# INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
# SHORT ABSTRACT OF THESIS

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Thesis Title: Pincer-Ruthenium Catalyzed (De)Hydrofunctionalization of Alcohols and Related Value-Added Transformations

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## SHORT ABSTRACT

The contents of the present thesis entitled ***"Pincer-Ruthenium Catalyzed (De)Hydrofunctionalization of Alcohols and Related Value-Added Transformation"*** have been divided into five chapters based on the results achieved from the experimental and computational work carried out during the entire course of the PhD research program.

**Chapter I** provides about a brief literature survey on organic transformations catalyzed by organometallic complexes. The use of various type of pincer-metal complexes having versatile activity towards organic transformations is also discussed. The chapter ends by identifying and defining the scope of the thesis.

**Chapter II** describes the synthesis of a series of new (*bis*)imino pincer-ruthenium complexes of type $(^{R2}NNN)RuCl_2(PPh_3)$ (R = Cy, R = Ph, R = $^{i}$Pr and R = $^{t}$Bu). The use of sodium results in the formation of sodium alkoxide as a base which is generated *in-situ* from the substrate alcohol, and also acts as a water scavenger for the *N*-alkylation of amines. The use of these new pincer-Ru complexes have provided high reactivity towards *N*-alkylation reaction of amines with alcohols and excellent turnovers (ca. 29000 TON) were obtained. The detailed mechanistic and computational studies provide a better understanding of the reaction. Apparently, the $\beta$-hydride elimination is the overall RDS. This protocol has also been used to transform benzene-1,2-diamines to benzimidazoles with high productivity (ca. 12000 TON).

**Chapter III** discusses about the synthesis of a series of a phosphine free (*bis*)imino pincer-ruthenium carbonyl complexes of the type $(^{R2}NNN)RuCl_2(CO)$ (R = Cy, R = Ph, R = $^{i}$Pr and R = $^{t}$Bu). The $\beta$-alkylation of 1-phenyl ethanol with benzyl alcohol at 140 °C under solvent-free conditions catalyzed by $(^{Cy2}NNN)RuCl_2(CO)$ in the presence of catalytic amount of NaOH provides very high turnover number (ca. 93 % yield, 372000 TONs at 12000 TO/h). DFT studies

are complementary to mechanistic studies and indicate the insertion of $\alpha$-alkylated ketone into the Ru-H bond to be the overall RDS.

**Chapter IV** investigates the upgrading of bio-ethanol to *n*-butanol which has been accomplished *via* the pincer-ruthenium catalyzed Guerbet reaction under thermal conditions as well as under microwave irradiation. Under the microwave irradiation, high efficiency has been achieved after only 2 h in the presence of 10 mol% sodium ethoxide (NaOEt). Among all the NNN pincer-ruthenium complexes that have been utilized, ruthenium catalysts based on 2,6-*bis*(benzimidazole-2-yl)pyridine ligands showed higher activity towards the Guerbet reaction. The highest rate (8534 TO/h, ca. 18 % yield of *n*-butanol at 90 % selectivity) was obtained and up to 72 % ethanol (42 % *n*-butanol yield) conversion was achieved under the microwave irradiation. The DFT calculations indicate the generation of hydrogen to be the rate-determining step (RDS). The catalytic system comprising of ($p$-OH$^{Bim2}$NNN)RuCl$_2$(CO) immobilized over neutral alumina resulted in best productivity of 15510 TON.

**Chapter V** describes a dehydration strategy that has been formulated for the selective etherification of secondary alcohols catalyzed by the pincer-ruthenium catalyst ($^{Ph2}$NNN)RuCl$_2$(CO) in the presence of molecular oxygen under solvent-free and base-free conditions at 140 °C. Up to 92 % yield (ca. 6133 TON) of the corresponding ethers are obtained at a very low catalyst loading. The detailed mechanistic studies provide the role of oxygen as a co-catalyst, non-labile nature of the ancillary CO ligand and the hemi-labile nature of the pincer-ligand arm. Ru(III) species formed *via* single electron transfer (SET) from O$_2$ is detected as the resting-state of the etherification. This work has been extended not only to the etherification of various aromatic secondary alcohols but also to the cross etherification and/or *o*-alkylation of 1-phenyl ethanols with a variety of phenols.

The current thesis demonstrates a synthetic protocol for a new series of pincer-ruthenium complexes. These complexes have been utilized for various organic transformations with a systematic understanding of the reaction mechanism.