Summary

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Chapter I

In this chapter, a brief survey on the area of C(aryl)-H bond activation following cyclometallation route has been made with an emphasis on recent advances. 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 2'-alkylsulfinylphenylazo-4-methoxy-1-naphthalenes(HL) by palladium(II). At room temperature, regioselective activation of C2(naphthyl)-H and C8(naphthyl)-H bonds have been achieved by palladium(II) resulting in *ortho*-palladate and *peri*-palladate respectively. Regiospecific activation of C2(naphthyl)-H bond by palladium(II) has been achieved in presence of Et_3N. On the other hand, the regiospecific activation of C8(napthyl)-H bond is achieved by palladium(II) in presence of acetic acid. The characterization of the resulting cyclopalladates has been done using spectroscopic techniques and single crystal X-ray crystallography. Palladium(II) binds the substrates *via* C(naphthyl), N(diazene), S(sulfinyl) donor set in terdentate fashion with the fourth position being occupied by a chloride ion. Both the *ortho*-palladates and *peri*-palladates contain five-membered carbopalladacycles [C, N], whereas the [N, S] chelate rings are five-membered in the *ortho*-isomer and six-membered in *peri*-isomer. The crystal packing of the cyclopalladates has been found to be stabilized by various non-covalent interactions. The time-dependent density functional theory (TD-DFT) calculation has been undertaken for better understanding of the electronic structure and nature of the spectral transitions. The TD-DFT calculations reveal that the high energy and low energy absorptions are predominantly due to intraligand π-π* and metal-to-ligand charge-transfer transitions. The simulated electronic spectra of the cyclopalladates are also presented.

Chapter III

Stoichiometric and catalytic oxygen insertion into the C(aryl)-metal bond (*metaloxylation*) of cyclopalladates is the core issue of Chapter III. At room temperature, regiospecific oxygen insertion into C(naphthyl)-Pd bonds of cyclopalladated thioazonaphthalenes and alkylsulfinylazonaphthalenes has been achieved by *m*-chloroperbenzoic acid (*m*-CPBA) with high yield. The molecular structure of a representative metaloxylated palladium(II) product has been elucidated by single crystal X-ray crystallography. Catalytic oxygen insertion into the Pd-C(naphthyl) bonds of the two sets of substrates has also been achieved by 'mild' hydrogen peroxide (H_2O_2) or *tert*-butylhydroperoxide (TBHP) with vanadyl acetylacetonate, $[VO(acac)_2]$ as catalyst. In case of the cyclopalladated thioazonaphthalenes (**1a′**, **1b′**), both metaloxylation (Ar-Pd→ Ar-OPd) and sulfoxidation (S → S=O) has been observed. On the other hand, only regiospecific metaloxylation (Ar-Pd→ Ar-OPd) is observed for cyclopalladates of sulfinylazonaphthalenes. Kinetics of oxygen insertion into Pd-C bonds has been examined by UV-vis spectroscopy. Moreover, the optical absorption spectra of oxygenated palladium(II) complexes in dichloromethane have been simulated using time dependent density functional study (TDDFT). Solvent effects in the oxygen insertion process have also been examined and reported.

Chapter IV

This chapter deals with the regiospecific activation of C(naphthyl)-H bond present in a group of substrates, 2′-alkylsulfinylphenylazo-4-methoxy-1-naphthalenes (HL), by platinum(II) complexes. Di-μ-chloro-bis(η^3-2-methylallyl)platinum(II) or tetrachloroplatinate has been used as metal precursor. The resulting cycloplatinates [Pt(II)LCl)] have been isolated and well characterized. Structures of the cycloplatinates of platinum(II) have been established by single crystal X-ray crystallography. It was observed that platinum(II) centers are surrounded by C(naphthyl), N(diazene), S(sulfinyl) donor set as terdentate ligand frame (L) and chloride ion in a 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 molecular halogens undergoing metal centered two electron oxidation affording platinum(IV) cycloplatinates. With alkyl halides (RX), the divalent cycloplatinates have been found to undergo oxidation followed by reductive elimination. The chloride in the cyclometallate [Pt(II)LCl] gets replaced by X^{1-} from RX leading to the formation of [Pt(II)LX]. The molecular structure of cycloplatinates [Pt(II)LX] have been determined by single crystal X-ray crystallography. Time dependent density functional study of both the platinum(II) cyclometallate has been done. Optical absorption spectra of the cycloplatinates in dichloromethane have been simulated using TD-DFT method.

Chapter V

Ruthenium(II) and ruthenium(III) mediated activation of C(naphthyl)-H bonds present in a group of 2-alkylsulfinylphenylazo-4-methoxy-1-naphthalenes (HL^{1-5}) constitute the core area of Chapter V. Regiospecific activation of C2(naphthyl)-H bonds in a group of 2-alkylsulfinyl-phenylazo-4-methoxy-1-naphthalene (HL^{1-5}) has been achieved with $[Ru(PPh_3)_3Cl_2]$ in refluxing ethanol and resulting cyclometallates $[Ru^{II}L(PPh_3)_2Cl]$ have been isolated. The higher-valent ruthenium (III) ($RuCl_3 \cdot xH_2O$) also regiospecifically activates C2(naphthyl)-H bond of alkylsulfinylazonaphthalenes (HL^{1-5}) in presence of excess triphenylphosphine (PPh_3) and affords divalent cycloruthenates $[Ru^{II}L(PPh_3)_2Cl]$. Single crystal X-ray crystallography of $[Ru^{II}L(PPh_3)_2Cl]$ shows that substrate, alkylsulfinylazonaphthalene, binds ruthenium(II) *via* C2(naphthyl), N(diazene) & S(sulfinyl) donors in terdentate fashion, resulting in two five-membered chelate rings. In the absence of PPh_3 $RuCl_3 \cdot xH_2O$ reacts with substrates HL (mole ratio 1:2) yielding interesting cycloruthenates with a general formula $[Ru(L)_2]$, where each ruthenium(II) is bound to two C2(naphthyl) from two substrate molecules. All the cycloruthenates have been successfully isolated in pure form and characterized by spectroscopic techniques. In the case of HL^5, two rotamers have been isolated. The structures of both the rotamers have been confirmed by X-ray crystallographic techniques. Weak intermolecular association due to C-H…π and π…π interactions was observed in solid state. Time dependent density functional study of the ruthenium(II) cycloruthenates has been done. Optical absorption spectra of the cycloruthenates in dichloromethane have been simulated using TD-DFT method and the excitation-simulated spectra were in agreement with the observed experimental data.

Chapter VI

Chapter VI deals with the C(naphthyl)-H bond activation by rhodium(I & III) and iridium(I). Rhodium(I) or iridium(I) precursors *viz.* [Rh(PPh_3)$_3$Cl] or [Ir(PPh_3)$_3$Cl] activates C(naphthyl)-H bonds present in a group of alkylsulfinylazonaphthalenes (HL) in refluxing toluene or dioxane leading to the formation of cyclometallates [ML(PPh_3) Cl_2] where M is rhodium(III) or iridium(III). Thus both the cyclometallation reactions are accompanied with metal centered two-electron oxidation. The representative members of cyclorhodates and cycloiridates have been characterized by single crystal X-ray crystallography. The substrates, $2'$-alkylsulfinylphenylazo-4-methoxy-1-naphthalenes (HL) are found to coordinate rhodium(III) or iridium(III) in a tridentate fashion *via* C2(naphthyl), N, S donors. The reactions of the substrates (HL) with Rhodium(III) chloride ($RhCl_3$ x H_2O) reacts with the substrates (HL) in refluxing ethanol and affords novel rhodium(III) complexes of the general formula [Rh(L)(L′)] where L′ is phenylazo-4-methoxy-1-naphthalene (HL′) resulting from C(aryl)-S bond cleavage. The X-ray crystallographic analysis of one representative cyclorhodate has been done. The HL fragment is found to coordinate in a monoanionic terdentate C(naphthyl), N(diazene), S(sulfinyl) fashion, whereas HL′ binds the same rhodium center in monoanionic bidentate C(phenyl), N(diazene) mode. The electronic structures of the representative cyclometallates have been examined using time-dependent density functional theory (TD-DFT). The simulated absorption spectra have been compared with the observed electronic spectra.