INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

The contents of the present thesis entitled "**Pincer-Ruthenium and Pincer-Cobalt Catalyzed Value-Addition of Alcohols**" 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 discusses a brief description on catalytic organic transformations reported in literature utilizing pincer-metal complexes. A large library of pincer-complexes that have been studied for various reactions such as alkane dehydrogenation, C-C or C-N bond formation and reduction of carbon dioxide, have been briefly reviewed in the chapter. The chapter ends with the identification and scope of the current thesis.

Chapter-II discusses the synthesis and characterization of three novel NNN pincer-Ru complexes based on *bis*(imino)pyridine ligands. These complexes along with other previously reported pincer-Ru complexes based on *bis*(imino)pyridine and 2,6-*bis*(benzimidazol-2-yl)pyridine ligands have been studied for the β-methylation of 2-phenylethanol and the selective β-dimethylation of 1-phenylethanol utilizing methanol as an alkylating agent. The optimization studies revealed that the pincer-ruthenium complex $[(^{MeBim2}NNN)RuCl(PPh_3)_2]Cl$ is the most efficient among the considered catalysts. In the presence of 0.5 mol % of $[(^{MeBim2}NNN)RuCl(PPh_3)_2]Cl$, 0.75 equivalents of KOH and 7.5 equivalents of methanol, up to 92% yield of β-methylated 2-phenylethanol was observed at 140 °C after 24 h. Under similar conditions, the β-dimethylation of 1-phenylethanol was achieved using 2 equivalents of Na and 24.8 equivalents of methanol. The synthetic protocol was further extended towards the β-methylation and selective β-dimethylation of about 35 substrates. The evidence for the homogeneous nature of the reaction was revealed from mercury drop experiments and kinetic studies. From the kinetic studies, it was observed that the rate of product formation has a linear dependence on the concentrations of both the pincer-ruthenium catalyst and 2-phenylethanol. DFT studies are in line with the observed secondary kinetic isotope effect (KIE) of 1.56 and suggest that dehydrogenolysis involving σ-bond metathesis of methanol with the Ru-H species leading to the evolution of hydrogen is the RDS with a barrier of 24.06 kcal/mol. The NMR and HRMS analysis have shown the presence of pincer-Ru-H and pincer Ru-OMe species, which are the lowest-energy intermediates of the catalytic cycle and are likely to be the resting states of the catalytic cycle.

Chapter-III formulates the decarboxylative coupling of alcohols to alkanes employing a plethora of new and known NNN pincer-Ru complexes of the type (^{R2}NNN)RuCl$_2$L (R = ^{i}Pr, ^{t}Bu, Cy, Ph, *p*-F-C$_6$H$_4$, *p*-OMe-C$_6$H$_4$ and L = PPh$_3$, CO and CH$_3$CN) based on *bis*(imino)pyridine ligands and [(^{RBim2}NNN)RuClL$_2$]Cl (R = H and Me, L = PPh$_3$ and CO) based on 2,6-*bis*(benzimidazole-2-yl)pyridine ligands. Notably, among the considered pincer-Ru complexes and their Ru precursors, a majority were either not very active or were unselective giving alkene/alkane mixtures. However, in the presence of 0.5 equivalents of NaOH in toluene at 140 °C, the complex (^{MeBim2}NNN)RuCl$_2$(PPh$_3$)$_2$ based on 2,6-*bis*(benzimidazole-2-yl)pyridine ligand gave excellent activity affording up to 91% yield of alkane (1,3-diphenyl propane) with 100% selectivity within 5 h of reaction. Experimental mechanistic studies point to the generation of hydrogen (detected by GC) and formic acid (detected by ^{1}H NMR) during the reaction along with involvement of organic intermediates such as *α*, *β*-unsaturated aldehydes. The [(^{MeBim2}NNN)RuCl(PPh$_3$)$_2$]Cl catalyzed transformation of 2-phenyl ethanol to 1,3-diphenyl propane demonstrated a first-order dependence of initial rate on both the catalyst concentration and the concentration of base. While catalyst poisoning experiments using mercury revealed the homogeneous nature of the catalyst, a few of these molecular species including the resting state [(^{MeBim2}NNN)RuH(PPh$_3$)$_2$]Cl have been detected by HRMS analysis and NMR studies. The experimental studies are nicely complemented by the DFT studies, that indicate the dehydrogenolysis step leading to the formation of 2-phenyl acetaldehyde and the resting state (^{MeBim2}NNN)RuHCl (experimentally trapped as PPh$_3$ adduct) to be the rate-determining step with a barrier of 22.81 kcal/mole at 140 °C. Furthermore, the corresponding cycle with the least active catalyst (^{iPr2}NNN)RuCl$_2$(PPh$_3$) that gave 14% yield of 1,3-diphenyl propane at 25% selectivity, involved insertion of 1,3-diphenyl propene into the Ru-H bond as the RDS that was kinetically unfavorable by 5 kcal/mole in comparison to the rate-determining dehydrogenolysis step of the cycle involving most active catalyst [(^{MeBim2}NNN)RuCl(PPh$_3$)$_2$]Cl. This work elaborates the direct access to jet-fuel-grade 1,3-diphenyl propane starting from 2-phenyl ethanol in a single-step one-pot reaction and offers great promise to open up exciting opportunities in this very important field of study.

Chapter-IV deals with the catalytic *β*-alkylation of alcohols using inexpensive and readily available cobaltous chloride under aerobic conditions at 140 °C. At higher loadings of cobaltous chloride (1 mol%) in the presence of 2.5 mol% NaO^{t}Bu, there is an instant formation of heterogeneous Co nanoparticles (NPs) which are apparently air-sensitive and lead to poor yields (*ca.* 25%) of *β*-alkylated products. On the other hand, performing the reaction in an inert atmosphere under otherwise identical conditions resulted in higher yields (*ca.* 44%). The heterogenization and gradual loss of activity in air could be mitigated by operating at a lower (0.01 mol%) CoCl$_2$ loading in the presence of 2.5 mol% NaO^{t}Bu at 140 °C. Under these conditions, the catalytic *β*-alkylation of alcohols afforded high yields (up to 89%) and unprecedented turnovers (ca. 8900) of the desired product. Mechanistic studies are indicative of the involvement of catalysts based on *in-situ* generated molecular Co complexes of alcohols. The involvement of C–H activation is confirmed by the deuterium labelling experiments, where a KIE of 1.61 was obtained. Kinetic studies indicate linear dependence of the rate on the concentration (in the regime of homogeneity) of cobaltous chloride and sodium *tert*-butoxide along with a non-linear dependence on the concentration of both the substrates.

Chapter-V describes the synthesis of pincer complexes of the type (^{R2}NNN)CoCl$_2$ (R = ^{i}Pr, ^{t}Bu, Cy, Ph, *p*-F-C$_6$H$_4$) derived from the inexpensive base metal cobalt. Among these complexes, (^{iPr2}NNN)CoCl$_2$ was found to be highly active for the catalytic β alkylation of alcohols in air at 140 °C. While the pincer-Co (0.0025 mol %) catalyzed β- alkylation in the presence of NaO^{t}Bu (2.5 mol %) took 24 h (85%, 34000 TON at 1417 TO/h) under conventional heating (140 °C), the corresponding reaction under microwave conditions (140 °C at 75 W) was complete in only 2 h with comparable yields (83%, 33200 TON), but with a better TOF (16600 TO/h). In contrast, CoCl$_2$ (0.0025 mol %) under similar conditions results in lower yields under both conventional (66%, 26400 TON at 1100 TO/h) and microwave heating (61%, 24400 TON at 12200 TO/h). The catalytic system has been successfully implemented (39 examples) to accomplish the β-alkylation of various secondary alcohols with several primary alcohols. EPR studies and magnetic moment measurements using the Evans method demonstrate that Co remains in its +2 oxidation state and in an octahedral geometry throughout the reaction. Significant evidence for the involvement of β- hydride elimination leading to acetophenone in the RDS of the pincer-Co catalyzed β-alkylation is obtained from competitive deuterium labelling experiments, which are indicative of a KIE of 6.14. The current report on base-metal catalysis in air under microwave conditions that leads to high yields of β-alkylation with unprecedented turnovers (33200 TON at 16600 TO/h) in a very short time (2 h) offers exciting atom-economical and greener possibilities for these class of synthetically valuable Guerbet-type reactions.