

Abstract

Studies on structures and reactivities of coordinatively unsaturated complexes have received much attention from organometallic chemists in terms of intermediates in transition metal catalyzed organic transformations. A number of transition metal catalysts have been used for various kinds of organic transformations. Ruthenium compounds have been used extensively as catalysts for different types of organic reactions. For example, ruthenium complexes have been utilized in metathesis, C-H activation, C-C bond formation, Oppenauer oxidation, and H₂-hydrogenation/transfer hydrogenation. In catalytic reductions of organic compounds, catalytic transfer hydrogenation can be an effective method for reducing a variety of organic substrates, which avoids some of the technical and safety concerns associated with using compressed hydrogen gas. Transfer hydrogenation (TH) using suitable donor molecules such as alcohols, formic acid or formic acid derivatives has gained importance over last few years for the relatively benign nature of the reagents and mild reaction conditions employed. Replacing organic solvents with water offers economic advantages, improves safety, and reduces the environmental impact of the waste stream, and thus offers great opportunities for 'green' chemistry. A literature survey reveals that the catalysts of choice for TH of ketones are ruthenium-based derivatives and only a few catalytic systems with this metal have been described for the TH of aldehydes. In addition, ruthenium catalyzed selective reduction of unsaturated organic substrates and selective alkylation of amines, under mild conditions are of interest. The thesis entitled "**Studies on Synthesis and Structure of Cationic Ruthenium(II) Complexes and Their Efficacy as Catalysts for Transfer Hydrogenation**" is primarily an effort for the development of new cationic ruthenium(II) complexes and study their catalytic activity towards transfer hydrogenation reactions from the viewpoint of developing environmentally benign organic synthesis.

The thesis has been divided into six chapters. The contents of each chapter are described briefly.

Chapter 1: General Introduction

Chapter 1 of the thesis describes non-exhaustive background information to the ruthenium chemistry and gives a brief overview on recent developments in transfer hydrogenation reactions. The ruthenium-mediated transfer hydrogenation and asymmetric transfer hydrogenation of carbonyl compounds and imines and mechanistic course of the reactions are discussed. In addition, a discussion on H₂-hydrogenation catalyzed by ruthenium complexes has been included. Finally, in view of the state of knowledge on the ruthenium catalyzed transfer hydrogenation, the aim and objective of the present work have been defined.

Chapter 2: General methods, Preparation and Purification of the Starting Materials and Particulars of Instruments/Equipment Used

This chapter provides particulars of instruments used for characterization and structural assessment and general methodologies adopted for the experimental work. Preparation and methods of purification of the starting materials are described in this chapter.

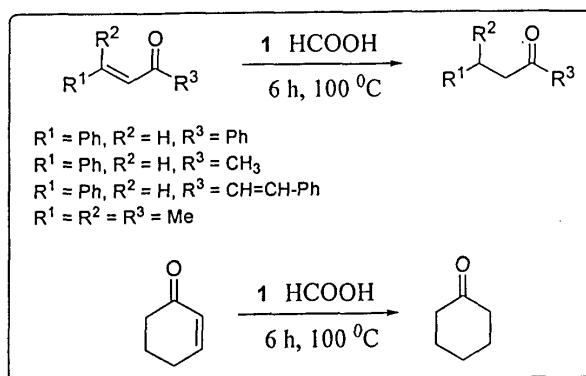
Chapter 3: Synthesis, Characterization and Structure of Cationic Ruthenium(II) Complexes Containing Triphenylphosphine Ligands and Their Efficacy as Catalysts for Transfer Hydrogenation of Aldehydes

This chapter deals with the synthesis, characterization and catalytic activity of the ruthenium(II) cationic compounds, [(PPh₃)₂Ru(CH₃CN)₃Cl][BPh₄] (**1**) and [(PPh₃)₂Ru(CH₃CN)₃Cl][ClO₄] (**2**). The complexes **1** and **2** have been characterized by elemental analyses, IR, UV-visible, mass spectra and ¹H NMR spectral studies, and also by electrochemical and magnetic measurements. Compound **1** has been

structurally characterized. The performance of the complex **1** as catalyst in transfer hydrogenation of aldehydes and ketones has been carried out. Although aldehydes are difficult to reduce by transfer hydrogenation catalysts from a solvent such as refluxing 2-propanol, compound **1** was found to be more effective for reduction of aldehydes rather than ketones. The catalytic activity of compound **2** has also been studied and a comparison between the catalytic activities of **1** and **2** has been done. Finally, based on the reported mechanistic works, a possible reaction pathway has been proposed.

Chapter 4: Effect of Hydrogen Donor on Transfer Hydrogenation: Chemoselective Transfer Hydrogenation of α,β -Unsaturated Carbonyl Compounds Catalyzed by $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ (1**)**

We were interested in the effect of hydrogen donor on the transfer hydrogenation of carbonyl compounds. Thus, in continuation of our studies, $[Ru(PPh_3)_2(CH_3CN)_3Cl]^+[BPh_4]^-$ (**1**) catalyzed transfer hydrogenation of various α,β -unsaturated ketones using formic acid as the hydrogen donor is described in this chapter (Scheme 1). The reactions are found to be chemoselective for reduction of olefinic double bonds in the presence of carbonyl group.

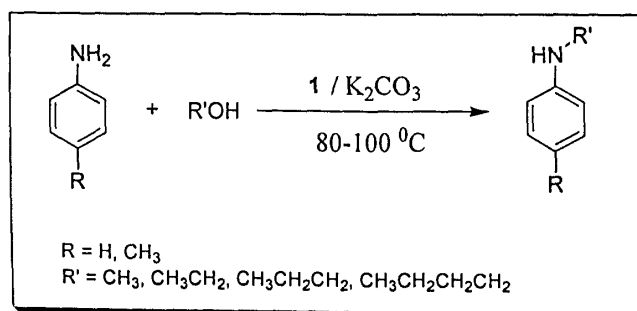


Scheme 1

2-Propanol was also used as hydrogen donor in these reactions. 2-Propanol was found to be not only less effective but also, its use resulted in a mixture of products, saturated ketones as well as saturated alcohols. The specificity of formic acid for hydrogenation of double bonds was further examined by the reaction of styrene and unsaturated aromatic acids with formic acid in the presence of **1**. Finally, a plausible mechanism of transfer hydrogenation of C=C double bonds has been proposed.

Chapter 5: Selective *N*-Monoalkylation of Anilines with Alcohols Catalyzed by [(PPh₃)₂Ru(CH₃CN)₃Cl][BPh₄] (1**)**

As a sequel to the studies described in Chapters 3 & 4 the efficiency of compound **1** as catalyst for reductive alkylation of amines by alcohols was taken up. Chapter 4 describes the successful use of ruthenium(II) cationic complex **1** as catalyst in the selective *N*-monoalkylation of anilines by alcohols under a mild conditions (Scheme 2). The reaction is specific for primary alcohols only.



Scheme 2

The alkylation of heteroaromatic amine and the effect of substituents on the aromatic ring have also been studied. Based on mechanistic work, a possible reaction pathway is proposed and the involvement of imine as intermediate has been established.

Chapter 6: Transfer Hydrogenation in Aqueous Medium: Synthesis, Structures and Properties of $[\text{Ru}(\text{L}_2)][\text{BPh}_4]_2$ and $[\text{RuL}(\text{CH}_3\text{CN})_3][\text{A}]_2$ [$\text{L} = N$ -{(2-Pyridyl)methyl}-2,2'-dipyridylamine and $\text{A} = \text{BPh}_4, \text{ClO}_4$]

This chapter incorporates synthesis, characterization and properties of the pyridine-based ligand, *N*-[(2-pyridyl)methyl]-2,2'-dipyridylamine (PMDA) and its ruthenium(II) complexes, $[\text{Ru}(\text{PMDA})_2](\text{BPh}_4)_2 \cdot 2\text{DMF}$ (**3**), $[\text{Ru}(\text{PMDA})(\text{CH}_3\text{CN})_3](\text{BPh}_4)_2$ (**4**) and $[\text{Ru}(\text{PMDA})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2$ (**5**). Compounds **3** and **4** have been structurally characterized. Their photophysical and electrochemical properties have been studied and finally efficacy of the cationic ruthenium complex, $[\text{Ru}(\text{PMDA})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2$ (**5**) as catalyst for transfer hydrogenation of aldehydes and ketones in aqueous medium have been explored.

The thesis concludes with a summary of the main results of the work and foreseeing the scope for the future investigation.