![Diagram of phosphine labelling](image)

Figure 4.11 – Simulated and experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of cis-$[\text{RuCl(CO)}(\text{depe})_2]^{+}$, showing ddd splitting of all resonances and 2nd order behaviour of the central two resonances, which is typical of an unsymmetrically substituted cis-diphosphine complex

Simulations were relatively straightforward for most complexes, although it was not possible to simulate the spectrum of cis-$[\text{RuCl(N_3)(depe)}_2]$ since the simulation converged poorly to an obviously incorrect result. Significantly, the chemical shift of the two axial phosphine groups in
$cis$-[RuCl(N$_3$)(depe)$_2$] differ so little that the intensities of the outer transitions are too low to be observed, preventing measurement of the trans phosphine coupling constant.

The collected information obtained from $^{31}$P{$^1$H} NMR simulation is presented in Table 4.6. There exist no obvious trends, although complexes with a strong π-acceptor in their ligand set (e.g., those of CO, MeCN and tBuNC) exhibit a significantly smaller trans coupling ($J_{(C,D)}$) than other complexes, however this correlation does not extend to the other three coupling constants.
Table 4.6 – Simulated $^{31}\text{P}^{(1)}\text{H}$ chemical shifts and coupling constants for a series of cis-[RuCl(X)(P-P)$_2$] complexes (P-P = dmpe, depe)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_A$(ppm)</th>
<th>$\delta_B$(ppm)</th>
<th>$\delta_C$(ppm)</th>
<th>$\delta_D$(ppm)</th>
<th>$J_{A,B}$(Hz)</th>
<th>$J_{A,C}$(Hz)</th>
<th>$J_{A,D}$(Hz)</th>
<th>$J_{B,C}$(Hz)</th>
<th>$J_{B,D}$(Hz)</th>
<th>$J_{C,D}$(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[RuCl(OTf)(depe)$_2$]</td>
<td>66.5</td>
<td>65.7</td>
<td>49.1</td>
<td>47.6</td>
<td>34.0</td>
<td>18.5</td>
<td>21.1</td>
<td>24.7</td>
<td>22.1</td>
<td></td>
</tr>
<tr>
<td>cis-[RuCl(BF$_4$)(depe)$_2$]</td>
<td>66.0</td>
<td>65.4</td>
<td>55.5</td>
<td>56.5</td>
<td>35.0</td>
<td>19.3</td>
<td>21.5</td>
<td>26.4</td>
<td>20.9</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="OTf">RuCl($^{15}$NH$_3$)(depe)$_2$</a></td>
<td>64.8</td>
<td>56.5</td>
<td>46.8</td>
<td>48.7</td>
<td>30.3</td>
<td>17.9</td>
<td>23.5</td>
<td>21.5</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="OTf">RuCl(H$_2$NNH$_2$)(depe)$_2$</a></td>
<td>62.2</td>
<td>54.3</td>
<td>47.1</td>
<td>46.8</td>
<td>30.2</td>
<td>19.5</td>
<td>22.3</td>
<td>26.4</td>
<td>20.9</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="OTf">RuCl(CN$_t$Bu)(depe)$_2$</a></td>
<td>60.4</td>
<td>54.8</td>
<td>49.6</td>
<td>48.7</td>
<td>30.1</td>
<td>17.9</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="OTf">RuCl(NCMe)(depe)$_2$</a></td>
<td>62.7</td>
<td>53.9</td>
<td>49.5</td>
<td>48.7</td>
<td>30.3</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="OTf">RuCl(CO)(depe)$_2$</a></td>
<td>56.6</td>
<td>53.9</td>
<td>49.1</td>
<td>48.4</td>
<td>30.2</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-[(RuCl(depe)$_2$)$_2$]$^{(\mu$-$N$<em>2$)} $(BArF$</em>{24}$)$_2$</td>
<td>64.4</td>
<td>53.9</td>
<td>43.2</td>
<td>48.4</td>
<td>30.6</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-[RuCl(OTf)(dmpe)$_2$]</td>
<td>54.1</td>
<td>53.5</td>
<td>43.2</td>
<td>48.4</td>
<td>30.6</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-[RuCl(BF$_4$)(dmpe)$_2$]</td>
<td>54.6</td>
<td>54.6</td>
<td>43.5</td>
<td>48.4</td>
<td>30.6</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="BArF$_%7B24%7D$">RuCl(N$_2$)(dmpe)$_2$</a></td>
<td>40.7</td>
<td>53.5</td>
<td>35.9</td>
<td>35.0</td>
<td>30.6</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>cis-[(RuCl(dmpe)$_2$)$_2$]$^{(\mu$-$N$<em>2$)} $(BArF$</em>{24}$)$_2$</td>
<td>50.0</td>
<td>53.5</td>
<td>35.9</td>
<td>35.0</td>
<td>30.6</td>
<td>19.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.7</td>
<td></td>
</tr>
</tbody>
</table>
4.5 Conclusions

Of all the ambient temperature reactions of cis-{Ru(depe)\textsubscript{2}}\textsubscript{2}(\textmu-Cl)\textsubscript{2}(OTf)\textsubscript{2} observed, the reaction with H\textsubscript{2} is the only one to involve an immediate change in geometry. Theoretical studies have shown that for complexes of the type [Ru(\eta\textsuperscript{2}-H\textsubscript{2})(P-P)\textsubscript{2}]\textsuperscript{+}, the trans geometry corresponds to the global energy minimum of the system and that the dihydrogen ligand prefers to coordinate trans to a ligand of high trans influence,\textsuperscript{41,42} which is entirely in line with the observed results. It is, however, unknown whether the isomerisation process occurs before or after initial dihydrogen coordination. Given the propensity of cis-{Ru(depe)\textsubscript{2}}\textsubscript{2}(\textmu-Cl)\textsubscript{2}(OTf)\textsubscript{2} to scramble its phosphine positions (Chapter 3, Section 3.4.3), presumably through the five-coordinate species [RuCl(depe)\textsubscript{2}]\textsuperscript{+}, there is obviously a low energy barrier involved with cis/trans isomerisation. Furthermore, other ligands such as NH\textsubscript{3}, NH\textsubscript{2}NH\textsubscript{2}, and MeCN exhibit sufficient lability to suggest that post-coordination isomerisation to a trans geometry is not impossible for complexes of these ligands; indeed, the complex cis-{RuCl(CN\textsuperscript{t}Bu)(depe)\textsubscript{2}} crystallises as the trans isomer.

The observation that these complexes do not observably undergo cis/trans isomerisation in solution within the time frames studied (< 48 hours) could arise due to a number of factors. One possibility is that the cis isomer is thermodynamically favoured for some ligands, however, on the basis of similar literature complexes this is unlikely. A more likely explanation is that the cis products are formed kinetically
from the initial complex cis-{Ru(depe)_2}$_2$(µ-Cl)$_2$(OTf)$_2$ and are stable at ambient temperature. Comparisons can be drawn with the literature five-coordinate complex [RuCl(dcpe)$_2$]$^+$, which reportedly forms the cis complexes of the type cis-[RuCl(L)(dcpe)$_2$]$^+$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane, L = CO, MeCN, PhCN) in dcm or acetone solution at −60°C that rapidly isomerise to the thermodynamically stable trans analogues upon warming to ambient temperature.$^{17}$ Whilst the complexes cis-[RuCl(L´)(depe)$_2$](OTf) (L´ = NH$_3$, NH$_2$NH$_2$, MeCN) do not display such thermal isomerisation behaviour at ambient temperature, mild heating may facilitate their transformation to the trans analogues.

The formation of isomeric cis-[RuCl(CO)(depe)$_2$]$^+$ and trans-[RuCl(CO)(depe)$_2$]$^+$ from cis-{Ru(depe)$_2$}$_2$(µ-Cl)$_2$(OTf)$_2$, through conditions which could hardly be more dissimilar, provides an interesting opportunity to study perturbations of the physical and spectroscopic properties caused by the different ligand arrangements. In particular the observation that the trans isomer possesses a $\nu_{\text{CO}}$ that is significantly lower in energy (44 cm$^{-1}$) than the cis analogue, highlights the dramatic effect the donor properties and structural geometry of co-ligands can have on the activation of end-on coordinated $\pi$-systems such as carbon monoxide or dinitrogen.

Overall, the fragment cis-[RuCl(depe)$_2$]$^+$, formed from the cleavage of cis-{Ru(depe)$_2$}$_2$(µ-Cl)$_2$(OTf)$_2$, successfully coordinated a number of hard
and soft $\sigma$-donor ligands, along with many ligands of various $\pi$-acidities. Thus, the question is begged: why not coordinate dinitrogen? The reaction between trans-$[\text{RuCl}_2(\text{depe})_2]$ and Tl(BArF$_{24}$) (Chapter 3, Section 3.1.7) produced cis-$[\{\text{RuCl(depe)}_2\}_2(\mu-N_2)](\text{BArF}_{24})_2$ as the major product, which crystallised as trans-$[\text{RuCl}(N_2)(\text{depe})_2](\text{BArF}_{24})$. Thus, the coordination of dinitrogen to both cis and trans isomers of $[\text{RuCl(depe)}_2]^+$ is not untenable.
Chapter 4  Reactions of [Ru₂Cl₂(depe)₄](OTf)₂

References


Chapter 4  
Reactions of \([\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2]\)


