

Summary

Summary

Chapter I

The recent advances in the area of C-H activation and oxygenation reactions with special emphasis on the catalytic oxygenation of hydrocarbons have been briefly reviewed in Chapter I. The scope and purpose of the present investigation is cast against this background.

Chapter II

Chapter II deals with C(phenyl)-H bond activation of arylazophenol by platinum(II) at room temperature under different reaction conditions. The cycloplatinates have been synthesized by the C(phenyl)-H bond activation of 2-(phenylazo)-4-methylphenol (H_2L) using di- μ -chloro-bis(η^3 -2-methylallyl)platinum(II) as metal precursor in presence of neutral Lewis base, D (4-picoline or PPh_3). The resulting cycloplatinates $[Pt^{II}(L)(D)]$ have been characterized on the basis of elemental analysis and spectroscopic techniques. The molecular structure of a representative cycloplatinate containing 4-picoline as donor has been elucidated by single crystal X-ray crystallography. It is observed that platinum(II) centre is surrounded by C,N,O donor set as tridentate ligand frame (L) and the donor atom of the Lewis base (D) in distorted square planar fashion. The crystal packing of the cycloplatinate has been found to be stabilized by various non-covalent interactions. The bivalent cycloplatinates prefer to undergo oxidative addition reaction rather than oxygenation of the Pt-C(phenyl) bond. The reactivity of the platinum(II) cycloplatinates towards oxidative addition reaction with halogens and alkyl iodide have been studied. The bivalent cycloplatinates undergo metal centred two electron oxidation affording platinum(IV) cycloplatinates. However, alkyl iodide fails to react with cycloplatinate having PPh_3 as donor. In case of cycloplatinate containing 4-picoline as donor, *trans* oxidative addition of electrophiles have been observed. In contrast, cycloplatinates containing PPh_3 as the neutral donor has been found to undergo *cis* oxidative addition. Structures of some representative tetravalent cycloplatinates have been determined by X-ray diffraction method. Time Dependent Density Functional Theory (TDDFT) calculation of both platinum(II) and platinum(IV) cycloplatinates has

been done. Optical absorption spectra of the cycloplatinates in dichloromethane have been simulated using TDDFT method. The experimentally observed spectra of bivalent and tetravalent cycloplatinates in dichloromethane are in good agreement with their corresponding simulated spectra.

Chapter III

In this chapter, stoichiometric and catalytic oxygen insertion into the C(naphthyl)-H bond of cyclopalladates has been studied. The cyclopalladates have been synthesized by the C(naphthyl)-H bond activation of [1-(2'-hydroxy-naphthylazo)naphthalene] by palladium(II) in presence of neutral Lewis base, D (4-picoline or PPh_3). At room temperature, regioselective activation of both C₂(naphthyl)-H and C₈(naphthyl)-H bonds have been achieved by palladium(II) affording *ortho*- and *peri*-palladate respectively. Oxygen-insertion into the Pd-C(naphthyl) bond of the orthopalladates ($\text{Pd-C} \rightarrow \text{Pd-O-C}$) has been achieved by *m*-CPBA at room temperature with high yield. The characterization of the oxygenated palladium(II) complexes has been done on the basis of elemental analysis and spectroscopic techniques. Structures of the oxygenated products have been further confirmed by single crystal X-ray crystallography. The palladium(II) centre is surrounded by O,N,O donor set of the oxygenated organic fragment in tridentate fashion with the fourth position being occupied by donor of the Lewis base in distorted square planar fashion. The crystal packing of the oxygenated products has been found to be stabilized by various non-covalent interactions. Catalytic oxygen insertion into the Pd-C(naphthyl) bond of the orthopalladates has also been achieved at room temperature with iron(III) porphyrin complex [$\text{F}_{20}\text{TPPFe(III)}\text{Cl}$; F_{20}TPP : meso-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin] as catalyst using environmentally benign and inexpensive H_2O_2 as terminal oxidant. However, the catalytic oxygenation of the orthopalladate containing sterically demanding PPh_3 as Lewis base proceeds at a much slower rate. Solvents effect in the catalytic oxygen insertion process has also been investigated. The electronic structures of the oxygenated palladium(II) complexes have been calculated using TDDFT model and the simulated spectra are in good agreement with the experimentally observed spectra in dichloromethane.

Chapter IV

To achieve catalytic oxygenation of hydrocarbons at room temperature, mononuclear non-heme iron(III) complexes with N,N'-bis(2-pyridylmethyl)diamine based neutral N₄-donor ligands have been synthesized and characterized. The catalytic properties of the synthesized complexes have been examined in the oxygenation of alkanes and alkenes with mild H₂O₂ and *t*-BuOOH as terminal oxidants. The involvement of radical-based reaction pathway in the catalytic oxygenation process has been confirmed from quenching the oxygenation reaction in presence of “radical scavenger” 2,4,6-tri-*t*-butyl phenol (TTBP) and predominately allylic oxidation in cyclohexene oxygenation reaction. The oxygenation of saturated hydrocarbons has also been achieved with *m*-CPBA as terminal oxidant with high selectivity, but with a poor yield. The selective oxidation of alcohols to carbonyl compounds has also been achieved at room temperature with environmentally friendly H₂O₂ with high yield. Finally, the rate of the catalyst oxidation with *m*-CPBA has been studied by monitoring the oxidation of 2,4,6-tri-*t*-butyl phenol (TTBP). Kinetic analysis of TTBP oxidation with *m*-CPBA follows the first order dependence of rate on the concentration of *m*-CPBA as well as on the concentration of the catalyst.

Chapter V

Chapter V describes the binuclear oxo-bridged non-heme iron(III) complex catalyzed oxygenation of alkanes and alkenes at room temperature using benign H₂O₂ and *t*-BuOOH as terminal oxidants. Remarkably increase in conversion and selectivity for the hydroxylation of saturated hydrocarbons (C-H → C-OH) has been achieved with H₂O₂ in presence of acetic acid. Oxygenation of alkanes has also been studied with *m*-CPBA as oxidant. The binuclear non-heme iron(III) complexes efficiently catalyze the epoxidation of various alkenes with high conversion and high selectivity with mild H₂O₂ in the presence of acetic acid at room temperature. The selective oxidation of both primary and secondary alcohols in the presence of H₂O₂ has also been achieved at room temperature with high yield. The kinetic data of catalytic oxidation of TTBP by H₂O₂ reveals first order dependence of the rate on both the catalyst and oxidant concentration.

Chapter VI

The synthesis and characterization of Mg/Al hydrotalcite-like layered double hydroxides (LDHs) with molybdate and tungstate as intercalating anions have been described in Chapter VI. The intercalated LDHs efficiently catalyze the epoxidation of a series of alkenes using environmental friendly and inexpensive H₂O₂ at room temperature. The epoxidation of alkenes has been found to be dependent on the nature of solvent, amount of catalyst and concentration of substrate. Reactions with non-intercalated anions and also with LDH-precursor confirm that the intercalated anions are responsible for the epoxidation. The heterogeneous catalysts are easily recovered from the reaction mixture and recycled.