INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

The contents of the present thesis entitled ***"Catalytic Transformation of Alcohols for the Production of Hydrogen, Fuels and Specialty Chemicals Using Pincer-Ruthenium and Pincer-Nickel Complexes"*** have been divided into four chapters based on the results achieved from the experimental work carried out during the entire course of the PhD research program.

Chapter I provides a concise overview of the literature regarding pincer-metal complexes and organic transformations facilitated by them. The transformation of alcohols and their tandem reactions using transition metal complexes is also discussed. The chapter concludes by outlining and defining the scope of the current thesis.

Chapter II describes the synthesis of pincer-ruthenium complexes based on *bis*(imino)pyridine ligands of the type (^{R2}NNN)$RuCl_2(CH_3CN)$. These complexes, in addition to their analogous phosphine and carbonyl complexes were studied for the reforming of methanol in presence of water and base. Among the complexes screened, (^{Cy2}NNN)$RuCl_2(PPh_3)$ (0.2 mol%) gave the best yield of formic acid (81%) and hydrogen (81%) with 100% selectivity for a 2:1 mixture of methanol and water at 100 °C. Further, for a 3:1 mixture of methanol and water, 84% H_2 with 81% formic acid at 95% selectivity were obtained at 0.8 mol% catalyst loading. The kinetic isotope effect studies resulted in an average value of 1.96, when CH_3OH was replaced with CD_3OD in the reaction. A combined kinetic and DFT (*vide infra*) analysis indicated that the methanol C–H bond activation occurs as a part of the mechanism and is not a part of the RDS, while the O-H bond activation is the RDS and contributes majorly to the observed average k_H/k_D value of 1.96. These results are well complimented by the DFT studies, which point towards the involvement of σ-bond metathesis leading to the generation of first hydrogen molecule as the rate determining step for the both the cycles *i.e* till formic acid and till CO_2. The cycle leading to the formation of formic acid is kinetically more favored by 4.54 kcal/mol as compared to the CO_2 formation cycle. The homogeneity of the reaction is proved by the kinetic

studies, where rate of the reaction is first-order relative to both catalyst and methanol. The current reaction has also been extended towards to the generation of D_2, which has been further employed for the deuteration of unsaturated compounds such as styrene, stilbene and medicinally important quinolines.

Chapter III investigates the catalytic aqueous–phase reforming of ethanol employing a series of NNN pincer–ruthenium complexes based on *bis*(imino)pyridine and 2,6–*bis*(benzimidazole-2-yl) ligands. These ruthenium complexes have been studied for H_2 production from ethanol in water in the presence of base at 120 °C. Among the complexes considered, the best results were obtained using (^{Cy2}NNN)$RuCl_2(PPh_3)$, which gave a yield of up to 70% of H_2 and 73% of acetic acid from a mixture of ethanol and water in a 2:1 ratio in the presence of 1.5 equivalents of KO^{t}Bu at 0.2 mol % of catalyst loading. Labelling studies provide key evidence for the involvement of C–H activation in the catalytic ethanol reforming reaction with an average KIE of 5.23. Kinetic studies have been performed which indicate the first order rate dependence on concentration of both pincer-ruthenium catalyst and ethanol, which also validates the homogeneity of the reaction. The HRMS and NMR studies provide conclusive evidence for the release of PPh_3 and generation of (^{Cy2}NNN)RuCl(H) species which plays a key role in catalytic aqueous ethanol reforming reaction. The Ru–H species involved in the catalytic cycle has also been detected as its phosphine adduct by NMR studies. The computational studies are in agreement with the control experiments, and it indicates that the σ-bond metathesis step resulting in the release of first molecule of H_2, is the rate–determining step (RDS).

Chapter IV deals with the synthesis of a series of novel NNN pincer-Ni(II) complexes based on *bis*(imino)pyridine ligands ((^{R2}NNN)$NiCl_2(CH_3CN)$; R = ^{i}Pr, ^{t}Bu, Cy, Ph and *p*-F-C_6H_4). These complexes have been well characterized and effectively used for the catalytic *β*–alkylation of various secondary alcohols with primary alcohols, achieving high yields and remarkable turnover numbers. Among all the complexes studied, very high TONs (up to 18400) have been observed for the reaction of benzyl alcohol with 1-(4-trifluoromethyl)phenyl)ethane-1-ol in the presence of 0.005 mol% of (^{Ph2}NNN)$NiCl_2(CH_3CN)$ and 5 mol% NaO^{t}Bu at 140 °C after 24 h. The kinetic studies point towards the aldol condensation being the rate determining step, with the overall reaction showing zero-order dependence of rate on the catalyst concentration and first-order dependence of rate on the concentration of base and substrates. The control experiments and HRMS studies are in accordance with the proposed mechanism which point towards the involvement of hydrogenolysis/alcoholysis pathway in the product formation step.

The current thesis describes the synthesis of novel pincer-ruthenium and pincer-nickel complexes based on *bis*(imino)pyridine ligands. These novel pincer-ligated ruthenium complexes along with the earlier reported pincer-Ru(II) complexes have been employed for the reforming of alcohols to generate hydrogen and industrially valuable chemicals. Further, the transformation of alcohols to higher alcohols *via* pincer-Ni(II) catalyzed *β*–alkylation of secondary alcohols with primary alcohols has been demonstrated.