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Solventless substitution chemistry of iron and ruthenium metal carbonyl complexes

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CHAPTER 1. INTRODUCTION

Chemical transformations have played a key role in the history of human kind from prehistorical time until the current era. This can be easily seen through different fields such as development of drugs in medical sciences, fertilizers in agriculture, improvement of diet due to food chemistry, clothes from textile industry, petroleum products in transport, to name a few examples.

Quite recently, it has been observed that negative consequences accompanying the development in chemistry are not trivial. For example, the depletion of the ozone layer by CFC compounds, problems arising from the use of chemicals in the medical field, a wide range of environmental pollution (soil, water, air) and toxicity issues that have emerged from chemical industries and research laboratories. This has led to the development of what is now known as *Green Chemistry*. Green chemistry is a new philosophy of carrying out chemical reactions that takes into account the whole process not only the formation of the desired product in order to minimize the environmental pollution as well as the degradation of human health due to the use of chemicals. Green chemistry was inspired by the adage that *it is better to prevent than to cure*. Green chemistry is governed by a number of principles one of them being that the use of auxiliary materials in a chemical reaction, such as a solvent, should be avoided wherever possible. This has led to the concept of solventless reactions.

The aim of this study was to evaluate the possibility of performing simple chemical reactions in the absence of solvent. To test the principle, solventless reactions of some substituted cyclopentadienyl metal complexes of Fe and Ru with two electron donor ligands like phosphines, phosphites, SO_2 and CO were studied.

Chapter two deals with a literature survey focused on green chemistry. The emphasis is placed on the twelve principles underpinning this approach, some new chemical synthesis methodologies inspired by the green chemistry philosophy as well as challenges facing green chemistry

Chapter three of this thesis explains the general laboratory working conditions as well as the characterization techniques used in the study.

Chapter four deals with the solventless reactions between $CpFe(CO)_2I$ and a range of phosphine ligands. The reactivity of the ligands and the melt issue have been discussed.

The solventless reactions between $MeCpFe(CO)_2I$ and phosphine ligands are dealt with in chapter five. The effect of the Me substituent on the Cp ring was studied.

Chapter six explores the solventless reactions between $RCpRu(CO)_2I$ (R = H, Me) and phosphine ligands. The effects of the presence of Ru as a metal centre as well as the R group have been discussed.

In chapter seven, phosphite ligands and $RCpM(CO)_2I$ (R = H, Me; M = Fe, Ru) were reacted under solventless conditions. The reactivity of phosphites was compared to the reaction of phosphine ligands.

Chapter eight discusses the ability of a range of cyclopentadienyl and palladium based compounds to catalyze the solventless reactions between $CpFe(CO)_2I$ and triphenylphosphine.

Chapter nine deals with the solventless reactions of substituted cyclopentadienyl iron complexes of the type $RCpFe(CO)_2R'$ (R = H, Me, CO_2H ; R' = Me, CH_2Ph) and solid phosphines as well as gaseous ligands like SO_2 and CO while chapter 10 gives a summary of the general conclusion for the thesis.

A short introduction is presented at the beginning of chapters 4 – 9 that explains the rationale for the study that follows. Each chapter also has a conclusion. Figures, tables and scheme are incorporated into the body of the text.