SUMMARY

I

The known chemistry of cyclometallation reaction with special reference to aromatic ring activation has been briefly reviewed in Chapter I. A brief discussion on relevance of cyclometallates has also made. The purpose of the present investigation is cast on this background.

II

Chapter II deals with C(naphthyl)-H bond activation by ruthenium. The selective activation of **C(2)-H** bond of naphthyl group has been achieved in presence of azo group at C(1) of naphthyl group along with phenol as auxiliary donor by ruthenium(II). The activation process is accompanied with oxidation of the metal centre. The end product is ruthenium(III) cyclometallate. The selective activation of **C(2)-H** bond of naphthyl group has also been achieved by ruthenium, where neutral thioether or ether group is auxiliary donor and primary donor is azo group at C(1) of naphthyl group. The selective activation of **C(3)-H** bond of naphthyl group is achieved by ruthenium(II) where phenol group is auxiliary donor and the primary donor is azo group at C(2) of naphthyl fragment. The activation of C(3)-H is also accompanied by the oxidation of metal centre and yields ruthenium(III) cyclometallate. All the cycloruthenates have been isolated in pure form and characterized on the basis of analytical and spectral data. Structures of two cycloruthenates have been determined by X-ray diffraction.

III

In this chapter, palladium(II) has been used to activate C(naphthyl)-H bonds. At room temperature, palladium(II) successfully activates both C(2)-H & C(8)-H bonds of 1-azonaphthyl fragment with neutral thioether as auxiliary donor. Both the isomeric cyclopalladates have been isolated and their structures have been determined by X-ray analysis. The cyclopalladate containing C(8)-Pd bond undergoes photochemical conversion into its isomer having C(2)-Pd bond in presence of sun light. The C(2)-Pd bond undergoes oxygenation reaction to C(2)-O-Pd with *m*-chloroperbenzoic acid in dichloromethane medium.

IV

In this chapter palladium (II) is used extensively to activate different C-H bonds of naphthyl moiety. The importance of auxiliary donor in the selection of metallation site has been observed.

When azo functionality is attached to C(1) of naphthyl group, palladium(II) activates :

(i) **C(8)-H** bond exclusively where auxiliary donor is phenol; (ii) **C(2)-H** bond exclusively where auxiliary donor is alkoxy group; (iii) both **C(2)-H & C(8)-H** bonds where auxiliary donor is naphthol group.

When azo functionality is attached to C(2) of naphthyl moiety, palladium(II) activates **C(3)-H** bond exclusively where auxiliary donor is phenol group.

All the cyclopalladates [PdL(D)] (where D = Lewis base) have been isolated in pure form and characterized. Structures of three cyclopalladates have been determined by X-ray diffraction. Some of the cyclopalladates [PdL(D)] have the potential to be used as acid-base indicators in non-aqueous media. At room temperature palladium-C(naphthyl) bond at C(2) & C(3) undergo smooth oxygenation (M-C → M-O-C) reaction with *m*-CPB acid.

V

Platinum (II) selectively activates **C(2)-H** bond of naphthyl moiety containing primary donor azo group attached to C(1) along with neutral thioether group as auxiliary donor. Unlike palladium(II), platinum(II) fails to activate the C(8)-H bond of naphthyl moiety of 1-naphthylazo group. With halogens (X_2), divalent cycloplatinates undergo metal centred oxidation and afford platinum cyclometallates having Pt (IV)-C(naphthyl) bond. Both the divalent and tetravalent cycloplatinates have been isolated in pure form and characterized. The structure of divalent cycloplatinate has been determined by X-ray diffraction.