CHAPTER 1

An Overview of C-H Bond Activation by Transition Metal Complexes: Scope and Purpose of the Present Investigation

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Abstract

A brief survey on the area of C-H bond activation by transition metal complexes has been made with an emphasis on recent advances. The discussion was mainly focused on stoichiometric and catalytic C-H bond activation. In this background, the scope and purpose of the present work have been delineated.

I.1 Introduction

In the course of development of science, area of focus changes with time and shifts from one area to newer pasture depending upon the necessity of knowledge and utility. Very few fields remain at focal point with the passage of time. Despite notable advances, the issue of C-H bond activation in chemical science is continuing to remain as a frontier area for a very long period.

Still, there is no unique catalytic route for selective and efficient functionalization of unactivated sp^3 C-H bonds present in different types of compounds. Saturated hydrocarbons (alkanes) are the main constituents of oil and natural gas, the feedstocks for chemical industry and functionalization of saturated, as well as aromatic, olefinic and acetylenic hydrocarbons constitute an extremely important field in contemporary chemistry. The development in this area is an absolute necessity to discover new economically viable routes for conversion of hydrocarbons to more valuable products, such as alcohols, ketones, epoxides, acids etc. In addition, improved hydrocarbon transformations could reduce petroleum pollution and other related environmental hazards. Finally the well-known inertness of saturated hydrocarbons makes their chemical transformation extremely challenging from the viewpoint of basic science. The transformation of hydrocarbons (both saturated and unsaturated) by catalytic action of transition metal complexes appears to be one of the promising fields.

Activation of a C-H bond is preceded by the binding of a substrate with a metal complex. This may be followed (i) stabilization of the metal-substrate complex with or without minor reorganization (ii) functionalization of the substrate and regeneration of the metal complex. The process (i) is known as stoichiometric C-H bond activation whereas process (ii) is termed as catalytic C-H bond activation. Thus C-H bond activation by transition metal complexes may broadly be classified under two heads: '*stoichiometric C-H bond activation*' and '*catalytic C-H bond activation*'.

I.2 *Inertness of Alkanes*

The well known inetness of alkanes is reflected from their old nomenclature, "paraffins", from the Latin word *parum affinis* meaning without affinity. Perhaps the only substance which 'activates' alkanes readily is the oxygen in air. Alkanes undergo oxidation (burning) in air to produce thermodynamically stable products: water and carbon dioxide.

In many respects, alkanes, notably the lower members (methane, ethane), are similar to hydrogen. Like alkanes, molecular hydrogen is inert toward oxygen at ambient temperature, but can be burned in air to produce the thermodynamically stable water. The values of C-H and H-H dissociation energies for methane and hydrogen molecules are almost exactly equal (104 kcal mol^{-1}). Ethylene, acetylene and benzene, which have much stronger C-H bonds (106, 120, and 109 kcal mol^{-1}, respectively) than methane, are known to exhibit much higher activities. The inertness of methane and dihydrogen is due to the fact that both are completely saturated molecules, which contain neither π- nor n-electrons.

I.3 *Reactions of C-H compounds with Metal Complexes: A Historical Survey*

In spite of the difficulties, initial success in activation of C-H bonds by transition metal complexes was achieved as early as 1898, when Fenton[1] reported that hydrogen peroxide and iron(II) salts can hydroxylate alkanes, but with poor conversion and yield. Fenton chemistry, also called Haber-Weiss chemistry, is believed to release HO$^{\bullet}$ radicals[2-4] by Fe-catalyzed decomposition of H_2O_2 via steps as shown below:

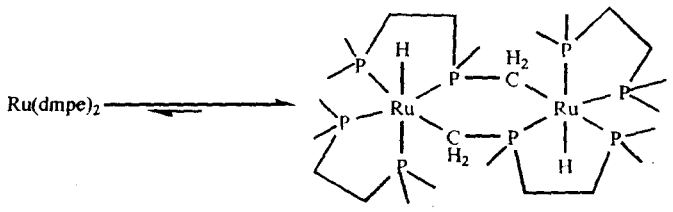
$$Fe(II) + H_2O_2 = Fe(III) + OH^- + {}^{\bullet}OH$$

$$R\text{-}H + {}^{\bullet}OH = R^{\bullet} + H_2O$$

$$R^{\bullet} + O_2 = R\text{-}O\text{-}O^{\bullet}$$

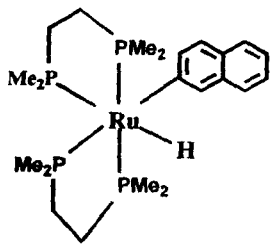
These radicals then react with alkane to form carbon radicals. The HO-H bond dissociation energy (BDE) of 119 kcal mol^{-1} easily allows HO$^{\bullet}$ to abstract an H atom from an sp^3 C-H bond (typical BDE range 90-105 kcal mol^{-1}). The ROO$^{\bullet}$ radical then goes on to give the observed products, such as alcohol and ketone.

During the 1930s, electrophilic aeration of arenes were described,[5] a radical-chain autooxidation of hydrocarbons initiated by the metal complexes was developed,[6] and a method for the metal-oxo complex promoted oxidation of alkenes and arenes by hydrogen peroxide was proposed.[7] A second spurt in pioneering research occurred in this field in the 1960s. In1965, Chatt[8] found cyclometallation[9,10] of CH bonds in a phosphine complex (**1**), essentially a CH oxidative addition driven by chelate effect.



(1)

The Chatt system also gave intramolecular CH activation of an arene (naphthalene) (**2**), but not of alkanes.

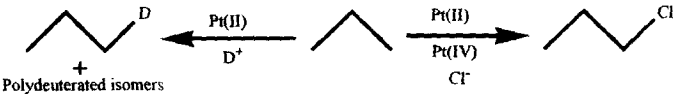


(2)

This was the first cyclometallation involving an sp^2 C-H bond. This pattern of enhanced arene reactivity versus alkanes has proved general. At first sight it seems unexpected because arene CH bonds are far stronger than those of alkanes. The reason has been traced in part to the much stronger M-aryl versus M-alkyl bond strengths.[11] In many cases where arene addition is exothermic, the corresponding reaction for alkanes is believed to be endothermic. A kinetic factor is the less hindered character of an arene CH bond and possibility of precoordination to the ring.[12] It is noteworthy that the ligand $Me_2PCH_2CH_2PMe_2$ (now called dmpe) has limited back bonding capability, so the zerovalent metal complexes prepared by Chatt have a very high tendency to give oxidative addition.[13]

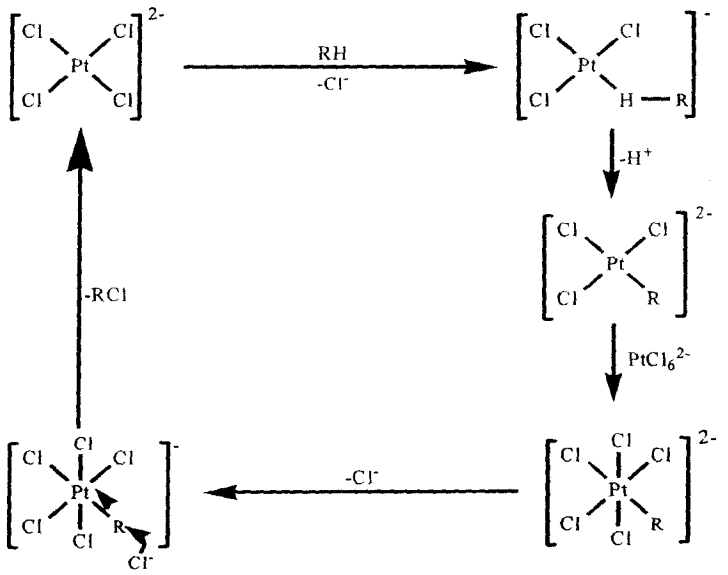
After the pioneering work of Chatt, the scientific community appreciated the potential importance of CH activation. Soon this field got another lift by the classical work of Shilov and coworkers.[14,15] They oxidized alkanes to ROH and RCl using Pt(II) as the catalyst and $[Pt(IV)Cl_6]^{2-}$ as primary oxidant (Scheme I.1). Earlier Garnett and coworkers[16-19] showed that platinum(II) salts in deuterated aqueous acid medium catalyze H/D exchange in polycyclic aromatic hydrocarbons and hetrocycles. Interestingly, activation of primary CH bonds in the terminal positions of long chain alkanes was preferred (Scheme I.1), in contrast with the preferential attack at secondary and tertiary

positions by classical radical and electrophilic reagents. In Shilov's case, terminal attack was still preferred with the same selectivity indicating that the Pt(IV) was intercepting the same intermediate alkyl that led to RD in the deuterated solvents. With methane as a substrate, methylplatinum intermediate was detected.[20]



Scheme I.1

The 1980s saw a growing number of C-H activation systems from a variety of research groups, with a great increase in attention to the topic and a growing awareness of the importance of the Shilov work.[21,22] Labinger and Bercaw[23] revisited the system in the 1990s using a series of mechanistic probes that confirmed Shilov's main points as well as extending the picture. Scheme I.2 shows the current mechanistic view. An alkane complex either leads to oxidative addition of the alkane and loss of a proton, or the alkane σ complex loses a proton directly. In isotope exchange, the resulting alkyl is cleaved by D^+ to give RD. In the alkane functionalization, oxidation of the Pt(II) alkyl by Pt(IV) gives a Pt(IV)alkyl by electron transfer and not by alkyl transfer. The Pt(IV) becomes a good leaving group, and Cl^- or OH^- can nucleophilically attack the R-Pt(IV) species with departure of Pt(II) to regenerate the catalyst. Only the latter possibility is shown in Scheme I.2.



Scheme I.2

In the 1970s it was shown that alkanes are oxidized by platinum(IV),[24] palladium(II),[25] ruthenium(IV)[26] and cobalt(III)[27,28] compounds and that complexes of iridium(III)[29] and titanium(II)[30] catalyze H-D exchange. The next decade was marked by vigorous development of the activation of alkenes and arenes by low valent metal complexes. These reactions proceed via an oxidative addition mechanism to form either alkyl or aryl derivatives of metals or alkenes.[31-37]

At the end of 1980s, interest gradually shifted to the oxidation of hydrocarbons by high valent metal-oxo compounds and dioxygen. Attention was being focused on biological and biomimetic oxidations. Cytochrome P450 model studies were propelled by the use of iodosylarenes as the oxygen donor in catalytic oxygenation reactions and by the use of metalloporphyrins as models for the active site of the enzyme.[38] The relatively recent Gif systems used for the selective oxidation alkanes were of considerable interest because of the unusual selectivity and mechanistic puzzle.[39]

I.4 *Activation of Hydrocarbons by Low-Valent Metal Complexes*

Oxidative addition reactions of hydrogen to metal complexes (Equation I.1) have been known since the 1960s. But oxidative addition reactions of hydrocarbons (Equation I.2) were discovered and investigated in detail since 1990s.

$$H—H + M \rightarrow H—M—H \qquad \text{..... I.1}$$

..... I.2

In some cases the intermediate metal hydride species can not be isolated, although the evidence supporting their formation is obtained.

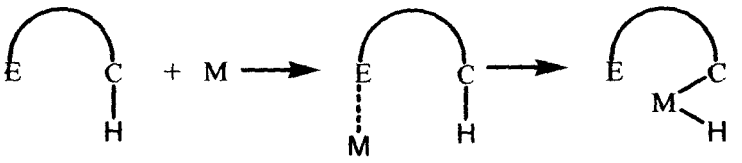
I.4.1 *Formation of σ-Organyl Hydride Complexes*

Reactions which proceed in accordance with the equation I.2 result an increase in the oxidation state of the metal by two units. Alkanes, alkenes, arenes and monosubstituted acetylene all undergo this type of oxidative addition reactions. Reactions generally take place at ambient temperature although in some cases heat or light is required. Either heat or light is essential for the abstraction of several ligands from the initial complex to form coordinatively unsaturated species capable of oxidatively adding the C-H bond. There are

mainly two pathways that lead to the formation of metal-carbon σ-bonds. They are discussed below.

I.4.1.1 *Cyclometallation*

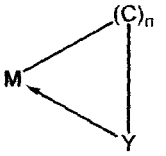
The intramolecular cleavage of a C-H bond occurs relatively easily than intermolecular activation and gives rise to a more stable σ-organyl hydride complex (scheme I.3). The intramolecular process is known as cyclometallation reaction.



Here E is a donor atom, such as N, P, or As.

Scheme I.3

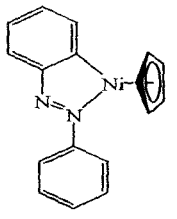
Cyclometallation reactions afford interesting intermediates (**3**), which are known as cyclometallates; the term being introduced by Trofimenko.[40]



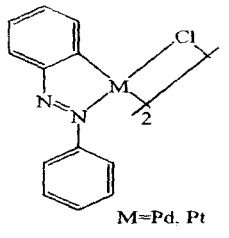
M=Metal ion; Y=coordinating atom; n= preferably 3 or 4

(**3**)

The cyclometallates or cyclic transition metal complexes containing a covalentmetal-carbon σ-bond and a metal-donor bond have been a topic of continuing interest since the discovery in the 1960s of the nickel(II) complex[41] and the chlorobridged platinum and palladium complexes[42] from the reaction of azobenzene with nickelocene and $[MCl_4]^{2-}$ (M=Pd, Pt), respectively (**4** & **5**).



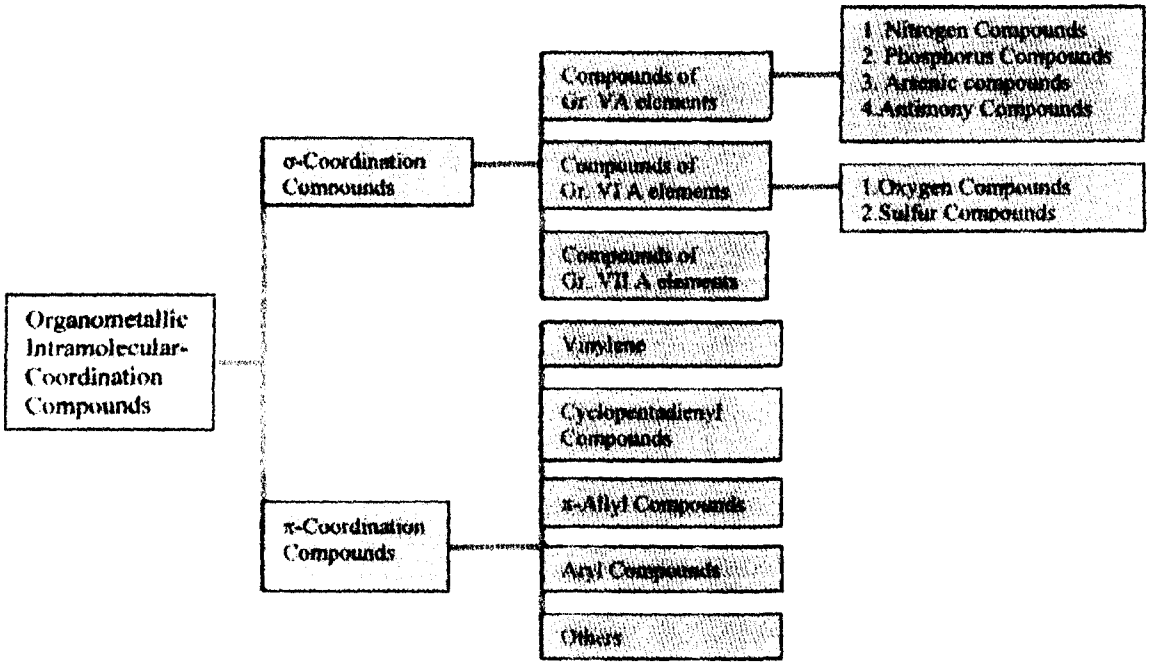
(**4**)



(**5**)

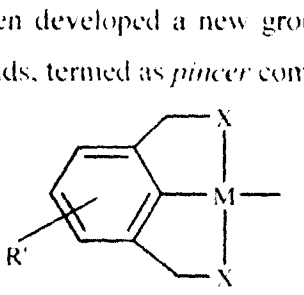
The systematic classification of intramolecular-coordination compounds has been done by Professor Omae.[9,43] The classification has been made on the basis of the nature of the

metal-carbon bond. Cyclometallates containing M-C σ-bonds are further classified on the basis of hetero donor atoms. On the other hand, cyclometallates containing M-C π-bonds has been classified on the basis of the nature of donating groups. The schematic representation has been shown below (Scheme I.4).



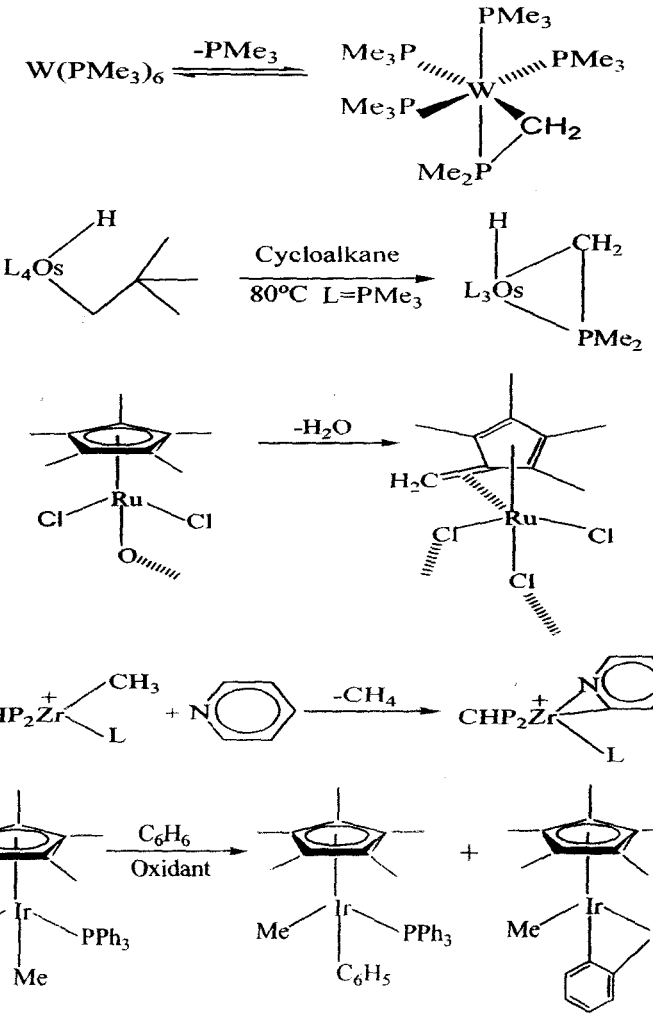
Scheme I.4 Classification of cyclometallates [Ref. 9]

Furthermore, Professor van Koten developed a new group of cyclometallates based on the mode of coordination of ligands, termed as *pincer* complexes (**6**).[44]



X -NR_2, -PR_2, -SR
M Metal ion
(**6**)

There has been intense interest in the chemistry of cyclometallated compounds over the last three decades.[43, 45-49] Besides providing unusual coordination environments,[50] they exhibit a good number of applications related to organic as well as to organometallic compounds, metallomesogens and catalysis.[51-63] Some important examples of the cyclometallation of sp^3- and sp^2-C-H bonds have been presented in Scheme I.5.

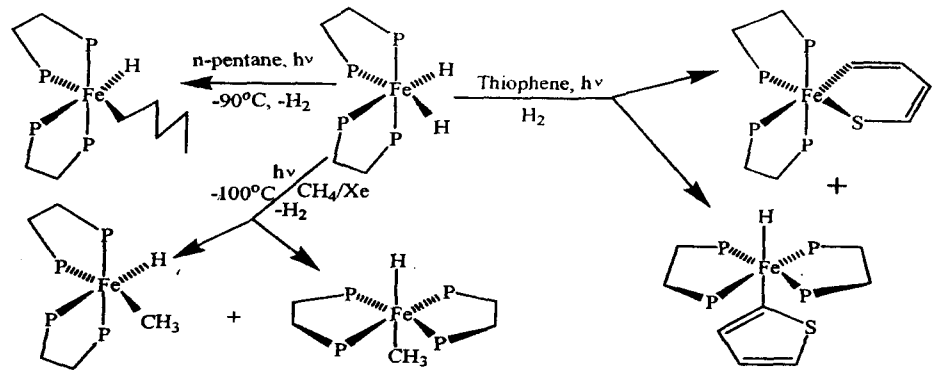


Scheme I.5 Selected examples of the cyclometallation of sp^3- and sp^2-C-H bonds

I.4.1.2 *Intermolecular Oxidative Addition*

In many cases, σ-organyl complexes are formed from the oxidative addition of alkanes, alkenes, arenes, monosubstituted acetylenes are fairly stable and can be isolated. The oxidative addition of alkanes to form alkyl hydride complexes was first demonstrated by Bergman.[69] He irradiated the iridium dihydrate derivative $Cp^*Ir(H)_2PMe_3$ (Cp^*=pentamethylcyclopentadienyl) in a cyclohexane or neopentane solution and produced $Cp^*(PMe_3)Ir(H)(C_6H_{11})$ and $Cp^*(PMe_3)Ir(H)(CH_2CMe_3)$ respectively.[67] A large number of reactions are known which form a coordinatively unsaturated species by elimination of molecular hydrogen or a hydrocarbon. These species then can react in a

similar way and form stable σ-organyl complexes. Some of the examples are shown in Scheme I.6.



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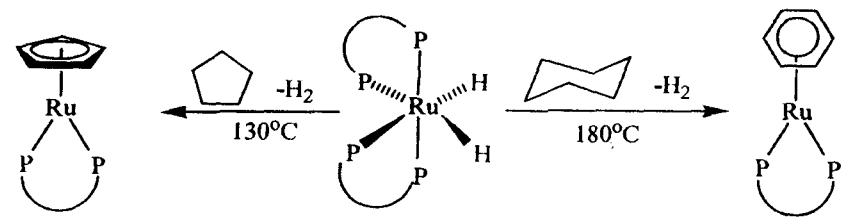

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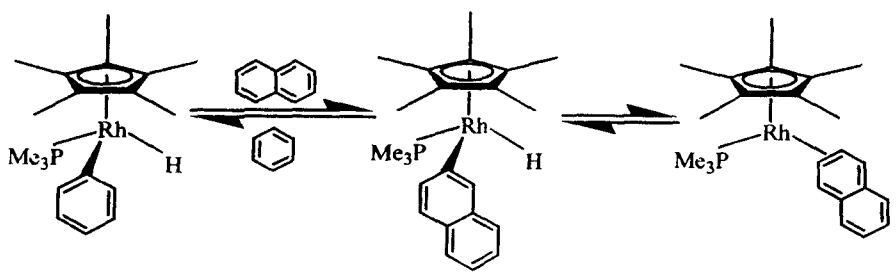

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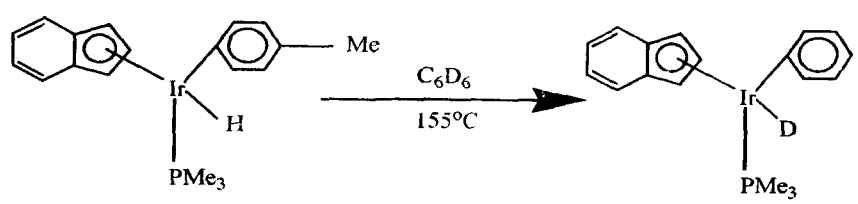

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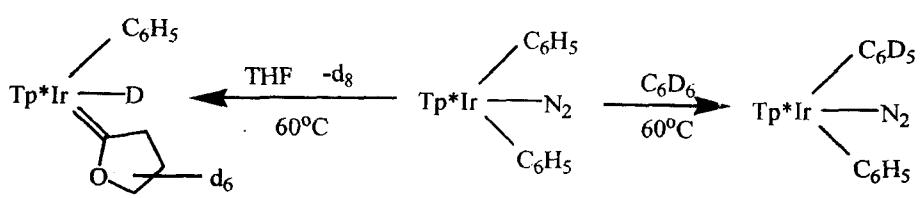

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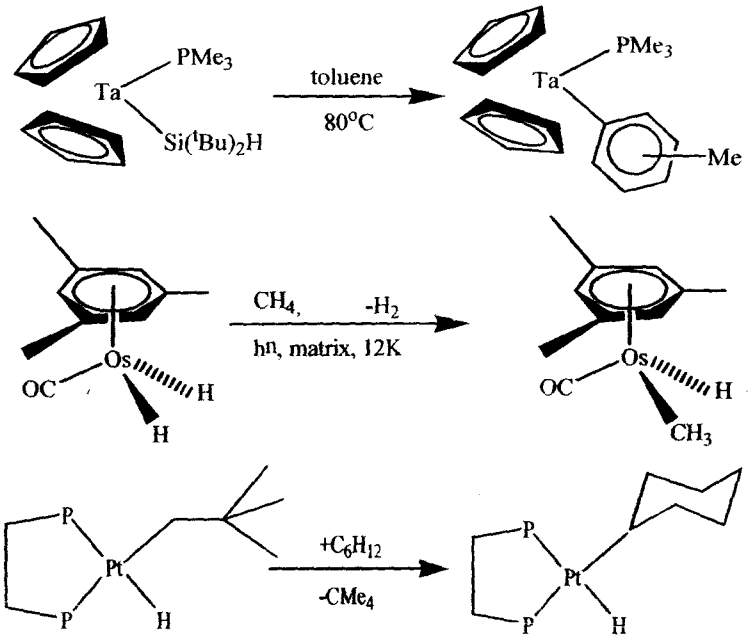


Scheme I.6 Selected examples of the cyclometallation of sp^3- and sp^2-C-H bonds

I.5 ***Activation of Hydrocarbons by Biological Systems and their Chemical Mimics***

Organic compounds can be very easily oxidized by dioxygen in the cells of bacteria, plants, incects, fish and mammals. The group of enzyme, called monooxygenases, catalyzes the hydroxylation of organic compounds by incorporating one atom of dioxygen into hydrocarbon substrates with concomitant reduction of the other oxygen atom to water. The creation of chemical models of the enzymatic oxidation of alkanes and arenes not only help to understand the mechanistic puzzles, but also makes it possible to develop fundamentally new processes for the conversion of hydrocarbon raw materials.[78] A brief survey of the most recent developments in biological C-H bond activation has been presented below.

I.5.1 ***Hydrocarbon Oxygenation by Cytochrome P-450 and their Chemical Models***

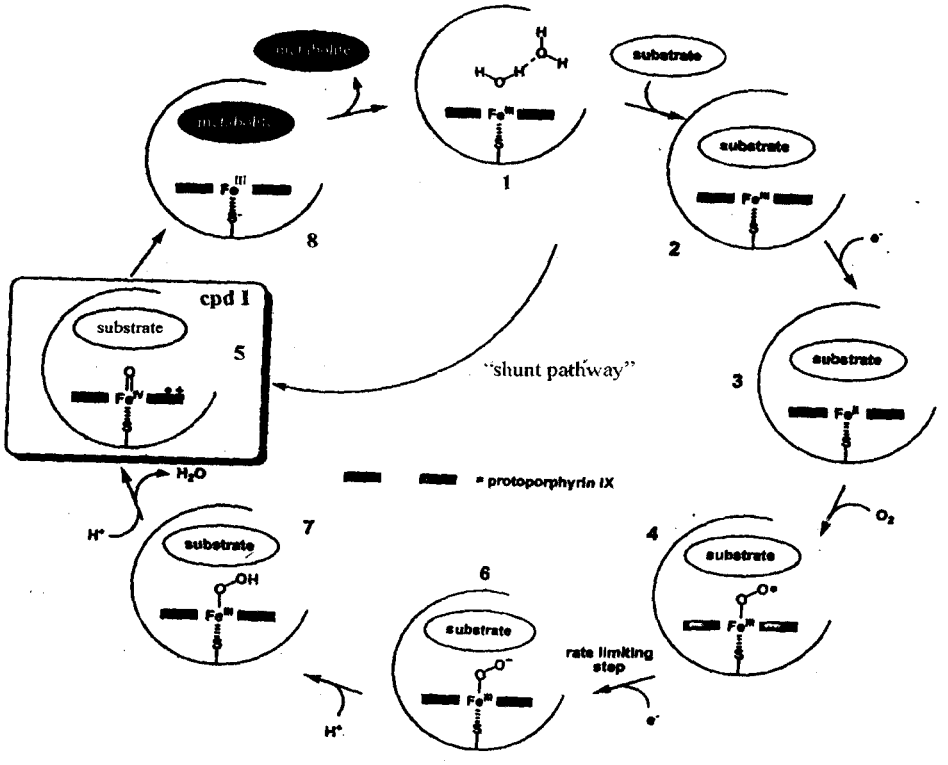
Mammalian Cytochrome P-450 is a ubiquitous membrane bound monooxygenase that catalyzes the hydroxylation of membrane-entrapped nonpolar substrates including drugs, steroids and pollutants, yielding partially water-soluble products that can be further metabolized.[79] Several other types of oxygen transfer reactions are also catalyzed by this enzyme, including epoxidation, N-dealkylation, O-dealkyaltion and sulfoxidation (Table I.1).

Table I.1 Major reactions catalyzed by cytochrome P-450.

Reaction type	Simplified examples	Typical substrates
Aliphatic hydroxylation	Cyclohexane→Cyclohexanol	Pentobarbital
Aromatic hydroxylation	Benzene→Phenol	Phenobarbital
Alkene epoxidation	Cyclohexene→Cyclohexene Oxide	Aldrin
N-dealkylation	$CH_3N(H)CH_3 \rightarrow CH_3NH_2 + H_2C{=}O$	Methadone
O-dealkylation	$C_6H_5OCH_3 \rightarrow C_6H_5OH + H_2C{=}O$	Codeine
Oxidative deamination	$(CH_3)_2CHNH_2 \rightarrow (CH_3)_2C{=}O + NH_3$	Amphetamine
S-oxidation	$CH_3SCH_3 \rightarrow (CH_3)_2S{=}O$	Chlorpromazine
Reductive dehalogenation	$C_6H_5CH_2Br \rightarrow C_6H_5CH_3$	Halothane

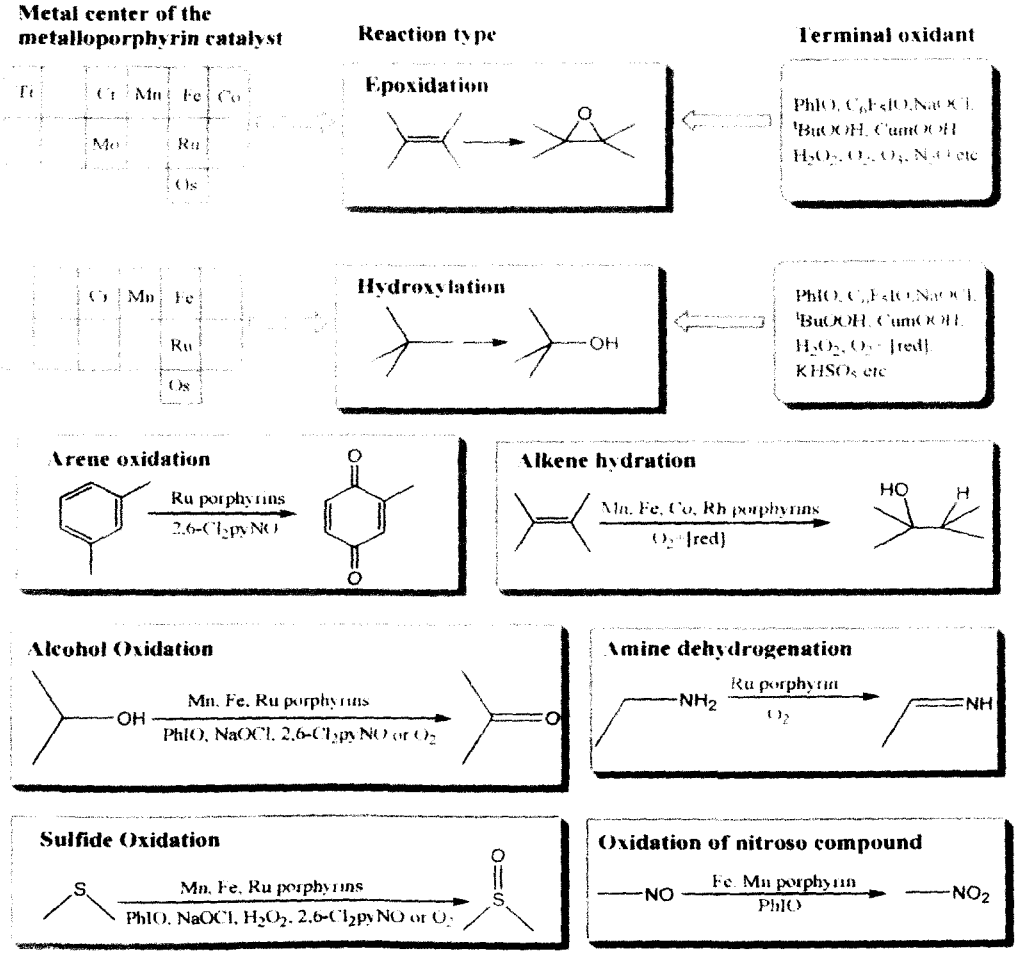
I.5.1.1 *Catalytic cycle of Cytochrome P450*

The main steps of the Cytochrome P450 catalytic cycle of O_2 activation and substrate hydroxylation were proposed in the early 70's, on the basis of spectral and enzymatic studies performed on purified $P450_{cam}$.[80] The proposed catalytic cycle[80] is shown in Scheme I.7. Nevertheless several aspects of P450 mechanisms are still elusive and subject to broad debate.



Scheme I.7 Catalytic cycle of Cytochrome P450. [ref. 80]

The catalytic cycle is initiated by substrate binding to Cytochrome P450. This causes a shift in spin equilibrium from predominantly low spin in the resting state (**1**) to high spin in the substrate bound state (**2**). This modification in spin state alters the redox potential of the metal centre from E_0= -0.3 to -0.17V (vs. SHE) and enable electron transfer from the reductase and thus triggering the catalytic cycle. Next one electron is donated to reduce the iron of the cofactor from the ferric (Fe^{III}) to the ferrous (Fe^{II}) from (**3**) which in turn, coordinate dioxygen to form a dioxygen adduct (**4**). Resonance Raman[81] and Mössbauer[82] spectroscopy both support the view of this intermediate as being a ferric superoxide (Fe^{III}-$O_2^{\cdot}$). The next step, donation of a second electron, being the rate determining step in the catalytic cycle, all other intermediates have eluded direct detection so far and hence still subject to debate.



Scheme 1.8 Metalloporphyrin-based oxidation systems.

Studies on peroxidases have identified a green high valent iron oxo species, compound I (cpdI) (**5**) as the reactive species. Studies on P450s with external oxidants using the so-called "shunt pathway", as well as extensive studies on model compounds and theoretical approaches support a similar electrophilic species to be the active species in P450s. The latter is formed via double protonation of the intermediately formed iron(III)-peroxo complex (**6**) to form an iron(III)-hydroperoxo complex (**7**), also referred to as compound 0 (cpd0), after the first protonation, and heterolytic cleavage of the O-O bond after second protonation to form water and (**5**). The so formed intermediate then oxidizes the bound substrate, generating the metabolite and the ferric P450 (**8**) which can coordinate a new substrate and enter a new cycle.

I.5.1.2 *Chemical Models*

For several decades, synthetic metalloporphyrins have been used as model for the iron(III)-peroxo and the iron(V)-oxo species, which are generated during the catalytic cycle of cytochrome P450 (Scheme I.7).

The first oxidation system with synthetic metalloporphyrin as a catalyst was developed by Grooves and co-workers in 1979.[83] This oxidation system, which consists of terminal oxidant iodosylbenzene (PhIO) and catalyst [Fe^{III}(por)Cl] (por = a porphirinato dianion), was shown to effect both epoxidation of styrene and cyclohexene, and hydroxylation of cyclohexane and adamantane. Subsequently, numerous reports on metalloporphyrin-catalyzed oxidation systems have appeared in the literature.[84-94] Among the most extensively studied systems are the epoxidation of alkenes and hydroxylation of alkanes catalyzed by iron, manganese and ruthenium porphyrins with terminal oxidants PhIO, NaOCl, 2,6-Cl_2pyNO (2,6-dichloro pyridine-N-oxide), including enantioselective oxidations. A brief outline of the metalloporphyrin-based oxidation systems previously reviewed in literature is shown in Scheme I.8.

Apart from metalloporphyrins various other synthetic systems have been found to mimic the function of Cytochrome P450 enzyme. The most important synthetic ligand systems, especially in the context of catalysis for the asymmetric oxidation of organic substrates, are the Schiff base derivatives, salens [salen= 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] and its derivatives.[95-99] The metallosalen derivatives, most notably those of manganese,[100, 101] chromium[102] and vanadium[103] have emerged as efficient

catalysts in various reactions. An increase in the enantioselectivities for these substrates has been achieved by modulating the steric and electronic properties of metallosalens.[100, 101]

Another interesting ligand framework which has been a subject of recent interest in the context of catalysis is the one carbon short analogue of porphyrin, the corrole.[104] Since the breakthrough discoveries of facile synthetic methodology for the preparation of corroles was made,[105] a tremendous amount of interest has been generated on the chemistry of this contracted macrocycles.[104] Due to their unique capacity to stabilize high metal oxidation states, various metallocorroles have been synthesized and examined successfully as catalysts for epoxidation,[106] hydroxylation,[107] cyclopropanation[108] and aziridination.[109]

I.6 Purpose of the present work

The present doctoral thesis focuses mainly on two fields:

A. Stoichiometric C-H bond activation by transition metals followed by isolation and characterization of the resulted cyclometallates.

B. Catalytic C-H bond activation by transition metal complexes with an aim to oxygenate different types of hydrocarbons.

Details of the purpose and work plan are described below.

A. Stoichiometric C-H bond activation

In the field of stoichiometric C-H bond activation, cyclometallation reaction (-C-H → -C-M) provides 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 the target group resulting in M-C bond formation.

The following factors influence the ease and mode of cyclometallation.

(i) The nature of carbon atom involved.

(ii) The nature of hetero donor atom or other functional groups attached to the target group.

(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 where more than one site are available.

(b) Influence of the donor group attached to aromatic ring.

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

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.[43,47]

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. Therefore, *regioselectivity* or *regiospecificity* of the processes becomes an issue due to the presence of multiple potential sites for metallation.

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

3. The choice of metal ions is to be restricted to *'soft'* metal ions like palladium (II), platinum (II) and rhodium(I) ions for the activation of C-H bond of naphthyl group.

4. Furthermore, a strategy has been drawn to incorporate an additional donor group (auxiliary donor) 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 diazene function. The influence of the auxiliary donor on the selection of metallation site would be investigated thoroughly.

Attempts would be made to isolate the end products containing M-C(naphthyl) bond, formed in the process of C(naphthyl)-H bond activation by different metal ions. The characterization of new cylometallates would be done using different spectroscopic techniques and X-ray diffraction method.

B. Catalytic C-H bond activation by transition metal complexes

Another area we wish to explore is the biomimmetic oxidation of hydrocarbons by soluble transition metal complexes as catalysts. In this area most of the reported works involve metalloporphyrins as catalysts.

1. We wish to exploit the well known 'salen' ligand framework, which is easy to synthesize and cost effective. The electronic and steric properties of metallosalens are to be tuned by incorporating suitable substituents with the ultimate goal of achieving effective catalytic performances.

The uses of iron(III)-salen complexes as catalyst in oxygenation of different types of hydrocarbons is almost rare. Although manganese(III)-salen complexes are well known for their catalytic activity in the area of asymmetric epoxidation, their uses in catalytic oxygenation of other hydrocarbons is least explored. Here, the catalytic behavior of iron(III)-salen as well as manganese(III)-salen complexes are to be examined in order to activate different types of C-H bonds with an aim to oxygenate hydrocarbons.

2. An important member of macrocyclic group is corrole, which is one *meso*-carbon short analogue of porphyrins. It is our objective to use metallocorroles in catalytic functionalization of C-H bonds. Recently the metallocorroles are receiving increasing attention in different areas of chemical science as catalysts. We wish to investigate the catalytic property of an electron deficient iron corrole complex, [Fe(tpfc)Cl] (tpfc = trianion of *meso*-tris(pentafluorophenyl) corrole) in oxygenation of different types of hydrocarbons. Catalytic hydroxylation of unactivated C-H bonds of alkanes will be the core area of investigation. Attempts would be made to elucidate the mechanistic aspects of the catalytic reactions.

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