Abstract

The present thesis entitled "***Synthesis and Catalytic Activities of Cationic Ruthenium Complexes: C−O and C−C Bond Formation via Activation of Terminal Alkynes and Allylic Nucleophilic substitutions***" is primarily an effort towards the synthesis and catalytic activity of various cationic and di-cationic ruthenium phosphine complexes with bidentate phosphine and aminophosphinite ligands for the activation of terminal alkynes and allylic nucleophilic substitutions leading to carbon–oxygen and carbon–carbon bond formation. The results are described in mainly four parts. They are summarized below.

The moisture- and air-stable cationic ruthenium(II) complexes, $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$ (**C1**), $[Ru(\eta^6\text{-p-cymene})(dppe)Cl][PF_6]$ (**C2**), $[Ru(\eta^6\text{-p-cymene})(dppp)Cl][PF_6]$ (**C3**) and $[Ru(DPMC)_2(CH_3CN)_2][2BPh_4]$ (**C4**) {DPMC = (S)-tert-butyl1-(diphenylphosphinooxy)-3-methylbutan-2-ylcarbamate} have been synthesized and characterized. All the ruthenium complexes are derived from very commonly used starting materials, $[Ru(PPh_3)_3Cl_2]$, $[\{Ru(\eta^6\text{-cymene})Cl_2\}_2]$ and cis-$[Ru(DMSO)_4Cl_2]$. The complex **C1** has been synthesized from the reaction of $[Ru(PPh_3)_3Cl_2]$ with diphenylphosphinopropane (dppp) by the procedure reported form this laboratory and complex **C2** and **C3** were synthesized form the reaction of $[\{Ru(\eta^6\text{-cymene})Cl_2\}_2]$ with diphenylphosphinoethane (dppe) and diphenylphosphinopropane (dppp), in acetonitrile in the presence of NH_4PF_6, respectively. The complexes have been characterized by elemental analyses, IR, ^1H and ^{31}P NMR spectroscopy and single crystal X-ray crystallography.

The catalytic activity of the new complexes was studied, and the ruthenium(II) cationic complexes have been found to activate terminal alkynes as well as propargylic alcohols towards the addition of both aromatic and aliphatic carboxylic acids to alkynes. From in-situ ^1H and ^{31}P NMR studies, we conclude that the activation of the terminal alkynes initially involves coordination of alkyne to the metal center followed by the formation of vinylidene complex. Regio- and stereoselective vinylation take place depending on the nature of ruthenium catalyst. By utilizing this methodology as the critical step, different fatty acid enol esters were synthesized from the addition long chain fatty acids with terminal alkynes. We also developed a one-pot synthesis of *O*-dienyl

esters through the regio- and the stereoselective addition of both aliphatic and aromatic carboxylic acids to different propargylic alcohols and one pot Tandem atom-transfer radical polymerization of the products 1,3-dienes. The initial addition reaction takes place through the formation of a carbon–oxygen bond followed by dehydration.

The regio- and the enantioselective addition of phenols and carboxylic acids to allylic chlorides was developed by using chiral di-cationic Ru(II) complex, **C4** as the catalyst and enantiomeric branched selective allylic ethers and allylic esters, respectively, were isolated. A number substituted phenols bearing both electron donating and electron withdrawing group smoothly underwent the allylation reaction with allyl chlorides with complete regioselectivity. The reaction is equally effective for substituted as well as unsubstituted aromatic acids. From in-situ ^{1}H and ^{31}P NMR studies, we found that first ruthenium η^3-allyl complex is formed followed by the addition of phenoxide or carboxylate ion on the allylic carbon to afford the intermediate. Then subsequent reductive elimination leads to the generation of active complex and liberation of the product.

A highly efficient metal-catalyzed allylic alkylation of allylic alcohol with various active methylene compounds has been developed. This ruthenium catalyzed direct carbon-carbon bond forming reaction produced mono-allylated products selectively with high yields using 2 mol% of **C3**. The use of additives like pyrrolidine and acetic acid was essential for preventing undesirable side reactions. From in situ NMR studies, we evaluated the role of these additives. It was found that pyrrolidine reacts with dicarbonyl compounds to generate enamines in the presence of acetic acid, which act as a reactive intermediate.

All the catalytic reactions have been investigated in detail from a synthetic viewpoint to assess their synthetic merit/limitations. In particular cases, efforts have been made to understand initial substrates activation in catalytic cycles.

Keywords: *Alkynes, Ruthenium, Enol Esters, Phosphine complexes, Fatty acids, Dienyl ester, Dienes , Propargylic alcohol, carboxylic acid, Polymerization, One pot, Tandem reaction, Allyl Chlorides, Allylic, Ester, Ether, chiral Aminophosphinite complexes, Phenol, Allyl alcohol, Alkylation, Active methylene, Mono-allylation, Pyrrolidine, Acetic acid, Enamines*