

*Syntheses, Spectral and Structural studies of  $\eta^5$  and  $\eta^6$   
cyclichydrocarbon complexes of some Platinum group metals  
with N,N and O,O Donor bidentate ligands*

*A thesis submitted in partial  
fulfillment of the requirements for the degree of  
Doctor of Philosophy*

By

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**August 2007**



## DECLARATION

I K. Pachhunga hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to anybody else to the best of my knowledge. I have not submitted the thesis for any research degree in any other University or Institution. This is being submitted to the North Eastern Hill University, Shillong for the degree of Doctor of Philosophy in Chemistry



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## CERTIFICATE

This is to certify that the thesis entitled "*Syntheses, Spectral and Structural studies of  $\eta^5$  and  $\eta^6$  - cyclichydrocarbon complexes of some Platinum group metals with N,N and O,O donor bidentate ligands*" is based on the original work done by K. Pachhunga, under my supervision in the Department of Chemistry, School of Physical Sciences, North Eastern Hill University, Shillong Meghalaya. This work has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title and that it represents entirely an independent work on the part of the candidate.

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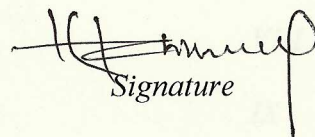
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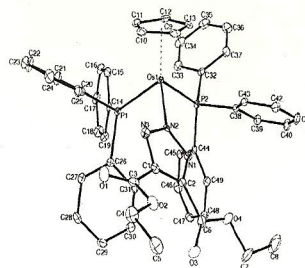
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Signature

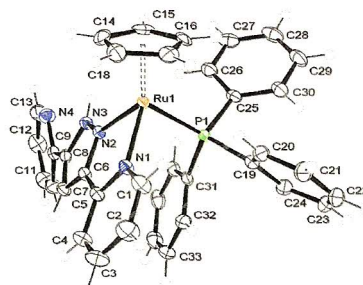
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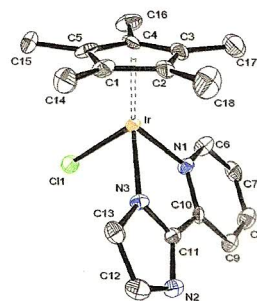


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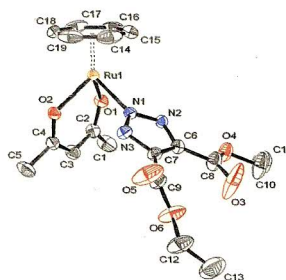
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## LIST OF ABBREVIATIONS

acac	=	acetylacetone
$\text{NH}_4\text{BF}_4$	=	ammonium tetrafluoroborate
$\text{NH}_4\text{PF}_6$	=	ammonium hexafluorophosphate
Cp ( $\text{C}_5\text{H}_5$ )	=	cyclopentadienyl
cym	=	<i>p</i> -cymene
arene	=	<i>p</i> -cymene or benzene
Cp* ( $\text{C}_5\text{Me}_5$ )	=	pentamethylcyclopentadienyl
2-PC	=	N-(pyridyl-2-ylmethylene)cyclophenylamine
2-PP	=	N-(pyridyl-2-methylene)phenylamine
$\text{PPh}_3$	=	triphenylphosphines
S	=	singlet
Sep	=	septet
M	=	multiplet
t	=	triplet
bzac	=	benzene acetylacetone
dbzm	=	methyl dibenzene
TCE	=	tetracyanoethylene
$\text{AgBF}_4$	=	silver tetrafluoroborate
pa	=	sodium salt of para-anisidic acid
ma	=	sodium salt of malonic acid
pz	=	Pyrazole
Hbpp	=	3,5-bis(2'-pyridyl)pyrazole

## PREFACE

Organometallic chemistry is one of the most important and interesting area in inorganic chemistry due to its catalytic properties and high reactivity. It is a broad interdisciplinary whose sphere of interest includes all compounds wherein metals are in low oxidation states and bounded with carbon atom of organic molecules, radicals and ions. In the mid of twentieth century and after the syntheses of the cyclopentadienyl, its analogues and arene transition metal complexes, there is a large number of work in organo transition metal chemistry which led to the development of new areas like homogeneous catalysis *etc.*, These compounds are potential precursors of organic polymers that shows interesting electrical and conducting properties. More recently, ( $\eta^6$ -arene) ruthenium complexes have been the subject of intensive studies due to their interesting antibacterial, antiviral and anticancer properties, coordination chemistry and its catalytic properties. They have the potential for inhibiting enzymes involving DNA biochemistry for example; ethylenediamine are cytotoxic to cancer. Thus, keeping this in mind the importance of these type of complexes, the research work is based on synthesis and characterization of new complexes arising from the versatile starting materials like  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene = benzene, *p*-cymene),  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{PPh}_3)_2\text{X}]$  where  $[\text{M} = \text{Ru}, \text{X} = \text{Cl}; \text{M} = \text{Os}, \text{X} = \text{Br}]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]_2$ ,  $\text{M} = \text{Rh}$  and  $\text{Ir}$ . The  $\sigma$ -donor and  $\pi$ -acceptor abilities of the cyclopentadienyl ligands stabilize transition metal complexes in low and high oxidation states. Thus the cyclopentadienyl group is one of the most important ligands in Organometallic chemistry. The importance of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  complex is evident from its appearance in literature and several papers reported that the catalytic property of this compound. Interestingly, there is

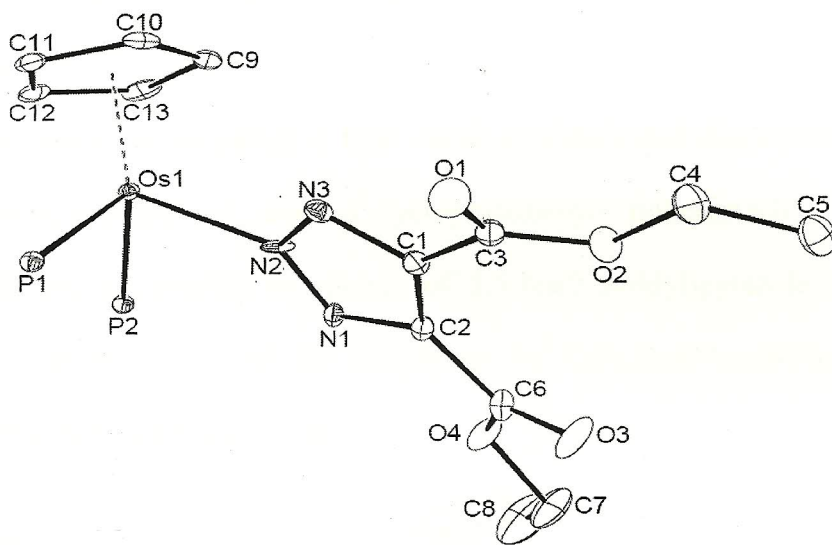
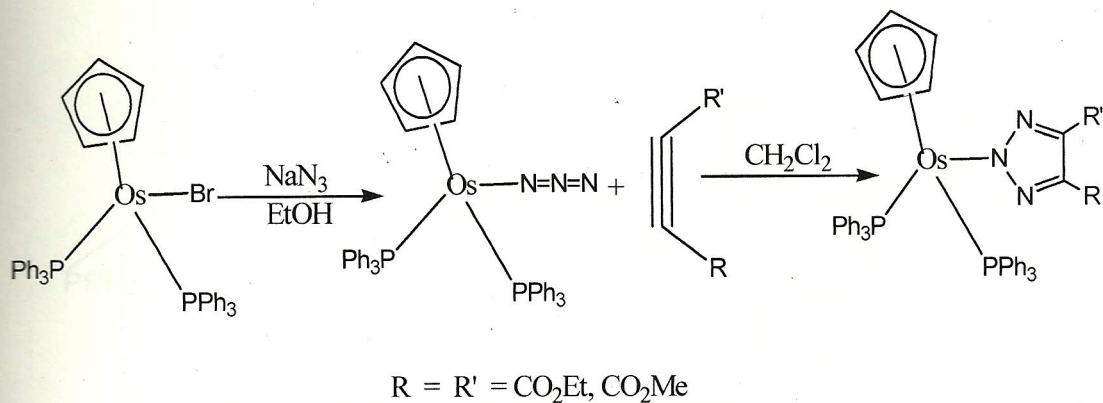
noticeable lack of emphasis on the osmium analogue,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$  as evident from the literature survey. This could be due to the lower kinetic lability of osmium relative to ruthenium and possibly the cost of osmium metal. Thus, this thesis consists of seven chapters mentioned as bellow:-

### **Chapter 1:**

This chapter gives a brief introduction to arene ruthenium (arene = benzene and *p*-cymene) cyclopentadienyl ruthenium(II), osmium(II); pentamethylcyclopentadienyl ruthenium(II), rhodium(III) and iridium(III) complexes, and their reactions towards bridge cleavage and its substitution reactions. These complexes undergo substitution reactions with various N,N'-donor and O,O'-donor ligands, and deals with their application in the field of catalytic activities.

### **Chapter 2.**

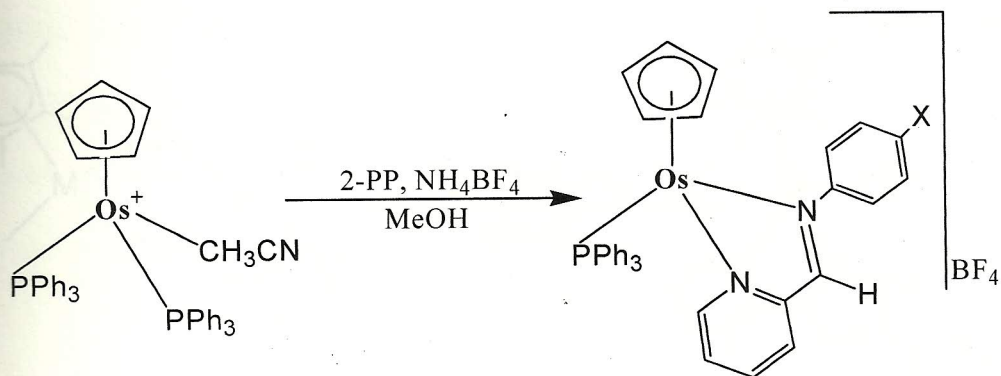
This chapter describes reactions of cyclopentadienyl osmium(II) biphosphine azido complexes with activated alkynes and nitriles and its isolation of osmium triazole complexes. The cyclopentadienyl osmium(II) biphosphine azido complexes thus generated undergo 1,3 dipolar cycloaddition reaction with various substituted acetylene, nitriles *etc.*, to gives triazolate and tetrazolato complexes. The single crystal X-ray structure of representative complex has been established.



ORTEP diagram of complex [CpOs(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>C<sub>2</sub>(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)] with 30% probability thermal ellipsoids displayed with out phenyl groups of phosphines and H atoms being omitted for clarity.

### Chapter 3.

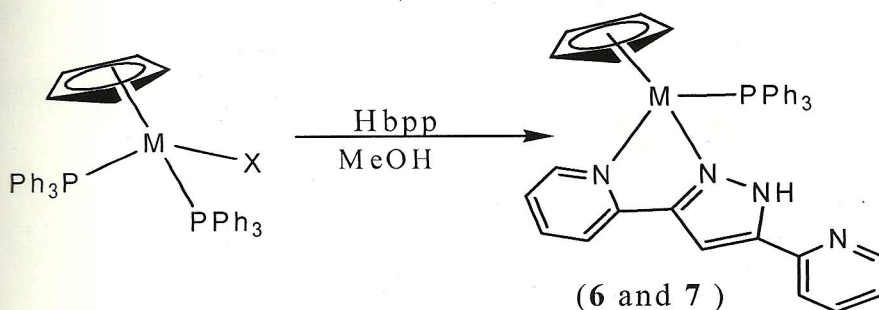
This chapter describes a brief synthetic methods and spectral characterization of the complexes results from the reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$  with N,N'-donor Schiff's bases *viz.* *para*-substituted N-(pyrid-2-ylmethylene)phenyl amines.



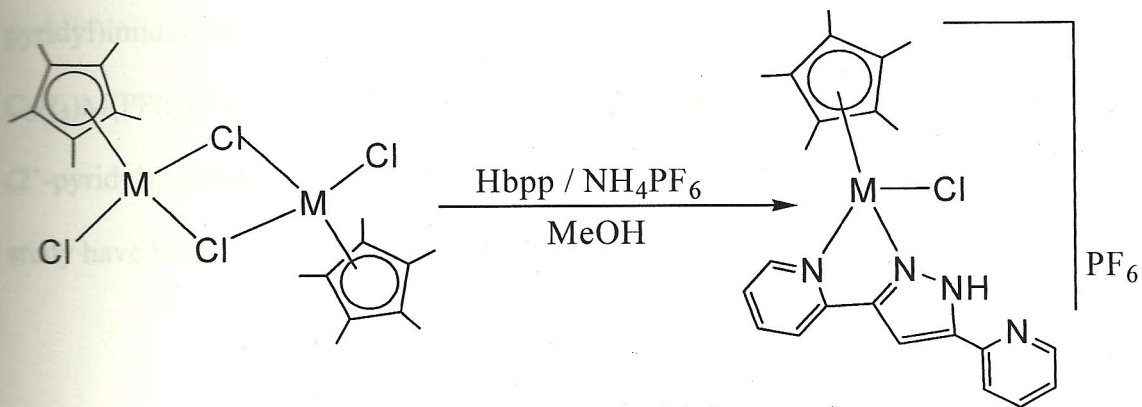
2-PP = N-(pyrid-2-ylmethylene)phenylamine  
 X = H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, NO<sub>2</sub>

#### Chapter 4.

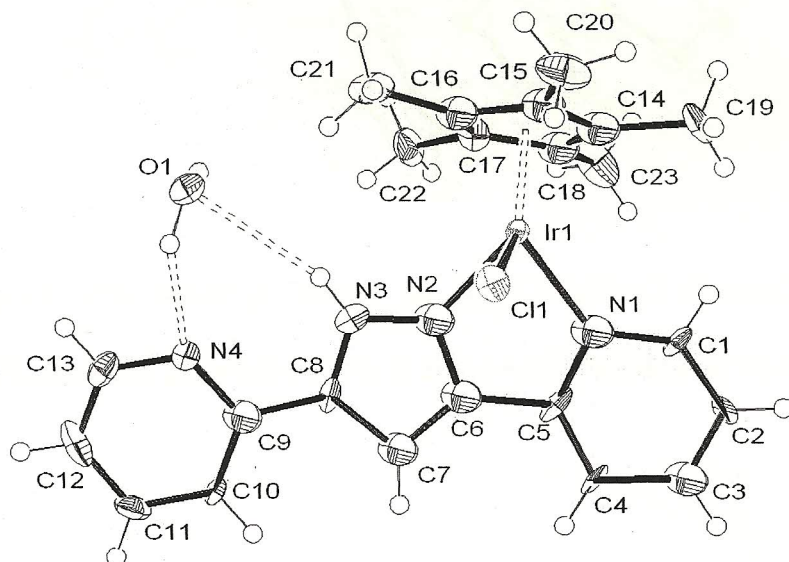
This chapter encompasses a brief detail syntheses and characterization of  $\eta^5$ -pentamethylcyclopentadienyl and  $\eta^5$ -cyclopentadienyl ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes of 3,5-bis(2-pyridyl)pyrazole (Hbpp). The molecular structural studies of the complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Hbpp})\text{PPh}_3]^+$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Hbpp})\text{Cl}]^+$  were carried out.



X = Cl or Br  
 M = Ru(II), Os(II).  
 Hbpp = 3,5-bis(2-pyridyl)pyrazole



Hbpp = 3,5-bis(2'-pyridyl)pyrazole  
 M = Rh(III) or Ir(III)

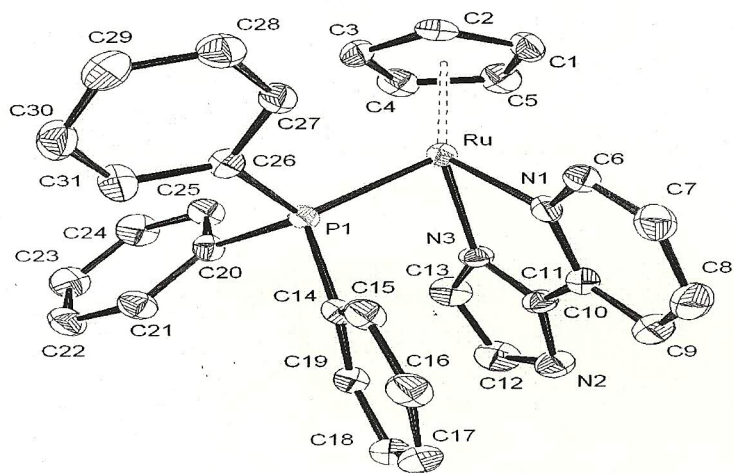


ORTEP diagram of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Hbpp})\text{Cl}]\text{PF}_6$  drawing with labelling scheme at 50% probability level,  $[\mathbf{10}]\text{PF}_6$  anion omitted for clarity

## Chapter 5.

This chapter encompasses reactivity studies of cyclopentadienyl ruthenium(II), osmium(II) and pentamethylcyclopentadienyl iridium(III) complexes towards 2-(2'-

pyridyl)imidazole derivatives. It describes substitution reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{PPh}_3)_2\text{Cl}]$  [ $\text{M} = \text{ruthenium(II)}$  and  $\text{osmium(II)}$ ], and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$  with 2-(2'-pyridyl)imidazole and 2-(2'-pyridyl)benzimidazole ligands. The single crystal X-ray study have been carried out for representative complexes.

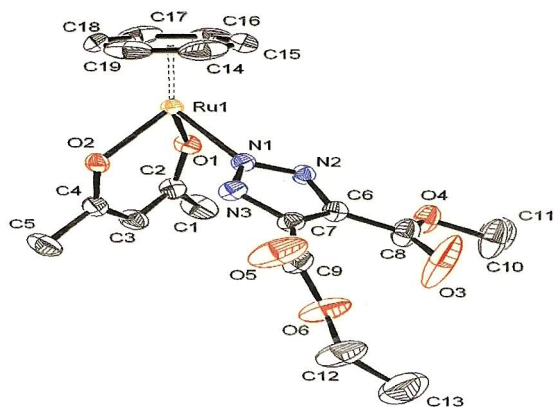
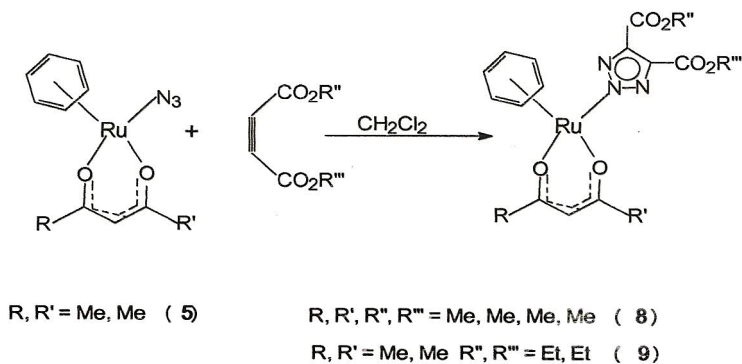


ORTEP diagram with labelling scheme for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{2\text{-}(2'\text{-pyridyl})\text{imidazole}\}(\text{PPh}_3)]^+$  ( $[\mathbf{1}]\text{PF}_6$ ), at 50% probability level, H atoms and  $\text{PF}_6^-$  anion omitted for clarity.

## Chapter 6.

This chapter deals with syntheses and characterization of  $\eta^6$ -arene ruthenium(II) (arene = benzene and *p*-cymene) azido complexes. The dinuclear complex  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$  obtained from the reaction of  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  with sodium azide in ethanol. The benzene ruthenium  $\beta$ -diketonato complexes of the general formula  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{LNL})\text{Cl}]$   $\{\text{LNL} = O,O'\text{-acac}; O,O'\text{-bzac}; O,O'\text{-dbzm}\}$  are obtained in methanol by the reaction of  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  with the corresponding  $\beta$ -diketonates. These complexes further react with sodium azide in ethanol to yield complexes of the

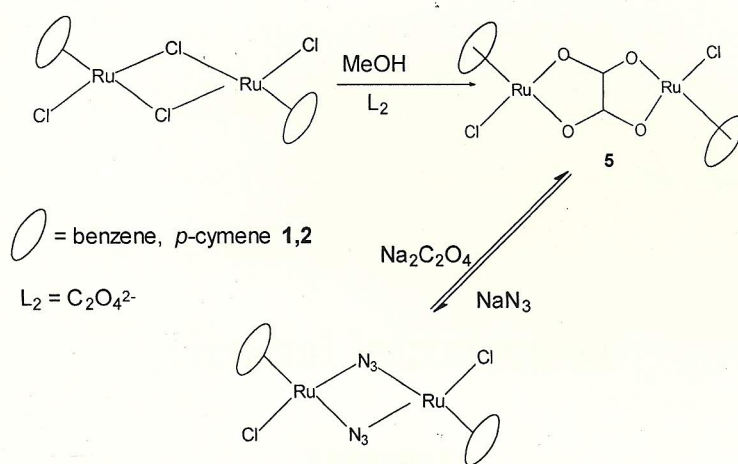
$\{N_3C_2(CO_2Et)_2\}$ ,  $[(\eta^6-C_6H_6)Ru(O,O'-acac)\{N_3C_2HCN\}]$ ,  $[(\eta^6-C_6H_6)Ru(O,O'-bzac)\{N_3C_2HCN\}]$  and  $[(\eta^6-C_6H_6)Ru(O,O'-dbzm)\{N_3C_2HCN\}]$ . These complexes are well characterized and the representative single crystal x-ray structure is established.



ORTEP diagram of complex **9** with labeling scheme at 50% probability level and H atoms being omitted for clarity

**Chapter 7:** This chapter deals with Syntheses of mono and di nuclear  $\eta^6$ -arene ruthenium carboxylato complexes; their reactions towards azide, acetate anions and some neutral ligands. The mono and di nuclear  $\eta^6$ - arene ruthenium carboxylato complexes thus obtained from the reaction of  $[(\eta^6\text{-arene})RuCl_2]_2$  with the corresponding sodium salts of the carboxylic acids further reacted with sodium azide in ethanol to give

**Chapter 7:** This chapter deals with Syntheses of mono and di nuclear  $\eta^6$ -arene ruthenium carboxylato complexes; their reactions towards azide, acetate anions and some neutral ligands. The mono and di nuclear  $\eta^6$ - arene ruthenium carboxylato complexes thus obtained from the reaction of  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  with the corresponding sodium salts of the carboxylic acids further reacted with sodium azide in ethanol to give known azide dimers  $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$  by the displacement of the carboxylate ligand.



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# General Introduction

Organometallic

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## CHAPTER 1

### General Introduction

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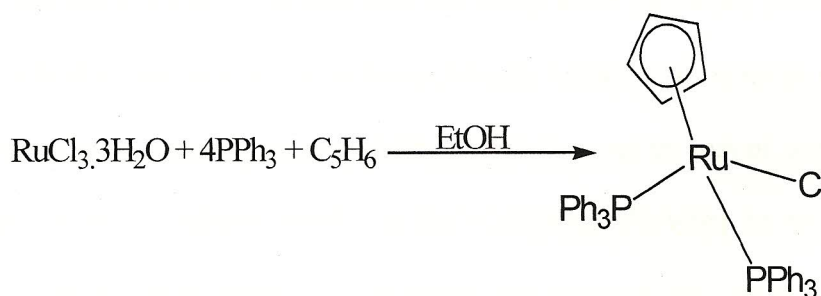
## General Introduction

Organometallic chemistry mainly dealt with compounds which contain organic groups, bound to the metal centre through one or more carbons atoms. The chemistry of such compounds provides a bridge between organic compounds and coordination complexes. Organic and organometallic chemists have extensively investigated arene-metal complexes for over forty years. The first sandwich complex ferrocene was obtained by Paulson and S. A. Miller and followed by E.O. Fischer the syntheses of sandwich complex of arene. Organometallic compounds have a wide range of application in catalysis [1], transformation of organic molecules [2] and are biologically important [3]. The transformation of organic molecules on industrial and laboratory scale involved catalysis by metals. Metals serve as reaction templates, which bond organic species providing a low-energy reaction pathway for their combination with other bonded species and producing a weakly bonded species. Arene complexes are used as versatile intermediates to access the reactive arene metal hydride or 16-electrons metal (0) intermediate that has been used recently for carbon-hydrogen bond activation. Classification of organometallic compounds is based on the nature of bonds *i. e.*, sigma ( $\sigma$ ), pi( $\pi$ ) or del( $\delta$ ) bond. Among the various half sandwich ruthenium complexes this work deals with penta- and hexa-hapto cyclichydrocarbons complexes *viz.* Cyclopentadienyl, pentamethylcyclopentadienyl,  $\eta^6$ -benzene and *p*-cymene ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes. The aim of this work is to study the synthetic route of these classes of complexes and their characterization with the help of spectroscopic data and single crystal X-ray analyses.

The first introductory chapter is divided into three sections. The first section mainly focussed on the chemistry of  $\eta^5$ -cyclichydrocarbon ruthenium complexes *i.e.* cyclopentadienyl and pentamethylcyclopentadienyl complexes giving a general presentation on the synthesis of precursor complexes and recent development of their chemistry. The second section concerned with the chemistry of arene ruthenium complexes. The third section is the brief discussion on various physical methods employed and preparation of selected starting materials which involved in this study.

### 1.1 $\eta^5$ -cyclichydrocarbons ruthenium (II) and osmium (II) complexes

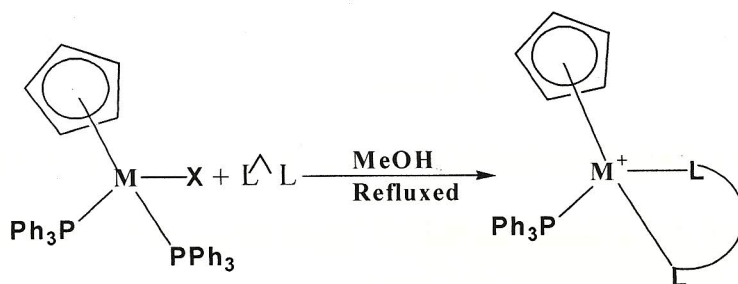
The most successful method of preparation of cyclopentadienyl ruthenium(II) triphenylphosphines complex was reported by Bruce *et al.*, [4], using cyclopentadiene, ruthenium trichloride trihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ), and triphenylphosphine which gave the complex in high yield (scheme 1.1). The advantage of this method is direct formation of the desired complex in a single pot with good yield. It has been shown that the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  is one of the most attractive molecules for synthetic manipulation.



**Scheme 1.1**

The complex dissolved in polar solvent and dissociates its Metal-chloride bond, whereas the triphenylphosphines groups dissociate in non-polar solvent. The cyclopentadienyl ruthenium(II) and osmium(II) complexes reacted with Nitrogen donor based ligands such

as N,N-donor bases and Schiff's bases to yield cationic and neutral complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{PPh}_3)\text{L}\cap\text{L}]^+$  where,  $\text{M} = \text{Ru}(\text{II}), \text{Os}(\text{II})$ ;  $\text{L}\cap\text{L} = \text{N}, \text{N}'\text{-donor ligands}$ . The complexes undergo substitution reaction whereby, substitution of chloride and one triphenylphosphine group is taken place (scheme 1.2).



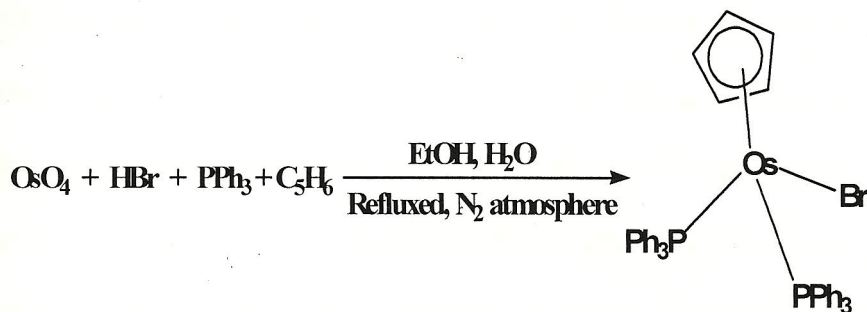
$\text{M} = \text{ruthenium (II) and osmium (II)}$

$\text{L}^{\wedge}\text{L} = \text{bidentate nitrogen base and Schiff's base ligands.}$

$\text{X} = \text{Cl, Br or CH}_3\text{CN}$

### Scheme 1.2

The closely related osmium analogue,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$  has been prepared by treatment of osmium tetra oxide with hydrobromic acid (HBr), cyclopentadiene ( $\text{C}_5\text{H}_6$ ) and triphenylphosphines, refluxed in ethanol under nitrogen atmosphere [5] (scheme 1.3). However, literature survey revealed that not much work has been carried out on this compound which could be due to the lower kinetic lability of osmium relative to the ruthenium complexes, other reasons might be due to the greater cost of osmium. The main objectives of our synthetic work on  $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$  is to study its reactivity towards N, N'-base ligands, to compare and contrast the structures and the properties with that of the corresponding cyclopentadienyl ruthenium(II) complexes.



Scheme 1.3

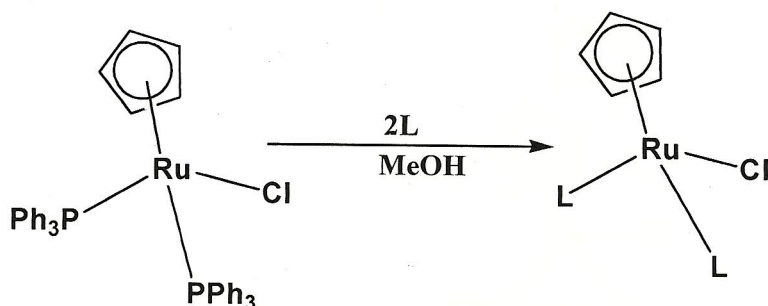
The pentamethylcyclopentadienyl analogue  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be prepared in good yield using a similar procedure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ , but longer reaction time is required [6]. The complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be prepared using less strenuous condition if ruthenium trichloride hydrate and pentamethylcyclopentadiene are first reacted to give polymeric pentamethylcyclopentadienyl-ruthenium dichloride, and treated with excess triphenylphosphine to produce the desired complex [7]. Recently, Bruce and his co-workers developed an improve method for the preparation of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  by using NaOEt base, which give a considerably good yield. In this method ruthenium trichloride and pentamethylcyclopentadiene was refluxed in ethanol followed by the addition of triphenylphosphine and NaOEt base [19]. It is noteworthy that studies on the ruthenium(II) complexes containing  $\eta^5$ -cyclichydrocarbons and triaryl and trialkylphosphine as co-ligands have been accompanied to a very large extent and interest in the ligand substitution processes at plus two valent metal centre. Generally two approaches have been applied to substitution reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ . The first approach centered around the reaction of Ru-Cl bond resulting in the replacement of chloride either by other anions or by neutral ligands to give neutral complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  or cationic complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{L})]^+$  [8].

Another approach is the substitution of  $\text{PPh}_3$  and chloride ligands or both the  $\text{PPh}_3$  with various ligands like heterocyclic molecules N, N'- donor bases to give neutral complex or one triphenylphosphine along with the chloride by N- base ligands to yield cationic complexes. A least common reaction is displacement of the organic moieties which is expected to be more common in complexes containing labile organic moieties such as  $\text{Cp}^*$  ligand. In addition there is another possibility of the reaction, though very little studied that is organic moiety (Cp) which could be activated towards substitution. The suggested factors for accounting these types of behaviors are: (a) the high electron density on ruthenium because of the presence of the two triphenylphosphine ligands and (b) the steric interaction between the two bulky  $\text{PPh}_3$  molecules [9]. The Ru-Cl bond of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be readily substituted with a variety of ligands to yield neutral or cationic complexes. Thus the complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  (X = NCS [10],  $\text{NO}_2$  [11]; CN [12]) can be readily prepared by treatment of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with methanolic solution of the appropriate sodium or potassium salts.

### 1.1 Exchange of $\text{PPh}_3$ ligands

The two triphenylphosphines ligands in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be replaced by others alkylphosphines and chelated phosphines to give neutral complexes. Thus, stepwise replacement of tertiaryphosphines occurs in the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$ , by alkylphosphine such as  $\text{PMe}_3$  in non-polar solvents to give  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}]$  at 80-100 degree centigrade and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{Cl}]$  at 110 degree centigrade [13]. Tertiary phosphine requires more severe conditions, short heating with decalin being required to form  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{P}(\text{OR})_3\}_2\text{Cl}]$  (R= Me, Ph). An

olefinic phosphines also displaces the two  $\text{PPh}_3$  ligands to give  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^2\text{-CH}_2\text{=CHC}_6\text{H}_4\text{PPh}_2)]$  [14] (Scheme 1.4).



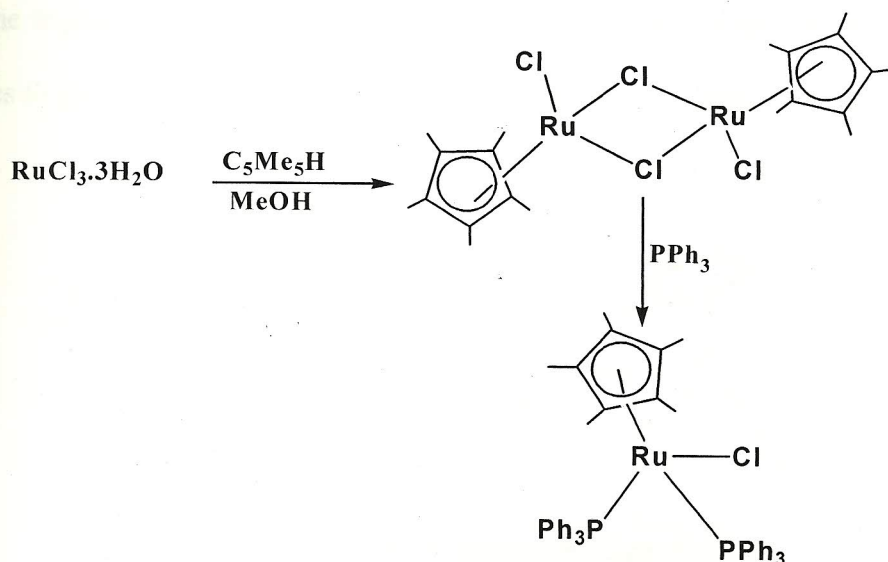
Scheme 1.4

## 1.2 Derivatives of nitriles, nitrosyls, carbonyl and N, N'-base ligands

Cyclopentadienyl complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  undergo a wide range of reactions with sulphur, nitrosyl and carbon bonded ligands. Thus, treatment of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with NaSH yielded complex of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{SH}]$  [15]. Treatment of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  complex with sodium thiocarbamate affords complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{S}_2\text{CX})(\text{PPh}_3)_2]$  [16]. Cyclopentadienyl complex of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{N},\text{N}')^+]$  are obtained by ready substitution of two facile coordination sites of the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with N, N' - base ligands [17].

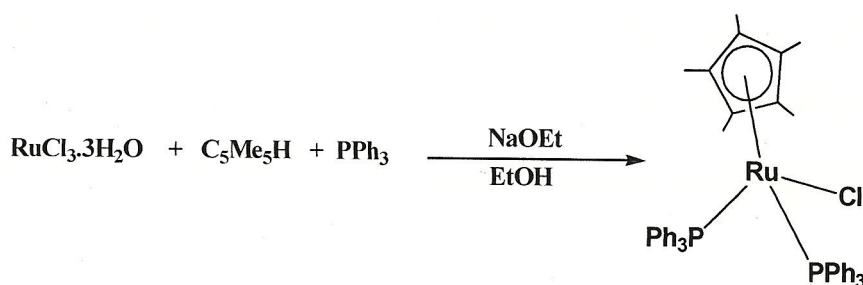
## 1.3 Pentamethylcyclopentadienyl ruthenium (II) complexes

The complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be prepared by the reaction between  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and pentamethylcyclopentadiene in methanolic solution to give dimeric pentamethylcyclopentadienyl ruthenium dichloride, which is further treated with excess of triphenylphosphine to yield the desired complex (scheme 1.5) [18].



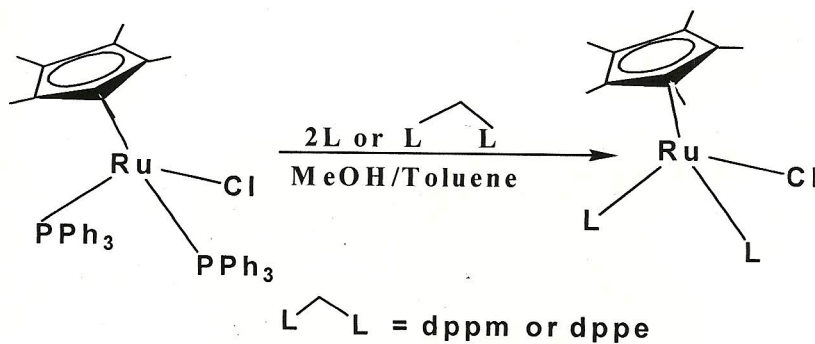
Scheme 1.5

An improved method of preparation of this complex was reported by Bruce and his co-workers by using NaOEt base, which give a considerably good yield. In this method ruthenium trichloride and pentamethylcyclopentadiene was refluxed in ethanol followed by the addition of triphenylphosphine and NaOEt base [19] to give the desired complex of the type  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  (scheme 1.6).



Scheme 1.6

Both of the triphenylphosphines can be replaced by the alkyl phosphines and chelating phosphines to give neutral complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{L})_2\text{Cl}]$  (scheme 1.7) [20].



Scheme 1.7

B. Steinmetz and his co-workers described a convenient route for the synthesis of a novel  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NCMe})_3]^+$  complexes by zinc reduction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$  in acetonitrile in the presence of  $\text{NaPF}_6$  [21].

#### 1.4 APPLICATION TO ORGANIC SYNTHESSES

The cyclopentadienyl and pentamethylcyclopentadienyl ruthenium(II) complexes are extensively used in organic molecules transformations. Ruthenium a catalyzed organic reactions are the most important and useful reactions in organic syntheses [22] mentioned as below:

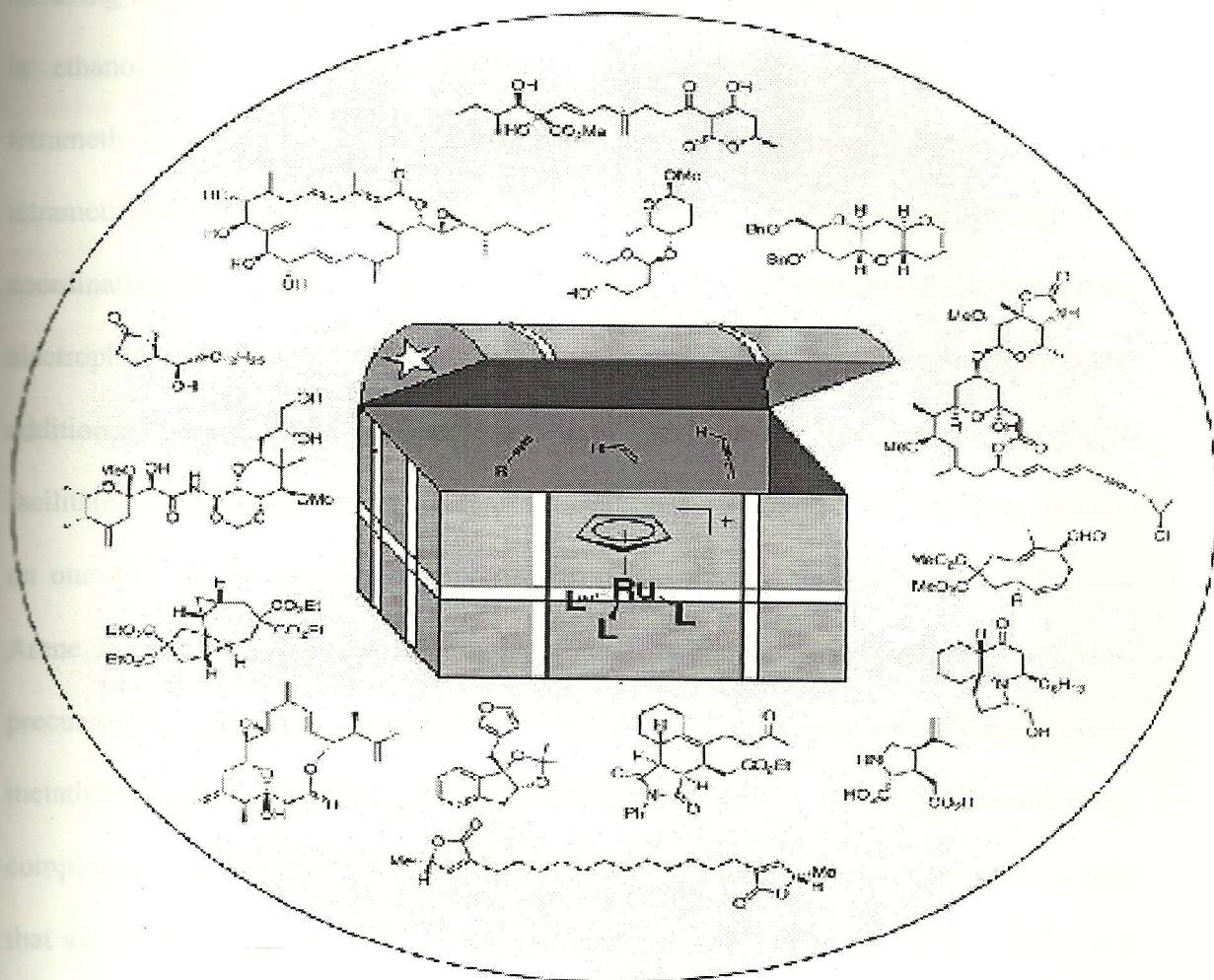


Figure: Ruthenium catalyzed reactions in organic syntheses.

### 1.5 $\eta^6$ -Cyclichydrocarbon ruthenium(II) complexes

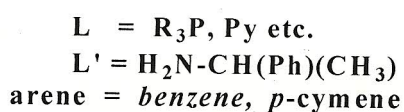
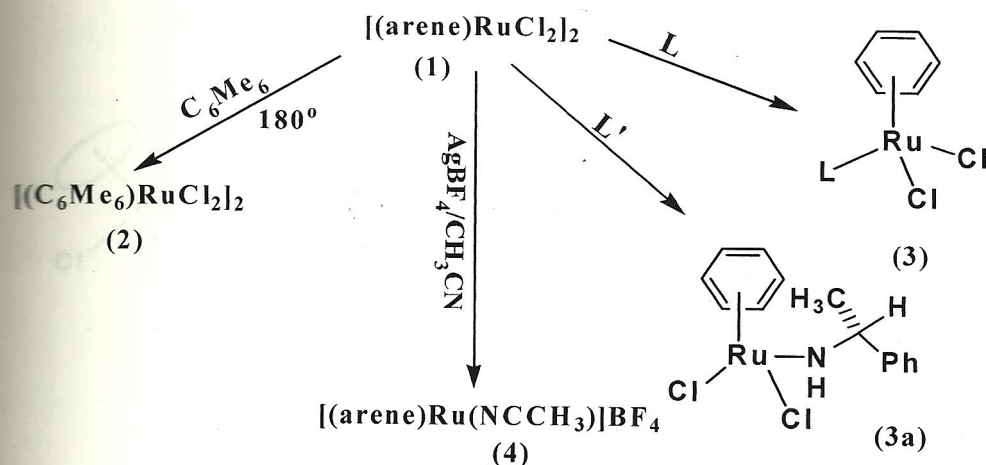
In recent years,  $\pi$ -arene metal complexes have generated considerable interest due to their potential roles in homogeneous catalysts. Its complexes have been extensively investigated by organic and organometallic chemists for over 40 years. In particular,  $\eta^6$ -arene complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [23]. The versatile starting materials  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  are usually prepared by

refluxing the appropriate cyclohexa-1, 3 diene or cyclohexa-1, 4-diene with  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  in ethanol [24]. The  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  complexes of mesitylene, 1, 2, 3, 4-tetramethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene and tetramethylthiophene [25] have been made similarly from  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ . The coordination of a metal fragment ( $\text{ML}_n$ ) to an arene ring dramatically increases the electrophilic character of the ligand. Thus, processes such as nucleophilic aromatic addition and substitution, arene deprotonation, and benzylic deprotonation are greatly facilitated. In addition, the presence of a transition metal centre (and ancillary ligands) on one face of the coordinated arene can serve as a valuable stereo control element. Arene metal complexes also have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis, and Diels-Alder cycloaddition [26]. More recently, planar chiral arene metal complexes have been employed as effective chiral auxiliaries and as asymmetric ligands that are capable of coordinating a second metal ion [27]. Thus, the utility of  $\eta^6$ -arene metal complexes emanates not only from the reactivity inherent to the coordinated ring but also from the control over three facially disposed coordination sites about a given metal centre afforded by incorporation of an arene ligands. While a number of transition metals form tractable  $\eta^6$ -arene complexes, those that incorporate the neutral tricarbonyl Chromium(0)  $\{\text{Cr}(\text{CO})_3\}$  fragment are the most thoroughly studied and the chemistry of arene chromium complexes has been summarized in a number of review articles [28]. In addition to chromium, arene complexes of manganese, iron, and ruthenium are important members of this family of organometallic materials. The most commonly encountered  $\eta^6$ -arene complexes prepared from these latter three metals are isoelectronic with their

tricarbonyl chromium analogues; hence, manganese is assigned a formal +1 oxidation state while iron and ruthenium are present in +2 oxidation states. Consequently, many of the arene complexes of Mn, Fe, and Ru are isolated as mono- coordination materials depending on the identity of the ancillary ligands. In turn, the cationic nature of these complexes often results in increased reactivity of the arene ring and enhanced Lewis acidity in coordinative unsaturated derivatives (an important feature for certain catalytic applications) relative to neutral chromium complexes.

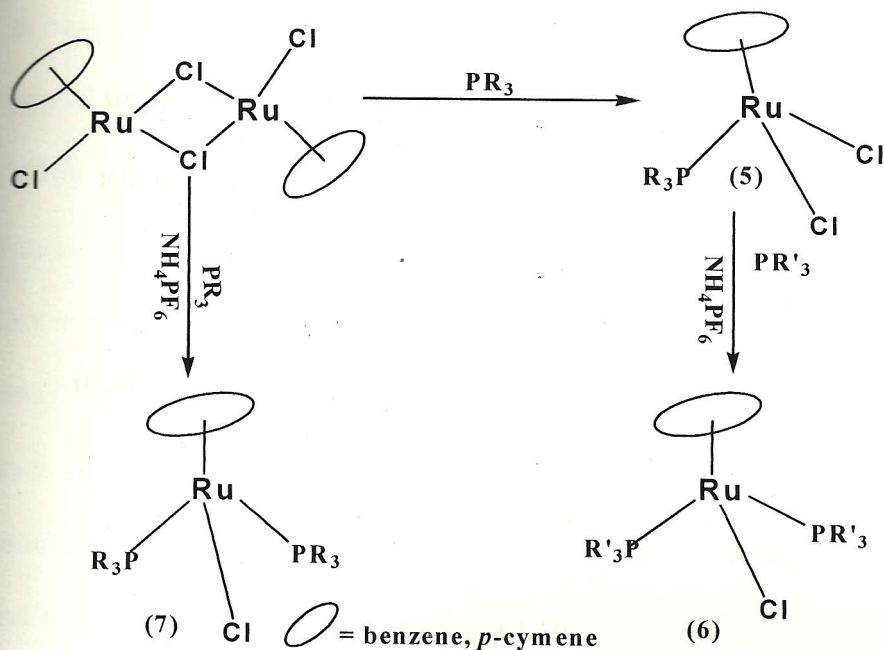
### 1.6 Arene ruthenium half sandwich complexes

Most half-sandwich complexes that contain an arene ruthenium moiety are conveniently prepared from chloro-bridged  $\eta^6$ -arene ruthenium(II) dimer. Majority of half sandwich arene chemistry based on ruthenium arises from the binuclear complexes  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene =  $\text{C}_6\text{H}_6$ ,  $\text{MeC}_6\text{H}_4\text{Pri}$ ) which results from the reactions of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with 1, 3-cyclohexadiene or  $\alpha$ - phellandrene as described by Zelonka and Baird as well as Bennett and Smith [29]. The  $\eta^6$ -*p*-cymene ruthenium dimer undergoes facile arene exchange at high temperature and this reaction provides a means of accessing new arene Ru (II) dimers [30] (scheme 1.8).



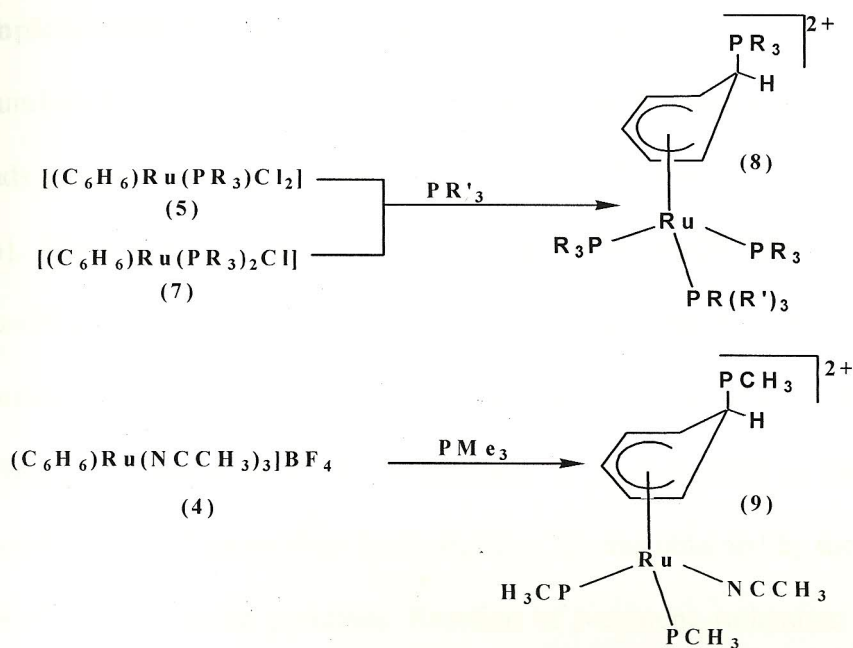
Scheme 1.8

The chloro bridges are labile and stirring dimeric complexes, such as **1** in coordinating solvents (*e.g.*,  $\text{CH}_3\text{CN}$ ,  $\text{DMSO}$ ) leads to formation of solvated monomeric derivatives. Simply treating **1** or **2** with suitable monodentate ligands (such as pyridines, phosphines, phosphites, arsines and amines) generates isolable monomeric air-stable arene ruthenium complexes **3** [31]. Reaction of (*S*)-(-)- $\alpha$ -methylbenzylamine with the dimer derived from *O*-toluic acid methyl ester eventually led to isolation of complex **3a** in greater than 90% diastereomeric excess. Complex **3a** was reported to be the first resolved planar chiral arene ruthenium (II) complex. Completely solvated arene ruthenium(II) dication (4) can be prepared from **1** or **2** and an excess of Ag (I) salt [32]. Ruthenium(II) dimers such as **1** serve as precursors for monomeric piano stool complexes with more than one added ligand as well. For example, conversion of **1** to **5** followed by treatment with a second monodentate phosphines in the presence of  $\text{NH}_4\text{PF}_6$  afforded complex **6** with two different phosphines bonded to the Ru(II) centre (Scheme 1.9) [33].



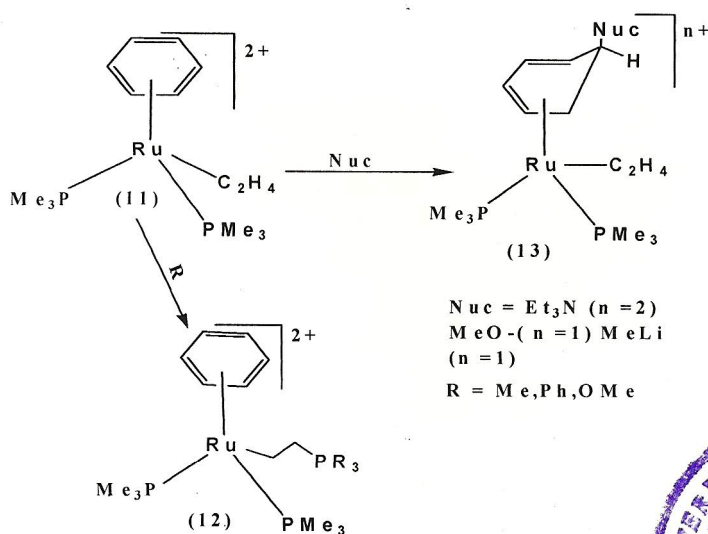
Scheme 1.9

Incorporation of two identical phosphine ligands **7** was accomplished directly by reacting **1** with excess of phosphine and  $\text{NH}_4\text{PF}_6$ . Complexes such as **5** and **7** were found to be susceptible to further attack by phosphine, ultimately providing phosphonio- $\eta^5$ -cyclohexadienyl ruthenium complexes **8** (Scheme 1.10), thus illustrating the activated nature of the coordinated arene ring [34]. Similarly, reaction of the tris-(acetonitrile) arene ruthenium dication **4** with an excess of  $\text{PMe}_3$  afforded the cyclohexadienyl complex **9** in which one acetonitrile ligand had been retained (Scheme 1.10). Spectroscopic studies confirmed that addition of the phosphine nucleophile had occurred exclusively from the *exo*-face of the arene ligand. Complexes **8-9** were reported to be reasonably air-stable but treatment with trifluoroacetic acid results in cleavage of the cyclohexadienyl-P bond with regeneration of an ( $\eta^6$ -arene)Ru(II) complex.

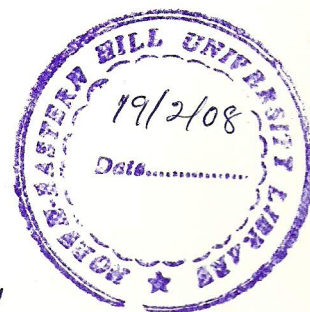


Scheme 1.10

The bis(phosphine)ethylene arene ruthenium complex **11** (Scheme 1.11) presents two  $\pi$ -ligands potentially susceptible to nucleophilic attack. Reaction with a phosphine or phosphites resulted in addition to the coordinated ethylene ligand, while treatment with harder nucleophiles ( $Et_3N$ ,  $MeO^-$ ,  $MeLi$ ) resulted in reaction at the arene ligand (from the *exo*-face) [35].

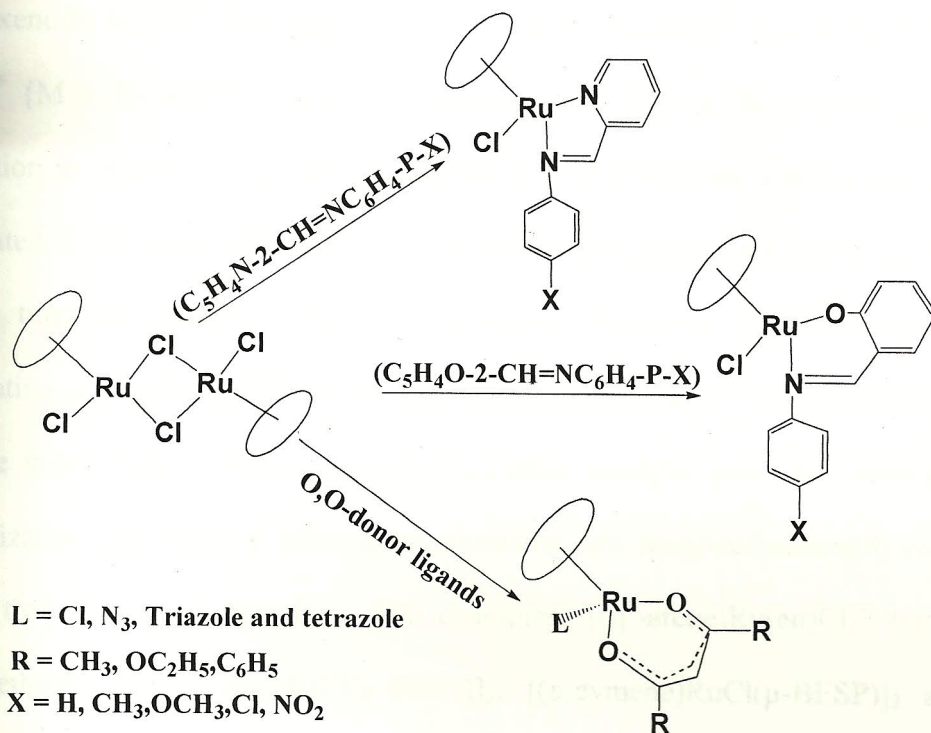


Scheme 1.11



## 1.7 Complexes with Nitrogen and oxygen donor ligands

A number of complexes of arene ruthenium fragment containing N, N'; and N,O donor ligands are generated by the reaction of  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  with the appropriate ligands [36]. The  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  complex reacts with NaOR/ROH to give  $[(\eta^6\text{-arene})\text{Ru}_2(\mu\text{-OR})_3]^+$  [37]. The complex  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  reacts with primary and secondary amines, neither at room temperature nor heating in non-polar solvents to gives  $[(\eta^6\text{-arene})\text{RuCl}_2(\text{L})]$  (arene = 1, 3, 5- $\text{C}_6\text{H}_3\text{Me}_3$ ; L =  $\text{C}_5\text{H}_{10}\text{NHPy}$ ) [38]. Similar complexes of the type  $[(\eta^6\text{-arene})\text{Ru}\{\text{Cl}_2\text{NC}_5\text{H}_4\text{NH}_3\text{-O}\}]$  was obtained by the reaction of  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  with amino pyridines. Reaction of *p*-cymene ruthenium dimer with N,N and N,O Schiff's base ligands generated cationic and neutral chelated complexes  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{N},\text{N}')\text{Cl}]^+$  and  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{N},\text{O})\text{Cl}]^+$  [39]. The similar reaction between  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  and O,O'- donor ligands produced complexes of the type  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{O},\text{O}')\text{Cl}]$ , which have been reported in this work (scheme 1.12).

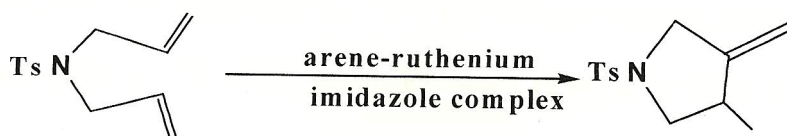


Scheme 1.12

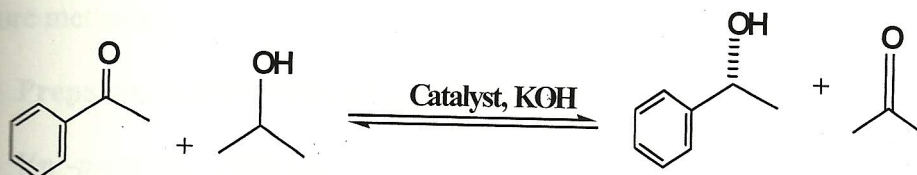
### 1.8 Application of arene ruthenium(II) complexes

Most of the arene ruthenium compounds are used in hydrogenation catalysts. The complexes  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene = benzene( $\text{C}_6\text{H}_6$ ), *p*-cymene, 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ , 1,3,5- $\text{C}_6\text{H}_3\text{Ph}_3$ ) [40] and  $[(\eta^6\text{-arene})\text{RuCl}_2(\text{DMSO})]$  were found to be catalyst precursors for hydrogenation of alkenes. Zero-valent ruthenium complex  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_6\text{Me}_6)]$  was found to be catalytically active for arene hydrogenation [41]. The complex  $[\text{RuH}(\eta^6\text{-C}_6\text{Me}_6)(\text{Ph})_3]$  was found to be an active catalyst for arene hydrogenation and for the transfer of hydrogenation from 1-phenylethanol to a variety of alkenes [42]. The analogous iridium and rhodium pentamethylcycloidylenyl complexes are reported to be hydrogenation catalysts of alkenes and arene [43]. In 1984 Pertici *et al.*, reported that hydrogenation of alkenes in the presence of the catalyst  $[\text{Ru}(\eta^6\text{-arene})(\eta^4\text{-COD})]$  (arene =  $\text{C}_6\text{H}_6$ , 1,4- $\text{C}_6\text{H}_4\text{Me}_2$ , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ ) [44]. Benzene was selectively reduced to

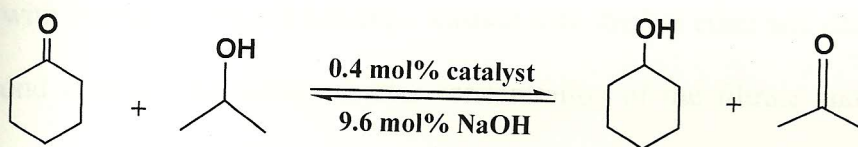
cyclohexene by hydride reduction of  $[\text{Ru}(\eta^6\text{-arene})(\eta^6\text{-C}_6\text{Me}_6)]^{2+}$  and  $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_6\text{H}_6)]^{2+}$   $\{\text{M} = \text{Rh and Ir}\}$ , followed by protonation. During the process of benzene protonation in presence of a weak coordinating counter-ion, the starting complex was regenerated. Under these conditions the protonation is formally catalytic in the complex, but the turnover number is low. In particular, transition metal complexes with coordinating group ( $\pi$ -electron bonded *e.g.*: arene ligands) have attracted much attention from the viewpoints of improving and elucidating catalytic processes such as olefin polymerization [45]. Interest arises for synthesizing new arene-ruthenium(II) complexes due to their biological activities. For examples:  $[(\eta^6\text{-arene})\text{Ru}(\text{en})\text{Cl}]^+$  (en = 1,2-ethanediamine),  $[(p\text{-cymene})\text{RuCl}(\mu\text{-BESE})]_2$ ,  $[(p\text{-cymene})\text{RuCl}(\mu\text{-BESP})]_2$  and  $[(p\text{-cymene})\text{RuCl}_2(\text{BESE})]\text{PF}_6$  (where, BESE = 1,2-bis(ethylsulfonyl)ethane, BESP = 1,2-bis(methylsulfonyl)ethane) has shown anti cancer activity [46-47]. The reaction of N-alkylimidazolines and N-arylalkylimidazoline with the arene-ruthenium(II) dimer gave the imidazoline complexes. These complexes are generated in situ and used as active catalysts for the cycloisomerization of 1, 6-diallyltosylamide into N-tosylpyrrolidine [48].



Diphosphine arene ruthenium(II) complexes  $[(\eta^6\text{-arene})\text{Ru}(\text{P-P})\text{Cl}]\text{CF}_3\text{SO}_3$  (arene =  $\text{C}_6\text{H}_6$ , *p*-cymene, mesitylene, hexamethylbenzene(HMB); P-P = 3,4-dimethyl-1-phenylphosphine, diphenylvinylphosphine) acting as catalyst for the hydrogenation of ketones [49],



Neutral and cationic arene-ruthenium(II) complexes containing the iminophosphine-phosphine ligand  $\text{PhPCH}_2\text{P(=N-p-C}_5\text{F}_4\text{N)Ph}_2$  are active catalyst for the hydrogenation of cyclohexanone [50].



## 1.9 Physical Measurements

**FT-IR:** FT-IR spectra were recorded on a Perkin-Elmer model-983 and BX-series spectrophotometer with samples prepared as KBr pellets.

**FT-NMR:** The NMR spectroscopic data  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR were recorded in suitable deuterated solvents using Bruker ACF-300 MHz or AMX 400 MHz instruments at sophisticated instruments Facility (SIF), IISc Bangalore, University of Barcelona-Spain, IIT Guwahati. For  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$   $\text{SiMe}_4$  is used as an internal standard while chemical shift for  $^{31}\text{P}\{^1\text{H}\}$  resonance were referred to 85%  $\text{H}_3\text{PO}_4$  and the coupling constant were given in Hertz. Elemental analyses and Micro analytical data were obtained from Sophisticated Analytical Instruments Facility (SAIF), NEHU using a Perkin-Elmer 2400CHN/S analyzer.

## Materials

The precursors complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  [4],  $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$  [5],  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  [21],  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  [31] and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ ,  $[(\eta^5\text{-$

$(C_5Me_5)RhCl_2)_2$  [51] and  $[(\eta^6\text{-}p\text{-cymene})RuCl_2)_2$  [30] were prepared by following the literature methods.

## 2.1 Preparation of starting materials

### 1. $[(\eta^6\text{-}p\text{-cymene})RuCl_2)_2$ [30]

1 g of  $RuCl_3 \cdot 3H_2O$  dissolved in 80 ml of ethanol and 5 ml of  $\alpha$ -phellandrene was added. The mixture was Refluxed for 4 hr and cooled to room temperature. Reduce the volume to about 40 ml and kept in the fridge. The precipitate is collected by filtration, washed with hexane 10 ml x 3 and then washed with diethyl ether and dried in vacuum. The second crop can be collected after concentration of the filtrate and followed the same procedure.

Yield: 1.2 g (81.63%)

### 2. $[(\eta^6\text{-}C_6H_6)RuCl_2)_2$ [31]

2 g of  $RuCl_3 \cdot 6H_2O$  in ethanol (100 ml) was heated under reflux with 1,4 or 1,3-cyclohexadiene (10 ml) for 4 hr. The brown precipitates was filtered off, washed with methanol and dried in vacuo.

Yield: 1.05 g (87.5%)

### 3. $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ [5]

An ample of  $OsO_4$  (1.0 g, 3.93 mmol) was broken in a flask containing 48% of HBr (37 ml) and the red solution was heated at reflux for 2 hr in air. Water and excess HBr were removed from the mixture by distillation at 50 °C under vacuum, leaving a dark red residue. The residue was dissolved in absolute ethanol (20 ml) and added to a stirred triphenylphosphines (6.30 g, 24.0 mmol) in ethanol (180 ml) immediately followed by a solution of freshly distilled cyclopentadienyl (10 ml) in ethanol (20 ml),

water (25 ml) was then added to the mixture *via* syringe, and the crimson suspension was heated at reflux for 2 hr; resulting in a colour change to orange. After the reaction mixture was cooled to room temperature, the resulting orange yellow powder was filtered, wash with hexane (2 x 10 ml). The solid compound was dried in vacuum to give pure product. The orange filtrate was concentrated to 40 ml and cooled to  $-30^{\circ}\text{C}$  to obtain the remaining products.

Yield: 2.55 g (74%)

#### 4. $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ [4].

4.2 g of triphenylphosphine was dissolved in 200 ml of ethanol and placed in a two necked round bottom flask (1000 ml), kept in an oil bath and refluxed ( $60^{\circ}\text{C}$ ) 30-40 mins with rapid stirring up to triphenylphosphine is dissolve. Immediately 9-10 ml of freshly distilled cyclopentadienyl, 1 g of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 40 ml of ethanol mixture is added. A dark brown colouration is observed. The mixture solution was refluxed for *ca.* 45-60 mins, the dark brown colour changes to orange colour. The orange colour product is filtered and washed with cold water, dried in vacuum.

Yield: 2.52 g (86%)

#### 5. $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ [21].

The compound  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (1 g, 2.41mmol) and pentamethylcyclopentadienyl (0.67 g, 4.82 mmol) were dissolved in ethanol (30 ml) and heated under refluxed for 90 mins, after which a solution of triphenylphosphines (2.53 g, 9.64 mmol) and sodium ethoxide (40 ml) was added drop wise. The solution was then refluxed for 18 hr. The orange yellow precipitates was collected and washed with ethanol (2 x 5 ml) and then with hexane (2 x 5 ml) to give the above complex.

Yields: 2.56 g (78%)

6.  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$  [51]

$\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (10 g), pentamethylcyclopentadienyl (6 g, 0.004 mmol), reagent grade methanol (300 ml) and a magnetic stirrer are placed in a 500 ml round bottom flask fitted with reflux condenser. A nitrogen bubbler is attached to the top of the condenser. The round bottomed flask is purged with nitrogen for 5 mins; the mixture was refluxed gently under nitrogen atmosphere for 48 hr with constant stirring. The reaction mixture was allowed to cool to room temperature and a dark red precipitate is filtered off in air through the glass sinter. The red filtrate is reduced to 50 ml in rotary evaporator, and kept in cool condition to get red crystalline product, washed with diethyl ether (3 x 20 ml). If required the product may be recrystallized from chloroform-hexane, gives an orange microcrystalline compound.

Yield: 10.7g (85%)

7.  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$  [51]

Method of preparation of this compound is same as above except rhodium trichloride trihydrate was used instead of iridium trichloride trihydrate.

Yields: 1.13 g (83%)

### Preparation of Ligands

**2-(2'-pyridyl)imidazole (L<sub>1</sub>)** [52]: An ice-cold solution of pyridine-2-carbaldehyde (10.7 g) in ethanol and glyoxal (20 ml. of 30 % aqueous solution) in ethanol (10 ml) were mixed and then, without delay, ice- cold concentrated aqueous ammonia solution (30 ml, of 20 N) was added. The yellow brown solution was kept at zero degree centigrade for 30 minutes, then allowed to stand overnight at room temperature. Most of

the ethanol was distilled off and the cold residue was extracted many times with diethylether. The solvent was removed from the combined, dried, ether extracts and the residual oil distilled in vacuo. It soon solidified and was obtained by recrystallization from ethyl acetate as yellow prism.

Melting point: 134 °C.

Analytical calculated for  $C_8H_7N_3$ : C, 66.2; H, 4.8; N, 29.0.

Found: C, 66.3; H, 4.9; N, 28.7

$^1H$  (NMR,  $\delta$ ): 8.5 (d,  $J_{HH} = 5.34\text{Hz}$ , 1H,  $H_6$  of py); 8.3 (d,  $J_{HH} = 4.75\text{Hz}$ , 1H,  $H_3$  of py); 7.8 (t, 1H,  $H_4$  of py); 7.3 (t, 1H,  $H_5$  of py).

#### Preparation of 2- (2'-pyridyl) benzimidazole ( $L_2$ ) [52].

2- (2'-pyridyl) benzimidazole has been prepared by many different methods. The material used for this experiment in this paper was made in rather poor yield by heating O-phenylenediamine and 2-picolinic acids together. A much more convenient method consists in careful heating together equimolecular amounts of O-phenylenediamine and 2-picolinthioamide. The purified product was melted at 221 degree centigrade. Commercially prepared by Aldrich company was available and can be used as received.

Analytical calculated for  $C_{12}H_9N_3$ : C, 73.85; H, 4.62; N, 21.54.

Found: C, 74.05; H, 4.82; N, 21.94

$^1H$  {NMR,  $\delta$ ): 8.6 (d,  $J_{HH} = 6.00\text{Hz}$ , 1H,  $H_6$  of Py); 8.3 (d,  $J_{HH} = 5.75\text{Hz}$ , 1H,  $H_3$  of Py); 7.5 (t, 1H,  $H_4$  of Py); 7.3 (t, 1H,  $H_5$  of Py); 7.0 (m, 4H).

#### 2-(2'-pyridyl)-4, 5-dimethylimidazole ( $L_3$ ).

Preparation method was similar to  $L_1$  except 2, 3 butanedione instead of glyoxal.

Analytical calculated for  $C_{14}H_{13}N_3$ : C, 75.34; H, 5.83; N, 18.83.

Found: C, 75.82; H, 5.28; N, 18.40

$^1\text{H}$  (NMR,  $\delta$ ): 8.5 (d,  $J_{\text{HH}} = 5.34\text{Hz}$ , 1H, H<sub>6</sub> of py); 8.3 (d,  $J_{\text{HH}} = 4.75\text{Hz}$ , 1H, H<sub>3</sub> of Py);

7.3 (t, 1H, H<sub>4</sub> of Py); 7.3 (t, 1H, H<sub>5</sub> of Py), 3.48(s, 6H of  $-\text{CH}_3$ ).

### 2-(2'-pyridyl)-4, 5-diphenylimidazole ( $\text{L}_4$ )

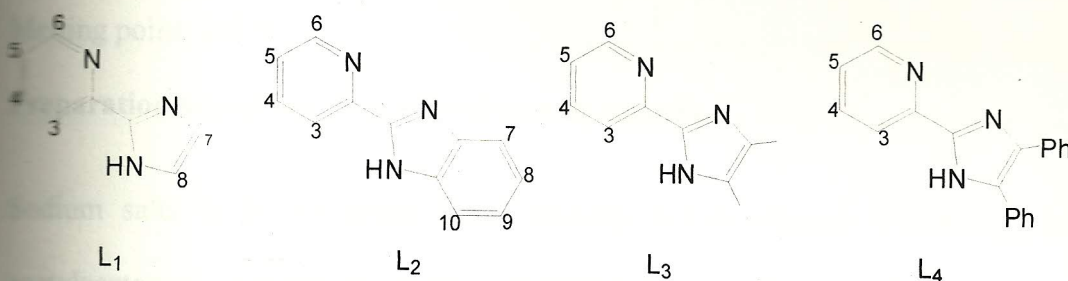
Preparation method was similar to  $\text{L}_1$  except benzil instead of glyoxal.

Analytical calculated for  $\text{C}_{20}\text{H}_{16}\text{N}_3$ : C, 80.54; H, 5.37; N, 14.09.

Found: C, 80.86; H, 5.75; N, 14.42

$^1\text{H}$  (NMR,  $\delta$ ): 8.4 (d,  $J_{\text{HH}} = 5.34\text{Hz}$ , 1H, H<sub>6</sub> of py); 8.3 (d,  $J_{\text{HH}} = 4.75\text{Hz}$ , 1H, H<sub>3</sub> of Py);

7.7 (t, 1H, H<sub>4</sub> of Py); 7.4 (t, 1H, H<sub>5</sub> of Py), 5.84(s, 10H of  $\text{C}_6\text{H}_6$ ).



### Preparation of 3,5-bis(2-pyridyl)pyrazole (Hbpp) [52]

This ligand is prepared by following three steps, given as bellow:

1. Preparation of NaOEt: 50 ml of ethanol and 1.67 g of sodium was added slowly to the stirred solution. When all sodium is dissolved or disappeared the solvent is removed under vacuum, a white solid compound was collected.
2. To this round bottomed flask, containing 250 ml of dry toluene was purged with nitrogen. Then 8.8 ml of methyl picolinate was added under stirring condition. To this mixture 11.6 ml of acetylpyridine was added drop wise. During the course of addition, a

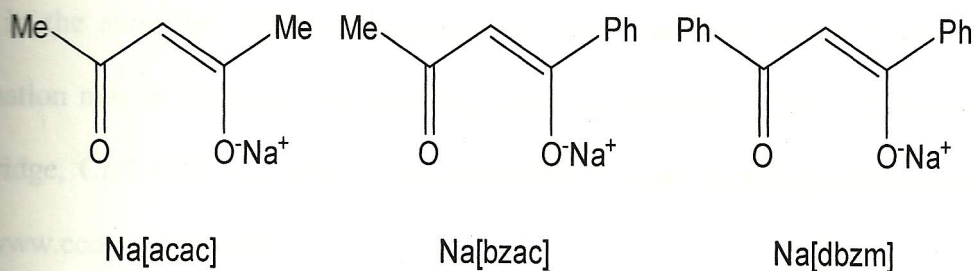
yellow colour changed was observed. The reaction mixture was stirred for another 50 mins, cool to room temperature, filtered and washed with toluene and hexane and dried *in vacuo*. The crude product was added to a mixture of 75 ml of acetic acids and 75 ml of water with 250 g of ice and shake rigorously. The precipitates were filtered off, washed with water and diethyl ether.

3. 5.8 g of diketone and 76 ml of absolute ethanol are taken in a flask. To this solution 9.5 ml of hydrazine hydrate was added. The mixture was boiled for 90 mins, and then cooled to a room temperature, the precipitated compound (Hbpp) was filtered off. The filtrate was concentrated to a minimum volume; the precipitates appeared which is collected. The compound was washed with ethanol and hexane and dried in vacuum.

Melting point: 167 °C;

#### **Preparation of sodium salts of $\beta$ -diketonate ligands**

Sodium salts of  $\beta$ -diketonates ligand namely; acetylacetonate {Na(acac)}, benzene acetylacetonate {Na(bzac)}, dibenzenemethylacetonate {Na(dbzm)} were prepared by reacting corresponding  $\beta$ -diketones with 2 equivalent of sodium hydroxide (NaOH) in ethanol as delineated here. 2 equivalent of sodium hydroxide in 100 ml of ethanol were stirred until sodium hydroxide was completely dissolved. To this stirring solution was added 1 equivalent of the corresponding  $\beta$ -diketones and stirred for 24 hr. The white precipitates were filtered and washed with cold ethanol and dried under vacuum.



### Crystallographic investigation

X-ray analyses of the complexes were performed by employing Bruker AXS Apex CCD, Rigaku Mercury CCD and Bruker Smart 1000 CCD diffractometer, using graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71069 \text{ \AA}$  and  $0.71073 \text{ \AA}$ ). Intensity data were corrected for Lorentz and polarization effects and absorption corrections were done using the SAINT program [53]. An empirical absorption correction was made by modelling a transmission surface by spherical harmonics employing equivalent reflections with  $I > 2\sigma(I)$  (Program SADABS) [54]. The structure were solved by direct methods (SIR 97) [56] and (SHELXS 97) [56]. Refinement by full matrix least squares base on  $F^2$  using (SHELXS 97) software packages [57]. The X-ray data of the complexes were corrected for the presence of disordered solvent using "SQUEEZE" [58]. The weighting scheme used were  $W = 1/[\sigma^2(F_0^2) + aP^2 + bP]$  where,  $P = F_0^2 + 2F_c^2/3$  and  $w = 1/[\sigma^2(F_0^2) + 0.0311P^2 + 3.5016P]$ . All the non-hydrogen atoms were refined anisotropically using the full-matrix, least squares technique on  $F^2$  using the SHELXL-97 software [59].

### Supplementary materials

Crystallographic data for the structural analysis of the complexes have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC Nos. of the complexes are

given in the summary of the crystallographic data collection tables. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223336033; email:deposit@ccdc.cam.ac.uk or <http://www.ccdc.ccdc.ac.uk>)

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