PREFACE

The work in this thesis entitled "C(aryl)-H Bond Activation: Isolation, Characterization and Reactivity of Cyclometallates" was initiated from an attempt to explore the possibility of activation of different types of C(aryl)-H bonds with special emphasis on the selectivity of the processes and the reactivities of the resultant organometallates. Another perspective of the present work is to insert oxygen into metal-carbon bonds under ambient conditions.

The thesis consists of six chapters. The main advances in the area of transition metal mediated C(aryl)-H bond activation have been summarized in Chapter I with emphasis on cyclometallation reactions. Current challenges in this area and the purpose of the present investigation are also outlined in the chapter.

Chapter II deals with the C(naphthyl)-H bond activation by palladium(II). All the cyclopalladates have been characterized by spectral data and X-ray diffraction. The nature of electronic transitions in the cyclometallates has been examined using Time Dependent Density Functional Theory (TD-DFT).

Oxygen insertion into palladium–C(aryl) bond (*metaloxylation*) under ambient conditions constitutes the core of Chapter III. The metaloxylation has been achieved under stoichiometric and catalytic reaction conditions. The isolated products have been characterized by spectral data and X-ray crystallographic analysis.

Chapter IV deals with the activation of C(naphthyl)-H bond by platinum(II) and the reactivities of the divalent cycloplatinates. Characterization by spectral studies, X-ray crystallographic analysis and also TDDFT study of the cycloplatinates has been presented.

Chapter V constitutes the C(naphthyl)-H bond activation by ruthenium(II) and ruthenium(III) metal precursors. The cycloruthenates have been isolated and characterized by spectral data and X-ray diffraction. TDDFT study of the cycloruthenates have been studied to delve into the origin of the electronic transition of the complexes.

The activation of C(naphthyl)-H bonds by rhodium(I), rhodium(III) and iridium(I) comprises the subject matter of Chapter VI. Rhodium exhibits a unique chemistry in bringing about C-S cleavage. This chapter also deals with the formation of cyclometallates of Rh(III) *via* regiospecific $C(sp^2)$-S cleavage of the alkylsulfinylazonaphthalenes. The isolation, characterization, X-ray crystallographic analysis and TD-DFT study of the resulting cyclometallates have been described.

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

In keeping with general practice of reporting scientific observations, due acknowledgement has been made whenever the work described was 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.

Satyadeep Sgh Chhetri
(SATYADEEP SINGH CHHETRI)

1st February , 2012

Department of Chemistry
University of North Bengal
Raja Rammohunpur
P.O. North Bengal University
Dt. Darjeeling,
West Bengal
Pin-734013