

PREFACE

The work described in this thesis entitled 'Oxygenation Reactions of Organic and Organometallic Compounds' is an attempt to explore the chemistry of oxygenation reactions mediated by transition metal complexes at room temperature. The stoichiometric and catalytic oxygenation of aromatic C-H bond was attempted following the selective activation of C-H bond by proper choice of metal ions *via* cyclometallation route. Another objective of the present work was to design suitable catalysts capable of oxygenating different types of hydrocarbons at room temperature.

The thesis consists of six chapters. A brief review of major advances in the area of oxygenation reactions of organic and organometallic compounds along with the purpose of the present investigation has been summarized in Chapter I.

Chapter II deals with the platinum(II) mediated C(phenyl)-H bond activation. The isolation, characterization and X-ray crystallographic analyses of the resultant bivalent cycloplatinates have also been described. The nature of electronic transitions in the cycloplatinates has been studied using Time dependent Density Functional Theory (TDDFT). The reactivity of platinum(II) cyclometallates towards oxidative addition with halogens and alkyl iodide has also been examined.

Oxygen insertion into the Pd-C(naphthyl) bond of cyclopalladated compounds constitute the subject matter of Chapter III. Oxygen insertion into the Pd-C(naphthyl) bond has been achieved by *m*-CPBA in dichloromethane medium at room temperature. The catalytic oxygenation of Pd-C(naphthyl) bond has also been achieved using environmental friendly H₂O₂ as oxidant in presence of iron(III) porphyrin as catalyst. The oxygenated palladium(II) complexes have been characterized by spectroscopic and X-ray crystallographic techniques. The TDDFT study of the oxygenated products has also been presented.

The synthesis and characterization of mononuclear non-heme iron(III) complexes of neutral N₄-based donor ligands have been described in Chapter IV. The synthesized complexes catalyze the oxygenation reactions of alkanes and alkenes with mild H₂O₂ and *t*-BuOOH as oxidants at room temperature. The hydroxylation of unactivated C-H bonds of alkanes has also been realized with *m*-CPBA as the terminal oxidant. Kinetic analysis of 2,4,6-tri-*t*-butyl phenol (TTBP) oxidation by *m*-CPBA has also been presented.

The room temperature oxygenation reactions of hydrocarbons by μ -oxo non-heme binuclear iron(III) catalysts is the major theme of Chapter V. The catalytic properties of the synthesized complexes towards oxygenation of alkanes and alkenes have been described at room temperature in presence of different terminal oxidants. Remarkable increase in conversion and selectivity for hydroxylation of saturated C-H bond and epoxidation of alkenes has been achieved by H_2O_2 in presence of acetic acid. Kinetic investigation of catalytic oxidation of TTBP with H_2O_2 has also been described.

Chapter VI describes the synthesis and characterization of molybdate and tungstate intercalated Mg/Al hydrotalcite-like layered double hydroxides (LDHs). The catalytic activities of the intercalated LDHs have been studied for the epoxidation of a series of alkenes using environmentally benign and inexpensive H_2O_2 at room temperature. A comparative study between the Mo and W-intercalated LDHs has been presented in this chapter.

The present work was initiated under the supervision of Dr. P. Bandyopadhyay in 2007 at Department of Chemistry, University of North Bengal.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made whenever the work described as based on the findings of other investigators. I must take the responsibility of any unintentional oversight and errors, which might have crept in spite of precautions.

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