Conclusions and future work

6.1 Conclusions

Attempts to prepare dinitrogen adducts of \([\text{RuCl}(\text{P-P})_2]^+\) (P-P = dmpe, depe) in this work highlight that dinitrogen coordination will only occur if all other potential products are less favourable. Oxidation of ruthenium(II) to ruthenium(III), coordination of anions and coordination of or reaction with solvent must all be avoided. Even if all such criteria are met, it may still be the case that a five-coordinate structure may be sufficiently stable sans dinitrogen, or that alternative means of filling the coordination sphere are realised, for example, dimerisation through chloride ligands.

Of the chloride abstraction agents used in this work, Na(BPh$_4$), Na(BArF$_{24}$), TMS(OTf), Ag(OTf), Tl(OTf), Tl(BArF$_{24}$) and Tl(BF$_4$), the thallium salts have proven to be the most successful, whilst the BArF$_{24}$ anion was the only anion for which no affinity to coordinate was observed. Tl(BArF$_{24}$) was shown to facilely abstract a single chloride from both cis and trans isomers of \([\text{RuCl}_2(\text{P-P})_2]\) at ambient temperature, resulting in precipitation of TlCl. For both isomers of \([\text{RuCl}_2(\text{depe})_2]\) and for the cis isomer of \([\text{RuCl}_2(\text{dmpe})_2]\), this resulted in formation of dinitrogen-bridged dimers of the form cis-\([\{\text{RuCl}(\text{P-P})_2\}_{2}\mu-N_2]\)(BArF$_{24}$)$_2$, whilst trans-\([\text{RuCl}_2(\text{dmpe})_2]\) reacted to give the five-coordinate complex trans-\([\text{RuCl}(\text{dmpe})_2](\text{BArF}_{24})\) as a stable product.
Trans-[RuCl(N₂)(dmpe)₂](BArF₂₄) was produced from the reaction of trans-[RuCl₂(dmpe)₂]·Tl(OTf) with Na(BArF₂₄) and displays an activated νₙₙ of 2012 cm⁻¹, which is the lowest reported νₙₙ for a ruthenium complex in the literature. This contrasts with cis-[{RuCl(P-P)₂}(µ-N₂)](BArF₂₄), which, despite the electron-rich ligand set and bridging dinitrogen coordination mode, exhibits (Raman) νₙₙ of 2284 cm⁻¹ and 2280 cm⁻¹ for the dmpe and depe complexes respectively. The substantial difference between cis and trans isomer highlights the importance of geometry in the activation of coordinated dinitrogen.

Reactions involving the triflate anion resulted mostly in the formation of complexes in which the anion coordinated to the ruthenium centre, however the reaction of trans-[RuCl₂(depe)₂] with Tl(OTf) formed the interesting product cis-[{Ru(depe)₂}(µ-Cl)₂](OTf)₂. This dichloride-bridged complex reacts with a wide range of neutral and anionic ligands such as CO, MeCN, 'BuNC, NH₃, NH₂NH₂, and N₃⁻ to give complexes of the form cis-[RuCl(L)(depe)₂]⁺⁺ (x = 0, 1). Reaction with hydrogen gas was the only reaction to involve an immediate change in geometry, forming the known complex trans-[RuCl(η²-H₂)(depe)₂]⁺.

Attempts to force dinitrogen coordination through driving conditions were unsuccessful, as reactions of trans-[RuCl₂(P-P)₂] performed at high temperature (150°C) and dinitrogen pressure (140 psi) resulted instead in carbonyl abstraction from both methanol and tetrahydrofuran. A similar
result was obtained when treating \( \text{cis-}{[\text{Ru(depe)}_2]_2(\mu-\text{Cl})_2(\text{OTf})_2} \) with \( \text{N}_2 \) under the same conditions, indicating that the five-coordinate ruthenium intermediate formed (\( [\text{RuCl}(\text{P-P})_2]^+ \)) is too reactive towards solvent at elevated temperatures to coordinate dinitrogen.

6.2 Future work

\( \text{Tl}(\text{BArF}_{24}) \) has proven to be an effective chloride abstraction agent for complexes of the form \( [\text{RuCl}_2(\text{P-P})_2] \). Nonetheless, the only dinitrogen adducts formed via this reagent were the dinitrogen-bridged dimers \( \text{cis-}{[\text{RuCl}(\text{P-P})_2]_2(\mu-\text{N}_2)}^{2+} \), where the \( \text{cis} \) geometry limits the \( \pi \)- acidity of the ruthenium centre and thus dinitrogen activation. Attempts to prepare \( \text{trans-}{[\text{RuCl}(\text{N}_2)(\text{P-P})_2](\text{BArF}_{24})} \) using \( \text{Tl}(\text{BArF}_{24}) \) resulted in isomerisation to a \( \text{cis} \) geometry for the depe complex (\( \text{cis-}{[\text{Ru(depe)}_2]_2(\mu-\text{Cl})_2(\text{OTf})_2} \)), whilst the dmpe analogue formed the stable five-coordinate complex \( \text{trans-}{[\text{RuCl}(\text{dmpe})_2](\text{BArF}_{24})} \). The choice of solvent has been demonstrated to significantly affect the outcome of chloride abstraction reactions, e.g., the reaction of \( \text{trans-}{[\text{RuCl}_2(\text{dmpe})_2]} \) with \( \text{Ag(OTf)} \) in methanol gives the oxidised complex \( \text{trans-}{[\text{RuCl}_2(\text{dmpe})_2](\text{OTf})} \) whilst in methanol the complex formed is \( \text{trans-}{[\text{RuCl}(\text{OTf})(\text{dmpe})_2]} \), thus it may be that chloride abstraction with \( \text{Tl}(\text{BArF}_{24}) \) in an alternative solvent will be sufficient to provide conditions conducive to dinitrogen coordination. This is both an obvious and simple area to explore in the future.
The five-coordinate species $\text{trans-}[\text{RuCl}(\text{dmpe})_2](\text{BArF}_2)_4$ is easily envisioned binding a number of ligands other than dinitrogen in a manner similar to that observed for $\text{cis-}[[\text{Ru}(\text{depe})_2](\mu-\text{Cl})_2](\text{OTf})_2$. Thus, the addition of potential ligands such as nitriles, isonitriles, amines and hydrogen to $\text{trans-}[\text{RuCl}(\text{dmpe})_2](\text{BArF}_2)_4$, or the abstraction of chloride from $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2]$ in the presence of such ligands are both fields worth exploring.

Whilst chloride abstraction from $\text{trans-}[\text{RuCl}_2(\text{depe})_2]$ invariably resulted in isomerisation to $\text{cis}$ products, reaction of one such species, $\text{cis-}[[\text{Ru}(\text{depe})_2](\mu-\text{Cl})_2](\text{OTf})_2$, with hydrogen gas gave $\text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](\text{OTf})$ in which the coordinated $\text{H}_2$ is labile. This complex may act as source of $\text{trans-}[\text{RuCl}(\text{depe})_2]^+$ for the addition of additional ligands, allowing isolation of the $\text{trans}$ analogues of the $\text{cis-}[\text{RuCl}(\text{L})(\text{depe})_2]^+$ (L = neutral or anionic ligand) complexes described in Chapter 4.

A number of reactions were performed under forcing conditions ($150^\circ\text{C}, 140$ psi $\text{N}_2$); however, in all cases the high temperature led to carbonyl abstraction from solvent in preference to dinitrogen coordination. Repeating the high pressure reactions at ambient temperature may avoid unwanted reactions involving solvent decomposition, and expanding this treatment to a number of other complexes such as $\text{trans-}[\text{RuCl}(\text{dmpe})_2](\text{BArF}_2)_4$ or $\text{trans-}[\text{RuCl}(\eta^2-\text{H}_2)(\text{depe})_2](\text{OTf})$ is a potentially worthwhile endeavour.
The successful coordination of dinitrogen, in both terminal and bridging modes to the electron-rich $[\text{RuCl}(P-P)_2]^+$ core enables the possibility of attempts at functionalising the dinitrogen molecule, whether by reduction of the dimeric system to give diazenido type complexes, or by addition of HX to the coordinated dinitrogen, ultimately working towards a goal of reduction of dinitrogen on ruthenium.