

ABSTRACT

SYNTHETIC AND MECHANISTIC STUDIES OF RUTHENIUM CATALYZED C-C,
C-N AND C-O BOND ACTIVATION REACTIONS

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Transition metal catalyzed selective C-C, C-N and C-O bond activation reactions are fundamentally important in organometallic chemistry and organic synthesis. Catalytic C-C, C-N and C-O activation are highly valuable for reforming processes of crude oils. Significant research has been devoted to transition metal mediated C-C, C-N and C-O bond cleavage reactions to form new compounds as these processes are expected to provide novel ways to transformation of inexpensive hydrocarbons into more commercially valuable products such as pharmaceuticals, agrochemicals and polymers.

A few examples of transition metal catalyzed cross coupling reactions involving C-N bond cleavage have been reported. A well-defined Ru catalytic system has been developed for oxidative alkylation of alcohol by deaminative coupling reactions of amines to form alkylated ketones. The catalytic method was successfully applied to the decarboxylative and deaminative coupling of amino acids with ketones.

Reductive deoxygenation of aldehydes and ketones has attracted considerable attention due to its many applications in fine-chemical synthesis and biofuel production. Classical methods for the deoxygenation of carbonyl compounds are generally associated with harsh reaction conditions and the use of stoichiometric amounts of toxic reagents, and poor functional-group tolerance. A well-defined Ru-H catalyst was found to mediate the reductive deoxygenation of carbonyl compounds to produce aliphatic compounds. Two different mechanistic pathways have been investigated in detail to probe the electronic nature of the catalysts and ligands.

Reductive etherification of ketones/aldehydes and alcohols have been studied intensively as cheaper and greener ways to synthesize ethers. A method for the reductive coupling of carbonyl compounds with alcohols has been developed, which involved a highly chemoselective formation of unsymmetrically substituted ether products. The catalytic etherification method employs cheaply available molecular hydrogen as the reducing agent, tolerates a number of common functional groups, and uses environmentally benign water as the solvent.