CHAPTER I

ASPECTS OF THE CYCLOMETALLATION REACTION AND THE PURPOSE OF THE PRESENT INVESTIGATION

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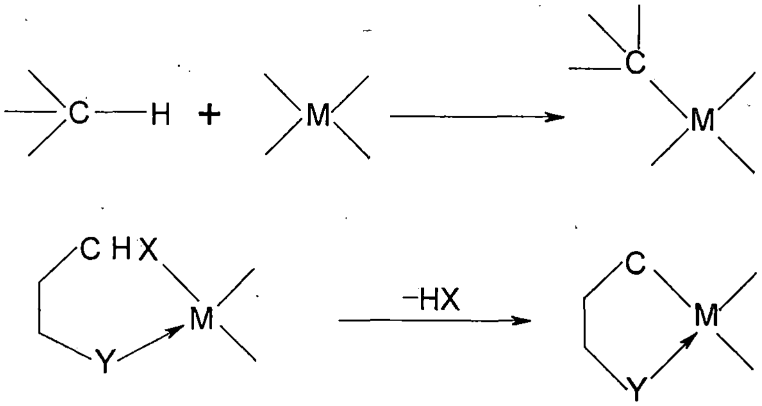
Abstract: In this chapter the significance of the cyclometallation reaction and its known chemistry is delineated. The scope and the purpose of the present work are also discussed.

I.1 INTRODUCTION

The C-H bond activation followed by functionalization at carbon is one of the most important reactions in chemistry, biology as well as industry [1-3]. The C-H → C-OH transformation in nature is executed by membrane bound enzyme cytochrome P-450 [4]. Extensive studies in both *vivo* and *vitro* are being done to mimic the above reaction. A large number of reactions involving C-H bond activation of organic substrates are carried out in presence of metal ions or metal complexes [5-10]. It is believed [11] that metal-carbon bond formation is involved in those C-H bond activation processes. Therefore it will provide a broad area to examine the possibility of diverse pattern of reactivity of those intermediates containing metal-carbon bond, if they can be isolated.

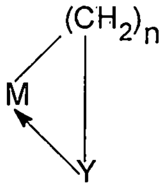
The C-H activation reaction between an organic substrate and a metal ion can occur through either inter- or intra-molecular step as represented bellow.



The intra-molecular process is known as *cyclometallation* reaction.

In this background we have chosen the route of cyclometallation reactions in our endeavour to activate C-H bond selectively.

Cyclometallation reactions afford interesting intermediates (1), which are known as cyclometallates. The term '*cyclometallates*' for compounds (1) was introduced by Trofimenko [12].

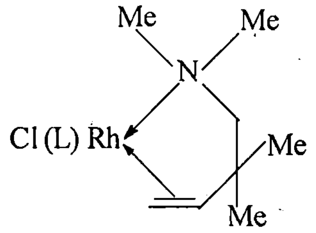


M = metal ion; Y = coordinating atom; n = preferably 3 or 4

(1)

In 1955 Bahr and Muller had defined the above class of compounds (1) as '*Metallorganische Innerkomplexe*' and proposed that they contain preferably five- or six-membered chelate ring [13-14]. They are also known as '*organometallic intramolecular-coordination compounds*' [15]. The compounds (1) are metal complexes in which the organic substrates undergo an intramolecular metallation with the formation of chelate rings containing a metal-carbon σ-bond.

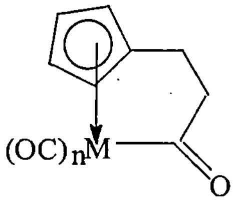
There are compounds [16] like (2) which contain metal-carbon π-bonds instead of metal-carbon σ-bond.



L = Ethylene, Acetonitrile, 4-cyanopyridine,
Pyridine

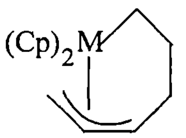
(2)

Groups such as cyclopentadienyl, [17-18], vinylene and -allyl [19] may behave as the Y of (1) as shown in (3) & (4) respectively. It is difficult to define ring size for the cyclometallates, which have metal-carbon π-bonds.



M(CO)n= Ni, Co, Fe(CO)$_2$,
Mo(CO)$_3$

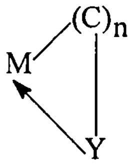
(3)



M = Zr, Hf

(4)

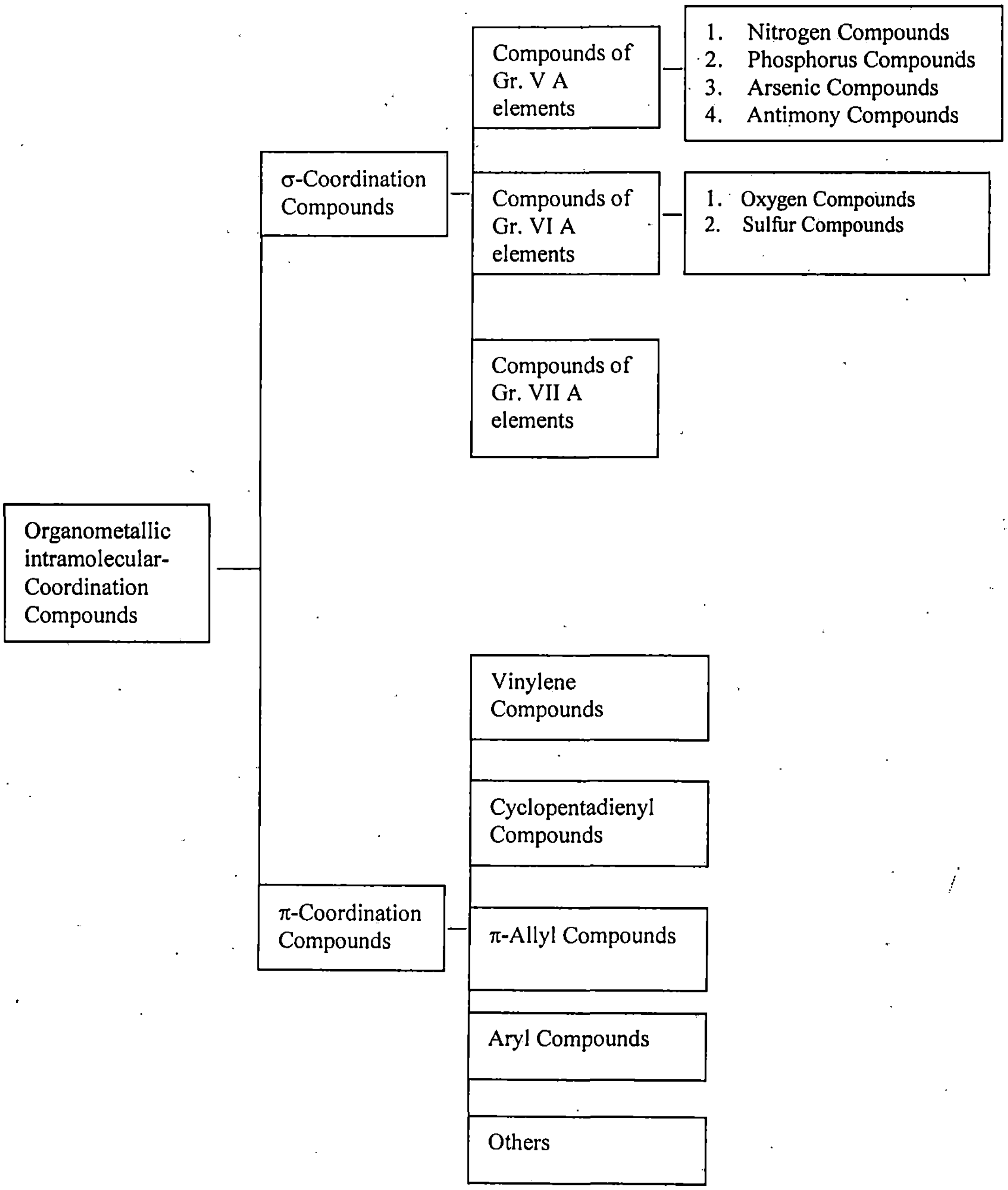
Omae considered [15] that the representation of cyclometallates as (5) would be more appropriate (n ≥1) to that shown in (1) to accommodate broader range of compounds.



M = metal ion
Y = Coordinating atom or group
(5)

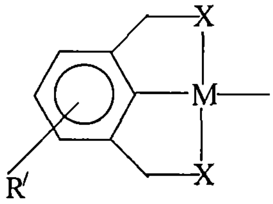
Classification of organometallic intramolecular-coordination compounds:

The systematic classification of intramolecular-coordination compounds has been introduced by Professor Omae [15]. The classification has been made on the basis of the nature of metal-carbon bond present in the cyclometallates. Cyclometallates containing metal-carbon σ- bonds are further classified on the basis of hetero donor atoms. The group of cyclometallates having metal-carbon π- bonds has been classified on the basis of the nature of donating groups. The schematic representation [15] is given below.



Scheme 1. Classification of cyclometallates [15].

Furthermore, Professor van Koten has classified [20] a group of cyclometallates based on the mode of coordination of ligands as ***pincer*** complexes of type **(6)**.



X = -NR$_2$, -PR$_2$, -SR
M = Metal ion
(6)

Typically, such a ligand, terdentate coordinating monoanionic array, encompasses an anionic aryl ring which is *ortho*, *ortho*-disubstituted with hetero donor atom like CH$_2$X which generally coordinate to the metal center and support the M-C σ bond. Studies on *pincer* complexes have emerged as an important area of cyclometallation chemistry [21 -29] and recent trends in this area [30 -38] are note worthy.

Relevance of cyclometallates :

There has been intense interest in the chemistry of cyclometallated compounds over last three decade [15, 39-43]. Cyclometallates are well known for their potential use in organic and organometallic synthesis [44-48]. Functionalization at metallated carbon is of special interest in organic synthesis. Reactions of cyclometallates with alkenes, alkynes, carbonmonooxide, isocyanides, halogens and oxo-transfering agents yield compounds, which are difficult or impossible to synthesize following conventional methods. In the field of catalysis cyclometallates find their extensive applications as catalysts [49-70]. Enantiopure '*pincer* ' type cyclometallates often behave as asymmetric catalyst [71-78].

Using the preferred stereochemistry of metal ions, a large number of cyclometallates have been designed and synthesised as metallomesogen [79-87]. Cyclometallates find applications in photochemistry [88-91]. Biological activities of some cyclometallates are also known [92-95].

I.2. PURPOSE OF THE PRESENT WORK

The study of cyclometallation reactions (-C-H → -C-M) may provide valuable insight into C-H bond activation process. The presence of hetero donor atom in the organic substrate activates the metal ion which in turn activates suitably oriented C-H bond of target group followed by M-C bond formation.

The following factors that influence the ease and mode of cyclometallation.

(i) The nature of carbon atom involved:

The cyclometalation of aromatic versus aliphatic C-H bond activation is an important topic in organometallic chemistry. It has been observed that there are many more examples of aromatic C-H bond activation than that of aliphatic or benzylic C-H bond activation.

Although the aliphatic or benzylic C-H bonds are weaker than the aromatic ones, the greater bond strength of the M-C $_{aryl}$ over the M-C $_{alkyl}$ or M-C $_{benzyl}$ bonds has been proposed as the explanation of the above observation [96]. In general, an intramolecular electrophilic attack of the metal at the carbon atom, a strong tendency for preferential activation of aromatic over aliphatic C-H bonds is widely accepted [41].

(ii) The nature of hetero donor atom or other functional groups with respect to the metal ion chosen.

(iii) The nature of metal ions.

The careful consideration of the importance of C-H bond activation following cyclometallation route, we wish to address the following issues:

(a) Controlling factors for selective activation of C(aromatic)-H bonds, if more than one option are available.

(b) Influence of the donor group attached to aromatic ring, on the different types of C(aromatic)-H bond activation.

(c) The roles of different metal ions in the selective C(aromatic)-H bond activation.

(d) Incorporation of additional donor groups (auxiliary donor) in the ligand framework and its influence on the selection of metallation sites, if any.

(e) The conditions for reactivity of C(aromatic)-M bond.

To address the above issues we wish to adopt the following strategy:

1. Studies in the field of C-H bond activation of aromatic rings by cyclometallation have been confined mainly within the area of C(phenyl)-H bond activation. Reports of C-H bond activation of other aromatic rings are relatively sparse. Few reports of C-H bond activation of naphthyl ring have appeared in literature [28, 97-108]. To the best of our knowledge only one report [109] concerning the activation of C-H bonds of anthracenyl group exists.

In this context it would be interesting to study the comparative ease of activation for different types of C(naphthyl)-H bonds by metal ions.

2. The azo group is well known to bind different metal ions in their different oxidation states. For this reason the azo group has been chosen as primary donor, which is to be attached with the target naphthyl group, to promote the site-selective activation of C(naphthyl)-H bonds.

3. In addition to the azo group (primary donor), another donor group (auxiliary donor) is to be incorporated in the organic substrate in such a fashion that auxiliary donor group, capable of binding the metal ion, would remain away from the target naphthyl group. The auxiliary donor site is to be provided as $2'$-substituted pendant phenyl or naphthyl group attached to the azo function. The potential terdentate donor framework is designed to prevent the formation of multinuclear compounds.The influence of the auxiliary donor center on the selection of metallation site would also be investigated.

4. The choice of metal ions is to be restricted to ruthenium (II), palladium (II) and platinum (II) ions for the activation of C-H bond of naphthyl group.
5. Finally, attempts would be made to examine the reactivity of the metal-C (naphthyl) bond present in the cyclometallate with special emphasis for oxygenation.

We intend to isolate the end products containing M-C(naphthyl) bond, formed in the process of C(naphthyl)-H bond activation by metal ions. The characterization of new cylometallates would be done using different spectroscopic techniques and X-ray diffraction method. Their electron transfer properties would be studied in nonaqueous media by cyclic voltammetry and coulometry. The photochemical behaviour of these compounds would be examined. The reactivity of these new cyclometallates towards oxo-transfer reagents would also be studied in solution.

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