

Chap 10 General Conclusion

CHAPTER 10. GENERAL CONCLUSION

The title of this thesis was called ‘solventless substitution chemistry of iron and ruthenium metal carbonyl complexes’ and this title summarises the work that was performed in the study. Most of these reactions studied have been previously carried out in a solvent medium. A solventless procedure was seen as an alternative synthetic methodology which complies with the principles of green chemistry.

Solventless reactions have been successfully conducted between $\text{CpFe(CO)}_2\text{I}$ and a range of phosphine ligands: PPh_3 , $\text{P(p-OCH}_3\text{C}_6\text{H}_4)_3$, $\text{P(m-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P(p-FC}_6\text{H}_4)_3$, $\text{P(p-ClC}_6\text{H}_4)_3$. Two products were typically formed, a salt product $[\text{CpFe(CO)}_2\text{PR}_3]\text{I}$ and a non-salt product $\text{CpFe(CO)(PR}_3)\text{I}$ in different ratios depending on the ligand. Generally the salt product was the major product formed in the reaction. Electron donating ligands: $\text{P(p-OCH}_3\text{C}_6\text{H}_4)$, $\text{P(m-CH}_3\text{C}_6\text{H}_4)_3$ and PPh_3 were found to be more reactive than the electron withdrawing ligands, $\text{P(p-ClC}_6\text{H}_4)_3$ and $\text{P(p-FC}_6\text{H}_4)_3$ suggesting a nucleophilic attack of the ligand during the reaction. However, the reactivity of $\text{P(p-FC}_6\text{H}_4)_3$ was unexpectedly high at 70°C and it was proposed that this was due to the reaction occurring in a melt phase reaction as was demonstrated by the DSC studies of the mixture.

At high temperature (100°C), the decarbonylation of the salt product to give the non salt product has been observed.

The effect of the Me substituent on the Cp ligand has been explored in the reaction between $\text{MeCpFe(CO)}_2\text{I}$ and the same range of phosphine ligands as those used with $\text{CpFe(CO)}_2\text{I}$. The Me group has been found to favour the formation of the salt product to the detriment of the non-salt product formation. In fact it has been established that the presence of an electron donating group on the Cp ring results in the strengthening of the Fe-CO bond. Therefore, the Fe-I bond breaks first leading to the salt product formation.

The iron dimer $[\text{CpFe}(\text{CO})_2]_2$ has been used to catalyse the solventless reactions between $\text{CpFe}(\text{CO})_2\text{I}$, $\text{MeCpFe}(\text{CO})_2\text{I}$ and phosphine ligands. The rates of reactions were markedly increased and again the salt was the major product of the reaction. This distribution between salt and non-salt products in the solventless procedures is in contrast to the results obtained in solvent procedures. In fact, when a solvent was used (e.g. refluxing benzene), the non-salt product was the major product of the reaction. This observation suggests that the mechanism taking place in a solventless procedure is not the same as the mechanism occurring in the presence of a solvent. In solventless conditions the reaction proceeds via a 19e intermediate, $[\text{CpFe}(\text{CO})_2\text{L}]^+$, while in a solvent medium, the reaction occurs via a 17e intermediate, $\text{CpFe}(\text{CO})\text{L}^+$. An experiment in which a stoichiometric amount of $\text{MeCpFe}(\text{CO})_2\text{I}$ and $[\text{CpFe}(\text{CO})_2]_2$ was used to catalyze the reaction with triphenylphosphine has confirmed this hypothesis.

Spectroscopic results for the salt and non salt products are consistent with the reported data for similar compounds prepared by conventional routes. Mass spectrometry analysis of the salt products revealed that the I atom is very labile. The fragmentation starts by the loss of I and then the two CO ligands. In the non salt compounds, it is the CO ligand which is removed before the I atom.

The solventless reactions between $\text{RCpRu}(\text{CO})_2\text{I}$ ($\text{R} = \text{H}, \text{Me}$) and phosphine ligands: PPh_3 , $\text{P}(\text{p-OCH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\text{m-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\text{p-FC}_6\text{H}_4)_3$, $\text{P}(\text{p-ClC}_6\text{H}_4)_3$ have been investigated. It has been observed that the Ru complexes are much less reactive than their Fe analogues. The same conclusion has been also made in solvent procedures. The Me group on the Cp ring favours salt formation rather than non salt product as was also observed in the reactions with the Fe complexes.

Although the melt phase was found to be a good medium for a reaction to occur, it is not a sufficient condition. In fact, the mixture $\text{MeCpRu}(\text{CO})_2\text{I} + \text{PR}_3$ melts at $36\text{--}42^\circ\text{C}$ but no reaction was observed, even at 70°C in the absence of catalyst for all the ligands used. The same problem was also observed for the reaction between $\text{MeCpFe}(\text{CO})_2\text{I}$ and PR_3 . Therefore, other factors such as energy requirements for the reaction, as well as electronic and steric properties of the ligands are responsible for the negligible reaction.

The solventless reactions between $\text{RCpM}(\text{CO})_2\text{I}$ ($\text{R} = \text{H, Me; M} = \text{Fe, Ru}$) and phosphite ligands : $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{OPh})_3$ have also been investigated. In contrast to the reactions with phosphine ligands, it has been observed that solventless reactions with phosphites are different. In fact, a very low conversion into non salt product was obtained while the salt product was not formed at all. Indeed reactions are slower than in a solvent. However when trimethylamine N-oxide was added to the reaction mixture using solventless conditions, the non salt product $\text{RCpM}(\text{CO})[\text{P}(\text{OR})_3]\text{I}$ was readily obtained.

A range of cyclopentadienyl based dimers : $[\text{CpFe}(\text{CO})_2]_2$, $[\text{MeCpFe}(\text{CO})_2]_2$, $[\text{CpRu}(\text{CO})_2]_2$, $[\text{MeCpRu}(\text{CO})_2]_2$, $[\text{CpMo}(\text{CO})_3]_2$, $[\text{MeCpMo}(\text{CO})_3]_2$ and palladium based compounds : Pd, PdO, Pd/CaCO₃ 5%, Pd/CaCO₃ 10% have been used to catalyze the solventless reactions between $\text{CpFe}(\text{CO})_2\text{I}$ and PPh_3 . The cyclopentadienyl metal dimers have been found to be the best catalysts for the reactions

Solventless migratory-insertion reactions between $\text{CpFe}(\text{CO})_2\text{Me}$ and a range of phosphine ligands : PPh_3 , $\text{P}(\text{p-OC}_6\text{H}_4)_3$, $\text{P}(\text{m-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\text{p-FC}_6\text{H}_4)_3$, $\text{P}(\text{p-ClC}_6\text{H}_4)_3$, $\text{P}(\text{p-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\text{o-CH}_3\text{C}_6\text{H}_4)_3$, PCy_3 were also investigated. Only the acetyl product $\text{CpFe}(\text{CO})(\text{PR}_3)(\text{COMe})$ was obtained in the reaction. The reaction was favoured by electron donor ligands and was very dependent on the steric effect of the incoming ligand.

Ligands with large cone angles such as P(o-CH₃C₆H₄) (194°C) did not react despite this ligand having a relatively good electron donating ability while ligands with small cone angles and relatively poor electron donor abilities like P(p-ClC₆H₄)₃ (145°C) were shown to form a significant amount of the product.

Solventless insertion reactions of SO₂ into RCpFe(CO)₂R' (R = H, Me, CO₂H; R' = Me, CH₂Ph) compounds to form S-sulfinate derivatives RCpFe(CO)₂SO₂R' have been investigated. It is worthy of note that SO₂ insertion into MeCpFe(CO)₂Me occurred very easily at room temperature while no reaction took place with CO₂HCpFe(CO)₂Me. This is consistent with the mechanism proposed earlier that the SO₂ insertion goes via a nucleophilic attack on the α-carbon leading to Fe-R' bond breakage. Therefore, an electron withdrawing group on Cp would strengthen the Fe-R' bond, blocking the SO₂ insertion while an electron donating group would weaken the Fe-R' bond, allowing an easy insertion of SO₂. A bulky R' group also will not favour the SO₂ insertion. Our results were consistent with this mechanism as the rate of SO₂ insertion into different substrates was as follows: MeCpFe(CO)₂Me > CpFe(CO)₂Me > CpFe(CO)₂CH₂Ph > CO₂HCpFe(CO)₂Me.

The solventless reactions described in this thesis have been performed on simple systems. The reactions that occurred between two reagents occurred in the melt phase. From this study it is apparent that the mere presence of a melt is an insufficient condition for a solventless reaction. However, *the melt is in principle a complex solvent system* in which reagents are in unusually high concentrations. Our study suggests that typical factors that influence reactions performed in solvents are also important in the melt. However, solvent effects due to the reactants can produce unexpected results e.g. the slow reaction between CpFe(CO)₂I and phosphites.

The thesis not only answers some questions but suggests further avenues of study. These include:

1. The use of DRIFTS and solid-state NMR spectroscopy to study reactions both in the melt and prior to melt formation. This should provide information on the mechanism of the reaction.
2. The focus of this study was on substitution reactions. Other reaction types should also (and some have been shown to) occur in the melt phase.
3. More complex reactions e.g. formation of metal carbenes should also be possible in the melt. This could lead to the facile synthesis of well known and novel organometallic compounds and catalysts.