

SUMMARY

Summary

Chapter I

In this chapter the main advances in the title area is reviewed with emphasis on both stoichiometric and catalytic functionalization of C-H bonds. Current challenges are discussed. The scope and purpose of the present investigation is cast against this background.

Chapter II

Chapter II deals with the C(naphthyl)-H bond activation of arylazonaphthalenes (HL) by palladium(II). Here, variation of the position of the diazene function (primary donor) attached to the naphthyl group and also the nature of the auxiliary donor, provided as 2'-substituted pendant phenyl or naphthyl group attached to the diazene function, have been made. The influence of the auxiliary donor and the position of the primary donor on the selection of metallation site has been investigated thoroughly. When the primary donor diazene is at C1 of the naphthyl group and the auxiliary donor is naphtholato function, palladium(II) has been found to activate C(2)-H and C(8)-H bonds regioselectively. When the naphtholato function is replaced by weak donor alkoxy group, regeospecific activation of C2(naphthyl)-H bond has been realized. Furthermore, when the primary diazene donor is at C2 of the naphthyl group, palladation reaction has been found to be regiospecific and only C(3)-H bond activation has been realised. The characterization of all the cyclometallates have been done on the basis of elemental analysis and spectral data. Single crystal X-ray crystallography of representative cyclopalladates have been done. The crystal packing of the cyclopalladates has been found to be stabilized by various non-covalent interactions. The Time-dependent density functional theory (TDDFT) calculation has been undertaken for better understanding of the electronic structure and nature of the spectral transitions. The TDDFT calculations reveal that the high energy and low energy absorptions are predominantly due to intraligand $\pi-\pi^*$ and metal-to-ligand charge-transfer transitions. The simulated spectra of cyclopalladates are in agreement with the experimental electronic spectra.

Chapter III

In this chapter, platinum(II) compound has been used in regiospecific activation of C(naphthyl)-H bonds in a group of naphthylazo-2'-hydroxyarenes (H_2L) under different reaction conditions and resulting cycloplatinates $[Pt(II)L(D)]$ have been isolated in presence of neutral Lewis bases (D). Structures of the cycloplatinates of platinum(II) have been established by single crystal X-ray crystallography. It is observed that platinum(II) centers are surrounded by C,N,O-terdentate ligand frame(L) and Lewis base(D) in distorted square planar fashion. Extensive intermolecular association due to C-H... π and π ... π interactions is also observed in solid state. These platinum(II) cycloplatinates have been found to react with halogens and methyl iodide undergoing metal centered two electron oxidation affording platinum(IV) cycloplatinates with distorted octahedral geometry. In reaction with halogens and methyl iodide, *trans* oxidative addition has been found for $[Pt(L)D]$ (D = 4-picoline) whereas *cis* addition has been observed for $[Pt(L)D]$ where D is sterically more demanding triphenylphosphine. Structures of two representative platinum(IV) cycloplatinates have been determined by single crystal X-ray crystallography. Time dependent density functional study 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 platinum(II) and platinum(IV) cycloplatinates in dichloromethane are in very good agreement with their corresponding simulated spectra.

Chapter IV

In this chapter, rhodium(I) compound $[Rh(PPh_3)_3Cl]$ has been used to activate C1(naphthyl)-H, C2(naphthyl)-H, C3(naphthyl)-H and C8(naphthyl)-H bonds of the naphthyl group present in a group of naphthylazo-2'-hydroxyarenes (H_2L). The cyclometallation is always accompanied by metal centered oxidation $[Rh(I) \rightarrow Rh(III)]$ and produces cyclometallate $[Rh(PPh_3)_2(L)Cl]$. All the cyclometallates have been isolated in pure form and characterized on the basis of elemental analysis and spectral data. The structures of the representative cyclometallates have been determined by X-

ray diffraction method. In all the cyclometallates, rhodium(III) is coordinated to naphthylazo-2'-hydroxyarenes via terdentate C, N, O donor centre & one chloride ion in a plane along with two axial *trans* PPh₃. In solid state intermolecular association is observed due to C-H... π and π ... π interactions. The magnetic susceptibility measurement shows that all the rhodium(III) cyclometallates [Rh(PPh₃)₂ (L)Cl] are diamagnetic. Compounds show an oxidative response within 0.93 to 1.11 V (vs. SCE) and a reductive response at \sim -1.0 V (vs. SCE). Both the responses are based on the coordinated diazene function and are irreversible in nature indicating limited stability of the oxidized and reduced species. The electronic structures of selected cyclometallates have been calculated using TD-DFT model and the simulated spectra are consistent with the observed spectra of those cyclometallates.

Chapter V

To achieve catalytic C-H bond activation and functionalization at room temperature, a group of chiral iron(III)-salen and manganese(III)-salen complexes were employed as catalysts in the oxidation of alkenes and alkane. Pentafluoroiodosylbenzene was used as terminal oxidant. A comparison has been drawn between these two sets of catalysts. The reactions were carried out in acetonitrile and dichloromethane. Iron(III)-salen catalyzed oxygenation reactions were found to be dependent upon the reaction media, whereas no distinct solvent effect had been noticed in the corresponding reactions catalyzed by manganese(III) salens.

Chapter VI

In this chapter, the catalytic property of iron complex with macrocyclic corrole ligand has been investigated. Electron deficient *meso* tris(pentafluorophenyl)corrolatoiron(IV) chloride [(F₁₅TPC)FeCl] has emerged as efficient catalyst in hydroxylating alkanes. At room temperature, cyclohexane and adamantane are oxidized to the corresponding alcohols using *m*-CPBA. Cyclohexane is converted to cyclohexanol in 45-50% yield. This reaction proceeds with 100% selectivity. Adamantane is hydroxylated up to 75% overall yield. Significantly high regioselectivity in adamantane oxidation has been observed. The reactive intermediates formed have been quantitatively trapped by

2,4,6-tri-*t*-butylphenol (TTBP). Kinetic analysis of the (F₁₅TPC)FeCl-catalysed oxidation of TTBP has been found consistent with rapid reaction of organic substrate with an intermediate formed in the first and rate determining step.

For the very first time, *t*-BuOOH has been used as oxidant in room temperature oxidation of alkane and alkene catalyzed by iron complex of 5,10,15-*tris*(pentafluorophenyl)corrole.

