



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Investigations on the Pincer-Ruthenium and Pincer-Nickel Catalyzed Organic Transformations

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SHORT ABSTRACT

The contents of the present thesis entitled “*Investigations on the Pincer-Ruthenium and Pincer Nickel Catalyzed Organic Transformations*” 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 programme.

Chapter 1 contains a brief introduction and the literature review on the chemistry of pincer-metal complexes and their versatile applications in catalytic organic transformations. The chapter winds up with a discussion on the scope of the current thesis.

Chapter 2 demonstrates an efficient and atom-economical Kharasch addition of CCl_4 to styrene that is catalyzed by a series of pincer-ruthenium complexes $(^{\text{R}^2}\text{NNN})\text{RuCl}_2(\text{PPh}_3)$ ($\text{R} = \text{Cy}, ^i\text{Bu}, ^i\text{Pr}, \text{and Ph}$). Gratifyingly, very high turnovers (ca. 5670) have been observed for the $(^{\text{Cy}^2}\text{NNN})\text{RuCl}_2(\text{PPh}_3)$ catalyzed Kharasch addition of CCl_4 to styrene. The reaction has also been probed to obtain a detailed mechanistic understanding.

Chapter 3 sheds light on the utility of NNN pincer-ruthenium complexes based on sterically less hindered 2,6-bis(benzimidazole-2-yl) pyridine ligands in catalyzing high yield (92%) transformation of glycerol selectively (98%) to lactic acid. Systematic mechanistic studies provide a clear understanding to the role of Ru–P bond and steric crowding around the Ru centre in favoring catalysis.

Chapter 4 illustrates the application of a new and well-defined pincer-nickel complex $(^{\text{iPr}^2}\text{NNN})\text{NiCl}_2(\text{NCCH}_3)$ for catalytic *N*-alkylation that proceeds with very high turnover (34000 TON). Detailed insight on the operative mechanism points to the involvement of both hydrogenation and alcoholysis steps in the *N*-alkylation reaction. The $(^{\text{iPr}^2}\text{NNN})\text{NiCl}_2(\text{NCCH}_3)$ catalyzed reactions have been extended to the dehydrogenative coupling of benzene-1,2-diamines with alcohols to yield the corresponding benzimidazoles.

Chapter 5 reports a computational study on cyanomethylation reaction. Here the energetics of the cyanomethylation catalytic cycle for a series of ten pincer-nickel systems with varying electronic demands have been compared with the corresponding Miller’s catalyst $(^{\text{iPr}^2}\text{POCCN}^{\text{Et}^2})\text{NiO}^t\text{Bu}$ that is reported to be active at room temperature. The study culminates with the identification of imine based pincers with C central atom as potential contenders for the Miller’s catalyst. Presence of strong σ -donors in the flanking groups and weak *trans* influencing pincer central atoms were found to lead to unfavorable energetics in the cyanomethylation catalysis.