



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
PhD-17 SHORT ABSTRACT OF THESIS

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Thesis Title: 3d-Metal Salts and their Pincer-Complexes for Catalytic Value-Addition of Alcohols to Hydrogen and Speciality Chemicals

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SHORT ABSTRACT

Chapter I provides a concise overview of the literature regarding transition metal salts, coordination compounds, organometallic complexes with a special focus on pincer-metal complexes and organic transformations catalysed by them. The dehydrogenative coupling of alcohols and aqueous reforming of alcohols using transition metal salts and pincer-metal complexes is also reviewed. The chapter winds up by defining the scope of the current thesis. Chapter II demonstrates an efficient β -alkylation of secondary alcohols with primary alcohols catalyzed by commercially available $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and its corresponding pincer-Cr complex $^{\text{Ph}_2}\text{NNN}(\text{CrCl}_3)$. High yields (ca. 90%) of the β -alkylated product was obtained with a selectivity of 91% at very low loadings (0.005 mol%) of the pincer-chromium catalyst based on bis(imino pyridine) under microwave conditions in the presence of 5 mol% NaO^tBu . The reaction mechanism was probed on the basis of control experiments. Chapter III illustrates the potential of commercially available first-row, 3d transition metal salt chromium (III) chloride (0.4 mol%) in catalyzing the selective α -alkylation of nitriles with benzyl alcohol in excellent yields (ca. 99%) in the presence of 30 mol% KO^tBu at 140 °C after 24 h using conventional heating in air. The reaction was found to reach completion within 2 h under microwave heating conditions, with comparable yields (ca. 93%). Detailed mechanistic studies are suggestive of a sole contribution from the alcoholysis path in the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ catalysed α -alkylation of benzyl nitrile with benzyl alcohol with β -hydride elimination as the RDS having a rate-determining barrier of 28.6 kcal/mol. Chapter IV deals with the net transfer dehydrogenation of glycerol (GLY) to lactic acid (LA) catalyzed by commercially available first-row transition metal salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and its corresponding pincer complexes based on bis(imino)pyridine ligands ($(^{\text{R}^2}\text{NNN})\text{CrCl}_3$; $\text{R} = \text{Ph}, \text{Cy}, ^i\text{Pr}$ and ^tBu) in the presence of a sacrificial hydrogen acceptor, acetone. The pincer-Cr complex, $(^{\text{Cy}^2}\text{NNN})\text{CrCl}_3$ (0.5 mol%) was found to efficiently bring about the catalytic net transfer dehydrogenation of glycerol in presence of 1.1 equivalents

of NaOH, at 160 °C to afford 94% lactic acid at 98% selectivity along with another value added product isopropanol (IPA). Thorough mechanistic investigations have suggested the homogeneous molecular nature of the Cr(II) active species in the reaction course. Chapter V describes the role of readily available, inexpensive, environmentally benign and earth-abundant base metal salt cobaltous chloride (0.5 mol%) which successfully catalysed the dehydrogenative conversion of glycerol to lactic acid in an acceptorless fashion as well as under transfer dehydrogenation conditions using acetone as a sacrificial acceptor at 160 °C in the presence of various bases. Up to 75% conversion of glycerol to lactic acid (33%), ethylene glycol (14%) and formic acid (27%) was observed in addition to hydrogen, under the acceptorless conditions, whereas a maximum of 93% lactic acid with 96% selectivity along with isopropanol was obtained in the presence of acetone as a sacrificial hydrogen acceptor in a sealed vessel. Mechanistic investigations shed light on the homogeneous nature of the reaction mixture involving Co(II) as the active species.

