Syntheses, Spectral and Structural studies of η^5 and η^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

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By

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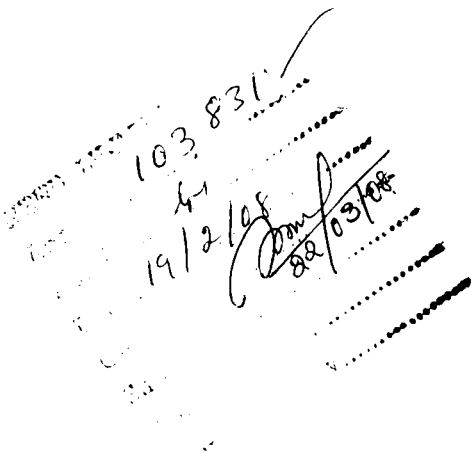

DECLARATION

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 η^5 and η^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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Signature

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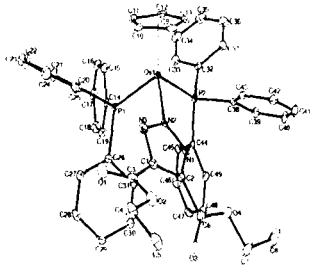

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LIST OF ABBREVIATIONS

acac	=	acetylacetone
NH_4BF_4	=	ammonium tetraflouroborate
NH_4PF_6	=	ammonium hexaflourophosphate
Cp (C_5H_5)	=	cyclopentadienyl
cym	=	*p*-cymene
arene	=	*p*- cymene or benzene
Cp* (C_5Me_5)	=	pentamethylcyclopentadienyl
2-PC	=	N-(pyridyl-2-ylmethylene)cyclophenylamine
2-PP	=	N-(pyridyl-2-methylene)phenylamine
PPh_3	=	triphenylphosphines
S	=	singlet
Sep	=	septet
M	=	multiplet
t	=	triplet
bzac	=	benzene acetylacetone
dbzm	=	methyl dibenzene
TCE	=	tetracynoethylene
$AgBF_4$	=	silver tetraflouroborate
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 interdisplinary 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, (η^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 $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, *p*-cymene), $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ where [M = Ru, X = Cl; M= Os, X = Br] and $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$, M = Rh and Ir. The σ-donor and π-acceptor abilities of the cyclopentadienyl ligands stabilize transition metal complexes in low and high oxidation states. Thus the cylopentadienyl group is one of the most important ligands in Organometallic chemistry. The importance of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ complex is evident from its appearance in literature and several papers reported that the catalytic property of this compound. Interestingly, there is

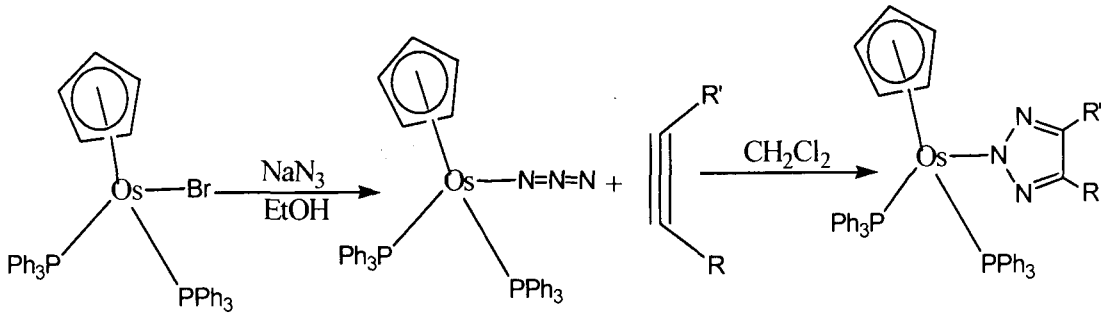
noticeable lack of emphasis on the osmium analogue, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ as evident from the literature survey. This could be due to the lower kinetic lability of osmium relative to ruthenium and possibly the cost of osmium metal. Thus, this thesis consists of seven chapters mentioned as bellow:-

Chapter 1:

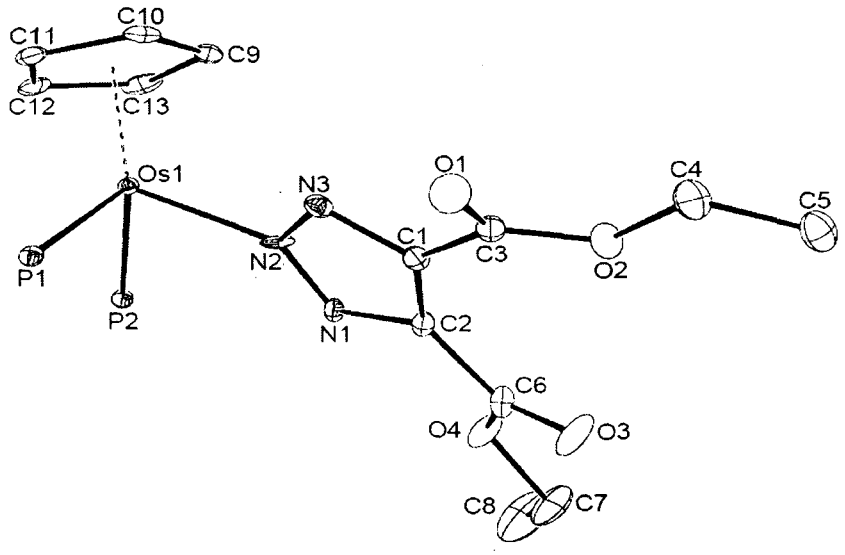
This chapter gives a brief introduction to arene ruthenium (arene = benzene and *p*-cymene) cyclopentadienyl ruthenium(II), osmium(II); pentamethylcyclopentadienyl ruthenium(II), rhodium(III) and iridium(III) complexes, and their reactions towards bridge cleavage and its substitution reactions. These 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.



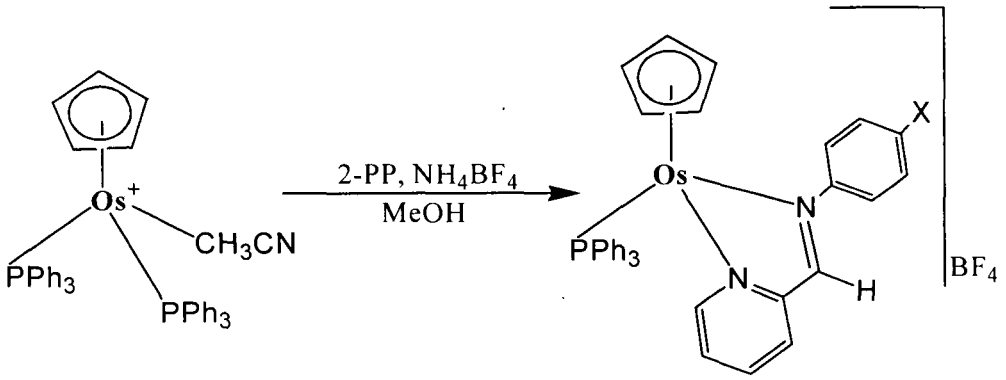
R = R' = CO_2Et, CO_2Me



ORTEP diagram of complex $[CpOs(PPh_3)_2(\ N_3C_2(CO_2C_2H_5)_2]$ with 30% probability thermal ellipsoids displayed with out phenyl groups of phosphines and H atoms being omitted for clarity.

Chapter 3.

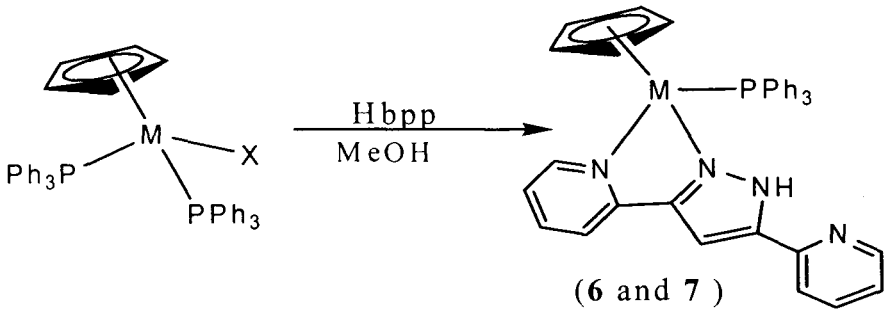
This chapter describes a brief synthetic methods and spectral characterization of the complexes results from the reaction of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ with N,N'-donor Schiff's bases *viz*. *para*-substituted N-(pyrid-2-ylmethylene)phenyl amines.



2-PP = N-(pyrid-2-ylmethylene)phenylamine
X = H, CH_3, OCH_3, Cl, NO_2

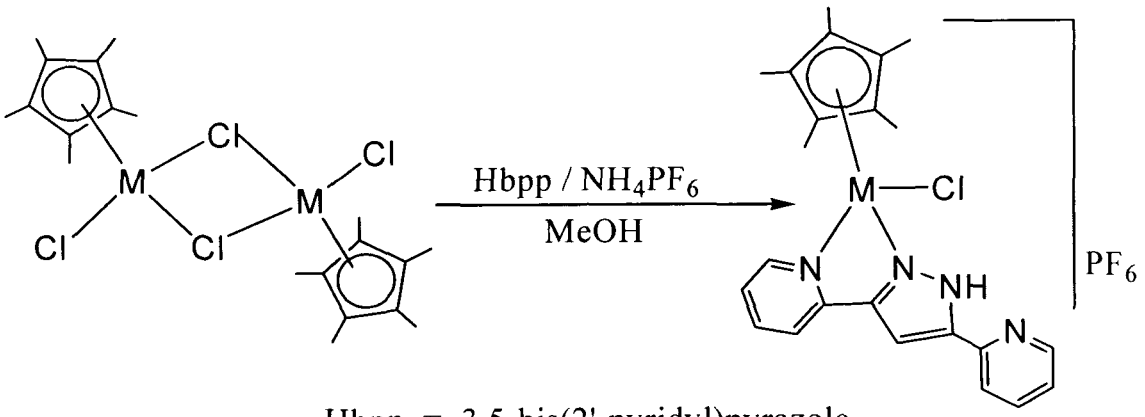
Chapter 4.

This chapter encompasses a brief detail syntheses and characterization of η^5-pentamethylcyclopentadienyl and η^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 $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)PPh_3]^+$ and $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl]^+$ were carried out.

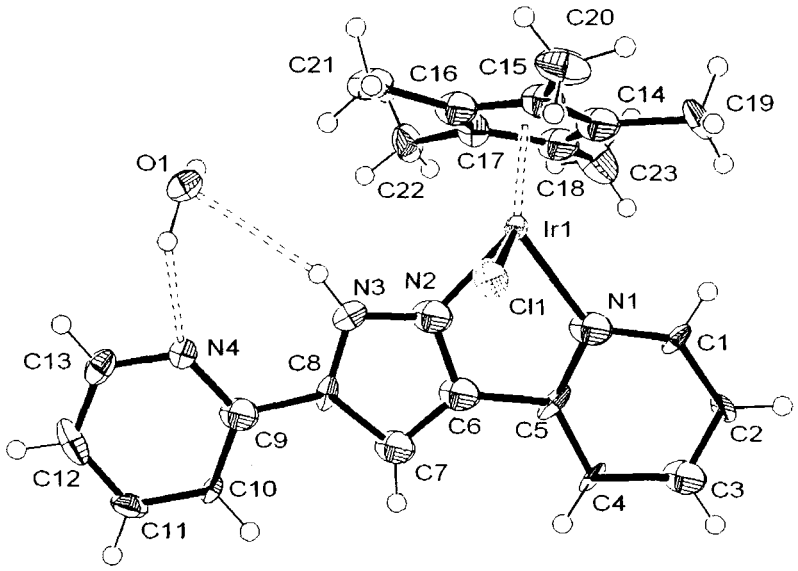


(**6** and **7**)

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)

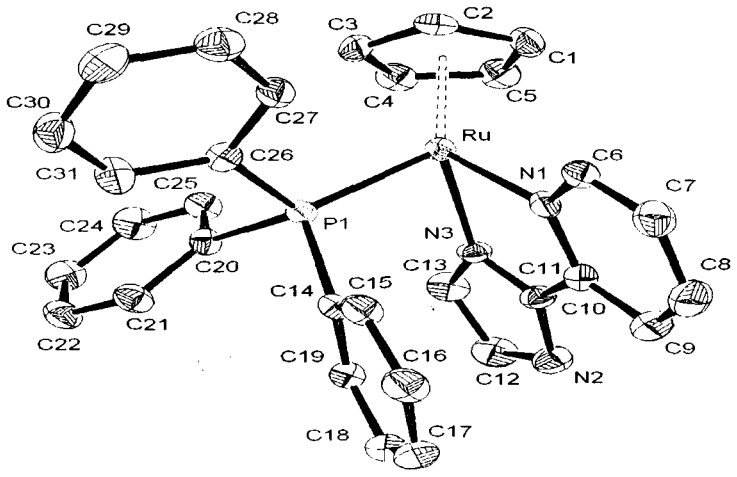


ORTEP diagram of $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl]PF_6$ drawing with labelling scheme at 50% probability level, **[10]**PF_6 anion omitted for clarity

Chapter 5.

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

pyridyl)imidazole derivatives. Its describes substitution reaction of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2Cl]$ [M = ruthenium(II) and osmium(II)], and $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ with 2-(2'-pyridyl)imidazole and 2-(2'-pyridyl)benzimidazole ligands. The single crystal X-ray study have been carried out for representative complexes.

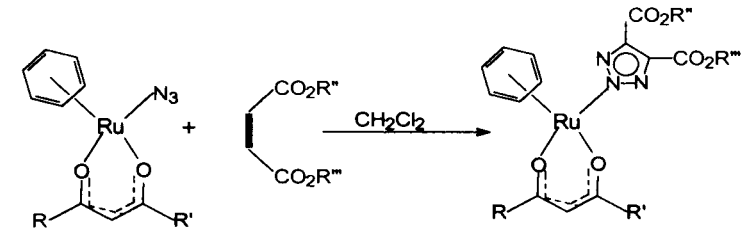


ORTEP diagram with labelling scheme for $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})imidazole\}(PPh_3)]^+$ ([**1**]PF_6), at 50% probability level, H atoms and PF_6 anion omitted for clarity.

Chapter 6.

This chapter deals with syntheses and characterization of η^6-arene ruthenium(II) (arene = benzene and *p*-cymene) azido complexes. The dinuclear complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl]_2$ obtained from the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with sodium azide in ethanol. The benzene ruthenium β-diketonato complexes of the general formula $[(\eta^6\text{-}C_6H_6)Ru(L\cap L)Cl]$ {L∩L = *O,O'*-acac; *O,O'*-bzac; *O,O'*-dbzm} are obtained in methanol by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the corresponding *β*-diketonates. These complexes further react with sodium azide in ethanol to yield complexes of the

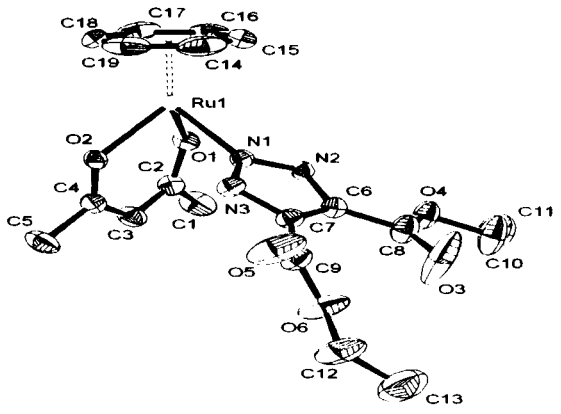
$\{N_3C_2(CO_2Et)_2\}]$, $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2HCN\}]$, $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-bzac})\{N_3C_2HCN\}]$ and $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-dbzm})\{N_3C_2HCN\}]$. These complexes are well characterized and the representative single crystal x-ray structure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



R, R' = Me, Me (5)

R, R', R", R''' = Me, Me, Me, Me (8)

R, R' = Me, Me R", R''' = Et, Et (9)



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 η^6-arene ruthenium carboxylato complexes; their reactions towards azide, acetate anions and some neutral ligands. The mono and di nuclear η^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

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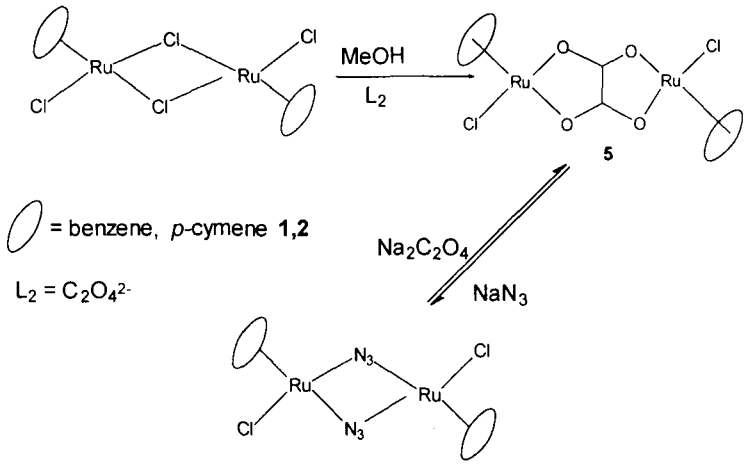

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CHAPTER 1

General Introduction

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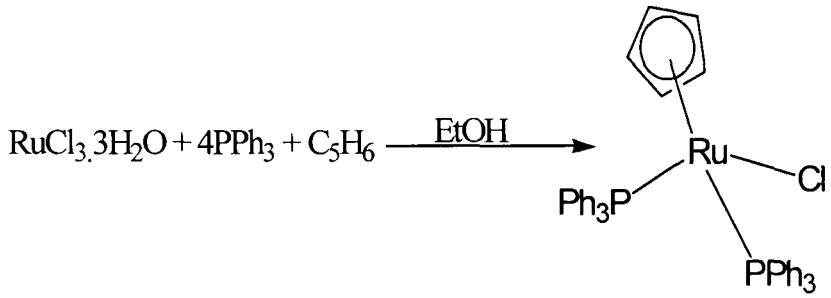
General Introduction

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 (σ), pi(π) or del(δ) bond. Among the various half sandwich ruthenium complexes this work deals with penta- and hexa-hapto cyclichydrocarbons complexes *viz.* Cyclopentadienyl, pentamethylcyclopentadienyl, η^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 η^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 η^5-cyclichydrocarbons ruthenium (II) and osmium (II) complexes

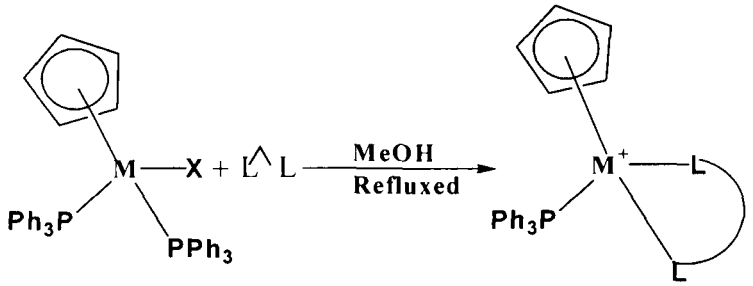
The most successful method of preparation of cyclopentadienyl ruthenium(II) triphenylphosphines complex was reported by Bruce *et al.*, [4], using cyclopentadiene, ruthenium trichloride trihydrate ($RuCl_3.3H_2O$), and triphenylphosphine which gave the complex in high yield (scheme 1.1). The advantage of this method is direct formation of the desired complex in a single pot with good yield. It has been shown that the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ 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 Schiffs' bases to yield cationic and neutral complexes of the type $[(\eta^5\text{-}C_5H_5)M(PPh_3)L\cap L]^+$ where, M = Ru(II), Os(II); L∩L = N, N'-donor ligands. The complexes undergo substitution reaction whereby, substitution of chloride and one triphenylphosphine group is taken place (scheme 1.2).



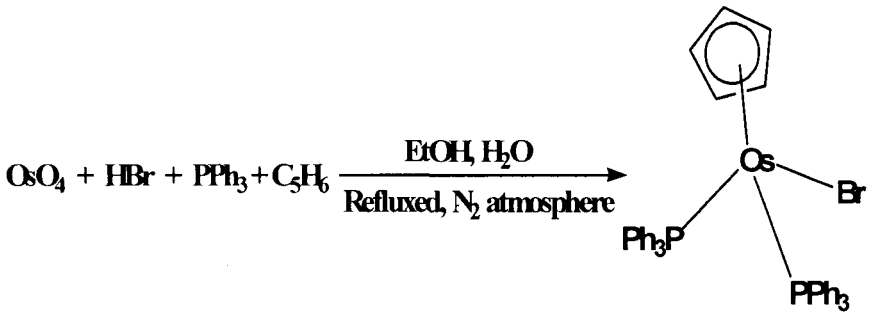
M = ruthenium (II) and osmium (II)

L^L = bidentate nitrogen base and Schiffs' base ligands.

X = Cl, Br or CH_3CN

Scheme 1.2

The closely related osmium analogue, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ has been prepared by treatment of osmium tetra oxide with hydrobromic acid (HBr), cyclopentadiene (C_5H_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 labiality 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 $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ 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

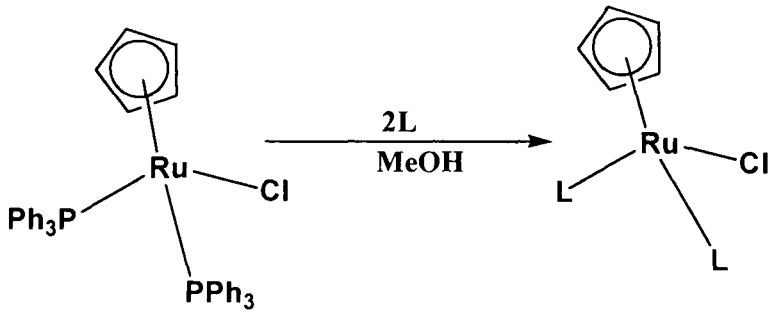
The pentamethylcyclopentadienyl analogue $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ can be prepared in good yield using a similar procedure of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, but longer reaction time is required [6]. The complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ can be prepared using less 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 $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ 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 η^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 $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$. 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 $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$ or cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(L)]^+$ [8].

Another approach is the substitution of PPh_3 and chloride ligands or both the 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 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 PPh_3 molecules [9]. The Ru-Cl bond of the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ can be readily substituted with a variety of ligands to yield neutral or cationic complexes. Thus the complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$ (X = NCS [10], NO_2 [11]; CN [12]) can be readily prepared by treatment of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with methanolic solution of the appropriate sodium or potassium salts.

1.1 Exchange of PPh_3 ligands

The two triphenylphosphines ligands in $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ can be replaced by others alkylphosphines and chelated phosphines to give neutral complexes. Thus, stepwise replacement of tertiaryphosphines occurs in the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$, by alkylphosphine such as PMe_3 in non-polar solvents to give $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)(PPh_3)Cl]$ at 80-100 degree centigrade and$[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ at 110 degree centigrade [13]. Tertiary phosphine requires more severe conditions, short heating with decalin being required to form $[(\eta^5\text{-}C_5H_5)Ru\{P(OR)_3\}_2Cl]$ (R= Me, Ph). An

olefinic phosphines also displaces the two PPh_3 ligands to give $[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)]$ [14] (Scheme 1.4).



L = PPh_2Me, $PPhMe_2$, PMe_3, PPh_2OMe, $P(OiPr)_3$

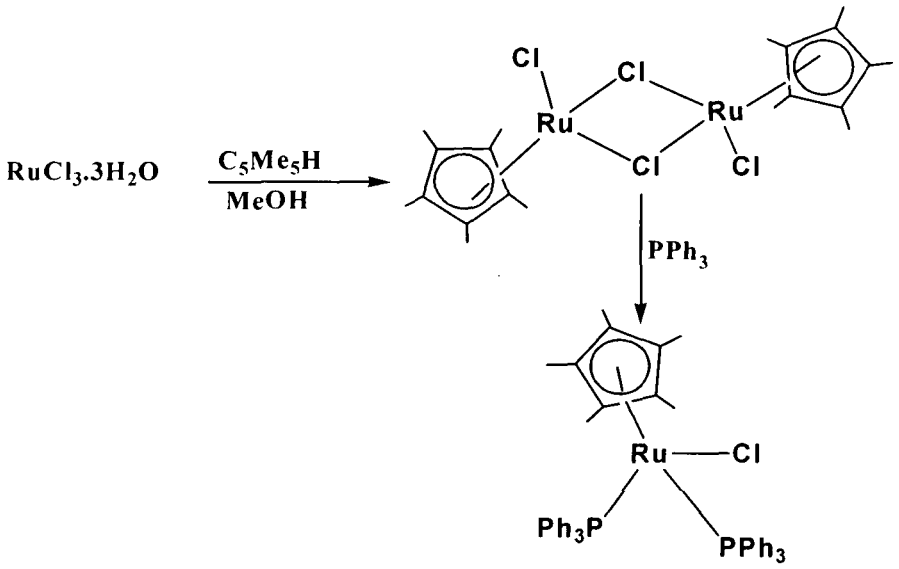
Scheme 1.4

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

Cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ undergo a wide range of reactions with sulphur, nitrosyl and carbon bonded ligands. Thus, treatment of the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with NaSH yielded complex of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2SH]$ [15]. Treatment of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ complex with sodium thiocarbamate affords complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(S_2CX)(PPh_3)_2]$ [16]. Cyclopentadienyl complex of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(N,N')]^+$ are obtained by ready substitution of two facile coordination sites of the complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with N, N'- base ligands [17].

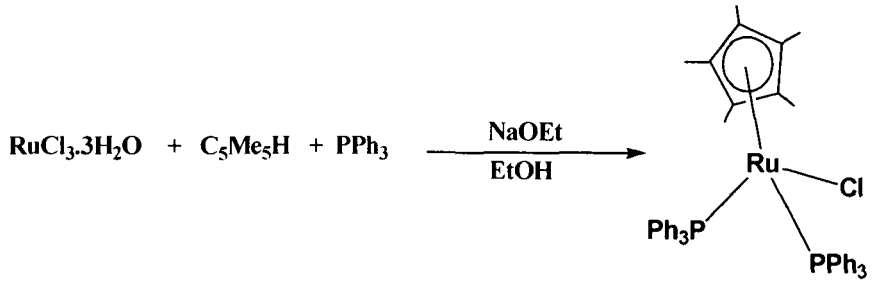
1.3 Pentamethylcyclopentadienyl ruthenium (II) complexes

The complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ can be prepared by the reaction between $RuCl_3.3H_2O$ 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].



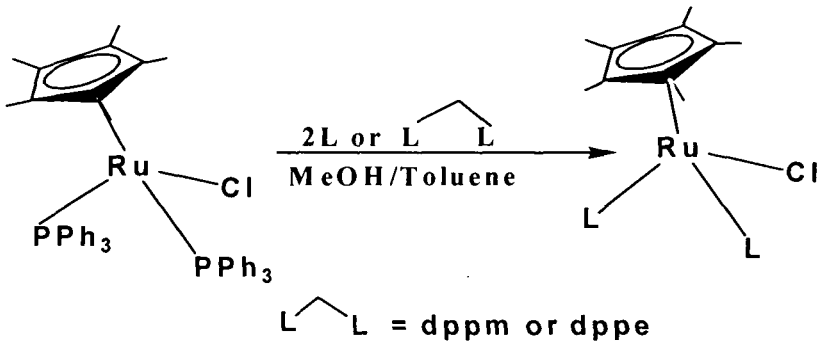
Scheme 1.5

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 $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (scheme 1.6).



Scheme 1.6

Both of the triphenylphosphines can be replaced by the alkyl phosphines and chelating phosphines to give neutral complexes $[(\eta^5\text{-}C_5Me_5)Ru(L)_2Cl]$ (scheme 1.7) [20].



Scheme 1.7

B. Steinmetz and his co-workers described a convenient route for the synthesis of a novel $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]^+$ complexes by zinc reduction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ in acetonitrile in the presence of $NaPF_6$ [21].

1.4 APPLICATION TO ORGANIC SYNTHESES

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:

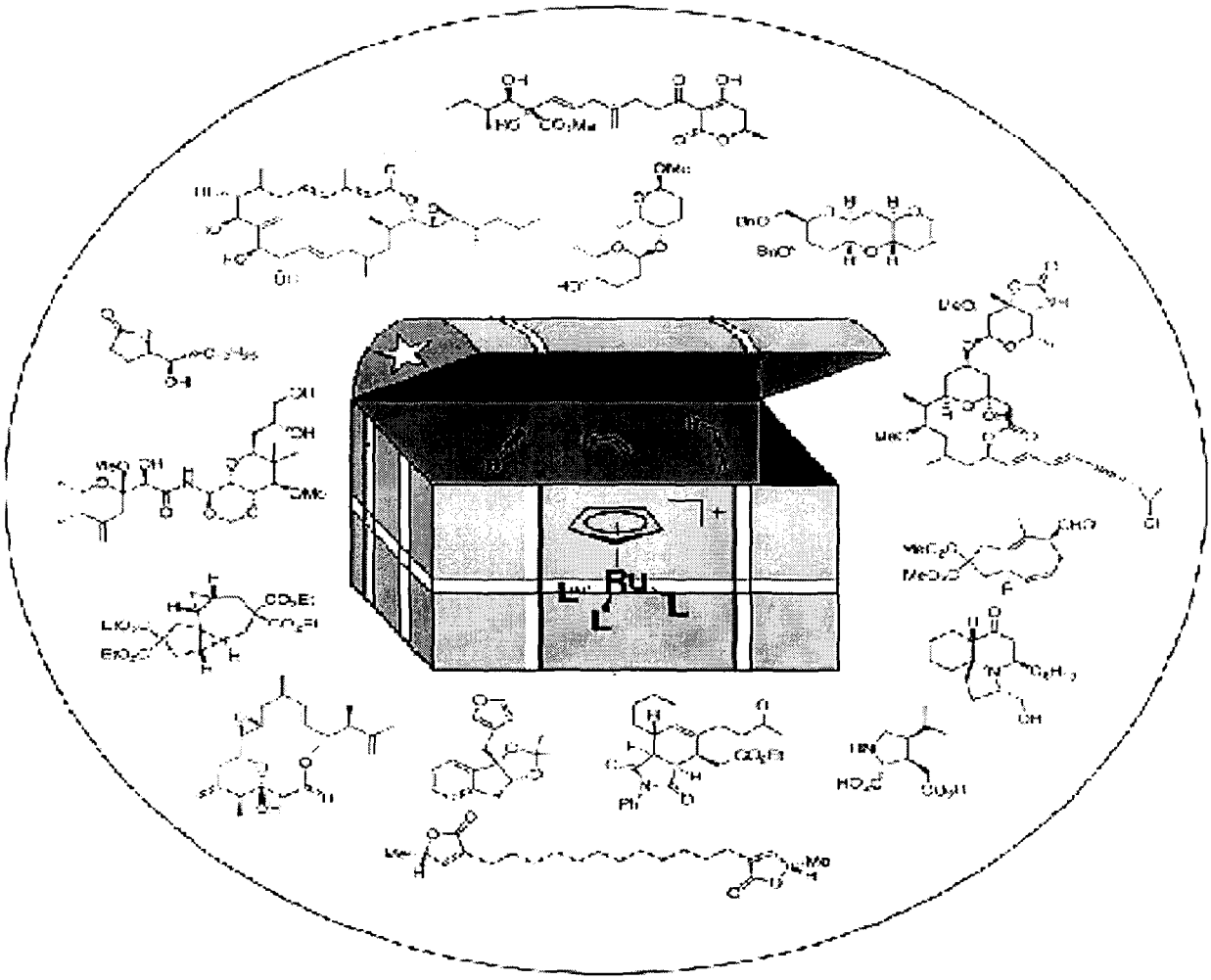


Figure: Ruthenium catalyzed reactions in organic syntheses.

1.5 η^6- Cyclichydrocarbon ruthenium(II) complexes

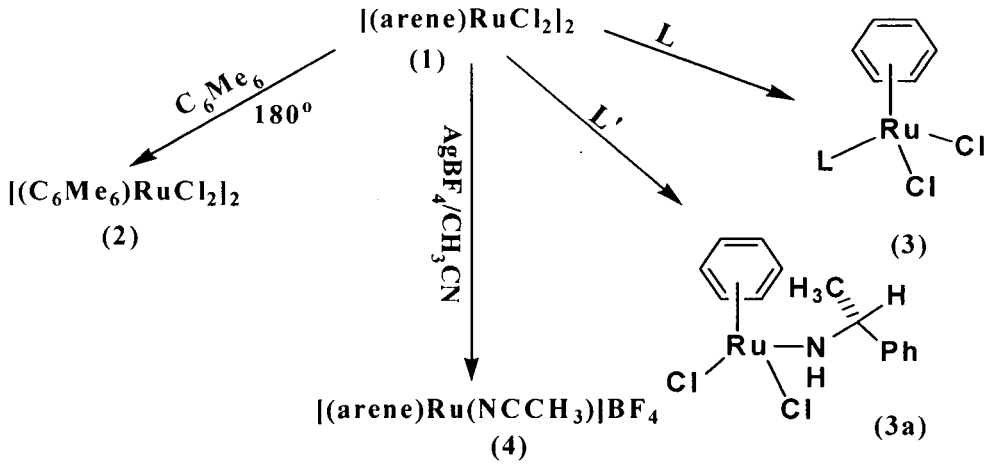
In recent years, π-arene metal complexes have generated considerable interest due to their potential roles in homogeneous catalysts. Its complexes have been extensively investigated by organic and organometallic chemists for over 40 years. In particular, η^6-arene complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [23]. The versatile starting materials $[(\eta^6\text{-arene})RuCl_2]_2$ are usually prepared by

refluxing the appropriate cyclohexa-1, 3 diene or cyclohexa-1, 4-diene with $RuCl_3.3H_2O$ in ethanol [24]. The $[(\eta^6\text{-arene})RuCl_2]_2$ complexes of mesitylene, 1, 2, 3, 4-tetramethylbenzene, 1,3,5–triethylbenzene, 1,3,5-triisopropylbenzene and tetramethylthiophene [25] have been made similarly from $[(\eta^6\text{-arene})RuCl_2]_2$. The coordination of a metal fragment (MLn) to an arene ring dramatically increases the electrophillic character of the ligand. Thus, processes such as nucleophillic 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 η^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 η^6-arene complexes, those that incorporate the neutral tricarbonyl Chromium(0) $\{Cr(CO)_3\}$ 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 η^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

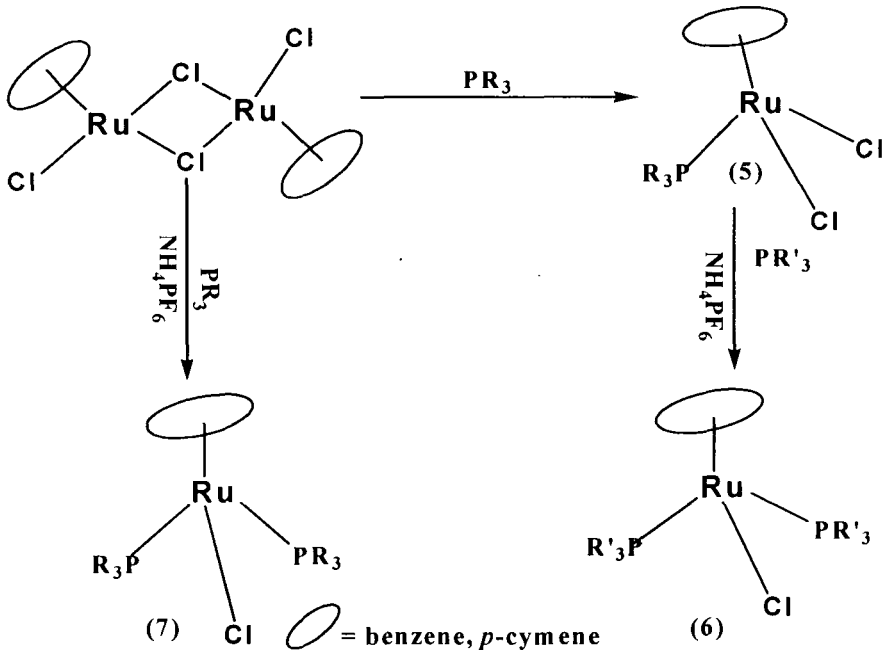
Most half-sandwich complexes that contain an arene ruthenium moiety are conveniently prepared from chloro-bridged η^6-arene ruthenium(II) dimer. Majority of half sandwich arene chemistry based on ruthenium arises from the binuclear complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6, MeC_6H_4Pri) which results from the reactions of $RuCl_3.3H_2O$ with 1, 3-cyclohexadiene or α- phellandrene as described by Zelonka and Baird as well as Bennett and Smith [29]. The η^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).



L = R_3P, Py etc.
L' = H_2N-CH(Ph)(CH_3)
arene = *benzene*, *p*-cymene

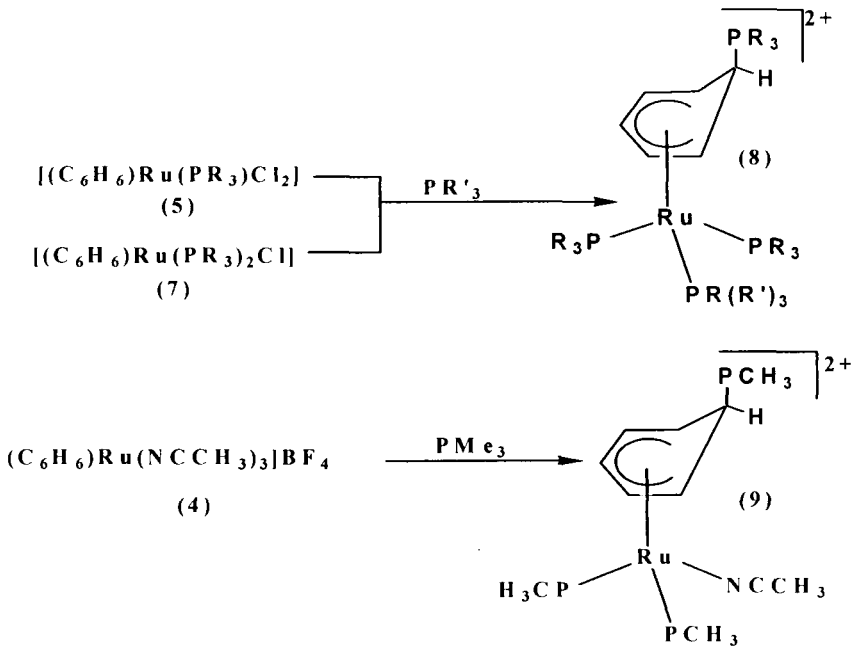
Scheme 1.8

The chloro bridges are labile and stirring dimeric complexes, such as **1** in coordinating solvents (*e.g.*, CH_3CN, 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)-(-)-α- 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) dications (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 NH_4PF_6 afforded complex **6** with two different phosphines bonded to the Ru(II) centre (Scheme 1.9) [33].



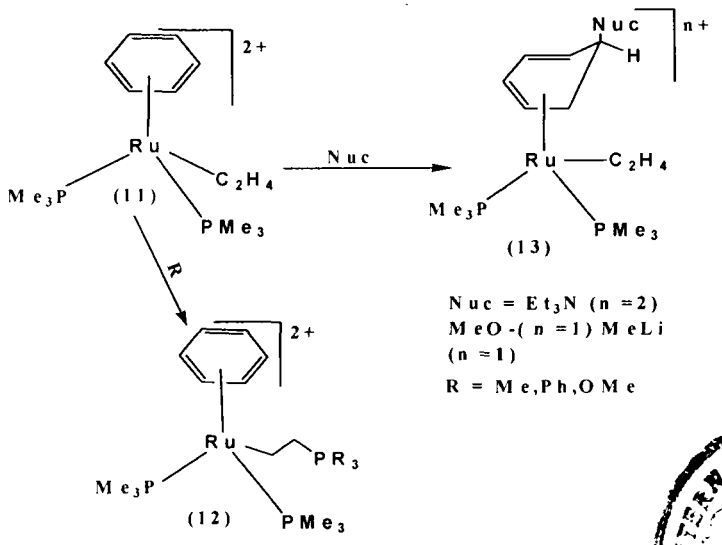
Scheme 1.9

Incorporation of two identical phosphine ligands **7** was accomplished directly by reacting **1** with excess of phosphine and NH_4PF_6. Complexes such as **5** and **7** were found to be susceptible to further attack by phosphine, ultimately providing phosphonio-η^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 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 (η^6-arene)Ru(II) complex.



Scheme 1.10

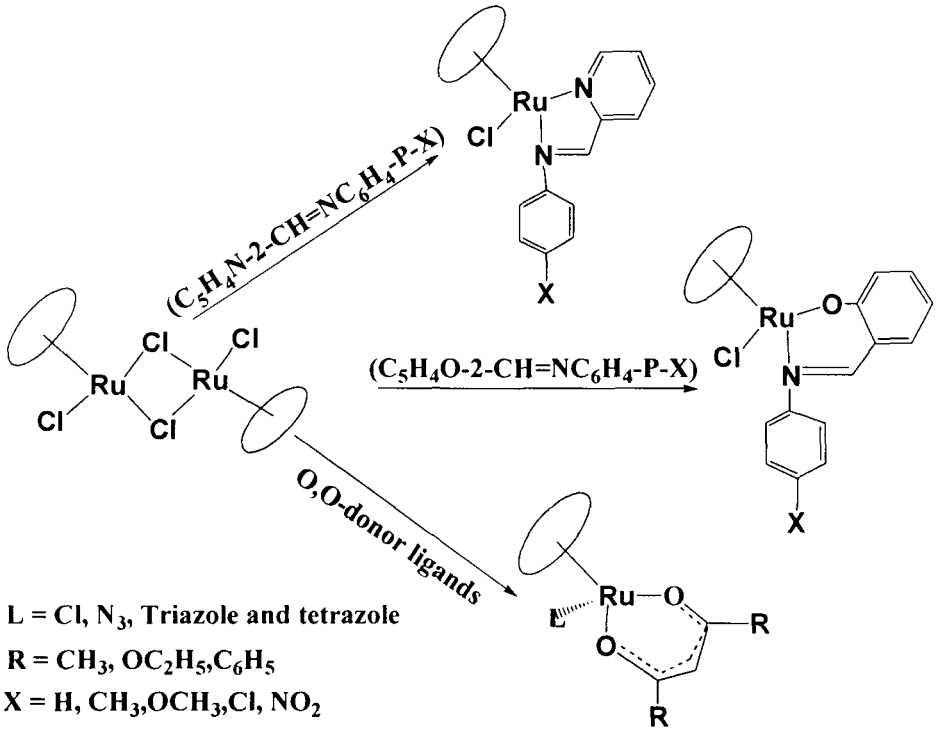
The bis(phosphine)ethylene arene ruthenium complex **11** (Scheme 1.11) presents two π-ligands potentially susceptible to nucleophillic attack. Reaction with a phosphine or phosphites resulted in addition to the coordinated ethylene ligand, while treatment with harder nucleophiles (Et_3N, MeO-, MeLi) 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 $[(\eta^6\text{-arene})RuCl_2]_2$ with the appropriate ligands [36]. The $[(\eta^6\text{-arene})RuCl_2]_2$ complex reacts with NaOR/ROH to give $[(\eta^6\text{-arene})Ru_2(\mu\text{-OR})_3]^+$ [37]. The complex $[(\eta^6\text{-arene})RuCl_2]_2$ reacts with primary and secondary amines, neither at room temperature nor heating in non-polar solvents to gives $[(\eta^6\text{-arene})RuCl_2(L)]$ (arene = 1, 3, 5-$C_6H_3Me_3$; L = $C_5H_{10}NHPy$) [38]. Similar complexes of the type $[(\eta^6\text{-arene})Ru\{Cl_2NC_5H_4NH_3\text{-}O\}]$ was obtained by the reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ 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 $[(\eta^6\text{-}p\text{-cymene})Ru(N,N')Cl]^+$ and $[(\eta^6\text{-}p\text{-cymene})Ru(N,O)Cl]^+$ [39]. The similar reaction between $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and O,O'- donor ligands produced complexes of the type $[(\eta^6\text{-}C_6H_6)Ru(O,O')Cl]$, which have been reported in this work (scheme 1.12).

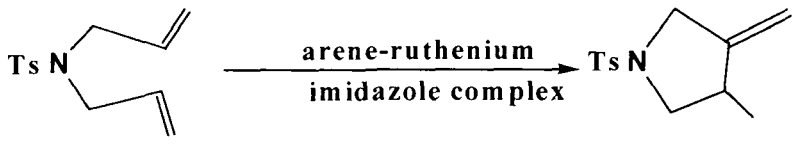


Scheme 1.12

1.8 Application of arene ruthenium(II) complexes

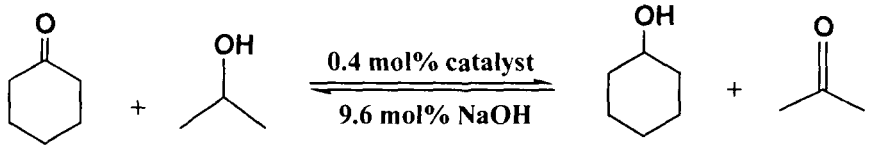
Most of the arene ruthenium compounds are used in hydrogenation catalysts. The complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene(C_6H_6), *p*-cymene, 1,3,5-$C_6H_3Me_3$, 1,3,5-$C_6H_3Ph_3$) [40] and $[(\eta^6\text{-arene})RuCl_2(DMSO)]$ were found to be catalyst precursors for hydrogenation of alkenes. Zero-valent ruthenium complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{ -}C_6Me_6)]$ was found to be catalytically active for arene hydrogenation [41]. The complex $[RuH(\eta^6\text{-}C_6Me_6)(Ph)_3]$ 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 pentamethylcyclodienyl complexes are reported to hydrogenation catalyst of alkenes and arene [43]. In 1984 Pertici *et al.*, reported that hydrogenation of alkenes in the presence of the catalyst $[Ru(\eta^6\text{-arene})(\eta^4\text{-COD})]$ (arene = C_6H_6, 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$) [44]. Benzene was selectively reduced to

cyclohexene by hydride reduction of $[Ru(\eta^6\text{-arene})(\eta^6\text{-}C_6Me_6)]^{2+}$ and $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^{2+}$ {M = 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 (π-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: $[(\eta^6\text{-arene})Ru(en)Cl]^+$ (en = 1,2-diaminoethane), $[(p\text{-cymene})RuCl(\mu\text{-BESE})]_2$, $[(p\text{-cymene})RuCl(\mu\text{-BESP})]_2$ and $[(p\text{-cymene})RuCl_2$ (BESE)$]PF_6$ (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 $[(\eta^6\text{-arene})Ru(P\text{-}P)Cl]CF_3SO_3$(arene = C_6H_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 $PhPCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$ 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 ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ 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 ^1H, ^{13}C $\{^1H\}$ $SiMe_4$ is used as an internal standard while chemical shift for ^{31}P $\{^1H\}$ resonance were referred to 85% H_3PO_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 $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ [4], $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ [5], $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ [21], $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ [31] and $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$, $[(\eta^5\text{-}$

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

2.1 Preparation of starting materials

1. $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ [30]

1 g of $RuCl_3.3H_2O$ dissolved in 80 ml of ethanol and 5 ml of α-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. $[(\eta^6$-$C_6H_6)RuCl_2]_2$ [31]

2 g of $RuCl_3.6H_2O$ 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. $[(\eta^5$-$C_5H_5)Os(PPh_3)_2Br]$ [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°C to obtain the remaining products.

Yield: 2.55 g (74%)

4. $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ [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 °C) 30-40 mins with rapid stirring up to triphenylphosphine is dissolve. Immediately 9-10 ml of freshly distilled cyclopentadienyl, 1 g of $RuCl_3.3H_2O$ 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. $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ [21].

The compound $RuCl_3.3H_2O$ (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. $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ [51]

$IrCl_3.3H_2O$ (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. $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ [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_1) [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 ^{o}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

^{1}H {NMR, δ}: 8.5 (d, J_{HH} = 5.34Hz, 1H, H_6 of py); 8.3 (d, J_{HH} = 4.75Hz, 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

^{1}H {NMR, δ}: 8.6 (d, J_{HH} = 6.00Hz, 1H, H_6 of Py); 8.3 (d, J_{HH} = 5.75Hz, 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}H {NMR, δ}: 8.5 (d, J_{HH} = 5.34Hz, 1H, H6 of py); 8.3 (d, J_{HH} = 4.75Hz, 1H, H3 of Py); 7.8 (t, 1H, H4 of Py); 7.3 (t, 1H, H5 of Py), 3.48(s, 6H of $-CH_3$).

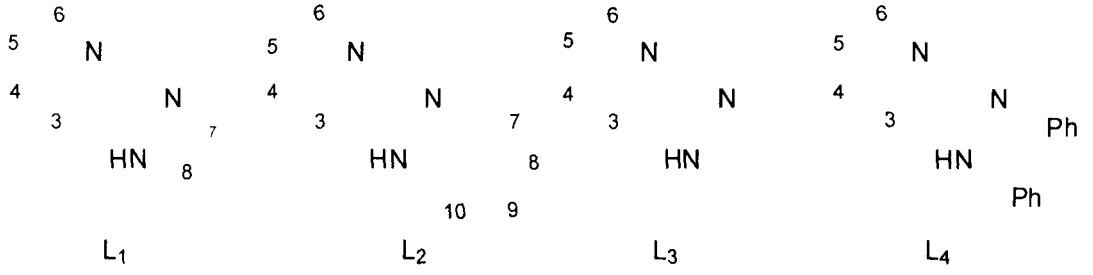
2-(2'-pyridyl)-4, 5-diphenylimidazole (L_4)

Preparation method was similar to L_1 except benzil instead of glyoxal.

Analytical calculated for $C_{20}H_{16}N_3$: C, 80.54; H, 5.37; N, 14.09.

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

^{1}H {NMR, δ}: 8.4 (d, J_{HH} = 5.34Hz, 1H, H_6 of py); 8.3 (d, J_{HH} = 4.75Hz, 1H, H_3 of Py); 7.7 (t, 1H, H_4 of Py); 7.4 (t, 1H, H_5 of Py), 5.84(s, 10H of C_6H_6).



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

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

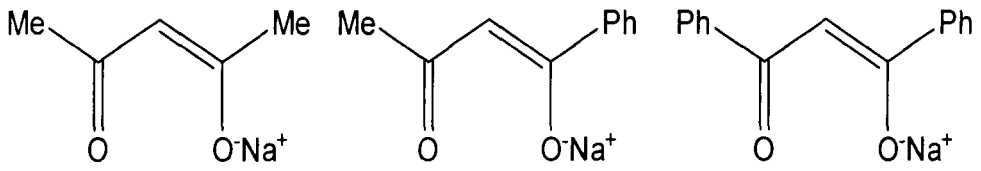
1. Preparation of NaOEt: 50 ml of ethanol and 1.67 g of sodium was added slowly to the stirred solution. When all sodium is dissolved or disappeared the solvent is removed under vacuum, a white solid compound was collected.
2. To this round bottomed flask, containing 250 ml of dry toluene was purged 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 ^{o}C;

Preparation of sodium salts of *β*-diketonate ligands

Sodium salts of *β*-diketonates ligand namely; acetylacetonate {Na(acac)}, benzene acetylacetonate {Na(bzac)}, dibenzenemethylacetonate {Na(dbzm)} were prepared by reacting corresponding *β*-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 *β*-diketones and stirred for 24 hr. The white precipitates were filtered and washed with cold ethanol and dried under vacuum.



Na[acac] Na[bzac] Na[dbzm]

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-Kα.(λ = 0.71069Å and 0.71073 Å). 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 > 2σ (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 F2 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)

References

[1] (a) T. Ando, M. Kamigaeto, S. Sawamoto, *Tetrahedron* 53 (1997) 15445; (b) H. Takahashi, T. Ando, M. Kamigaeto, S. Sawamoto, *Macromolecules*, 32 (1999) 3820; (c) Y. Watanabe, T. Ando, M. Kamigaeto, S. Sawamoto, *Macromolecules* 34 (2001) 4370.

[2] K. Mashima, Koh-hei Kusano, N. Sato, Y. Matsumura, K. Nozaki, H. Kumobayashi, N. Sayo, Y. Hori, T. Ishizaki, S. Akutagawa, H. Takaya, *J. Org. Chem.* 59 (1994) 3064.

[3] (a) R. E. Aird, J. Cummings, A. Ritchie, M. Muir, R. Morris, H. Chen, P. J. Sadler, D. I. Jodrell, *Brit. J. Cancer* 86 (2002) 1652.

[4] (a) M. I. Bruce, N. J. Winsor, *Aust. J. Chem.* 30 (1977) 1601; (b) M. I. Bruce, Hameister, A. G. Swincer, R. C. Wallis, *Inorg. Synth.* 21 (1982) 78.

[5] (a) P. W. Wanandi, T. D. Tilley, *Organometallics*, 16 (1997) 4299; (b) M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887.

[6] P. M. Treichl, D. A. Komar, P. J. Vincnti, *Synth. React. Inorg. Chem.* 14 (1984) 383.

[7] (a) H. Lehmkuhl, M. Bellenbaum, J. Grundk, H. Mauermann, C. Kruger, *Chem. Ber.* 121 (1988) 1719.

[8] R. J. Haines, A. L. du Preez, *J. Organomet. Chem.* 210 (1981) C5.

[9] M. I. Bruce, F. S. Wong, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.*, (1982) 687.

[10] T. Welczewski, M. Bochenska, J. F. Beirnat, *J. Organomet. Chem.*, 215 (1981) 87.

[11] P. M. Treichel, D. A. Komar, *Synth. React. Inorg. Met. Org. Chem.*, 10 (1990) 205.

[12] T. Welczewski, M. Bochenska, J. F. Beirnat, *J. Organomet. Chem.*, 215 (1981) 87; M. I. Bruce, R. C. Wallis, *Aust. J. Chem.*, 34 (1981) 209.

[13] F. M. Conroy,-Lewis, S. J. Simpson, *J. Organomet. Chem.*, 286 (1985) 343.

[14] J. W. Faller, Y. Ma, C. J. Smart, M. J. Diverdi, *J. Organomet.Chem.*, 420 (1991) 237.

[15] P. M. Treichel, D. A. Komar, *Synth. React. Inorg. Chem.*, 10 (1990) 205; G. S. Ashby, M. I. Bruce, I. B. Tomkins, R. C. Wallis, *Aust. J. Chem.*, 32 (1979) 1003.

[16] M. I. Bruce, A. G. Swincer, R. C. Wallis, unpublished results.

[17] L. B. Reventos, A. Guttierrez Alonso, *J. Organomet. Chem.*, 309 (1986) 179.

[18] P. M. Treichel, D. A. Komar, P. J. Vincenti, *Synth. React. Inorg. Met. Org. Chem.*, 14 (1984) 383.

[19] (a) P. M. Treichel, D. A. Komar, P. J. Vincenti, *Synth. React. Inorg. Met. Org. Chem.*, 14 (1984) 383; (b) H. Lehmkuhl, M. Bellenbaum, J. Grundke, H.

Mauermann, C. Kruger, *Chem. Ber.*, 121 (1988) 1719; (b) N. Oshima, H. Suzuki, Y. Moro-Oka, *Chem. Lett.*, (1984) 1161.

[20] M. I. Bruce, Ben C. Hall, Natasha N. Zaitseva, Brian W. Skelton, Allan H. White, *J. Chem. Soc. Dalton Trans.*, (1998) 1793.

[21] P. M. Treichel, D. A. Komar, P. J. Vincenti, *Synth. React. Inorg. Met. Org. Chem.*, 14 (1984) 383.

[22] B. M. Trost, Mathias U.Frederiksen, Michael T. Rudd, *Angew.Chem. Int.Ed.* 44 (2005) 6630-6666.

[23] T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc.*, A (1971) 2376.

[24] J. Maussa, C. G. Duhayon, P. Herson, H. Amouri, M. N. Rager, A. Jutand, *Organometallics* 23 (2004) 213.

[25] (a) L. S. Hegedus*Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausalito, CA, 1999; Chapter. 10. (b) Pike, R. D.,Sweigart, D. A. *Coord. Chem. Rev.*, 187(1999) 183.

[26] J. W. Hull, Jr, W. L. Gladfelter, *Organometallics*, 3 (1984) 605

[27] J. R. Lockemeyer, T. B. Rauchfuss, A. L. Rheingold, S. R. Wilson, *J. Am. Chem. Soc.*, 111 (1989) 8828.

[28] (a) R. Noyori, S. Hashiguchi, *Acc.Chem. Res.*, 30 (1997) 97. (b) G. C. Fu, *Acc. Chem. Res.*, 33 (2000) 412.

[29] G. B. Jones, M. Guzel, *Tetrahedron Lett.*, 41(2000) 4695 (a) C. Bolm, K. Muñiz, *Chem. Soc. Rev.*, 28 (1999) 51. (b) G. B. Jones, M. Guzel, S. B. Heaton, *Tetrahedron: Asymmetry* 11 (2000) 4303.

[30] (a) M. F. Semmelhack, In *Comprehensive Organometallic Chemistry II*; L. S. Hegedus, Ed., Elsevier Science, Ltd.: Oxford, 1995; Vol. 12, pp. 979-1038; (b) S. G. Davies, T. D. McCarthy, In *Comprehensive Organometallic Chemistry II*; L. S. Hegedus, Ed., Elsevier Science, Ltd.: Oxford 1995; Vol. 12, pp.1039-1070.

[31] R. A. Zelonka, M. C. Baird, *Can. J. Chem.*, 50 (1972) 3063.

[32] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans* 1974, 233

[33] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 21 (1982) 74.

[34] H. Werner, R. Werner, *Chem. Ber.*, 115 (1982) 3766.

[35] H. Werner, R. Werner, *Chem. Ber.*, 117 (1984) 142.

[36] H. Werner, R. Werner, *Chem. Ber.*, 118 (1985) 4543.

[37] S. K. Mandal, A. R. Chakravarty, *J. Organomet. Chem.*, 417 (1991) C5; (b) S. K. Mandal, A. R. Chakravarty, *Polyhedron* 11 (1992) 823.

[38] (a) T. Arthur, D. R. Robertson, D. A. Tocher, T. A. Stephenson, *J. Organomet. Chem.*, 208 (1981) 389; (b) R. O. Gould, D. A. Tocher, T. A. Stephenson, *J. Organomet. Chem.*, 263 (1984) 375; (c) M. R. J. Elsegood, D. A. Tocher, *Inorg. Chim. Acta.*, 161 (1989) 147.

[39] L. Carter, D. L. Davies, J. Fawcett, D. R. Russell, *Polyhedron* 12 (1993) 1123.

[40] S. K. Mandal, A. R. Chakravarty, *J. Organomet. Chem.*, 417 (1991) C5; (b) S. K. Mandal, A. R. Chakravarty, *Polyhedron* 11 (1992) 823.

[41] (a) A. G. Hinze, Recl. Trav. Chim., Pays-Bas, 92 (1973) 542; (b) R. Iwata, I. Ogata, *Tetrahedron* 29 (1973) 2753; (c) R. Iwata, I. Ogata, Y. Ikeda, *Tetrahedron Lett.*, (1970) 3011.

[42] (a) E. O. Fischer, C. Elschenbroich, *Chem. Ber.*, 103 (1970) 162; (b) G. Huttnet, S. Lange, *Acta. Cryst.*, B28 (1972) 2049.

[43] M. A. Bennett, T. N. Huang, T. W. Turney, *J. Chem. Soc., Chem. Comm.*, (1979) 312.

[44] M. J. H. Russel, C. White, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1977) 427.

[45] P. Pertici, G. Vitulli, C. Bigelli, R. Lazzaroni, *J. Organomet. Chem.*, 275 (1984) 113.

[46] (a) B. M. Trost, J. A. Marting, R. J. Kulawiec, A. F. Indoles, *J. Am. Chem. Soc.*, 115 (1993) 10402; (b) M. A. Bennett, K. Khan, E. Wenger, *Comprehensive Organometallic Chemistry* (and references cited therein), Elsevier, Oxford, 1995.

[47] (a) Y. K. Yan, M. Melchart, A. Habtemariam, P. J. Sadler, *Chem. Commun.*, (2005) 476; (b) R. Fernandez, M. Melchart, A. Habtemariam, P. J. Sadler, S. Parsons, *Chem. Eur. J.* 10 (2004) 5173.

[48] L. A. Huxham, E. L.S. Chen, B.O. Patrick, B. R. James, *Inorg. Chim. Acta.*, 352 (2003) 238.

[49] I. Ozdemir, B. Cetinkaya, S. Demir, E. Cetinkaya, N. Gurbuz, M.Cicek, *Appl' Organomet. Chem.*, 18 (2004) 15.

[50] K. Y. Ghebreyessur, J. H. Nelson, *J. Organomet. Chem.*, 669 (2003) 48.

[51] (a) R. A. Zelonka, M. C. Baird, *J. Chem.*, 50 (1972) 2063; (b) M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* (1974) 233.

[52] B. Chiswell, F. Lions, B. S. Morris, *Inorg. Chem.*, 31 (1964) 110.

[53] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 21 (1982) 74.

[54] XRD Single Crystal Software; Bruker Analytical X-ray systems, Madison, USA, 2002.

[55] M. Sheldrick, SHELXS-86, Program for Crystal structure solution, University of Gottengen, Germany, 1986.

[56] A. Altomare, M. Burla, M. Camalli, G. Casarano, C. Giacovazzo, A. Guagliarde, A. Molitrni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 32 (1999) 115.

[57] M. Sheldrick, SHELXS 97 Program for Crystal structure refinement, University of Gottengen, Germany 1997.

[58] (a) M. Sheldrick, SHELXS 97 Program for Crystal structure refinement, University of Gottengen, Germany 1997.

(b) P. V. D. Sluis, A. L. Spek, *Acta Crystallogr.*, Part A 46 (1990) 194.

[59] C. K. Johnson, ORTEP-II: A Fortran Thermal ellipsoid plot Program for Crystal structure illustrations, ORNL-5138, 1976.

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CHAPTER 2

Reactivity study of cyclopentadienyl osmium(II) bisphosphine azido complexes with activated alkynes and nitriles: isolation of osmium triazolato and tetrazolato complexes by 1,3 dipolar addition.

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Reactivity study of cyclopentadienyl osmium (II) bisphosphine azido complexes with activated alkynes and nitriles: isolation of osmium triazolato and tetrazolato complexes by 1,3 dipolar addition*.

Abstract:

The cyclopentadienyl osmium(II) complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2X]$ [X = Br (**1**), CH_3CN (**2**)] reacts with sodium azide (NaN_3) to yield the corresponding azido complex of the type $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$ (**3**). The azido complex thus generated undergoes [3+2] dipolar cycloaddition reaction with activated alkynes such as diethylacetylenedicarboxylate and dimethylacetylenedicarboxylate to yield triazolato complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_3C_2(CO_2R)_2\}]$ [R = $-CH_2CH_3$ (**4**) and $-CH_3$ (**5**)]. The complex **3** also reacts with nitriles such as tetracyanoethylene (TCE), fumaronitrile and p-nitrobenzonitrile to yield complexes of the type $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_4C_2(CN)=C(CN)_2\}]$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_3C_2HCN\}]$ (**7**) and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_4C(C_6H_4\text{-}p\text{-}NO_2)\}]$ (**8**). These complexes were fully characterized on the basis of microanalyses, FT-IR and NMR spectroscopic data. Molecular structure of the representative complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_3C_2(CO_2CH_2CH_3)_2\}]$ (**4**) was determined by single crystal X-ray analysis.

Keywords: Osmium complexes, cyclopentadienyl, dimethylacetylenedicarboxylate, diethylacetylenedicarboxylate, fumaronitrile, tetracyanoethylene, *p*-nitrobenzonitrile.

**Communicated Inorganica Chimica Acta*

2.1 Introduction

The σ-donor and π-acceptor abilities of the cyclopentadienyl ligands stabilize transition metal complexes in low and high oxidation states. The half sandwich cyclopentadienyl ruthenium and osmium biphosphine complexes *viz.*, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**), have generated a great deal of interest for the last few decades due to high reactivity [1] and catalytic activity [2]. However, the chemistry of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**) is less research in compared to its analogue ruthenium complexes [3]. This could be due to the lack of convenient osmium synthetic precursor [4] and the higher kinetic stability of the cyclopentadienyl osmium $((\eta^5\text{-}C_5H_5)OsL_3)^+$ compounds in comparison with the related cyclopentadienyl ruthenium complexes [5]. Our interest arises due to catalytic potential in organic reactions, which is particularly important for synthesizing heterocyclic compounds [6]. In addition, tetrazoles are not only important in precursors to a variety of nitrogen containing heterocycles [7] but also to diverse application in pharmaceuticals [8], explosives [9] and corrosion inhibitors [10]. The presence of a coordinated azide in certain metal complexes has been reported to react with electron-poor nitriles [11] and isonitriles [12] under relatively mild conditions to produce metal-nitrogen and metal-carbon bonded tetrazoles respectively. Similar reactions with alkynes produce triazolates, whereas alkenes react very slowly and mostly afford an impure product [13]. Similarly, it has been reported that azido complexes react with carbon disulfides to produce thiothiatriazolate [14]. A number of azido complexes have been found to react with organic isothiocyanates and alkyl thiocyanates to give tetrazolinethionates and 5-(thioalkyl) tetrazolates respectively [15].

Recently cyclopentadienyl ruthenium triazolato and tetrazolato complexes have been reported [16]. We recently reported the triazolato complexes of the type [(η^6-arene)Ru(LL){$N_3C_2(CO_2R)_2$}] and [(η^5-indenyl)Ru(LL){$N_3C_2(CO_2R)_2$}] (LL = β-diketonates, dppe, dppm) which result from the reaction of [(η^6-*arene*)Ru(μ-N_3)(LL)] and [(η^5-indenyl)Ru(LL)(N_3)] respectively with various substituted acetylenes [17]. The study revealed two important observations, these are:- (i) η^5-indenyl ruthenium(II) complexes containing bulky triphenylphosphine ligands did not undergo 1, 3 cyclo-addition and (ii) in our study, the ethoxy substituted complex exclusively produces the isomer with the metal bonded to the terminal nitrogen atom (N1) of triazolato ring. To understand the role of steric factors in 1,3 –dipolar cyclo-addition reactions, we carried out the reaction between activated alkynes / nitriles and cyclopentadienyl osmium azido complex [(η^5-C_5H_5)Os(PPh_3)$_2N_3$] (**3**). The work presented here is an elaborate study on cycloaddition reaction of cyclopentadienyl osmium azido complexes.

2.2 Experimental Section

All solvents were dried in appropriate drying agents and distilled prior to use [22]. Osmium tetraoxide (Arora Matthey Limited), dimethylacetylenedicarboxylate, diethylacetylenedicarboxylate, tetracyano-ethylene (TCE), fumaronitrile (Aldrich) and *p*-nitrobenzonitrile (Across) were used as received. ^{1}H NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 (^{1}H), or 100.61 MHz (^{13}C) and 161.97 (^{31}P) with $SiMe_4$ or 85% H_3PO_4 as references and coupling constants were given in Hertz. Infrared spectra were recorded as a KBr pellets on a Perkin-Elmer Model 983 spectrometer. Elemental analyses were carried out at the Sophisticated Analytical Instrumentation facility (SAIF), NEHU - Shillong, using a Perkin-Elmer 2400 CHN/S

analyzer. The precursor complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2CH_3CN][PF_6]$ (**2**) were prepared by following a literature method [21].

2.3 *Synthesis of the complex* $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$ (3)

Two routes were used to prepare for this complex:

(Caution: Reactions with azide salts and their complexes should perform with extreme care)

Route (a): A solution of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**) (100 mg, 0.12 mmol) and NaN_3 (50 mg, 0.75 mmol) in ethanol (30 ml) was refluxed for *ca.*, 5 hrs. During the period of reaction, the color of the solution progressively changed from pale yellow to an orange colored. The solution was concentrated to *ca.* 5 ml and left at room temperature for overnight; a pale green crystalline compound was deposited on the beaker. The crystalline compound was collected and washed with cold ethanol (3 x 10 ml) and air dried.

Route (b): A mixture of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_3CN)][BF_4]$ (**2**) (100 mg, 0.10 mmol) and NaN_3 (20 mg, 0.31 mmol) in ethanol (30 ml) was refluxed for *ca.*, 3 hrs. The solvent was removed under reduced pressure; the solid residue was extracted with dichloromethane and filtered to remove NaCl and excess NaN_3. The filtrate on concentration to *ca.* 5 ml and addition of excess hexane gave a pale green crystalline solid of compound (**3**), and washed with cold ethanol (3 x 10 ml).

Yield: 72 mg, 84.61 %

Elemental analyses: (%) for. Calc.$C_{41}H_{35}P_2N_3Os$: C 59.2; H 4.2; N 5.1; found: C 59.75; H 4.87; N 5.64.

IR (KBr, cm^{-1}): 2034 (ν_{N3}).

^{1}H NMR ($CDCl_3$, δ): 7.82-7.01 (m, 30H, Ph); 4.47 (s, 5H, C_5H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 133.5-127.6 (Ph), 79.7 (C_5H_5).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 1.15.

2.4 *Synthesis of [(η^5-C_5H_5)Os(PPh_3)$_2${$N_3C_2(CO_2C_2H_5)_2$}] (4)*

General Procedure:

Diethylacetylenedicarboxylate (175 mg, 1.23 mmol) and dichloromethane (20 ml) were added to a round bottom flask charged with the corresponding azido complex (**3**) (100 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for *ca.*15 hrs. The solvent was evaporated under reduced pressure to *ca.* 5 ml. To this solution was added 30 ml of hexane, whereby the compound precipitated out as a light yellow solid. The solid compound was collected by centrifuge and washed with hexane (2 x 20 ml) and dried under vacuum to yield the N(2)-bound triazole complex [(η^5-C_5H_5)Os(PPh_3)$_2$.$N_3C_2(CO_2C_2H_5)_2$] (**4**)

Yield: 85 mg, 62.69 %.

Elemental analyses: (%) for $C_{49}H_{45}N_3P_2O_4Os$. Calc.: C 59.3; H 4.5; N 4.2; found: C 59.9; H 4.1; N 4.8.

IR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$), 1433 ($\nu_{N=N}$), 1245 (ν_{C-O}).

^{1}H NMR ($CDCl_3$, δ): 7.45-7.03 (m, 30H; Ph); 4.51 (s, 5H, C_5H_5); 3.23 (q, 2H, -OCH_2CH_3); 1.94 (t, 3H, OCH_2CH_3).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 1.15 (s).

2.5 ***Synthesis of*** ***[(η^5-C_5H_5)Os(PPh$_3$)$_2${N$_3$C$_2$(CO$_2$CH$_3$)$_2$}]*** **(5)**

This complex was prepared in a similar manner to that of the preparation of complex **4**, except the ligand dimethylacetylenedicarboxylate [$C_2(CO_2Me)_2$] was used instead of [$C_2(CO_2C_2H_5)_2$] to yield a light yellow complex (**5**)

Yield: 85 mg, 64.52 %

Elemental analyses: (%) for $C_{47}H_{41}N_3P_2O_4Os$. Calc.: C 58.6; H 4.3; N 4.4; found: C 58.1; H 4.8; N 4.2.

IR (KBr, cm^{-1}): 1735 ($\nu_{C=O}$), 1439 ($\nu_{N=N}$).

^{1}H NMR ($CDCl_3$, δ): 7.45-7.03 (m, 30H, Ph); 4.51 (s, 5H, C_5H_5); 3.06 (s, 3H, OCH_3).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 162.9 (CO_2); 135.2{$\underline{C}(CO_2CH_3)$}; 133.8 (Ph); 82.81 (C_5H_5); 51.4 (O$\underline{C}$H$_3$).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 1.19(s).

2.6 ***Synthesis of*** ***[(η^5-C_5H_5)Os(PPh$_3$)$_2$N$_4$C{(CN)C=C(CN)$_2$}]*** **(6)**

Dichloromethane (20 ml) was added to a round bottom flask charged with complex **3** (100 mg, 0.12 mmol) and tetracyanoethylene (0.60 mmol). The reaction mixture was stirred at room temperature for *ca.* 36 hrs. The solvent was evaporated under reduced pressure to *ca.* 5 ml. To the solution was added 20 ml of n-hexane, whereby a deep blue compound was precipitated. The precipitate was filtered, washed with n-hexane (2 x 10 ml) and dried under vacuum to yield [(η^5-C_5H_5)Os(PPh$_3$)$_2${N$_4$C{(CN)C=C(CN)$_2$}] (**6**)

Yield: 83 mg, 64.0 %

Elemental analyses: (%) for $C_{47}H_{35}N_7P_2Os$. Calc.: C 59.4; H 3.7; N 10.3; found: C 58.9; H 3.2; N 9.8.

IR (KBr, cm^{-1}): 2227, 2183 (s, $\nu_{C\equiv N}$), 1430 (s, $\nu_{N=N}$).

^{1}H NMR ($CDCl_3$, δ): 7.73-6.96 (m, 30H, Ph); 4.05 (s, 5H, C_5H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 154.2 {$C(CN)_2$}, 139.4 {C(CN)}, 132.1-126.4 (Ph), 125.3 (C=N), 112. 6, 110.4, 108.5 (CN), 81.4 (s, C_5H_5).

^{31}P {^{1}H} NMR ($CDCl_3$ δ): 1.26 (s).

2.7 *Synthesis of [(η^5-C_5H_5)Os(PPh_3)$_2N_3C_2HCN$]* (7)

The mixture of azido complex [(η^5-C_5H_5)Os(PPh_3)$_2N_3$] (**3**) (100 mg, 0.12 mmol) and fumaronitrile [$C_2H_2(CN)_2$] (0.60 mmol) was stirred at room temperature for 36 hrs in dichloromethane (20 ml), then the solution was concentrated to *ca.* 5 ml. To this solution was added 30 ml of n-pentane, whereby the compound precipitated as a deep green solid. The solid compound was centrifuged, collected and washed with n-pentane (2 x 10 ml) to yield the complex [(η^5-C_5H_5)Os(PPh_3)$_2N_3C_2HCN$] (**7**) and further dried under vacuum.

Yield: 86 mg; 72.1 %

Elemental analyses: (%) for $C_{46}H_{36}N_6P_2Os$. Calc.: C 59.7; H 3.9; N 9.1; found: C 59.0; H 4.1; N 8.7.

IR (KBr, cm^{-1}): 2221 (s, $\nu_{C=N}$), 1433 (s, $\nu_{N=N}$).

^{1}H NMR ($CDCl_3$, δ): 7.50-7.13 (m, 30H, Ph); 6.2 (s, 1H, CH); 4.05 (s, 5H, C_5H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 137.2 {C(CN)}, 136.02 (CH); 132.1-126.4 ({^{1}H} Ph), 113.8 (CN); 82.8 (s, C_5H_5).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 1.25.

2.8 *Synthesis of [(η^5-C_5H_5)Os(PPh_3)$_2N_4C(C_6H_4$-p-NO_2)]* (8)

The mixture of azido complex [(η^5-C_5H_5)Os(PPh_3)$_2N_3$] (**3**) (100 mg, 0.12 mmol) and para-nitrobenzonitrile (NO_2-C_6H_4-C≡N) (0.60 mmol) in dichloromethane (20 ml) was

stirred at room temperature for one week, and the solution was concentrated to *ca.* 5 ml. To this solution was added 30 ml of n-pentane, whereby the compound precipitated as a deep green solid. The solid compound was centrifuged, collected and washed with n-pentane (2 x 20 ml) to yield the complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C(C_6H_4\text{-}p\text{-}NO_2)]$ (**16**) and dried under vacuum.

Yield: 75 mg, 71.0 %

Elemental analyses: (%) for $C_{48}H_{39}N_5\ O_2P_2Os$. Calc.: C 59.4; H 4.0; N 7.2; found: C 58.9; H 4.7; N 7.9.

IR (KBr, cm^{-1}): 1475 (ν_{NO2}), 1430 ($\nu_{N=N}$).

^1H NMR ($CDCl_3$, δ): 4.82 (s, 5H, C_5H_5); 7.0-7.56 (m, 30H, Ph); 8.3 (d, $J_{H\text{-}H}$ = 5.92Hz, 1H); 9.3 (d, $J_{H\text{-}H}$ = 5.6Hz, 1H).

^{13}C {^1H} NMR ($CDCl_3$, δ): 36.02 (CH); 132.1-126.4 (Ph); 82.0 (C_5H_5).

^{31}P {^1H} NMR ($CDCl_3$, δ): 1.19 (s)

Results and discussion

2.9 *Preparation of azido complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$*

Treatment of the complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Os\text{-}(PPh_3)_2\text{-}(CH_3CN)]BF_4$ (**2**) with an excess of sodium azide (NaN_3) in ethanol under refluxed condition for 5 hrs, affords a pale yellow product of cyclopentadienyl osmium azido complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$ (**3**) in good yield (Scheme 2.1). The azido complex **3** is air stable and soluble in polar solvents such as CH_2Cl_2, $CHCl_3$ and acetone, also stable in solution. The infrared spectrum of the complex exhibits a strong band at 2034 cm^{-1} due to terminal azido group (Figure 2.1). The ^{31}P NMR spectrum of the complex **3** displays a singlet at δ 1.15 corresponds to triphenylphosphines. The ^1H NMR spectrum

of the complex **3** displays a singlet resonance at δ 4.47, assigned to the protons of cyclopentadienyl group. The cyclopentadienyl protons showed a down field position in compared to the starting complex (δ 4.31) is presume as due to the increased steric factor on the metal centre of the complex (**3**). Also the spectrum displays a multiplet in the range of δ 7.82-7.01 corresponds to the protons of the triphenylphosphines.

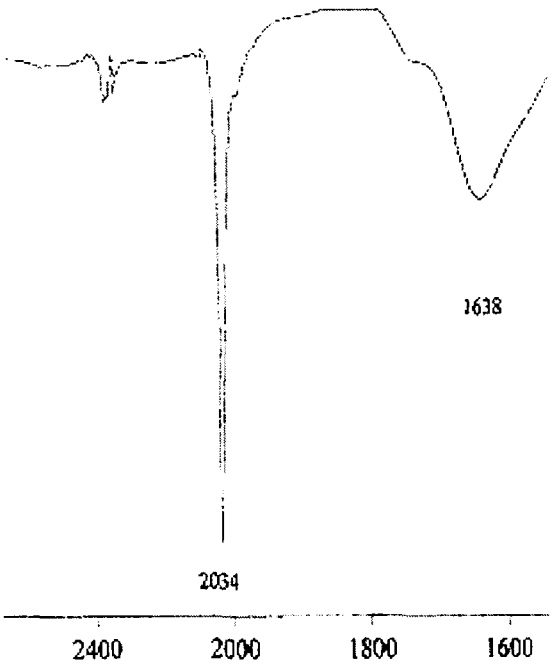


Figure 2.1: Infrared spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$ (**3**)

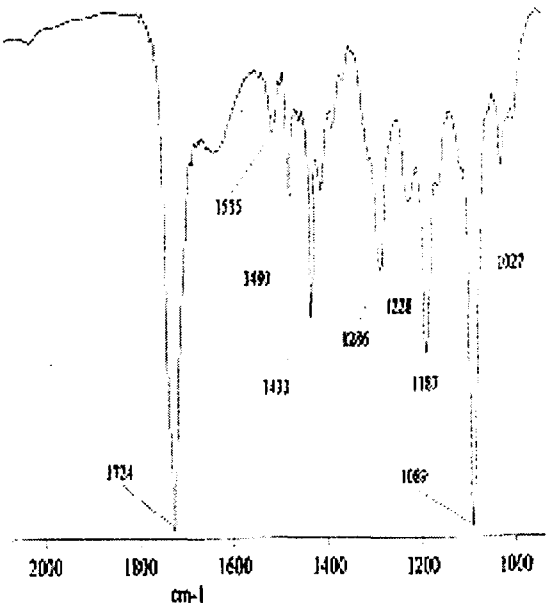


Figure 2.2: Infrared spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_3C_2(CO_2C_2H_5)_2\}]$(**4**)

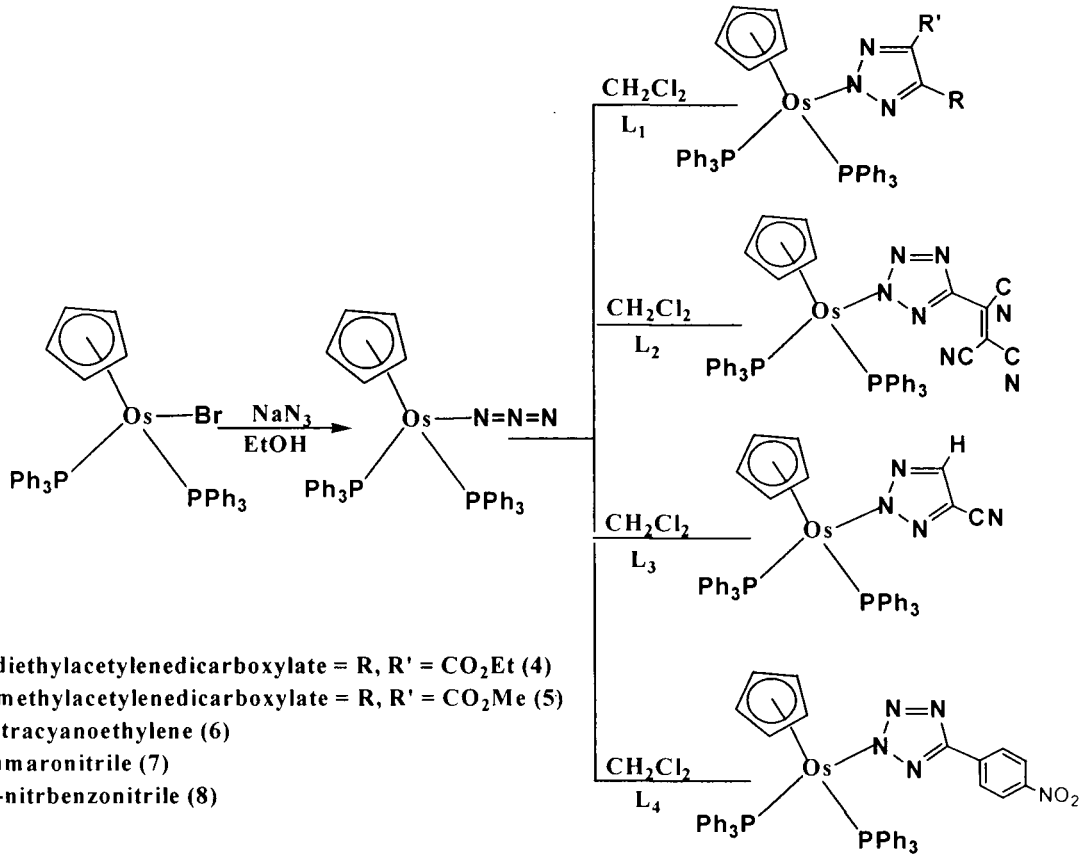
2.9.1 *Reaction of complex 3 with diethylacetylenedicarboxylate:*

Azido complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3]$ (**3**) is treated with excess of diethylacetylenedicarboxylate in dichloromethane and stirred at room temperature for 15 hrs, and results in a light yellow solid compound **4** in good yield. The formation of the complex can be readily confirmed by the disappearance of characteristic azide peak

and the subsequent appearance of a sharp peaks at 1724 and 1433 cm^{-1} corresponds to the characteristic stretching frequency of C=O and N=N respectively(Figure 2.2). The formation of the complex is supported by the single crystal X-ray analysis. The proton NMR spectrum shows a quartet at δ 3.23, triplet at δ 1.94, and singlet δ 4.51 for the ten ethoxy protons and five protons of cyclopentadienyl group. It has been reported that the triazole anion could be coordinated by a metal centre through either its N(1) or N(2) nitrogen atoms [18]. Evidence obtained to date indicates that either two isomers N(1) and N(2) are formed simultaneously. In our case, the N(2) bound isomer is produced exclusively. The ^{1}H NMR spectrum is also displays multiplet in the aromatic region due to phenyl groups of triphenylphosphines.

2.9.2 *Reaction of complex* **3** *with dimethylacetylenedicarboxylate*

Treatment of complex **3** with excess of dimethylacetylenedicarboxylate in dichloromethane at room temperature for 15 hrs affords 4,5-bis(methoxycarbonyl)-1,2,3-triazolato complex **5** in good yield. The infrared spectrum shows sharp peaks at 1724 and 1433 cm^{-1} which are assigned to the stretching frequencies of C=O and N=N of the complex. The proton NMR spectrum displays a singlet at δ 3.06 and δ 4.51 corresponds to methoxy and cyclopentadienyl protons. ^{31}P NMR resonance of the complex **5** appears at δ 1.19 which is comparable to the starting complex (**3**). The complex is soluble in polar solvents but insoluble in non-polar solvents, and is air stable.



L_1 = diethylacetylenedicarboxylate = R, R' = CO_2Et (4)
= dimethylacetylenedicarboxylate = R, R' = CO_2Me (5)
L_2 = tetracyanoethylene (6)
L_3 = fumaronitrile (7)
L_4 = p-nitrbenzonitrile (8)

Scheme 2.1

2.9.3 *Reaction of complex* 3 *with tetracyanoethylene* (TCE):

The azido complex **3** is reacted with excess of tetracyanoethylene (TCE) in dichloromethane at room temperature. The reaction mixture is turned to deep green colouration after one hour and continued to stirring up to 36 hrs to ensure complete reaction. This affords the tetrazolato complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C\{(CN)C{=}C(CN)_2\}]$ (**6**) in good yield. The infrared spectrum exhibited a sharp peaks at 2925 cm^{-1}, 2197 cm^{-1} and 1430 cm^{-1} assigned to the stretching frequencies of C≡N and N=N groups (Figure 2.3), agreeable to the reported values [17]. The ^1H NMR spectrum shows a singlet at δ 4.05 for cyclopentadienyl group, the up field chemical shift of this

compound is due to more electron density on the metal centre. Multiplets observed at the aromatic region correspond to the protons of the triphenylphosphines.

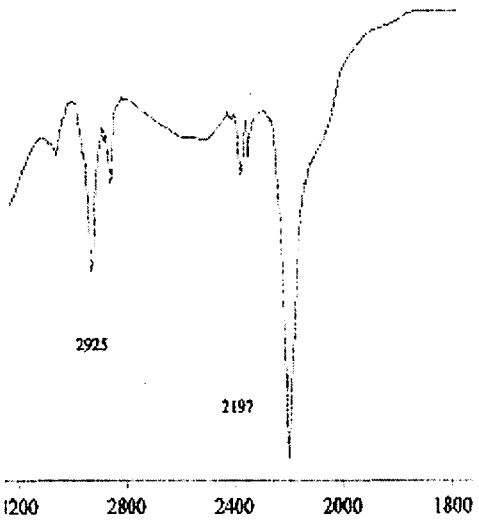


Figure 2.3: IR spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C\{(CN)C{=}C(CN)_2\}]$ (**6**)

^{31}P NMR resonance of this complex displays singlet at δ 1.26. The formation of complex **6** can also be confirmed by the disappearance of terminal azide peak, which is observed at 2057 cm^{-1} and the appearance of stretching frequency of C≡N group. In general, most of the tetrazoles are prepared from the corresponding nitriles by reaction of sodium azide and ammonium chloride [19]. Our effort to get single crystals for X-ray analysis was not succeed.

2.9.4 *Reaction of complex 3 with fumaronitrile*:

Treatment of complex **3** with excess of fumaronitrile at room temperature affords a chocolate coloured 4-cyano-1, 2, 3-triazolato complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2\{N_3C_2HCN\}]$ (**7**) in good yield. The infrared spectrum of the complex shows as a sharp peaks at 2221 and 1433 cm^{-1} assignable to the stretching frequency of C≡N and N=N

groups. The ^{1}H NMR spectrum displays a characteristic singlet resonance at δ 6.2 assigned to the proton (-CH) of triazole group and a singlet resonance at δ 4.05 attributed to the protons of cyclopentadienyl ligand (Figure 2.4). The ^{31}P NMR resonance of this complex appears at δ 1.25 for two triphenylphosphine groups. The complex is soluble in dipolar solvents such as acetone, chloroform, methanol *etc.*, and air stable. The cycloaddition reaction of fumaronitrile to coordinated azide can take place *via* C=C or C≡N bond. In addition, the reaction of coordinated azide in Ni (II) with CH_2=CHCN gave triazolinato complex [18]. A pathway *via* direct cyclization of HC≡CCN with azide resulting in the formation of triazalato has been reported [20]. The formation of this complex can also be readily confirmed by the disappearance of the azide peak at 2037 cm^{-1}, and the simultaneous appearance of the peak for C≡N group. Our effort to get single crystals for x-ray analysis is not successful.

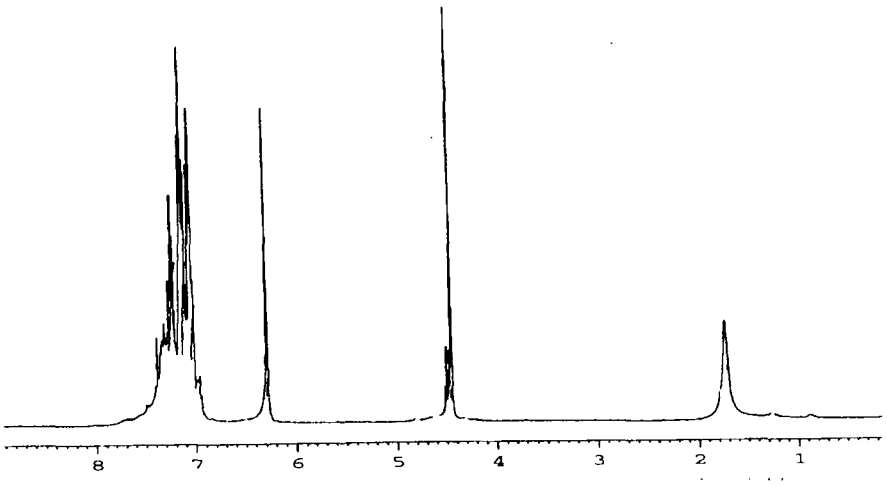


Figure 2.4: ^{1}H NMR spectrum of [$CpOs(PPh_3)_2N_3C_2HCN$] (**7**)

2.9.5 *Reaction of complex* **3** *with p-nitrobenzonitrile*:

Treatment of complex **3** with five fold excess of *p*-nitrobenzonitrile at room temperature for one week gives a deep green coloured complex [(η^5-C_5H_5)$Os(PPh_3)_2$

$\{N_4C(C_6H_4\text{-}p\text{-}NO_2)\}]$ (**8**), in good yield. The formation of the complex is enviable from the appearance of $-NO_2$ peak at 1474 cm^{-1} and the disappearance of the terminal azide peak (Figure 2.6). The ^1H NMR spectrum shows a singlet peak at δ 4.82 assigned to the protons of cyclopentadienyl ligand which is very down field to the chemical shift of the starting complex (δ 4.47) (Figure 2.7). The *p*-nitrobenzonitrile ligand exhibited two doublets at δ 9.3, δ 8.2 which correspond to the 1,2 and 3,4 protons of benzyl group.

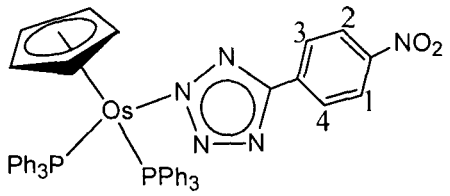


Figure 2.5: Triazolato complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C(C_6H_4\text{-}p\text{-}NO_2)]$ (**8**) with numbering scheme.

The phenyl protons of PPh_3 group displays in the aromatic region. Moreover, only a slight shift of phosphorus resonance (δ 1.19) in the ^{31}P NMR was observed in comparison to the starting complex (δ 1.15). The complex is a deep green colour solid, soluble in polar solvents such as acetone, dichloromethane; chloroform and methanol *etc.*, and is air stable.

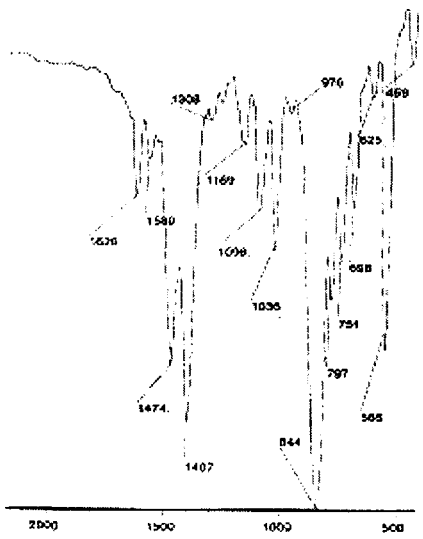


Figure 2.6: IR spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C(C_6H_4\text{-}p\text{-}NO_2)]$ (**8**)

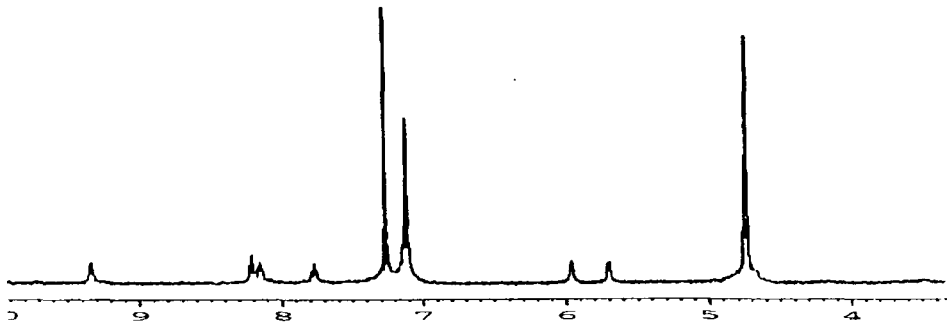


Figure 2.7: ^1H {NMR} spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_4C(C_6H_4\text{-}p\text{-}NO_2)]$ (**8**)

2.9.6 *Crystal structure*

Crystal structure determination of the compound $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2 \cdot \{N_3C_2(CO_2C_2H_5)\}]$ (**4**) has been carried out. Details of crystallographic data collection parameters are summarized in table 1. ORTEP diagram of the complex with atom labelling scheme are shown in figure 2.8 and 2.9. ORTEP 2.7 exhibits clear view of the molecule due to removal of phenyl groups of triphenylphosphine. In this complex the

osmium atom is π-bonded to the cyclopentadienyl group in η^5- fashion with the distance between osmium atom and the centroid of the cyclopentadienyl being 1.66 Å which is similar to the ruthenium analogues. The geometry around the osmium atom is a distorted octahedral assuming the cyclopentadienyl ligand which occupies three facial coordination sites. The remaining coordination sites are occupied by the P atom of triphenylphosphines and an N-atom of the coordinated triazolato group. The complex **4** adopts the well–known piano stool geometry with P and N atoms forming the legs. The planar five–membered triazolato ring is coordinated to Os *via* N(2). The N(1)-N(2) and N(2)-N(3) bond distances are 1.331 (4) Å and 1.343 (3) Å respectively (Table 2.2), which are comparable to the reported values of its ruthenium analogues [17]. The Os-P(1) and Os-P(2) bond lengths are 2.323 Å and 2.326 Å which are slightly longer than the average Os-P distance (2.293 Å) [21].

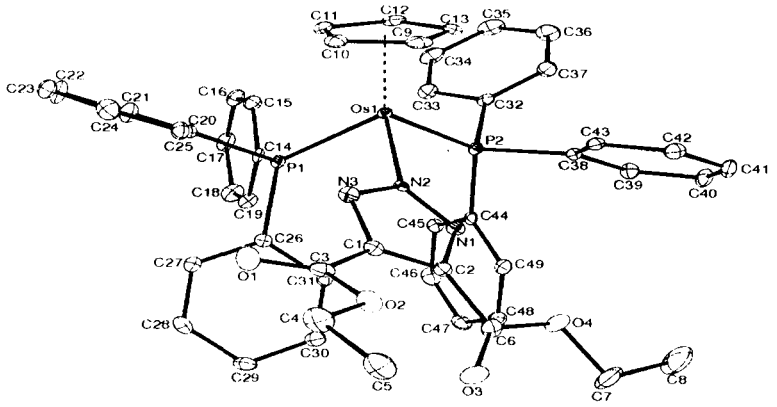


Figure 2.8: ORTEP diagram of complex **4** with 30% probability thermal ellipsoids displayed and H atoms being omitted for clarity.

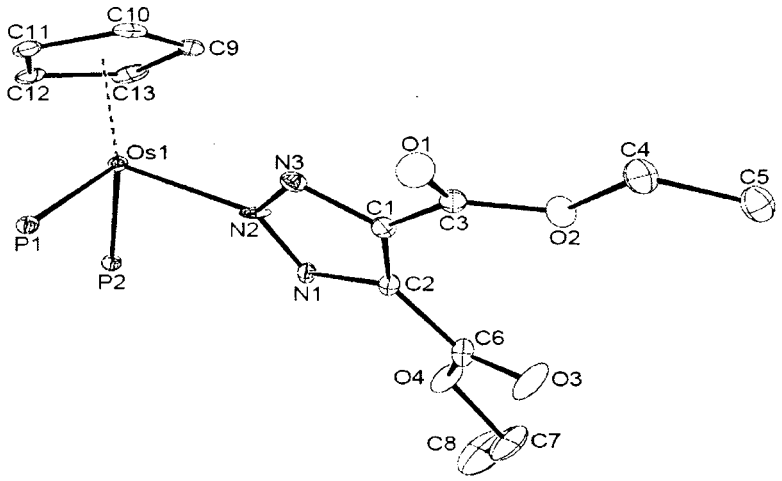


Figure 2.9: ORTEP diagram of complex 4 with 30% probability thermal ellipsoids displayed with out phenyl groups of phosphines and H atoms being omitted for clarity.

2.9.7 *Single-crystal X-ray structures analyses*

Crystals suitable for X-ray diffraction study was grown by slow diffusion of diethylether into dichloromethane solution of the complex **4**. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (α = 0.71069 Å) at a temperature of 143 K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 410 rotation images were collected with a crystal to detector distance of 35 mm, a 2 α swing angle of -12°, rotation widths of 0.5° and exposures of 20 seconds. Rotation images were processed using Crystal Clear [23] producing a listing of unaveraged F^2 and α (F^2) values which were then passed to the crystal structure [24] program package for further processing and structure solution on a Dell Pentium III computer. A total of 21130 reflections were measured over the ranges $5.08 \leq 2\theta \leq 54.98$ °, $-15 \leq h \leq 16$, $-26 \leq k \leq 32$, $-17 \leq l \leq 17$ yielding 9051 unique reflections (R_{int} = 0.0193). The

intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB [23] (minimum and maximum transmission 0.836, 1.000). The structure was solved by direct methods (SIR97) [25]. Refinement was by full-matrix least squares based on F^2 using SHELXL-97 [26]. All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2)+ 0.0112P^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to R_1= 0.0214 and wR_2 = 0.0387 for 7407 reflections for which $F > 4\sigma(F)$ and R_1 = 0.0286, wR_2=0.0404 and GOF = 0.914 for all 9051 unique, non-zero reflections and 535 variables. The maximum Δ/σ in the final cycle of least squares was 0.003 and the two most prominent peaks in the final difference Fourier were +1.579 and -0.923 e/Å^3. Crystallographic details are summarized in table 2.1. The figure 2.8 and 2.9 were drawn with ORTEP -II [27] representation of the molecule with 30 % probability thermal ellipsoids displayed.

2.9.8 Concluding remarks: This study described the 1,3-dipolar addition of [(η^5-C_5H_5)Os(PPh_3)$_2N_3$] complex with activated alkynes and nitriles to generate cyclopentadienyl osmium triazolato and tetrazolato complexes in spite of complex having bulky triphenylphosphine groups. Where as its analogue ruthenium complexes [(η^5-C_5H_5)Ru(PPh_3)$_2N_3$] and [(η^5-*indenyl*)Ru(PPh_3)$_2N_3$] do not undergo such type of addition reaction, this could be due to bulkiness of triphenylphosphine. It may be due to the larger size of the osmium atom in compared to its analogue ruthenium yielded these complexes. Unlike *p*-cymene ruthenium triazolato complexes, central nitrogen atom of triazolato ring is bonded to the osmium metal in these complexes. *These reactions*

indicated that size of the central metal atom played a very important role in 1,3 dipolar-cycloaddition reaction. Another fascinating point is that in contrast to ruthenium complexes, the less steric complexes of the type $[(\eta^5\text{-}C_5H_5)Os(dppe)N_3]$ and $[(\eta^5\text{-}C_5H_5)Os(dppm)N_3]$ complexes did not undergo cyclo-addition reactions with diethylacetylenedicarboxylate and dimethylacetylene dicarboxylate, investigation is under process.

Table 2.1: Summary of structure determination for $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3C_2(CO_2C_2H_5)_2]$ **(4).**

Empirical formula	$C_{49}H_{45}N_3P_2O_4Os$
CCDC. Number	649330
Formula weight	992.02
Temperature (K)	143 K
Crystal system, space group	Monoclinic, $P2_1/n$ (no.14)
Unit cell dimensions	
a (Å)	12.4947(7)
b (Å)	24.8362(13)
c (Å)	13.7755(8)
β (°)	99.558(2)
Volume ($Å^3$)	4215.5(4)
μ	31.50 cm^{-1}
Z	4
Calculated density (mg/cm^3)	1.563
Radiation Å	Mo-kα (λ=0.71069)

F (000)	1992
Crystal size (mm^3)	0.35 x 0.20 x 0.18
hkl collected	$-15\leq h\leq 16;-26\leq k\leq 32;-17\leq l\leq 17$
No. reflections measured	21130
No. unique reflections	9051
(R_{int} = 0.0193)	7407
No. observed reflections (F> 4σ)	535
Completeness to 2 θ (%)	5.08-54.98
Data/restraints/parameters	535
Goodness-of-fit on F^2	0.914
R_1 [I>2σ(I)], wR_2	R_1= 0.0214, wR_2= 0.0387
R_1, R_2 (all data)	R_1= 0.0286, wR_2= 0.0404
Largest diff. peak and hole ($eÅ^{-3}$)	+1.579-0.923

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$

$$GOF = \{\sum w (F_o^2 - F_c^2)^2 / (n - p)\}^{1/2}$$

Where, n = the number of reflections and p = the number of parameters refined.

Table 2.2: Selected bond lengths and angles of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2N_3C_2(CO_2C_2H_5)_2]$ **(4)**

Os(1)- P(2) 2.3263(6)	N(1)-N(2)-N(3) 114.9(2)
N(1)-N(2) 1.302(3)	N(3)-N(2)-Os(1) 118.20(14)
N(2)-N(3) 1.343(3)	N(1)-N(2)-Os(1) 126.7(2)
N(1)-Os(1) 2.078(3)	N(2)-N(3)-C(1) 104.8(2)

N(3)-C(1) 1.343(3)	N(2)-Os(1)-P(1) 87.11(6)
N(1)-C(2) 1.346(3)	N(2)-Os(1)-P(2) 92.19(5)
C(1)-C(3) 1.502(4)	Os(1)-N(2) 2.110(2)
C(2)-C(6) 1.478(3)	P(1)-Os(1)-P(2) 102.77(2)
Os(1)-Centroid of Cp 1.66	

References

1. M. A. Bennett, K. Khan, E. Wenger, in: *Comprehensive Organometallic Chemistry (II),* Elsevier, Oxford, 7 (1995) Ch. 8, 473 and references cited in.
2. B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem. Int. Ed.*, 44 (2005) 6630.
3. M. I. Bruce, F. S. Wong, *J. Organomet. Chem.*, C5 (1981) 210; (b) M. I. Bruce, M. G. Humphrey, G. A. Koutsantonis, M. J. Liddell, *J. Organomet. Chem.*, 247 (1987) 326; (c) D. A. Freedman, T. P. Gill, A. M. Blough, R. S. Koefod, K. R. Mann, *Inorg. Chem.*, 36 (1997) 95.
4. M. I. Bruce, N. J. Windsor, *Aust. J. Chem.*, 30 (1977) 1601; (b) W. A. Hermann, E. Herdtweck, A. Schäfer, *Chem. Ber.*, 121 (1988) 1907.
5. P. Crochet, M. A. Esteruelas, A. M. López, N. Ruiz, J. I. Tolsa, *Organometallics.* 17 (1998) 3479.
6. (a) H. W. Fruhäuf, *Chem. Rev.*, 97 (1997) 523; (b) Z. Dori, R. F. Ziolo, *Chem. Rev.* 73 (1973) 247.
7. D. Moderhack, *J. Prakt. Chem.*, 340 (1988) 687.

8. H. Singh, A. S. Chawla, V. K. Kapoor, D. Paul, R. K. Malhotra, *Prog. Med. Chem.*, 17 (1980) 151.

9. M. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bome, Proc. Int. *Pyrotech. Semi.*, *27* (2000) 3.

10. E. Szocs, I. Bako, T. Kosztolanyi, Bertoti, E. Kalman, *Electrochem. Acta., 49* (2004) 1371.

11. L. Busetto, A. Pallazzi, R. Ros, *Inorg. Chim. Acta.*,13 (1975) 233; (b) W. Rigby, P. M. Bailey, J. A. Mc Cleverty, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* 1979, 371; (c) R. B. Silverman, D. Dolphin, *J. Am. Chem. Soc.* 98 (1976) 4626.

12. (a) W. Beck, W. P. Fehlhammer, *Angew. Chem., Int. Ed,. Engl.*, 6 (1967) 169; (b) P. M. Treichel, W. J. Knebel, R. W. Hess, *J. Am. Soc.* 93 (1971) 5424; (c) W. Beck, K. Burger, W. P. Fehlhammer, *Chem. Ber.*, 104 (1971) 1816; (d) W. P. Fehlhammer, T. Kemmerich, W. Beck, *Chem. Ber.*, 112 (1979) 468.

13. T. Kammerich, J. H. Nelson, N. E. Takach, H. Boeheme, B. Jablonski, W. Beck, *Inorg. Chem.*, 21 (1982) 1226.

14. (a) P. Paul, K. Nag, *Inorg. Chem.*, 26 (1987) 2969; (b) T. Kammerich, J. H. Nelson, N. E. Takach, H. Boeheme, B. Jablonski, W. Beck, *Inorg. Chem.*, 21 (1982) 1226; (c) L. Busetto, A. Pallazzi, R. Ros, *Inorg. Chim. Acta.*, 13 (1975) 233; (d) T. Kammerich, W. Beck, C. Spencer, R. Z. Mason, Naturforch, B: *Inorg. Chem., Org. Chem., Biochem., Biophs., Biol.*, 27B (1972) 745.

15. P. H. Kreutzer, J. C. Weis, H. Bock, J. Erbe, W. Beck, *Chem. Ber.*, 116 (1983) 2691.

16. Chao-Wan Chang, Gene-Hsiang Lee, *Organometallics,* 22 (2003) 3107.

17. K. Sarjit Singh, K. A. Kreisel, G. P. A. Yap, K. Mohan Rao, *J. Organomet. Chem.*, 691(2006) 3509; (b) K. Sarjit Singh, C. Thöne, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 4222; (c) K. Sarjit Singh, K. A. Kreisel, G. P. A. Yap, K. Mohan Rao, *J. Coord. Chem.*, 60 (2007) 505.

18. (a) J. H. Nelson, D. L. Schmitt, R. A. Henty, D. W. Moore, H. B. Janassen, *Inorg. Chem.*, 9 (1970) 2678; (b) R. L. Kieft, W. M. Peterson, G. L. Blundell, S. Horton, R. A. Hendry, H. B. Jonasson, *Inorg. Chem.*, 15 (1976) 1721.

19. A. Palazzi, S. Stagni, S. Bordoni, M. Monari, S. Selva, *Organometallics*. 21(2002) 3774; (b) K. Koguro, T. Oga, S. Mitsui, R. Orita, *Synthesis*. (1998) 910; (c) Z. P. Demko, K. B. Sharpless, *J. Org. Chem.*, 66 (2001) 7954.

20. P. Paul, S. Chakladar, K. Nag, *Inorg. Chim. Acta.*, 27 (1990)170.

21. (a) P. W. Wanandi, T. D. Tilley, *Organometallics*. 16 (1997) 4299; (b) M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887; (d) R. Lalrempuia, P. J. Carroll, K. Mohan Rao, *Polyhedron* 22 (2003) 1301; (e) S. A. Westcott, A. K. Kakkar, G. Stringer, J. Taylor, T. B. Marder, *J. Organomet. Chem.*, 394 (1990) 777; (f) R. Lalrempuia, H. Suante, H. P. Yennawar, K. Mohan Rao, *Polyhedron* 26 (2007) 867.

22. A. I. Vogel, "*A. I. Vogel text book of practical organic chemistry*" ELBS, Fourth Edition. (1984) 264.

23. Rigaku Corporation, 1999.

24. R. A. Jacobsen, 1994. Private Communication.

25. Altomare, A., M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, 32 (1999) 115.

26. Program for the Refinement of Crystal Structures, Sheldrick, G. M. 1997, University of Göttingen, Germany.

27. A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, C. K. Johnson. 1976. ORNL-5138.

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CHAPTER 3

Syntheses and spectral characterization of

$[(\eta^5\text{-}C_5H_5)Os(PPh_3)(N\cap N)]BF_4$ complexes

(N∩N) = Schiff's base ligands.

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Syntheses and spectral characterization of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(N\cap N)]BF_4$ complexes (N∩N) = Schiff's base ligands.

Abstract:

The reaction of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_3CN)]$ (**2**) with bi-dentate (N∩N) base ligands (L = $C_5H_4N_2$-CH=NC_6H_4-p-X)], [X = H, CH_3, OCH_3, Cl, NO_2] in dry methanol yielded cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(N\cap N)X]$ (N∩N = $C_5H_4N_2$-CH=NC_6H_4-p-X)]$^+$ {X = H, (**3**), X = CH_3, (**4**), X = OCH_3, (**5**), X = Cl, (**6**), X = NO_2, (**7**)}. The cationic complexes were isolated as BF_4 salts. These complexes were fully characterized on the basis of microanalyses, FT-IR and FT-NMR spectroscopy.

Keywords: Osmium(II), cyclopentadienyl, N-(pyrid-2-ylmethylene)phenylamines(2-PP); pentamethylcyclopentadienyl.

INTRODUCTION

Cyclopentadienyl ruthenium half sandwich complexes are the most extensively studied class of cyclopentadienyl chemistry among the transition metal complexes. The spectrum of reactivity and chemical properties to date for this system is remarkable, especially considering the limited number of synthetic precursors, *viz.*, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ [1]. The chemistry of these complexes is characterized by the ready displacement of one or both triphenylphosphine and chloride ligands which occur under mild conditions [2]. The electron rich metal center contributes to the stabilization of unusual ligands such as vinyllidines and allenylidines [3]. The steric interactions of the two triphenylphosphines ligands often leads to the displacement of either both the triphenylphosphine units or one of them along with chlorides to yield neutral or cationic complexes [4]. No reports are available on the reactions where all the three ligands are replaced. However, the corresponding analogues $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ chemistry have not been studied extensively due to lower kinetic labiality of the phosphines compared to its ruthenium. However, not much work has been carried out in the case of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ which could be due to lower kinetic labiality of the phosphines compared to its ruthenium analogues. For instance, in the case of ruthenium, the substitution of two triphenylphosphines by chelating diphos-ligands takes place readily in boiling benzene or toluene, whereas the same reaction requires boiling decalin for several hours in the case of its Osmium analogue [5]. Until recently far fewer studies had been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with chelating N, N'-donor bases [6]. But it was observed that the dissociation of the M-X bond takes

place at room temperature in polar solvents such as methanol for both the cases. We had recently reported that the reaction of η^6-arene ruthenium(II) and η^5-indenyl ruthenium(II) [7] with Schiff's base ligands. During the reactions involving the analogous pentamethylcyclopentadienyl or indenyl system, the product did not show evidence of binding of these organic ligands, simple coordination compound being formed instead. However, no reports are available in the literature for the analogous cyclopentadienyl osmium(II) Schiff's base complexes. In this paper, we would like to report the syntheses and characterization of new cationic cyclopentadienyl osmium(II) complexes with N∩N base ligands, *viz.*, various para-substituted N-(pyrid-2-ylmethylene)phenylamines (N∩N or 2-PP) because of their photochemical and catalytic activities [8]

Experimental

3.2 General remarks:

All reactions were carried out in distilled and dried solvents under dry nitrogen atmosphere. OsO_4 was purchased from Sd. Fine Chem. Limited and used as such. Pyridine-2-carbaldehyde (Fluka) was purchased and used as received. All ligands amines were reagent grade and distilled prior to use, while solid amines were used as such. Elemental analyses were performed in a Perkin-Elmer model 983 spectrophotometer, the sample were prepared as KBr pellets. The ^1H NMR spectra were recorded in $CDCl_3$ solvents (tetramethyl silane as the internal standard) on a Bruker ACF-400 spectrometer. ^{31}P $\{^1H\}$ NMR chemical shift were recorded relative to H_3P0_4 (85%). The ligands $C_5H_4N_2$-CH=C_6H_4-p-X (where X = H, CH_3, Cl, N0, OCH_3) were

prepared by known literature method. [9] The precursor complex [(η^5-C_5H_5)Os(PPh_3)$_2$Br] (**1**) is prepared by following the literature procedures [10].

3.2.1 Preparation of [(η^5-C_5H_5)Os(PPh_3)$_2$Br] (1).

An ample of OsO_4 (100 mg, 3.93 mmol) was broken in a flask containing HBr (47% w/v, 36 ml), and the red solution was refluxed for 2 h. The solution was reduced to 5 ml, methanol (20 ml) added, and the whole mixture was added rapidly to a stirred, boiling solution of triphenylphosphine (1370 mg, 52 mmol) in methanol (380 ml), followed immediately by a solution of freshly distilled cyclopentadiene (10 ml) in methanol, small volume of water also added via syringe. Refluxing the stirred dark red suspension for 18 h resulted in a colour change to orange. After cooling the resulting orange powder was filtered off, washed with ethanol (2 x 10 ml), water (2 x 10 ml), ethanol (2 x 10 ml) and light petroleum (2 x 10 ml), and dried under vacuum. The yellow filtrate was reduced in volume to a few milliliters and cooled for 2 hr in the refrigerator to separates the rest of the product.

Yield: 2.55 g (74%)

Melting point: 180-181°C

^{1}H NMR ($CDCl_3$, δ): 7.25 (m, 30H, Ph), 4.31 (s, 5H, C_5H_5).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): - 3.85 (s).

3.2.2. Preparation of [(η^5-C_5H_5)Os(PPh_3)$_2$(CH_3CN)]BF_4 (2)

A mixture of [(η^5-C_5H_5)Os(PPh_3)$_2$Br] (100 mg, 0.116 mmols) and NH_4BF_4 (25 mg, 0.24 mmol) was refluxed in acetonitrile (20 ml) under nitrogen atmosphere. The insoluble starting materials were slowly dissolved and the color changed to very pale yellow solution after one hour. The solvent was then evaporated under reduced pressure. The

residue was then extracted with acetone, filtered and the volume of the filtrate was reduced. Subsequently an addition of hexane yielded a cream colored product. The compound was recrystallised from dichloromethane-diethyl ether giving grey needle shaped crystals.

Yield: 86 mg, 82 %.

Elemental analyses (%) for $C_{43}H_{38}BF_4NP_2Os$: C, 56.89; H, 4.21; N, 1.54; found: C, 56.88; H, 4.20; N, 1.59.

IR (KBr): 2282 (m, $\nu_{C\equiv N}$), 1082 ($\nu_{B\text{-}F}$).

^{1}H NMR {$CDCl_3$, δ}: 7.34 – 7.01(m, 30H, Ph), 4.56 (s, 5H, Cp); 2.41 (s, 3H, CH_3).

^{31}P {^{1}H} NMR, ($CDCl_3$ δ): 2.11 (s).

Synthesis of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(N\cap N)]BF_4$ (3-7)

N∩N or 2-PP = $C_5H_5N_2$-CH=N-C_6H_4-p-X

X = H (**3**), CH_3 (**4**), OCH_3 (**5**), Cl (**6**), NO_2 (**7**).

The following general procedure was used for the preparation of these five complexes:

Mixture of the starting complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_3CN)]BF_4$ (100 g, 0.112 mmols), the appropriate Schiff's base ligands (N∩N or 2-PP) (40 g, 0. 224 mmol) and NH_4BF_4 was refluxed in methanol (40 ml) under dry nitrogen atmosphere whereby the orange yellow color suspension gradually changed to a dark red solution. The mixture was refluxed *ca.* 12 hr, and the solvent was evaporated in rotary evaporator under

reduced pressure. The residue was dissolved in dichloromethane and filter through a short silica gel column to remove insoluble materials. The filtrate was again concentrated to about 2 ml, whereupon addition of excess hexane gave the desired complexes (**3-7**) as dark brown solids. The solids was washed with diethyl ether and dried under vacuum to afford 56-60 % yield of the complexes.

Complex [(η^5-C_5H_5)Os(PPh_3)($C_5H_5N_2$-CH=N-C_6H_4-p-H)]BF_4 [3]BF_4

Elemental analysis (%) for $C_{35}H_{30}N_2OsPBF_4$: C, 49.9; H, 3.6; N, 3.34; found: C, 50.2; H, 3.9; N, 3.04

IR (KBr pellets, cm^{-1}): 1587 ($\nu_{C=N}$); 1084 (ν_{B-F}).

^1H NMR ($CDCl_3$, δ): 4.66 (s, 5H, C_5H_5); 8.31 (d, J_{H-H} = 5.00 Hz, 1H); 8.15 (d, J_{H-H} = 5.65 Hz, 1H of Py), 6.80 - 7.49 (m, 23H);

^{31}P {^1H} NMR ($CDCl_3$, δ): 2.25 (s).

Complex [(η^5-C_5H_5)Os(PPh_3)($C_5H_5N_2$-CH=N-C_6H_4-p-CH_3)] BF_4 [4]BF_4

Elemental analysis (%) for $C_{36}H_{33}N_2OsPBF_4$: C, 50.5; H, 3.9; N, 3.3; found: C, 50.00; H, 3.24, N, 3.87

IR (KBr pellets, cm^{-1}): 1593 ($\nu_{C=N}$); 1089 (ν_{B-F}).

^1H NMR ($CDCl_3$, δ): 3.59 (s, 3H, CH_3); 4.66 (s, 5H, C_5H_5); 7.05 (d, J_{H-H} = 4.8 Hz,1H); 7.01- 7.83 (m, 22H); 8.45 (d, J_{H-H} = 5.00 Hz, 1H of Py).

^{31}P {^1H} NMR ($CDCl_3$, δ): 2.50 (s).

Complex [(η^5-C_5H_5)Os(PPh_3)($C_5H_5N_2$-CH=N-C_6H_4-p-OCH_3)]BF_4 [5]BF_4

Elemental analysis (%) for $C_{35}H_{30}N_2OsOPBF_4$: C, 49.54; H, 3.78; N, 3.21; found: C, 49.83; H, 3.28; N, 3.76

IR (KBr pellets, cm^{-1}): 1590 ($\nu_{C=N}$); 1084 (ν_{B-F}).

^1H NMR ($CDCl_3$, δ): 3.69 (s, 3H, OCH_3), 4.66 (s, 5H, C_5H_5); 7.45 (d, J_{H-H} = 5.18 Hz, 1H); 7.58- 7.89 (m, 22H); 8.45 (d, J_{H-H} = 5.00 Hz, 1H of Py).

^{31}P {^1H} NMR ($CDCl_3$, δ): 2.45 (s).

Complex [(η^5-C_5H_5)Os(PPh_3)($C_5H_5N_2$-CH=N-C_6H_4-p-Cl)]BF_4 [6]BF_4

Elemental analysis (%) for $C_{35}H_{30}N_2OsClPBF_4$: C, 47.89; H, 3.31; N, 3.33; found: C, 47.06; H, 3.92; N, 3.71.

IR (KBr pellets, cm^{-1}): 1602 ($\nu_{C=N}$), 1084(ν_{B-F})

^1H NMR ($CDCl_3$, δ): 4.91 (s, 5H, C_5H_5); 9.15 (d, J_{H-H} = 5.18 Hz, 1H)

8.16 (d, J_{H-H} = 5.00 Hz, 1H of Py); 7.18 - 7.38 (m, 22H);

^{31}P {^1H} NMR ($CDCl_3$, δ): 2.05 (s).

Complex [(η^5-C_5H_5)Os(PPh_3)($C_5H_5N_2$-CH=N-C_6H_4-p-NO_2)]BF_4 [7]BF_4

Elemental analysis (%) for $C_{35}H_{30}N_3OsOPBF_4$: C, 47.35, H; 3.38; N, 4.73; found: C, 47.01; H; 3.82, N, 5.05.

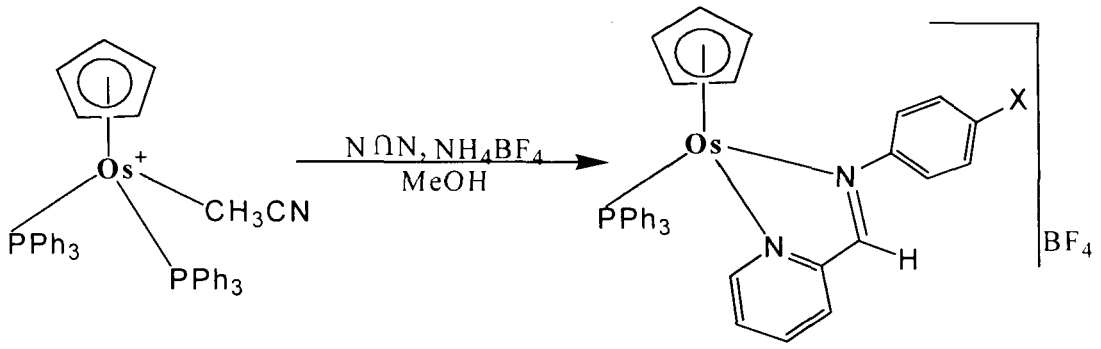
IR (KBr pellets, cm^{-1}): 1604 ($\nu_{C=N}$), 1084 (ν_{B-F})

^{1}H NMR ($CDCl_3$, δ): 4.65 (s, 5H, C_5H_5); 6.64 (d, J_{H-H} = δ4.8Hz, 1H); 7.01- 7.33 (m, 22H); 8.06 (d, J_{H-H} = 5.2 Hz, 1H of Py).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 2.32 (s).

3.3 Results and discussion

The synthetic reaction of the cyclopentadienyl complexes **3-7** with an excess of N, N'- donor Schiff's base ligands, *viz.*, N∩N or 2-PP, in dry methanol under dry nitrogen atmosphere refluxing condition resulted in the formation of dark-red colored compounds which is an air stable cationic complexes of the type [(η^5-C_5H_5)Os(PPh_3)(C_5H_5N-2-CH=N-C_6H_4-*p*-X)]BF_4 (X = H (**3**), CH_3 (**4**), OCH_3 (**5**), Cl (**6**), NO_2 (**7**) (Scheme 3.1) by dissociation of one of the triphenylphosphine and chloride ligands. Here, we would like to highlight that the substitution of two triphenylphosphines by chelating diphos ligands takes place readily in boiling decalin or toluene for several hours. But it was observed that the dissociation of the M-X bond takes place readily in polar solvents such as methanol [11]



N ∩N = N-(pyrid-2-ylmethylene)phenylamine
X = H, CH_3, OCH_3, Cl, NO_2

Scheme 3.1

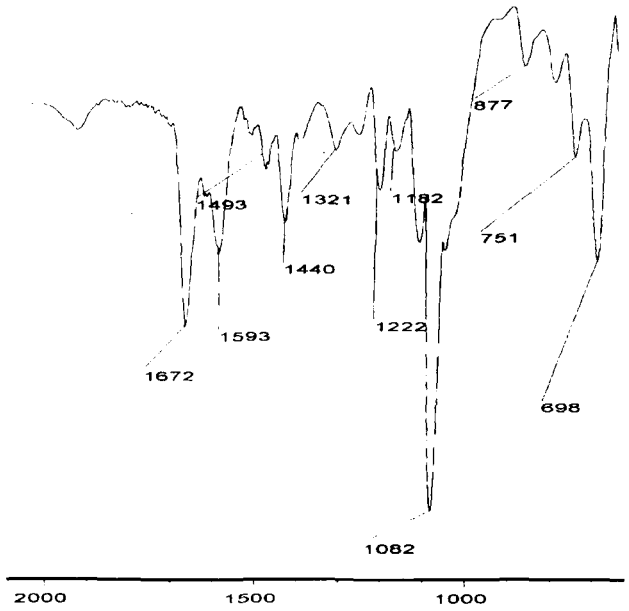


Figure 3.2: Infrared spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}H)]BF_4$

[3]BF_4

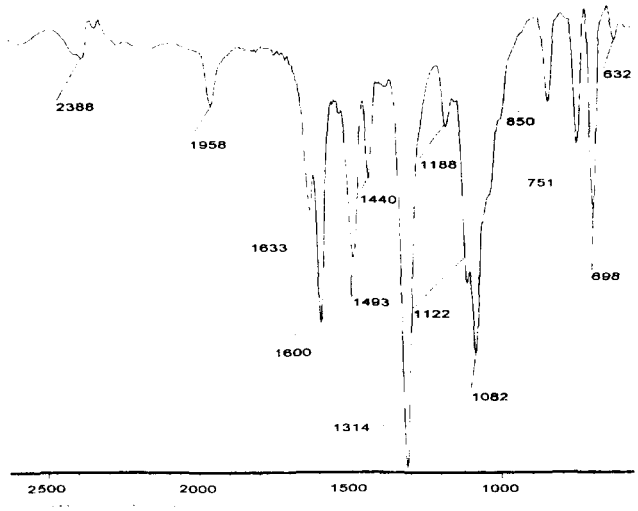


Figure 3.1: IR- spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]BF_4$

[7]BF_4

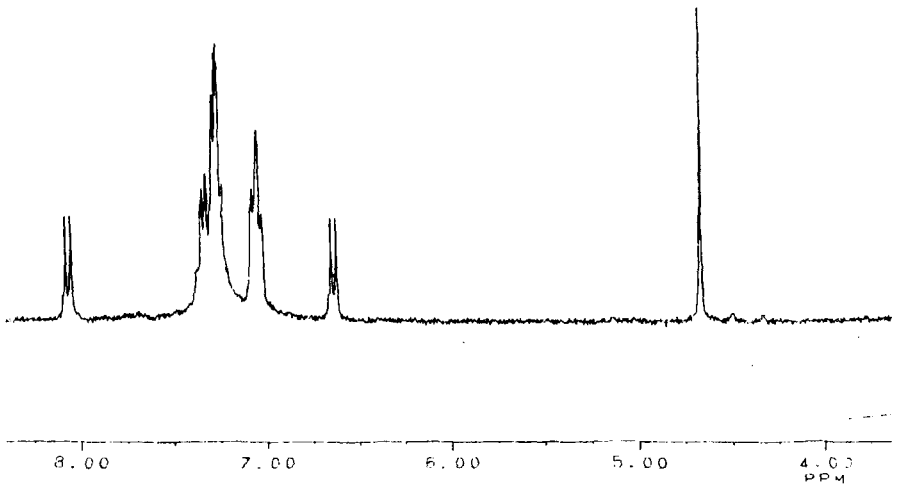


Figure 3.3: ^{1}H {NMR} spectrum of $[(\eta^{5}\text{-}C_5H_5)Os(PPh_3)(C_5H_4N_2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]BF_4$

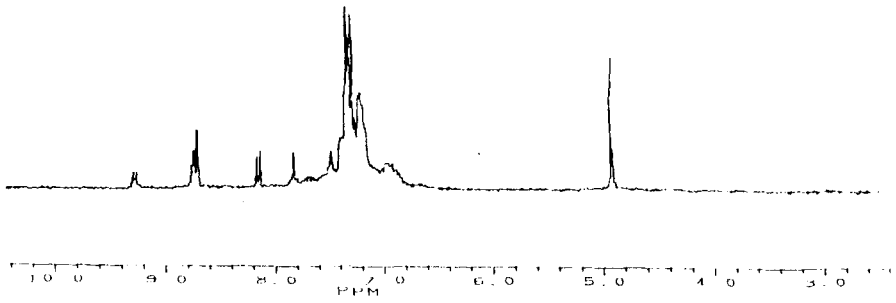


Figure 3.4: ^{1}H NMR spectrum of $[(\eta^{5}\text{-}C_5H_5)Os(PPh_3)(C_5H_4N_2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}OCH_3)]BF_4$ **[5]**BF_4

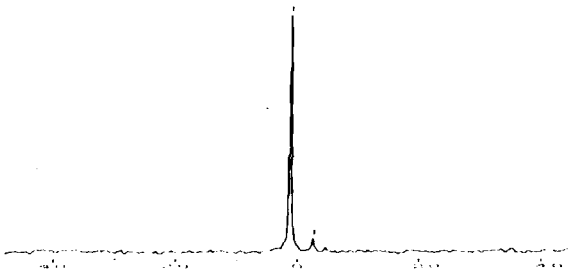


Figure 3.5: ^{31}P {NMR} spectrum of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(C_5H_4N_2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}Cl)]BF_4$ [**6**]BF_4

The complexes (**3-7**) are highly soluble in polar solvents such as chloroform, dichloromethane, acetone, acetonitrile *etc.*, but insoluble in non-polar solvents such as hexane, pentane *etc*. These complexes were characterized by using analytical, infrared (IR), proton (^1H) NMR and phosphorus (^{31}P) NMR spectroscopic techniques. C, H, N analyses, Infrared, ^1H and ^{31}P NMR spectroscopic data given in experimental parts support the formulation of these complexes (**3-7**). The infrared spectra of all these complexes shows a strong bands due to phenyl groups of triphenylphosphines, $\nu_{C=N}$ group of the Schiff's base ligands at around 1580 cm^{-1} and BF_4 exhibited strong band for $\nu_{B\text{-}F}$ in the range of 1082-1089 cm^{-1} respectively. In addition, complex $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]BF_4$ (**7**) shows the characteristic bands for ν_{NO2} (asymmetric stretch at 1493 cm^{-1} and symmetric stretch 1314 cm^{-1}). The infrared spectra of the representative complexes **3** and **7** were shown in figures 3.1 and 3.2. The proton NMR spectra of these complexes are presented in fig 3.3 to 3.7. The cyclopentadienyl ring protons displayed a sharp singlet at 4.65 ppm - 4.80 ppm. The downfield shift of cyclopentadienyl ligand from the starting complex (4.56 ppm)

indicates that cationic nature of these complexes after substituting one tri-phenylphosphine and CH_3CN group with N-donor ligands. The presence of Cyclopentadienyl, triphenylphosphine and N∩N ligand in a 1:1:1 ratio is inferred from the areas obtained upon peak integration of the ^1H NMR spectra. A doublet observed in the range 8.5 ppm-7.9 ppm is assigned to the ortho-proton of the pyridine ring of the ligand (N∩N), a triplet observed in the range 6.85 -7.30 ppm corresponds to the meta-proton and para-proton of the pyridine ring of the ligand (N∩N). The methine protons displayed a doublet in the range 6.6 - 7.0 ppm. The ^{31}P NMR spectra of these complexes (**3-7**) exhibit a single sharp resonance for triphenylphosphine in the range of 2.05 - 2.50 ppm, whereas the starting complexes $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_3CN)]BF_4$ [**2**]BF_4 exhibits at 2.11 ppm as a singlet for triphenylphosphine indicating the cationic nature of these complexes **3-7**. The ^1H NMR and ^{31}P $\{^1H\}$ NMR spectrums of complex [**3**] as the representative complexes is shown in figure 3.4. On the basis of spectral studies the following structure was proposed:

3.4 Conlusions: The reaction of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2(CH_3CN)]BF_4$ [**2**]BF_4 with Schiff's base *viz.*, para-substituted N-(2-pyridinylmethylene)cyclohexylamine (N∩N or 2-PP) yielded cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(C_5H_4N_2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)]BF_4$ resulting from the substitution of CH_3CN and one triphenylphosphine.

References

1. (a) M. A. Bennett, K. Khan, E. Wenger, in G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds.), *Comprehensive Organometallics Chemistry*, Ch. 8, Vol.7, 2nd ed., Elsevier, Oxford, (1995) 473; (b) S. G. Davies, J. P. McNally, A. J. Smallridge, *Adv. Organomet. Chem.*, 30 (1991) 1; (c) M. I. Bruce, C. Hameister, A. G. Swincer, R. C. Wallis, *Inorg. Synth.*, 21(1982) 78.

2. T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc.*, A (1971) 2376.

3. (a) G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem.*, 32 (1979) 1003; (b) S. G. Davies, S. J. Simpson, H. Felkin, T. Fillebeen-Khan, *Organometallics* 2 (1983) 539; (c). S. G. Davies, S. J. Simpson, H. Felkin, T. Fillebeen-Khan, F. Tadjand O. Watts, *J. Chem. Soc., Chem. Commun.*, (1981), 341.

4. M. I. Bruce, S. F. Wong, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.*(1981) 1398.

5. R. Lalrempuia, P. J. Carroll, K. Mohan Rao, *Polyhedron* 22 (2003) 1391.

6. D. L. Davies, J. Fewcett, R. Krafczyk, D. R. Russel, *J. Organomet. Chem.*, 545 (1997) 581

7. Sarjit Keisham Singh, Yurij A. Mozharivskyj, Patrick J. Carroll, K. Mohan Rao, *J. Organomet. Chem.*, 689 (2004) 1249.

8. (a) F. Teixidor, R. Garcia, J. Pons, J. Casabo. J. *Polyhedron* 7 (1998) 43; (b) J.

Casabo, J. Pons, K. S. Siddiqi, F. Teixidor, E. Molins, C. Miravitles. *J. Chem. Soc.*, Dalton Trans. (1989) 1401; (c) R. Levine, J. K. Sneed. *J. Am. Chem. Soc.* 73 (1951) 5614.

9. (a) R. N. Dominey, B. Hauser, J. Hubbard, J. Dunham, *Inorg. Chem.*, 30 (1991) 4754; (b) E. V. Dose, L. J. Wilson, *Inorg. Chem.*, 17 (1978) 2660.

10. M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887.

11. (a) T. Wilczewski, M. Bchenska, J. F. Biernat, *J. Organomet. Chem., 87 (1981) 215; (*b) T. Wilczewsk, *J. Organomet. Chem., 224 (1982) C1;* (c) T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc.* (A) (1971) 2376.

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CHAPTER 4

Syntheses and characterization of ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes containing cyclichydrocarbons and 3,5-bis(2-pyridyl)pyrazole(Hbpp) as a Ligands.

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Syntheses and characterization of ruthenium(II), osmium(II), rhodium(III) and iridium (III) complexes containing η^5-cyclichydrocarbons and 3,5-bis(2-pyridyl)pyrazole (Hbpp) as a ligands.

Abstract

The compound $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X= Cl (**1**); M = Os, X = Br (**2**)}, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2X]$ (**3**) and $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ {M = Rh(III) (**4**) and Ir(III) (**5**)} reacts with N,N'-donor chelating ligand *viz.*, 3,5-bis(2-pyridyl)pyrazole (Hbpp) in methanol to afford the cyclopentadienyl ruthenium and osmium complexes of the type $[(\eta^5\text{-}C_5H_5)M(Hbpp)(PPh_3)]PF_6$ (M = Ru(II) (**6**); M = Os(II) (**7**); and pentamethyl - cyclopentadienyl ruthenium, rhodium and iridium complexes of the type $[(\eta^5\text{-}C_5Me_5)Ru(Hbpp)(PPh_3)]$ (**8**) and $[(\eta^5\text{-}C_5Me_5)M(Hbpp)Cl]PF_6$ where M = Rh(III) (**9**) and Ir(III) (**10**) respectively. These compounds were characterized by FT-IR and FT-NMR spectroscopy as well as analytical data. The molecular structures of the hexaflourophosphate salts of $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)(PPh_3)]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl]^+$ (**10**) were established by single X-ray diffraction studies.

Keywords: Pentamethylcyclopentadienyl, cyclopentadienyl, rhodium and iridium complexes, 3, 5-bis(2-pyridyl)pyrazole(Hbpp)

4.1 INTRODUCTON

The chemistry of transition metal complexes having pentamethylcyclopentadienyl and cyclopentadienyl ruthenium(II) complexes have been mainly considered as useful model compounds and have been successfully employed as catalyst in a series of C-C bond forming reaction [1]. Similarly, ligand substitution reactions of pentamethylcyclopentadienyl rhodium and iridium complexes [2] are of considerable importance, especially in view of the utility of these complexes for many types of reactions [3]. The dimeric chloro bridged complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) display some rich chemistry by cleavage of the chloro-bridge, leading to the formation of a series of interesting neutral and cationic mononuclear complexes [4]. Many studies of cyclopentadienyl ruthenium(II) complexes with bidentate ligands have shown that substitution reaction at the metal centre [5].We had already reported that the syntheses and characterization of cationic complexes of cyclopentadienyl ruthenium(II) [6], osmium(II) [7], pentamethylcyclopentadienyl ruthenium(II), rhodium(III) and iridium(III) [8] with a variety of nitrogen based ligands, principally because these complexes and its derivatives have generated a lot of interest due to their high reactivity [9] and catalytic activity [10].

As a part of our continuing study, we here report on complexes of cyclopentadienyl ruthenium(II), osmium(II) and pentamethylcyclopentadienyl ruthenium(II), osmium(II), rhodium(III) and iridium(III) with tetradentate N,N'-donor ligand *viz.*, 3,5-bis(2-pyridyl)pyrazole (Hbpp). The 3,5-bis(2-pyridyl)pyrazole (Hbpp) transition metal complexes are associated with extremely interesting considered as water oxidation catalyst [11]. This ligand has been acting as a bidentate as well as tetradentate

depends on the ratio of metal to ligand. The molecular structures of representative compounds are solved by X-ray crystallography and are reported as well.

4. 2. Experimental

4.2.1 Physical measurements

Elemental analyses were performed on a Perkin-Elmer-2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The ^1H NMR spectra were recorded on a Bruker ACF-300 (300 MHz) spectrometer in $CDCl_3$ solvents with TMS as internal reference. All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents. Ruthenium trichloride, iridium trichloride, rhodium trichloride and osmium tetraoxide (OsO_4) were purchased from Arora Matthey Ltd and Aldrich. The 3,5-bis(2-pyridyl)pyrazole (Hbpp) was prepared by following a literature procedure [12]. The precursor's complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ [13], $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ [14], $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$, $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ [15] and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ [16] were prepared by following the reported literature methods.

4.2.2 Preparation of [CpM(Hbpp)(PPh$_3$)]PF$_6$ {M = Ru [6]PF$_6$, Os [7]PF$_6$}

A mixture of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X = Cl (**1**) and M = Os, X = Br (**2**)} (100 mg, 0.11 mmol), 3,5-bis(2-pyridyl)pyrazole (Hbpp) (49 mg, 0.22 mmol) and NH_4PF_6 (36 mg, 0.22 mmol) in dry methanol (15 ml) were refluxed under dry nitrogen for 8 hrs until the colour of the solution changed from pale yellow to orange. The solvent were removed under vacuum, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium halide. The orange solution was

concentrated to 5 ml, when addition of excess diethylether gave the orange-yellow complex, which was separated and dried under vacuum.

Complex $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)(PPh_3)]PF_6$ [6]PF_6

Yield: 75 mg, 68.4%

Elemental Anal (%) Calc. for $C_{36}H_{30}N_4P_2F_6Ru$: C 54.3; H 3.7; N 7.1; found: C 54.87; H 4.13; N 7.94.

IR (KBr pellets, cm^{-1}): 3429 ($\nu_{N\text{-}H}$); 1460 ($\nu_{C\text{-}N}$); 850 ($\nu_{P\text{-}F}$);

^1H NMR ($CDCl_3$, δ): 4.75 (s, 5H, C_5H_5); 7.1 (t, 1H, CH of Pz); 7.2 (t, 1H, CH of Py); 7.3 (t, 1H, CH of Py); 7.5 (t, 1H of Py); 7.7 (t, 1H,CH of Py); 7.85 (t, 1H, CH of Py); 8.6 (d, $J_{H\text{-}H}$ = 4.53Hz, 1H, α-proton of Py); 9.3 (d, $J_{H\text{-}H}$ = 4.97Hz, 1H, α-proton of Py); 11.8 (s, 1H, NH of Pz).

Complex $[(\eta^5\text{-}C_5H_5)Os(Hbpp)(PPh_3)]PF_6$ [7]PF_6

Yield: 65 mg, 66.7%.

Elemental Anal (%) Calc. for $C_{36}H_{30}N_4P_2F_6Os$: C 48.9; H 3.4; N 6.3; found: C 49.2; H 3.91; N 6.87

IR (KBr pellets, cm^{-1}): 3425 ($\nu_{N\text{-}H}$); 1474 ($\nu_{C\text{-}N}$); 850 ($\nu_{P\text{-}F}$);

^1H NMR ($CDCl_3$, δ): 4.69 (s, 5H, C_5H_5); 6.9 (t, 1H, CH of Pz); 7.1 (t,1H,CH of Py); 7.3 (t, 1H,CH of Py); 7.4 (t,1H,CH of Py); 7.6 (t, 1H,CH of Py); 7.7 (t,1H,CH of Py); 8.4 (d, $J_{H\text{-}H}$ = 5.0Hz,1H, α-proton of Py); 8.9 (d, $J_{H\text{-}H}$ = 5.2Hz, 1H, α-proton of Py);12.23 (s, 1H, NH of Pz).

4.2.4 Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(Hbpp)(PPh_3)]PF_6$ [8]PF_6

A mixture of $[(\eta5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), 3,5-bis(2-pyridyl)pyrazole (Hbpp) (56 mg, 0.25 mmol) and NH_4PF_6 (40 mg, 0.25 mmol) in dry

methanol (15 ml) were refluxed under dry nitrogen for 12 hrs until the colour of the solution changed from pale yellow to orange. The solvents were removed in rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The orange solution was concentrated to 5 ml, when addition of excess hexane gave the orange-yellow complex, which was separated and dried under vacuum.

Yield: 70 mg, 64.3%.

Elemental Anal (%) Calc. for $C_{41}H_{45}N_4P_2F_6Ru$: C 56.6; H 5.2; N 6.4; found: C 57.0; H 5.9; N 6.8

IR (KBr pellets, cm^{-1}): 3424(ν_{N-H}); 1613 ($\nu_{C=N}$); 850(ν_{P-F}).

^1H NMR ($CDCl_3$, δ): 1.45 (s, 15H, C_5Me_5); 6.89 (t, 1H, CH of Pz); 7.1 (t, 1H, CH of Py); 7.28 (t, 1H,CH of Py); 7.6 (t, 1H, CH of Py); 7.8 (t, 1H, CH of Py); 8.5 (d, J_{H-H} = 3.42Hz, 1H, α-proton of Py); 8.7 (d, J_{H-H} = 4.5Hz, 1H α-proton of Py), 11.92 (s, 1H, NH of Pz)

4.2.5 Preparation of [(η5-C_5Me_5)M(Hbpp)Cl]PF_6 {M = Rh (9), Ir (10)}

A mixture of [(η^5-C_5Me_5)M(μ-Cl)Cl]$_2${M = Rh (**9**), Ir (**10**)} (100 mg, 0.162 mmol), 3,5-bis(2-pyridyl)pyrazole (Hbpp) (70 mg, 0.325 mmol) and NH_4PF_6 (50 mg, 0.325 mmol) in dry methanol (15 ml) were stirred at room temperature for 6 hrs until the colour of the solution changed from pale yellow to pale green. The solvents were removed in rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (5 ml), and the solution filtered to remove ammonium chloride. The pale green solution was concentrated to 2 ml, when addition of excess hexane gave the orange-yellow complex, which was separated and dried under vacuum.

Complex [9] PF6: Yield: 70 mg, 76%.

Elemental Anal (%) Calc. for $C_{23}H_{25}N_4PClF_6Rh$: C 37.8; H 3.4; N 7.7; found: C 38.0; H 3.9; N 7.0

IR (KBr pellets, cm^{-1}): 3426 (ν_{N-H}); 1612 ($\nu_{C=N}$); 850 (ν_{P-F});

^1H NMR ($CDCl_3$, δ): 1.48 (s, 15H, C_5Me_5); 7.2 (t, 1H, CH of Pz); 7.4 (t, 1H, CH of Py); 7.5.7 (t, 1H, CH of Pz); 8.0 (t, 1H, CH of Py); 8.2 (t, 1H, CH of Py); 8.6 (d, J_{H-H} = 3.42 Hz, 1H, α-proton of Py); 8.9 (d, J_{H-H} = 4.8 Hz, 1H, α-proton of Py),11.80 (s, 1H, NH of Pz)

Complex [10] PF6: Yield: 68 mg, 74.1%.

Elemental Anal (%) Calc. for $C_{23}H_{25}N_4ClPF_6Ir$: C 43.1; H 3.9; N 8.7; found: C 43.6; H 4.2; N 8.0.

IR (KBr pellets, cm^{-1}): 3429 (ν_{N-H}); 1613 ($\nu_{C=N}$); 850 (ν_{P-F});

^1H NMR ($CDCl_3$, δ):1.45 (s, 15H, C_5Me_5); 7.2 (t, 1H, CH of Pz); 7.4 (t, 1H, CH of Py); 7.5 (t, 1H, CH of Py); 8.24 (t, 1H, CH of Py); 8.45 (t, 1H, CH of Py); 8.58 (d, J_{H-H} = 3.42 Hz, 1H, α-proton of Py); 8.75 (d, J_{H-H} = 4.8 Hz, 1H, α-proton of Py), 11.86 (s, 1H, NH of Pz)

4. 3. Results and discussion

The cyclopentadienyl and pentamethylcyclopentadienyl ruthenium(II), cyclopentadienyl osmium(II) reacted with 3,5-bis(2pyridyl)pyrazole (Hbpp) in the presence of ammonium hexaflorophosphate in methanol to form the mononuclear cationic pentamethylcyclopentadienyl ruthenium and cyclopentadienyl osmium complexes having the general formula $[CpM(Hbpp)PPh_3]^+$ {Cp = C_5H_5, M = Ru (**6**); Cp = C_5H_5, M = Os (**7**); Cp* = C_5Me_5, M = Ru (**8**)} (Scheme 4.1). The complexes are

orange yellow colored; they are non-hygroscopic, air stable, crystalline solids. They are soluble in polar solvents like methanol, dichloromethane, chloroform, acetone *etc.*, but insoluble in hexane, petroleum ether and diethylether.

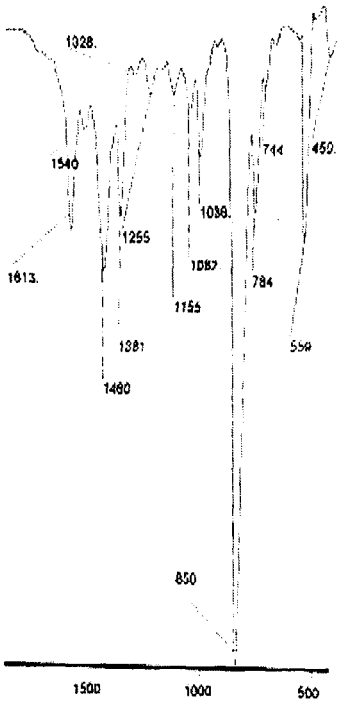


Figure 4.1: Infrared spectrum of $[(\eta^5\text{-}C_5Me_5)\ Rh\ (Hbpp)Cl]PF_6$ [**9**]PF6

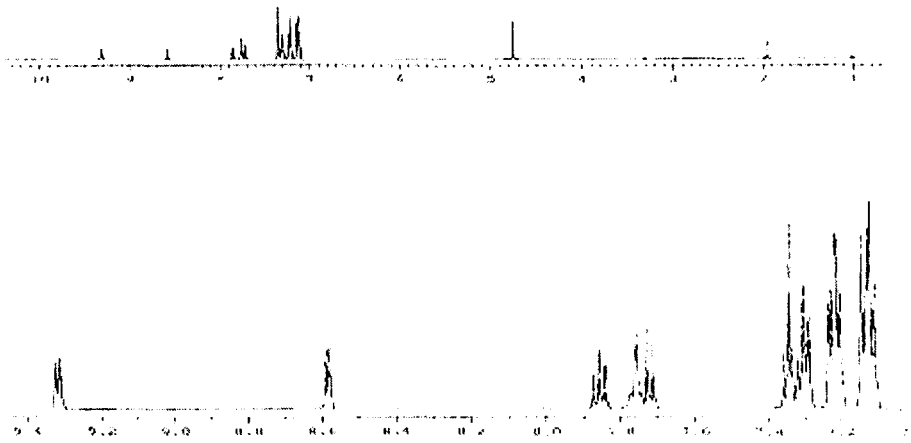


Figure 4.2: ^{1}H NMR spectrum of [(η5-C_5H_5)Ru(Hbpp)PPh_3]PF_6 [**6**]PF_6

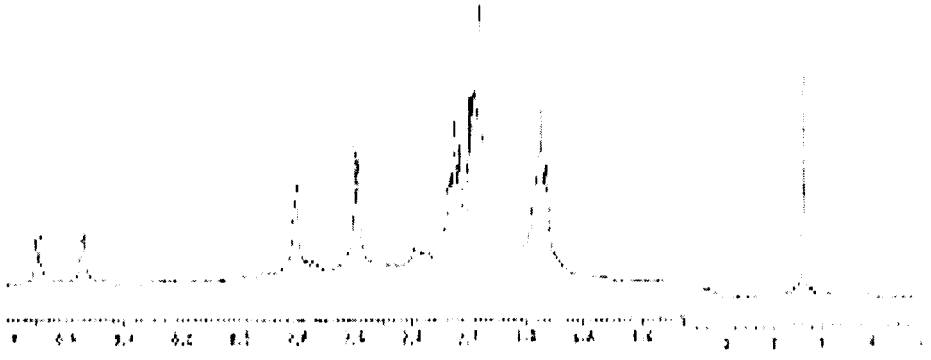
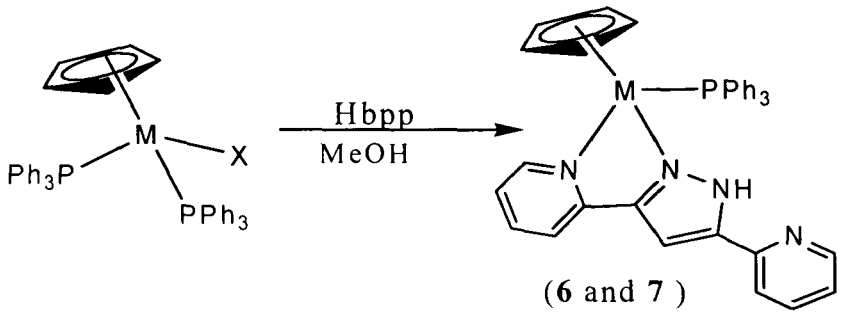


Figure 4.4: ^{1}H NMR spectrum of [(η5-C_5Me_5)Ru(Hbpp)PPh_3]PF_6 [**8**]PF_6

4.3.1 Cyclopentadienyl ruthenium [6]PF_6 and osmium complexes [7]PF_6

The analytical data of these compounds are consistent with the formulations. The infrared spectra of the complexes **6** and **7** exhibit a chelated N,N'-bidentate ligand as

strong bands at 3429 cm^{-1}, 3425 cm^{-1}, 1460 cm^{-1} and 1474 cm^{-1} corresponding to the stretching frequencies of N-H bond of pyrazole ring and C-N bond of the pyridine ring of the ligand. In addition, the infrared spectra contained a strong band at 850 cm^{-1} due to the stretching frequency of P-F bond for both the complexes. The proton NMR spectra of these complexes **6** and **7** exhibit a singlet at 4.75 and 4.69 ppm for the cyclopentadienyl ring protons, indicating a downfield shift from the starting complex **1** and **2**. Downfield shift in the position of cyclopentadienyl protons might result from a change in electron density on the metal centre due to chelation of the 3, 5-bis(2-pyridyl)pyrazole (Hbpp) ligand through it nitrogen atoms. The 3, 5-bis(2-pyridyl)pyrazole (Hbpp) protons of the complexes **6** and **7** showed singlet at the range of 6.9 and 7.1 ppm corresponding to the CH proton of pyrazole. The spectra also display five triplets in the range of 7.1-7.85 ppm corresponding to the CH-protons of pyridine groups of the ligand. The spectra also showed two doublets in the range of 8.4 - 9.3 ppm corresponding to the α-proton of pyridine group of the ligand for these complexes (Figure 4.2). In addition, singlet peak observed at the range of 11.8 - 12.23 ppm corresponding to the N-H proton of pyrazole ring for both the complexes.



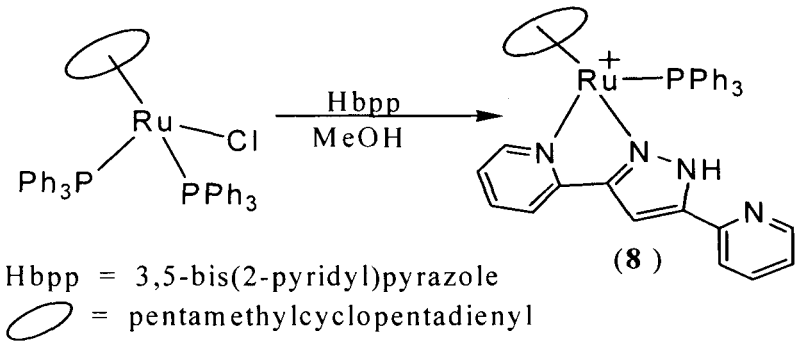
(**6** and **7**)

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

Scheme 4.1

4.3.2 Pentamethylcyclopentadienyl ruthenium complex [8]PF_6

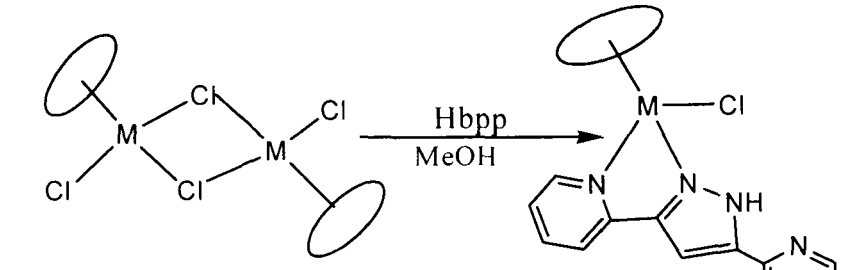
The 3,5-bis(2-pyridyl)pyrazole (Hbpp) ligand reacted with the pentamethylcyclopentadienyl ruthenium(II) complexes in presence of hexafluorophosphate counter ion, in methanol to yield mononuclear cationic complex **8** (scheme 4.2). The complex is orange coloured, crystalline solids, soluble in polar solvents and air stable. The infrared spectrum displays a sharp singlet at 3424 cm^{-1}, 1613 cm^{-1} and 850 cm^{-1} corresponding to the stretching frequencies of N-H bond of the pyrazole ring, C-N bond of the pyridine ring and P-F bond of the counter ion of the complex. The proton NMR spectrum displays singlet peak at 1.45 ppm corresponding to the CH proton of the pentamethylcyclopentadienyl ring and four triplets were observed in the range of 7.1 ppm to 7.8 ppm corresponding to the CH protons of the pyridine group. In addition, singlet peak appeared at 11.92 ppm due to the NH proton of the pyrazole ring of the ligand (Figure 4.4).



Scheme 4.2

4.3.3 Pentamethylcyclopentadienyl rhodium [9]PF_6 and iridium complexes [10]PF_6

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ {M = Rh (**9**) or Ir (**10**)} undergo a bridge cleavage reaction with N,N'-bidentate nitrogen base (Hbpp) ligand in methanol at room temperature to yield cationic complexes **5** and **6** (Scheme 4.3). These complexes are isolated as the hexaflourophosphate salts. The orange-yellow complexes are air stable, dissolved in polar solvents but in soluble in hexane, petroleum ether and diethylether. The complex **9** showed a pale green coloured when it's in solution form. The infrared spectra of the complexes **9** and **10** exhibit a chelated N,N'-bidentate ligand as strong bands at 3426, 1612, 3429 and 1613 cm^{-1} corresponds to the stretching frequencies of C-N bond of pyridine group and N-H bond of pyrazole ring [17]. In addition, the infrared spectra contain a strong band at 850 cm^{-1} due to the counter ion PF_6. The proton NMR spectra of compounds **9** and **10** displays singlet at 1.48 and 1.45 ppm corresponding to the protons of the pentamethylcyclopentadienyl group. The five triplets were observed in the range of 7.0-8.0 ppm corresponding to the proton of pyrazole and pyridine group. Another two doublets were observed at the range of 8.0 - 8.7 ppm due to the α-proton of pyridine. In addition, the spectra displays singlet at the range of 11.80 – 11.86 ppm corresponding to the NH-proton of the pyrazole ring.



(**9** and **10**)

= pentamethylcyclopentadienyl

Hbpp = 3,5-bis(2-pyridyl)pyrazole

M = Rh(III) or Ir(III)

Scheme 4.3

4.4. Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for compound [**6**]PF_6 and [**10**]PF_6 were grown by slow diffusion of diethylether into dichloromethane solution of complexes [**6**]PF_6, and [**10**]PF_6 respectively. The bright orange crystals of compound [**6**]PF_6 and pale green crystal of compound [**10**]PF_6 were mounted on a Stoe-Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0-200°, increment of 1.2°, D_{max}-D_{min} = 12.45-0.81 Å. X-ray intensity data were collected with Mo-Kα graphite monochromated radiation at 120 (2) K, with 0.3°ω scan mode and 10 second per frame. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [18]. Refinement and all further calculations were carried out using SHELXL-97 [19]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

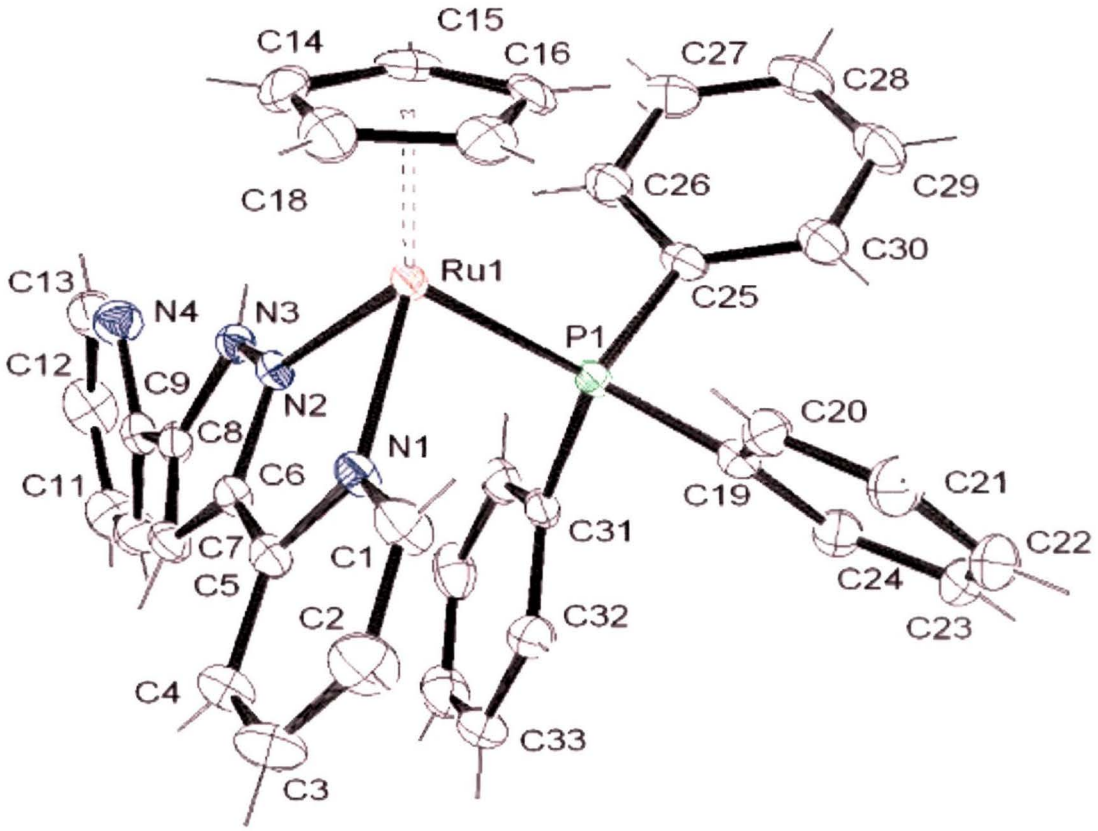


Figure 4.5: ORTEP drawing with labelling scheme at 50% probability level, [**6**]PF_6 anion omitted for clarity. Selected bond distances (Å) and angles (°) are N1-Ru1 2.188(2); N2-N3 1.342(3); P1-Ru12.311(7); C(14)-C(18) 1.398(5); N3-N2-Ru1 135.69(15); N2-Ru-N75.56(8); N2-Ru1-P1 89.93(6); N1-Ru1-P1 89.87(6).

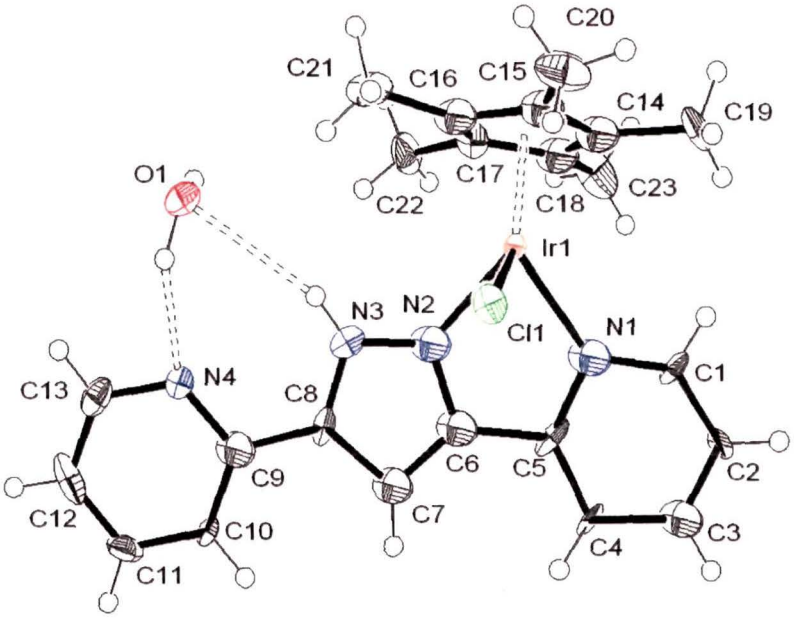


Figure 4.6: ORTEP drawing with labelling scheme at 50% probability level, [**10**]PF_6 anion omitted for clarity. Selected bond distances(Å) and angles(°) are N(1)-Ir(1) 2.07(8); N(2)-Ir(1) 2.01(5); N(2)-N(3) 1.37(8); Cl(1)-Ir(1) 2.398(17); N(3)-N(2)-Ir(1) 135(4); N(2)-Ir(1)-N(1) 77(2); N(2)-Ir(1)-Cl(1) 83.1(15); N(1)-Ir(1)-Cl(1) 87.9(15).

4.5 Molecular structure

Single crystals X – ray structure determination were carried out for compound **6** and **10** for confirmation of their formulae and structure. The ruthenium atom of compound **6** and the iridium atom of compound **10** are coordinated to two nitrogen atoms of the 3,5-bis(2-pyridyl)pyrazole (Hbpp) ligand, chlorine atom and the cyclopentadienyl and pentamethylcyclopentadienyl molecule in a η^5-fashion where one triphenylphosphine in the case of complex **6** and leading to the usual "three-legged piano stool" structures. The geometry around the metal atom can be regarded as distorted octahedral if the η^5-cyclopentadienyl and pentamethylcyclopentadienyl

moieties are assumed to occupy three facial-coordinated positions. A summary of single crystal X – ray structure analyses are shown in Table 4.1. The ORTEP drawing of compounds **6** and **10** are shown in Figs 4.5 and 4.6 respectively.

The hexaflourophosphate salt of complex $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)PPh_3]$ $[PF_6]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl][PF_6]$ (**10**) crystallizes in the monoclinic space group (Figs 4.5 and 4.6). The average bond distances of Ru-C (compound **2**) and Ir-C(**6**) of cyclopentadienyl group is 2.190 Å and 2.140Å. There are no significant differences in the C-C bond lengths in the pentamethylcyclopentadienyl ring, all being about 1.337Å and pointing to π-electron delocalization in the ring. Further more; the five membered ring is planar as evident in the nearly equal bond distances between metal atom and the ring carbons. The Ru-N and Ir-N bond distances are 2.188(2) Å and 2.07(8) Å. Here, we observed that the bond distance of Ru-N is longer than the bond distance of Ir-N, this could be due to the size of the metal atom. The Ir-Cl bond distance is 2.398 Å, which is closely to another related two-coordinated chelating N,N'-base ligands iridium and rhodium complexes.

4.6. Concluding remarks:

The reaction of 3,5-bis(2-pyridyl)pyrazole(Hbpp) ligand with pentamethyl-cyclopentadienyl and cyclopentadienyl ruthenium, osmium, rhodium and iridium complexes yielded cationic complexes. The complexes may able to bind with another metal to form dinuclear complexes through the nitrogen atom, which is not carried out in this work.

Table 4.1. Crystal data and experimental details for $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)PPh_3][PF_6]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl][PF_6]$ (**10**)

Compund	[(η5-C_5Me_5)Ir(Hbpp)Cl][PF_6](**10**)	(η^5-C_5H_5)Ru(Hbpp)PPh_3][PF_6](**6**)
Empirical formula	$C_{23}H_{27}ClF_6IrN_4OP$	$C_{36}H_{30}F_6N_4P_2Ru$
Formula weight	748.11	795.65
Temperature	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, P $2_1/n$
Unit cell dimensions		
a (Å)	8.7598(10)	8.7598(10)
b (Å)	13.9029(16)	13.9029(16)
c (Å)	13.706(2)	17.1718(12)
β(°)	129.184(10)	129.184(10)
Volume (A^3)	293.8(3)	3280.1(4)
Z, Calculated density (Mg/m^3)	2, 1.920	4,1.611
Absorption coefficient (mm^{-1})	5.393	0.644
F(000)	728	1608
Crystal size(mm)	0.42 x 0.38 x 0.24	0.42 x 0.38 x 0.24
θ range for data collection (deg) .	1.46 to 34.82	2.09 to 26.00

Index ranges	-10<=h<=10,-13<=k<=13,-20<=l<=20	-16<=h<=16,-17<=k<=17,-21<=l<=21
Reflections collected / unique [R_{int} = 0.2224]	9464 / 4814	25474/6310
Refinement method(F^2)	Full-matrix least-squares on	
Completeness to 2 θ (°)	34.82, 44.8	26.00, 97.8
Data/restraints/parameters	4814/ 2 /339	6310/0/442
Goodness-of-fit on (F^2)	2.390	1.108
Final R indices [I>2σ(I)]	R1=0.1886, wR2=0.4351	R1=0.0324, wR_2=0.0854
R indices (all data)	R1=0.2292, wR2= .4720	R1=0.0414, wR_2= 0.0940
Absolute structure parameter	0.60(10)	
Largest diff. peak and hole(A^{-3})	18.211 and -9.924	0.662 and -1.640

References

1. B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.*, 101 (2001) 2067; V. Guerchais, *Eur. J. Chem.*, (2002) 783.
2. J. W. Kang, P. M. Maitlis, *J. Organomet. Chem.*, (1981) 101.
3. A. H. Janowicz, R. G. Bergman. J. Am. Chem. Soc., 104 (1982) 352; *ibid*, 105 (1983) 3929.
4. (a) E. Carmona, A. Cingolani, F. Marchetti, C. Pettinari, R. Pettinari, B.W. Skelton, A. H. White, *Organometallics*. 22 (2003) 2820.
5. (a) Y. Inoguchi, B. Milewski Marla, H. Schmidbauer, *Chem. Berichte.*, 115 (1982) 3085; (b) M. M. Olmstead, A. Maisonnat, J. P. Farr, A.L. Balch, *Inorg. Chem.*, 20 (1981) 4060.
6. D. Drommi, C. Arena, F. Nicolo, G. Bruno, F. Faraone, *J. Organomet. Chem.*, 485 (1995) 115.
7. P. Govindaswamy, Y. A. Mozharivskyj, K. Mohan Rao, *J. Organomet. Chem.*, 689 (2004) 3265.
8. P. Govindaswamy, Y. A. Mozharivskyj, K. Mohan Rao, *Polyhedron* 24 (2005) 1710.
9. M. A. Bennett, K. Khan, E. Wenger, in: *Comprehensive Organometallic Chemistry (II),* Elsevier, Oxford, 7 (1995) Ch. 8, 473 and references cited in
10. B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem. Int. Ed.*, 44 (2005) 6630.
11. C. Sens, I. Romero, M.Rodriguez, A. Llobet, T. Parella, J. Benet-Buchholz, *J. Am. Chem. Soc.*, 126 (2004) 7798.

12. (a) F. Teixidor, R. Garcia, J. Pons, J. Casabó. *Polyhedron* 7 (1988) 43; (b) J. Pons, F. J. Sánchez, X. López, F. Texidor, J. Casabó. *Polyhedron.* 9 (1990) 2839.

13 (a) M. I. Bruce, N. J. Windsor, Aust. J. Chem., 30 (1977) 1601; (b) G. Consiglio, F. Morandini, *Chem. Rev.*, 87 (1987) 761.

14. (a) P. W. Wanandi, T. D. Tilley, *Organometallics*. 16 (1997) 4299; (b) M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887.

15. J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.*, 91 (1969) 5970; (b) C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.*, 29 (1992) 228.

16. M. I. Bruce, N. J. Windsor, *Aust. J. Chem.*, 30 (1977) 1601; (b) M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887.

17. P. Govindaswamy, Chittaranjan Sinha, K. M. Rao, *J. Organomet. Chem.*, 690 (2005) 3465.

18. M. Sheldrick, *Acta Cryst.* A 46 (1990) 467.

19. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany (1999).

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CHAPTER 5

Reactivity Studies of Cyclopentadienyl Ruthenium(II), Osmium(II) and Pentamethyl-cyclopentadienyl Iridium(III) Complexes Towards 2-(2'-Pyridyl)Imidazole Derivatives

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Reactivity studies of cyclopentadienyl ruthenium (II), osmium (II) and pentamethylcyclopentadienyl iridium(III) complexes towards 2-(2'-pyridyl)imidazole derivatives.

Abstract

The reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ with chelating 2-(2'-pyridyl)imidazole (N∩N) ligands and NH_4PF_6 yields cationic complexes of the type $[(\eta^5\text{-}C_5H_5)M(N\cap N)(PPh_3)]^+$ (**1**: M = Ru, N∩N = 2-(2'-pyridyl)imidazole; **2**: M = Ru, N∩N = 2-(2'-pyridyl)benzimidazole; **3**: M = Ru, N∩N = 2-(2'-pyridyl)-4,5-dimethylimidazole; **4**: M = Ru, N∩N = 2-(2'-pyridyl)-4,5-diphenylimidazole; **5**: M = Os, N∩N = 2-(2'-pyridyl)imidazole; **6**: M = Os, N∩N = 2-(2'-pyridyl)benzimidazole). They have been isolated and characterized as their hexafluorophosphate salts. Similarly, in the presence of NH_4PF_6, $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ reacts in dry methanol with N∩N chelating ligands to afford in excellent yield $[(\eta^5\text{-}C_5Me_5)Ir(N\cap N)Cl]PF_6$ (**7**: N∩N = 2-(2'-pyridyl)imidazole; **8**: N∩N = 2-(2'-pyridyl)benzimidazole). All the compounds have been characterized by infrared and NMR spectroscopy and the molecular structure of [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6 by single-crystal X-ray structure analysis.

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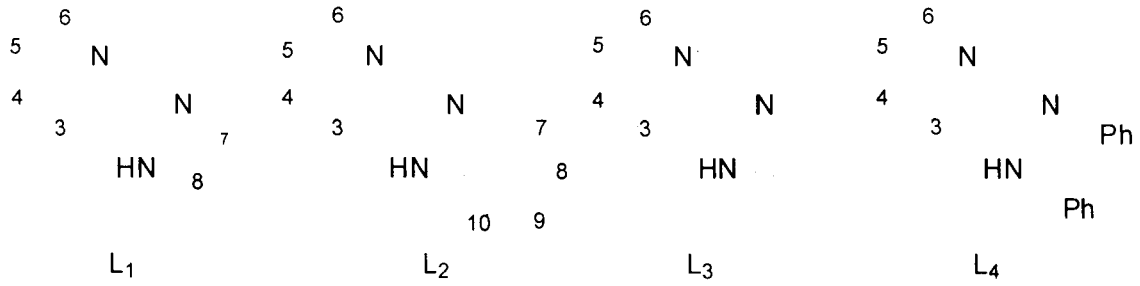
5.1 Introduction

The chemistry of cyclopentadienyl bisphosphine ruthenium complexes [(η^5-C_5H_5)$Ru(PPh_3)_2X$] is the family of an area of active research [1] due to their high reactivity and catalytic activities [2-3]. These properties have prompted widespread interest regarding both the synthetic applications and the mechanistic features of cyclopentadienyl complexes for a large number of transition metals. Similarly, there is an increasing interest in the organometallic chemistry of osmium as the nature of the differences from its lighter congener ruthenium becomes more apparent [4]. However, the complex [(η^5-C_5H_5)$Os(PPh_3)_2Br$] chemistry have not been studied extensively due to lower kinetic labiality of the triphenylphosphines compared to its ruthenium analogue [5]. Until recently far fewer studies had been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with chelating N∩N-donor bases [6]. The chemistry of [(η^5-C_5H_5)$Ru(PPh_3)_2Cl$] is characterized by facile displacement of either chloride or one or both triphenylphosphine ligands, affording cationic or neutral compounds, respectively, depending on the solvent and reaction conditions [7]. The electron rich metal center contributes to the stabilization of unusual ligands such as vinyllidines and allenylidines [8]. We had reported that the reactions of cyclopentadienyl ruthenium (II), [(η^5-C_5Me_5)$Ru(PPh_3)_2(CH_3CN)$]$^+$ and [(η^5-C_9H_7)$Ru(PPh_3)_2(CH_3CN)$]$^+$ [9] with a variety of nitrogen based ligands. In this paper, as a part of our continuing study, we would like to report the syntheses and characterization of new cationic cyclopentadienyl (Cp) ruthenium(II), osmium(II) and pentamethylcyclopentadienyl (Cp*) iridium(III) complexes with chelating N∩N-donor ligands [L_1 = 2-(2'-pyridyl)imidazole, L_2 = 2-(2'-pyridyl)benzimidazole, L_3 = 2-(2'-

pyridyl)-4,5-dimethylimidazole, L_4 = 2-(2'-pyridyl)-4,5-diphenylimidazole) (Scheme 5.1). In order to confirm the nature of bonding, the molecular structures of $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})imidazole\}(PPh_3)]PF_6$ ([**1**]PF_6), $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})benzimidazole\}\text{-}(PPh_3)]PF_6$ ([**2**]PF_6) and $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})imidazole\}Cl]PF_6$ ([**7**]PF_6) have been solved by x-ray crystallography.



Scheme 5.1: Ligands and numbering scheme used in this study.

5.2. Experimental

Elemental analyses were performed on a Perkin-Elmer-2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The ^1H NMR spectra were recorded on a Bruker ACF-300 (300 MHz) spectrometer in $CDCl_3$ solvents with TMS as internal reference. All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents. Ruthenium trichloride, iridium trichloride and osmium tetraoxide were purchased from Arora Matthey Ltd and Aldrich. The 2-(2'-pyridyl)imidazole and its derivatives were prepared by following a literature procedure [10]. 2-(2'-Pyridyl)benzimidazole (Aldrich), pyridine-2-aldehyde (Fluka), glyoxal (Aldrich), 2,3-butanedione (Aldrich) and benzyl (Sd Fine) were used as received. The precursor's complexes $[(\eta^5\text{-}$

$C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ [11] and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ [12] were prepared by following the reported literature methods.

5.2.1. *Synthesis of $[(\eta^5\text{-}C_5H_5)Ru(N\cap N)(PPh_3)]PF_6$*

The following general procedure was used for the preparation of complexes [1]PF_6 to [4]PF_6.

Preparation of [**1**]PF_6: A mixture of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (0.1 g, 0.14 mmol), 2-(2`-pyridyl)imidazole (0.04, 0.28 mmol) and NH_4PF_6 (0.046 g, 0.28 mmol) was refluxed in dry methanol (20 ml) under a nitrogen atmosphere for 6 hrs. The yellow suspension turns to a light yellow color. The solvent is evaporated at reduced pressure. Then the residue was dissolved in dichloromethane (5 ml), and the solution filtered to remove ammonium chloride. The yellow solution was concentrated (2 ml) and by addition of an excess of hexane the orange yellow product precipitates. The compound is filtered and dried under vacuum to give [**1**]PF_6.

Complex $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})imidazole\}(PPh_3)]PF_6$ [1]PF_6

Yield: 63mg, 64 %.

Elemental Anal (%) Calc. for $C_{31}H_{27}N_3F_6P_2Ru$: C, 51.81; H, 3.76; N, 5.85.

Found: C, 51.54; H, 4.17; N, 5.44.

IR (KBr pellets, cm^{-1}): 1606 ($\nu_{C=C}$), 1480, 1440 ($\nu_{C=N}$), 857 (ν_{PF6}),

^1H NMR ($CDCl_3$, δ): 12.01 (s, 1H, NH); 9.04 (d, $J_{H\text{-}H}$ = 5.74 Hz, 1H, H_6); 8. 75 (d, $J_{H\text{-}H}$ = 6.08 Hz, H_7); 8.50 (d, $J_{H\text{-}H}$ = 6.02Hz, H_8); 8.00 (d, $J_{H\text{-}H}$ = 5.12 Hz, 1H, H_3); 7.78 (m, 15H, Ph); 7.70 (t, 1H, H_4); 7.32 (t, 1H, H_5); 4.68 (s, 5H, C_5H_5).

Complex [(η^5-C_5H_5)Ru{2-(2'-pyridyl)benzimidazole}(PPh_3)]PF_6 [2]PF_6

Yield: 65 mg, 62 %.

Elemental Anal (%), Calc. for $C_{35}H_{29}F_6P_2N_3Ru$: C, 54.69; H, 3.78; N, 5.47; found: C, 54.87; H, 4.12; N, 5.67.

IR (KBr pellets, cm^{-1}): 1613 ($\nu_{C=C}$), 1447 ($\nu_{C=N}$), 850 (ν_{P-F}),

^1H NMR ($CDCl_3$, δ): 8.74 (d, J_{HH} = 5.42Hz, 1H, H_6); 8.07 (d, J_{HH} = 5.80Hz, 1H, H_3); 7.98 (t, 1H, H_4); 7.90 (t, 1H, H_5); 7.48 (m, 15H, Ph); 7.32 (m, 4H H_{7-10}); 4.64 (s, 5H, C_5H_5).

***Complex [(η^5-C_5H_5)Ru{2-(2'-pyridyl)-4,5-dimethylimidazole}(PPh_3)]PF_6* [3]PF_6**

Yield: 64 mg, 62 %.

Elemental Anal. (%) Calc. for $C_{33}H_{31}F_6P_2N_3Ru$: C, 53.08; H, 4.16; N, 5.63; found: C, 53.28; H, 4.66; N, 5.77.

IR (KBr pellets, cm^{-1}): 1604 ($\nu_{C=C}$), 1480, 1447 ($\nu_{C=N}$); 855 (ν_{P-F}),

^1H NMR ($CDCl_3$, δ): 8.50 (d, J_{H-H} = 5.74Hz, 1H, H_6); 8.18 (d, J_{H-H} = 5.00 Hz, 1H, H_3); 7.53 (m, 15H, Ph); 7.39 (t, 1H, H_4); 7.28 (t, 1H, H_5); 4.67 (s, 5H, C_5H_5); 3.21 (s, 6H, CH_3).

Complex [(η^5-C_5H_5)Ru{2-(2'-pyridyl)-4,5-diphenylimidazole}(PPh_3)]PF_6 [4]PF_6

Yield: 70 mg, 60%.

Elemental Anal (%), Calc for $C_{43}H_{35}N_3P_2F_6Ru$: C, 59.31; H, 4.02, N, 4.83; found: C, 60.23; H, 4.23; N, 5.13.

IR (KBr pellets, cm^{-1}): 1600 ($\nu_{C=C}$), 1480, 1440 ($\nu_{C=N}$), 850 (ν_{P-F}),

^1H NMR ($CDCl_3$, δ): 8.50 (d, J_{H-H} = 5.0 Hz, 1H, H_6); 8.27 (d, J_{H-H} = 5.73 Hz, 1H, H_3), 7.92 (m, 25H, Ph); 7.60 (t, 1H, H_4); 7.37 (t, 1H, H_5); 4. 62 (s, 5H, C_5H_5)

5.2.2. *Synthesis of [(η^5-C_5H_5)M(N∩N)(PPh_3)]PF_6*

These complexes were prepared by the same method given in section 2.1 using of [(η^5-C_5H_5)Os(PPh_3)$_2$(CH_3CN)]PF_6 instead of [(η^5-C_5H_5)Ru(PPh_3)$_2$Cl].

Complex [(η^5-C_5H_5)Os{2-(2'-pyridyl)imidazole}(PPh_3)]PF_6 [5]PF_6

Yield: 48 mg, 57 %.

Elemental analysis (%) for $C_{31}H_{27}N_3P_2F_6Os$. Calc.: C, 46.09; H, 3.35; N, 5.21; found: C, 46.36; H, 4.03; N, 5.65.

IR (KBr pellets, cm^{-1}): 1600 ($\nu_{C=C}$), 1480, 1440 ($\nu_{C=N}$), 885 (ν_{P-F})

^{1}H NMR ($CDCl_3$, δ): 8.95 (d, J_{H-H} = 5.7 Hz, 1H, H_6); 8.78 (d, J_{H-H} = 6.05 Hz, 1H, H_3); 8.63 (d, J_{H-H} = 6.12Hz, 1H, H_7); 8.59 (d, J_{H-H} = 5.52Hz, 1H, H_8); 7.89 (m, 15H, Ph); 7.75 (t, 1H, H_4); 7.48 (t, 1H, H_5); 4.59 (s, 5H, C_5H_5).

Complex [(η^5-C_5H_5)Os{2-(2'-pyridyl)benzimidazole}(PPh_3)]PF_6 [6]PF_6

Yield: 46 mg, 52 %.

Elemental analysis (%) for $C_{35}H_{29}N_3P_2F_6Os$. Calc.: C, 49.01; H, 3.38; N, 4.90; found: C, 49.15; H, 3.56; N, 5.15.

IR (KBr pellets, cm^{-1}): 1613 ($\nu_{C=C}$), 1447 ($\nu_{C=N}$), 850 (ν_{P-F}).

^{1}H (NMR, $CDCl_3$, δ): 8.50 (d, J_{H-H} = 5.2Hz, 1H, H_6); 8.10 (d, J_{H-H} = 5.2Hz, 1H, H_3); 7.0-7.27 (m, 15H, Ph); 7.9 (t, 1H, H_4); 7.45 (t, 1H, H_5); 7.37 (q, 4H H_{7-10}); 4.65 (s, 5H, C_5H_5).

5.2.3. *Synthesis of [(η^5-C_5Me_5)Ir(N∩N)Cl]PF_6*

These complexes were prepared by the same method given in section 2.1 using 0.5 equivalent of [(η^5-C_5Me_5)Ir(μ-Cl)Cl]$_2$ instead of 1 equivalent of [(η^5-C_5H_5)M(PPh_3)$_2$Cl].

Complex [(η^5-C_5Me_5)Ir{2-(2'-pyridyl)imidazole}Cl]PF_6 [7]PF_6

Yield: 52 mg, 64 %.

Elemental Anal (%), Calc for: $C_{18}H_{22}ClN_3F_6PIr$. Calc.: C, 33.13; H, 3.37; N, 6.44; found: C, 32.87; H, 3.88; N, 6.23.

IR (KBr pellets, cm^{-1}): 1600 ($\nu_{C=C}$), 1460-1327 ($\nu_{C=N}$), 850 (ν_{P-F}),

^1H NMR ($CDCl_3$,δ): 8.94 (d, J_{H-H} = 6.4 Hz, 1H, H_6); 8.50 (d, J_{H-H} = 6.12 Hz, 1H, H_3); 8.00 (d, J_{H-H} = 6.03 Hz, 1H, H_7); 7.90 (d, J_{H-H} = 5.23 Hz, 1H, H_8); 7.73 (t, 1H, H_4); 7.43 (t, 1H, H_5); 1. 9 (s, 15H, C_5Me_5)

Complex [(η^5-C_5Me_5)Ir{2-(2'-pyridyl)benzimidazole}Cl]PF_6 [8]PF_6

Yield: 54 mg, 62 %.

Elemental Anal (%), Calc for: $C_{22}H_{24}ClN_3F_6PIr$. Calc.: C, 37.61; H, 3.42; N, 5.98. found: C, 37.52; H, 3.87; N, 6.15.

IR (KBr pellets, cm^{-1}): 1600 ($\nu_{C=C}$), 1474-1407 ($\nu_{C=N}$), 850 (ν_{P-F}),

^1H NMR ($CDCl_3$, δ): 8.97 (d, J_{H-H} = 5.63Hz, 1H, H_6); 8.90 (d, J_{H-H} = 5.29 Hz, 1H, H_3); 7.85 (t, 1H, H_4); 7.43 (t, 1H, H_5); 7.24 (m, 4H, $H_{7\text{-}10}$); 1.82 (s, 15H, C_5Me_5)

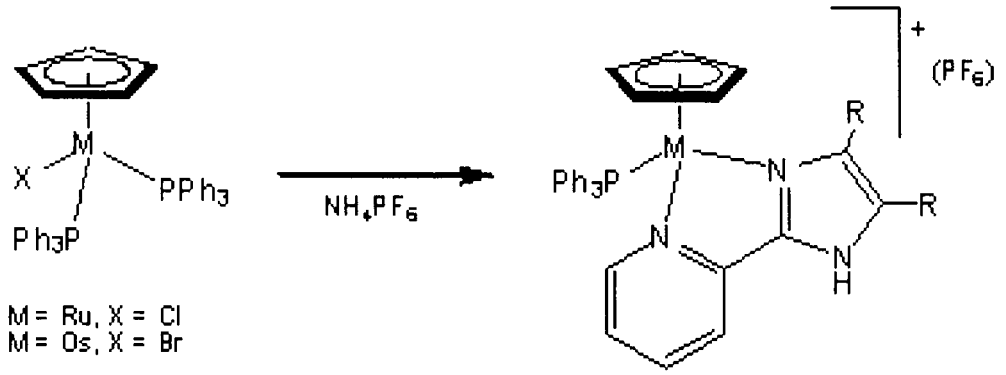
5.2.3. *Single-crystal X-ray structures analyses*

Crystal suitable for X-ray diffraction study for compound [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6 were grown by slow diffusion of diethylether into dichloromethane solution of complexes [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6, respectively. The orange reddish crystals of compound [**1**]PF_6 and [**7**]PF_6 were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0-200°, increment of 1.2°, D_{max}-D_{min} = 12.45-0.81 Å. Whereas crystal of [**2**]PF_6 was mounted on a Bruker Apex CCD diffractometer in a full

reciprocal sphere equipped with a CCD detector, X-ray intensity data were collected with Mo-Kα graphite monochromated radiation at 120 (2) K, with 0.3°ω scan mode and 10 second per frame. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [13]. Refinement and all further calculations were carried out using SHELXL-97 [14]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. In [**2**]PF_6 H_2O, the $-C_5H_4NC_3N_2H-$ fragment of the 2-(2'-pyridyl)benzimidazole was found to be disordered over two positions and the partial occupancy factor was refined at 76:24. Crystallographic details are summarized in Table 1. Figures 1, 2 and 4 are drawn with ORTEP32 [15] while Figures 3 and 5 are drawn with MERCURY [16].

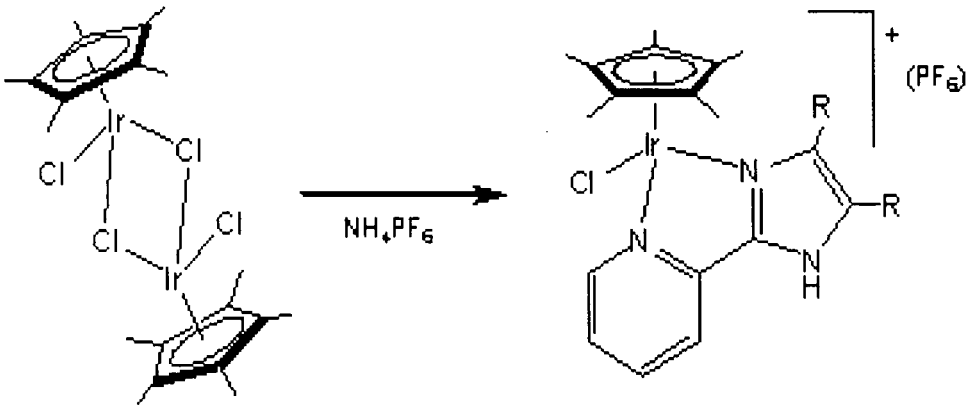
5.3. Results and discussion

The reactions in dry methanol of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ with an excess of chelating N∩N ligands and NH_4PF_6 result, under refluxing conditions, in the dissociation of one triphenylphosphine and the halide ligands to yield the monocationic complexes $[(\eta^5\text{-}C_5H_5)M(N\cap N)(PPh_3)]^+$ (**1**: M = Ru, N∩N = 2-(2'-pyridyl)imidazole; **2**: M = Ru, N∩N = 2-(2'-pyridyl)benzimidazole; **3**: M = Ru, N∩N = 2-(2'-pyridyl)-4,5-dimethylimidazole; **4**: M = Ru, N∩N = 2-(2'-pyridyl)-4,5-diphenylimidazole; **5**: M = Os, N∩N = 2-(2'-pyridyl)imidazole; **6**: M = Os, N∩N = 2-(2'-pyridyl)benzimidazole), see Scheme 5.2. The compounds are isolated and characterized as hexafluorophosphate salts.



Scheme 5.2

In the case of the reaction of the dinuclear iridium(III) complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ with two equivalents of chelating N∩N ligands in the presence of NH_4PF_6, cleavage of the chloride-bridge followed by dissociation of one chloride ligand, affords the complexes $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})imidazole\}Cl]PF_6$ ([**7**]PF_6) and $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})benzimidazole\}Cl]PF_6$ ([**8**]PF_6), see Scheme 5.3.



Scheme 5.3

The complexes (**1-8**) are pale yellow to orange reddish colored. They are highly soluble in polar solvents such as chloroform, acetone, methanol, dichloromethane *etc.*, but insoluble in non-polar solvents such as hexane, pentane *etc.*, C, H, N analyses, IR, ^1H

NMR spectroscopic data were given in the experimental section, which supported the formation of these complexes (**1-8**). The X-ray structures of representative complexes **1**, **2** and **7** were determined to confirm the structure of the complexes (**1-8**).

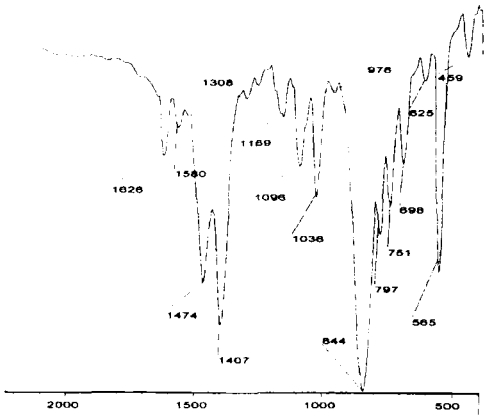
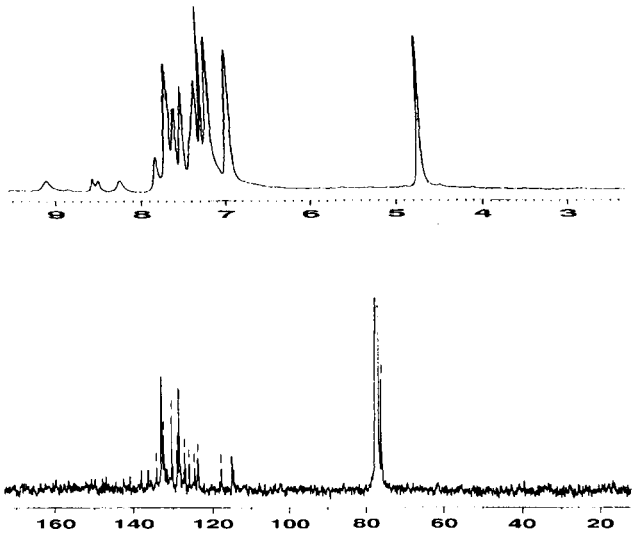


Figure 5.1: Infrared spectrum of $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})imidazole\}Cl]PF_6$ [**7**]

The infrared spectra of complexes (**1-6**) exhibited very strong bands at 1613-1600 cm^{-1} and 1480-1440 cm^{-1} corresponding to phenyl groups of triphenylphosphine and N-bases, while in complexes **7** and **8** prominent peaks were observed at 1600 cm^{-1} and 1474-1327 cm^{-1}. The counter ion (PF_6) exhibit a strong band around 845 cm^{-1} for $\nu_{P\text{-}F}$ group (Figure 5.1). The protons' corresponding to the cyclopentadienyl ligands appear in the region of 4.6-4.7 ppm while the triphenylphosphine peaks are observed as multiplets in the aromatic region between 7-8 ppm. The chemical shifts of cyclopentadienyl groups are shifted to down field as compared to the precursor complexes (4.43-4.31 ppm) (Figure 5.2 and 5.3).



'igure 5.2: ^{1}H NMR, ^{13}C spectra of $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})benzimidazole(PPh_3)]PF_6$[**2**]

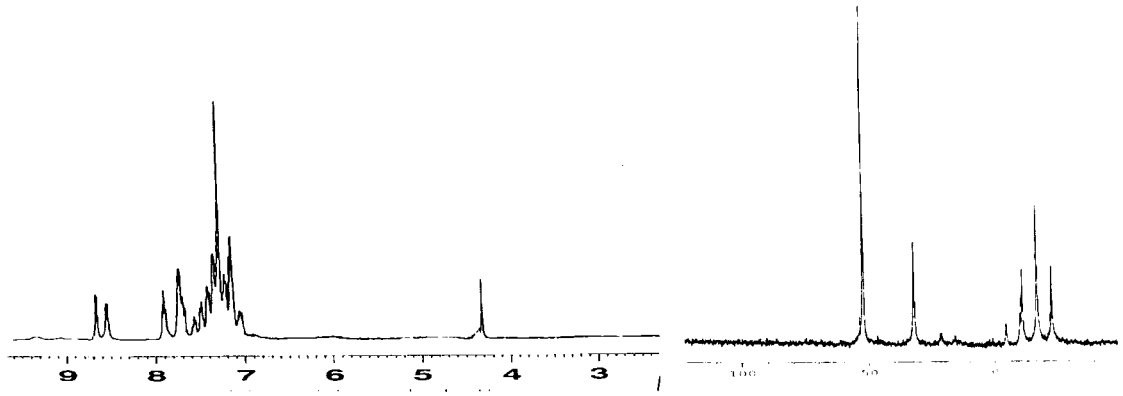


Figure 5.3: ^{1}H and ^{31}P {NMR}, spectra of $[(\eta^5\text{-}C_5H_5)Os\{2\text{-}(2'\text{-pyridyl})benzimidazole\}(PPh_3)]PF_6$

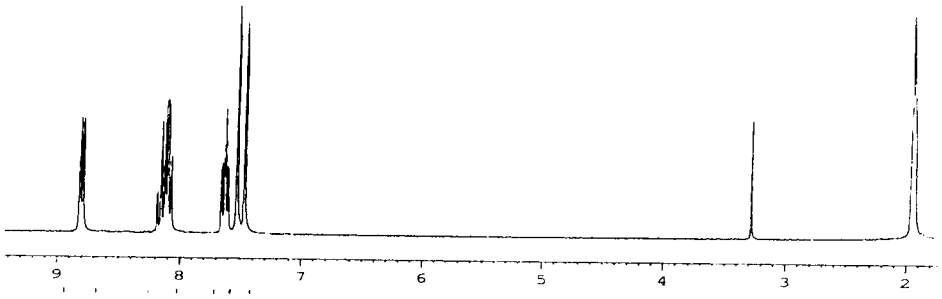


Figure 5.4: ^{1}H NMR, spectrum of $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})benzimidazole\}Cl]PF_6$ **[8]**PF_6

The down field shift position of the cyclopentadienyl protons in complexes **1-6**, which might results from the change in electron density on the metal center due to chelation of the nitrogen base ligands through the nitrogen atoms of the 2-(2'-pyridyl)imidazole derivatives ligands. The ^{1}H NMR spectra of complexes **1-6** also showed two pseudo-triplets in the range of 7.85 - 6.32 ppm due to the pyridine protons (H_4 and H_5) of the N∩N-donor ligands. The spectra of the Cp* complexes **7** and **8** showed resonance for the methyl protons of the Cp* ligand as singlet at 1.86 ppm and 1.82 ppm respectively (Figure 5.4). Molecular structure of the representative hexafluorophosphates salts **[1]**PF_6, **[2]**PF_6 and **[7]**PF_6 are presented in Figures 1, 2 and 4 respectively. Selected bond lengths and angles are recorded in Table 2. The molecular structures of $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})imidazole\}(PPh_3)]^+$ (**1**) and $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-pyridyl})benzimidazole\}(PPh_3)]^+$ (**2**) have been established by single-crystal X-ray structure analysis of **[1]**PF_6 and **[2]**PF_6--- H_2O, respectively. Both complexes show typical piano-stool geometry with the metal center coordinated by a cyclopentadienyl ligand, a PPh_3 ligand and a chelating N∩N-ligand, *see* Figures 5.1 and 5.2.

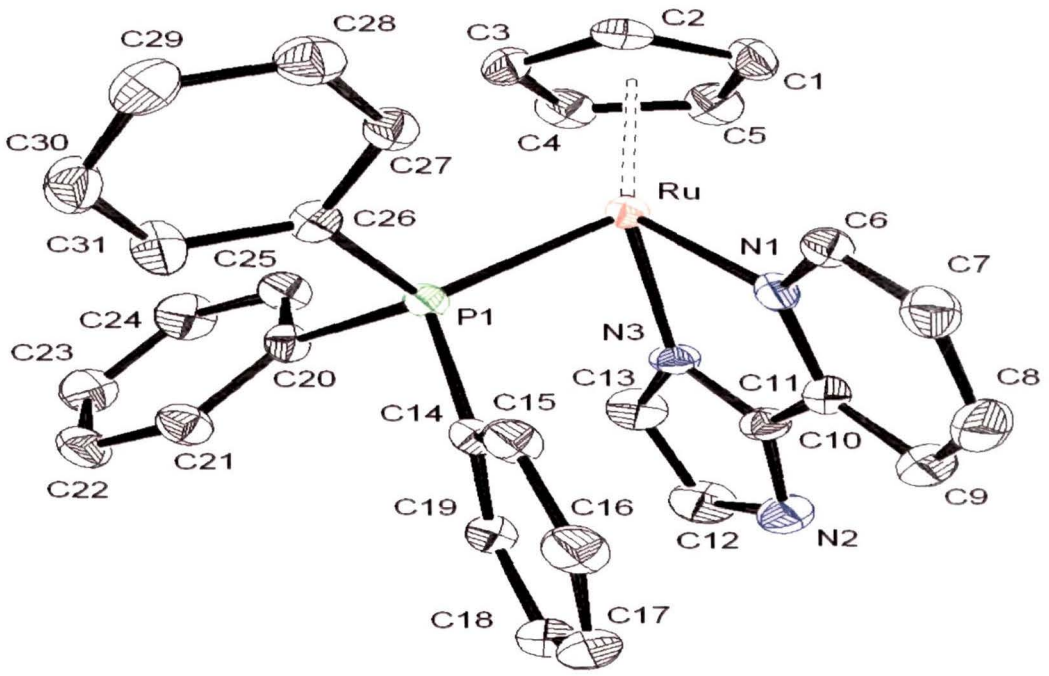


Figure 5.5: ORTEP diagram with labelling scheme for $[(\eta^5\text{-}C_5H_5)Ru\{2\text{-}(2'\text{-}pyridyl)imidazole\}(PPh_3)]^+$ ([**1**]PF_6), at 50% probability level, H atoms and PF_6 anion omitted for clarity.

The Ru-N bond distances [2.113(3) and 2.093(3) Å in **1**; 2.117(2) and 2.094(2) in **2**] are comparable to those in $[(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)RuCl(2,3\text{-bis}(2\text{-pyridyl})pyrazine)]BF_4$ [17] and $[(\eta^6\text{-}C_6H_6)RuCl(2\text{-}(1\text{-imidazole-2-yl})pyridine)]PF_6$ [18a]. Accordingly, there is no significant difference in the Ru-P bond length in **1** [2.316(1) Å] or **2** [2.325(1) Å] with reported values [9d, 19]. The N(1)-Ru-N(3) bond angle in complexes **1** [76.0(1)°] and **2** [76.1(2)°] are similar to those of compounds $[(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)RuCl(2,3\text{-bis}(2\text{-pyridyl})pyrazine)]^+$ [N-Ru-N = 76.5(2)°] [17] and $[(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)RuCl(2,3\text{-bis}(\alpha\text{-pyridyl})quinoxaline)]^+$ [N-Ru-N = 76.2(2)°] [18b]. The angles between the least-square

planes of η^5-C_5H_5 and that of the N∩N ligand are 57.8(2)° in **1** and 55.3(2)° in **2** (Table 5.2).

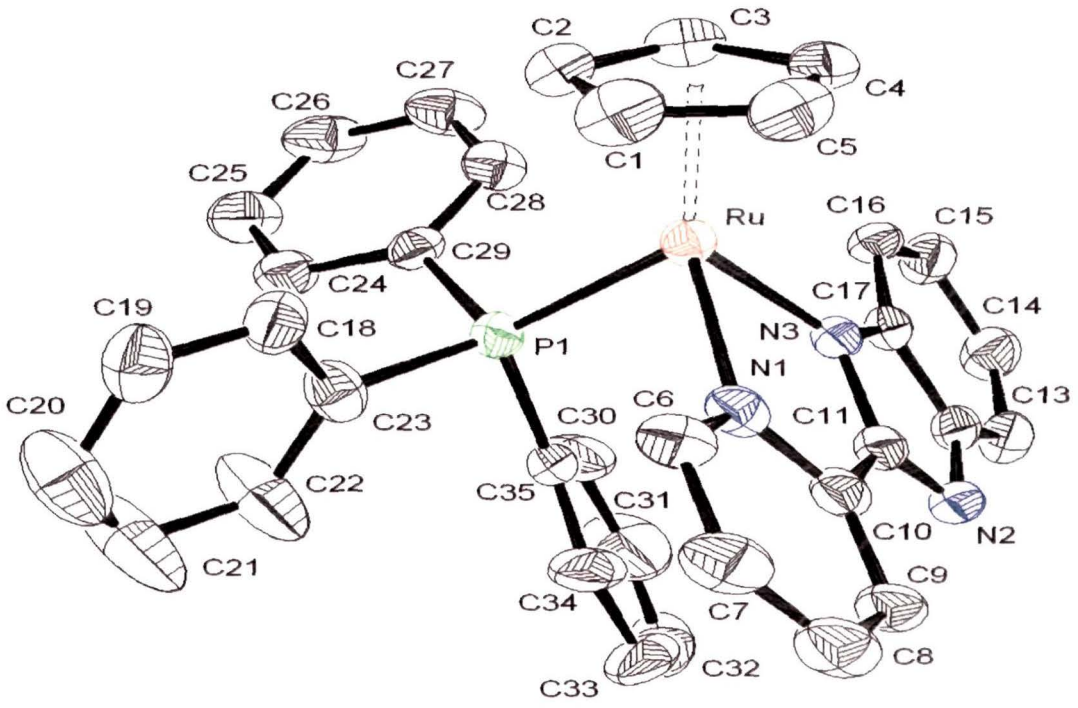


Figure 5.6: ORTEP diagram with labelling scheme for [(η5-C_5H_5)Ru{2-(2'-pyridyl)benzimidazole} $(PPh_3)]^+$ ([**2**]PF_6 · H_2O) at 50% probability level, H atoms, PF_6 anion and water molecule omitted for clarity.

Complex [**2**]PF_6 crystallizes with one molecule of water per asymmetric unit, which forms a hydrogen-bonded network with two hexafluorophosphate anions and the N-H group of the N∩N ligand, see Figure 3. The N-O and O-F distances of the hydrogen bonds are respectively, 2.820(3) Å for the N-H of the 2-(2'-pyridyl)benzimidazole ligand and H_2O, and 2.941(4) and 2.907(4) Å between the hexafluorophosphate anions and the water molecule (Table 5.2). The N-H···O angle is 167.1° while the O-H···F angles are 178 and 153°, respectively.

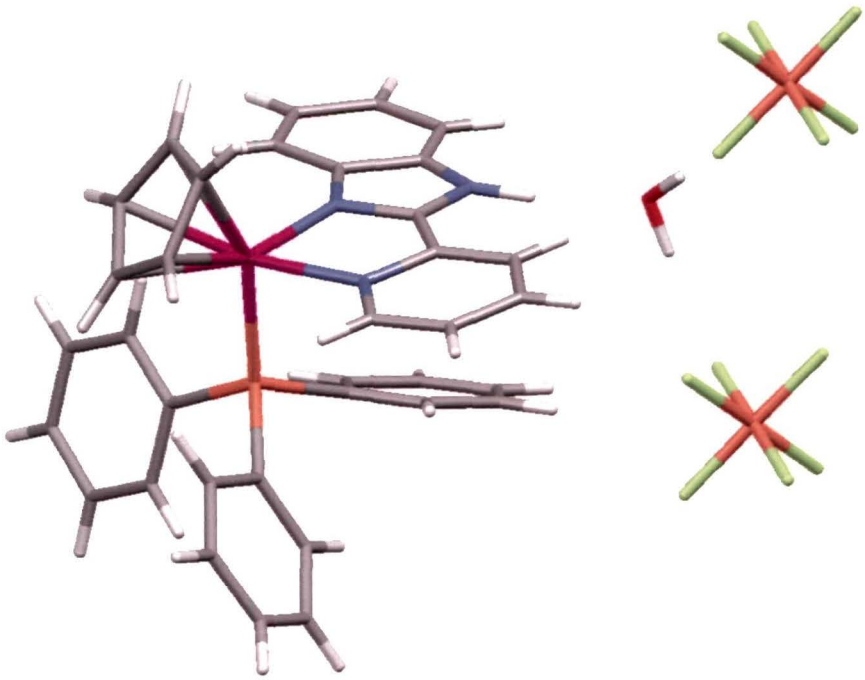


Figure 5.7: Hydrogen-bonded system observed in [**2**]PF_6

The molecular structure of $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})imidazole\}Cl]^+$ (**7**) has been established by single-crystal X-ray structure analysis of [**7**]PF_6 (see Figure 4). The complex shows a typical piano-stool geometry with the metal center coordinated by the pentamethylcyclopentadienyl ligand, a terminal chloride and the 2-(2'-pyridyl)imidazole ligand. The Ir-N bond distances [2.106(5) and 2.080(5) Å] are slightly shorter to those in [**1**]PF_6 and [**2**]PF_6. The average distance between the metal atom and the carbon atoms of the η^5-C_5Me_5 ring is 2.16 Å. This average bond length is comparable to that in the related η^5-C_5Me_5 iridium complex [(η^5-C_5Me_5)IrCl((*S*)-1-phenylethylsalicylaldiimine)] [2.17 Å] [20]. The Ir-Cl bond length is 2.4183(14) Å in **7**, which is slightly longer to the reported iridium complex [(η^5-C_5Me_5)IrCl((*S*)-1-phenylethylsalicylaldiimine)] [2.4017(16) Å] [20] (Table 5.2).

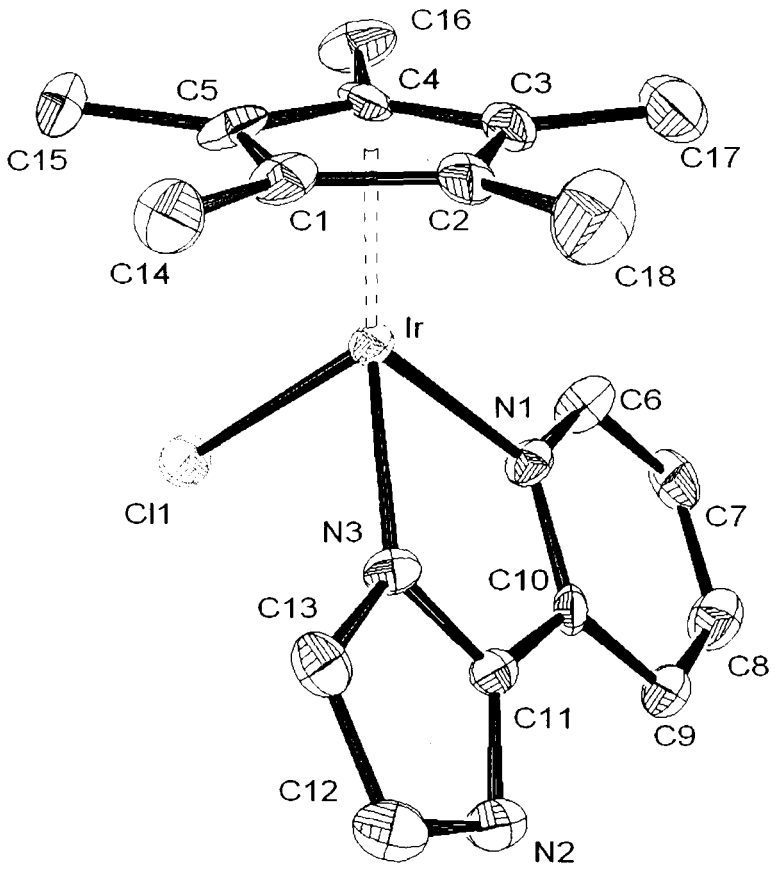


Figure 5.8: ORTEP diagram with labelling scheme for $[(\eta^5\text{-}C_5Me_5)Ir\{2\text{-}(2'\text{-pyridyl})imidazole\}Cl]^+$ ([7]PF_6) at 50% probability level, H atoms and PF_6 anion omitted for clarity.

In the crystal packing of [7]PF_6, two molecules of **7** form a dimer through N-H--Cl contacts and π-stacking interactions, *see* Figure 5. The N--Cl separation is 3.254(5) Å with an N-H···Cl angle of 162.1°. The distance observed between the π-stacking interacting systems (centroid---centroid 3.76 Å) is in good agreement with the theoretical value calculated for this stacking mode [21]. The distance observed between the two iridium centres of the dimer is 7.841(1) Å and excludes any possible metal-metal interactions.

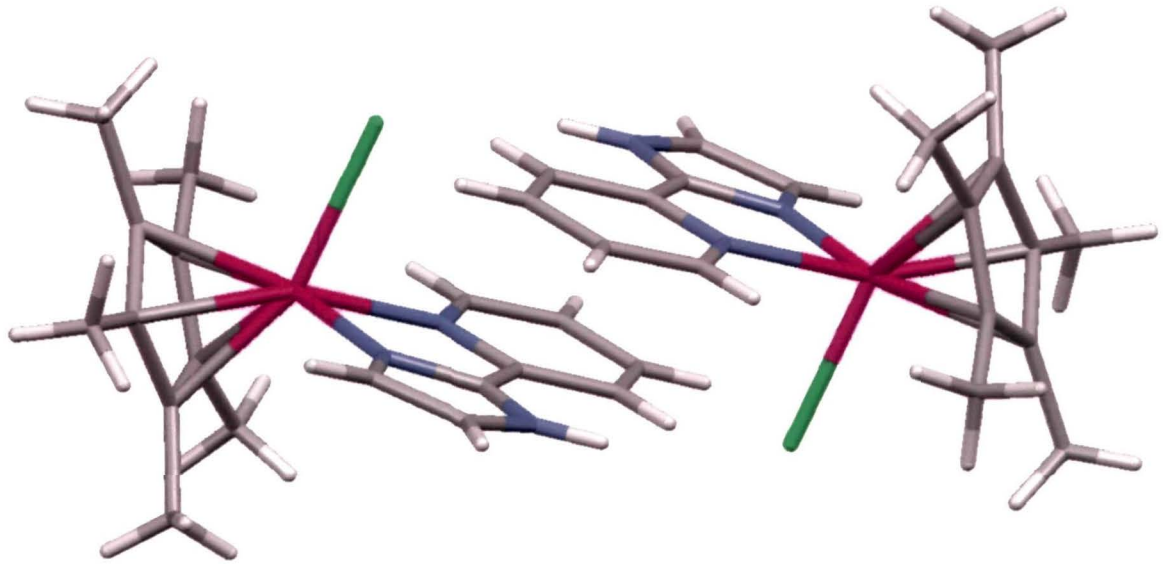


Figure 5.9: Dimeric structure of [**7**]PF_6 showing the intermolecular NH···Cl hydrogen contacts and π-π interacting system.

5.4. Conclusions:

The present study describe the syntheses of eight new (η^5-C_5H_5)Ru, (η^5-C_5H_5)Os and (η^5-C_5Me_5)Ir complexes containing 2-(2'-pyridyl)imidazole ligands. Representative complexes have been characterized by single X-ray study. In the crystal packing of [**7**]PF_6, two molecules of **7** form a dimer through N-H--Cl contacts and π-stacking interactions.

Table 5.1: Crystallographic and structure refinement parameters for complexes [**1**]PF_6, [**2**]$PF_6 \cdot H_2O$ and [**7**]PF_6

	[**1**]PF_6	[**2**]$PF_6 \cdot H_2O$	[**7**]PF_6
Chemicalformula	$C_{31}H_{27}F_6N_3P_2Ru$	$C_{35}H_{31}F_6N_3OP_2Ru$	$C_{18}H_{22}ClF_6N_3PIr$
Formula weight	718.57	786.64	653.01
Crystal system	monoclinic	Triclinic	Triclinic
Space group	P $2_1/c$ (no. 14)	P -1 (no. 2)	P -1(no.2)
Crystal colour and shape	orange block	red block	red block
Crystal size	0.32 x 0.20 x 0.200.	28 x 0.23 x 0.18	0.35 x 0.26 x 0.21
a (Å)	13.552(3)	10.379(4)	8.0428(9)
b (Å)	14.582(3)	11.285(4)	11.4031(14)
c (Å)	17.920(6)	15.601(6)	11.7074(13)
α (°)	90	108.602(5)	93.585(14)
β (°)	126.31(2)	91.211(5)	96.862(14)
γ (°)	90	104.887(5)	98.154(14)
V ($Å^3$)	2853.6(13)	1663.0(10)	1051.8(2)
Z	4	2	2
T (K)	173(2)	120(2)	173(2)
D_c ($g.cm^{-3}$)	1.673	1.571	2.062
μ (mm^{-1})	0.729	0.635	6.613
Scan range (°)	$1.86 < \theta < 29.24$	$1.98 < \theta < 28.23$	$2.58 < \theta < 26.03$
Unique reflections	6277	7437	3821

Reflections used [I>2σ(I)]	4388	6379	3518
R_{int}	0.0588	0.0261	0.0501
Final R indices [I>2σ(I)]*	0.0387, wR_2 0.0860	0.0457, wR_2 0.1073	0.0323,wR_2 0.0782
R indices (all data)	0.0605, wR_2 0.0926	0.0543, wR_2 0.1131	0.0373,wR_2 0.0884
Goodness-of-fit	0.910	1.016	1.112
Max, Min Δρ/e (Å^{-3})	0.763, -1.038	0.754, -0.530	1.775, -1.850

- Structures were refined on F_0^2: $wR_2 = [\sum[w(F_0^2 - F_c^2)^2] / \sum w(F_0^2)^2]^{1/2}$, where w^{-1}
- $= [\sum(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$

Table 5.2: Selected bond lengths and angles for complexes [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6.

Distances (Å)	**1**	**2**	**7**
Ru-P	2.316(1)	2.325(1)	
Ir-Cl			2.4183(14)
M-N1	2.113(3)	2.1169(17)	2.106(5)
M-N3	2.093(3)	2.0939(15)	2.080(5)
M-C1	2.208(4)	2.109(4)	2.178(6)
M-C2	2.177(4)	2.157(3)	2.149(5)
M-C3	2.150(4)	2.226(3)	2.158(6)
M-C4	2.180(4)	2.219(3)	2.144(6)
M-C5	2.215(4)	2.146(4)	2.164(6)
Angles (°)			
N1-M-N3	75.98(10)	76.08(17)	76.48(19)
N1-M-P1	90.12(8)	92.15(6)	

N3-M-P1	87.66(8)	89.02(6)	
N1-Ir-Cl1			84.60(14)
N3-Ir-Cl1			86.95(14)

References

1. (a) W. Baratta, E. Herdtweck, W. A. Hermann, P. Rigo, J. Schwarz, *Organometallics*, 21 (2002) 2101; (b) M. A. Bennett, K. Khan, E. Wenger, in: G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds.), Comprehensive Organometallic Chemistry II, Second Ed., Vol. 7, Elsevier, Oxford, 1995 (Chapter 8) (and references cited therein).
2. (a) S. G. Davies, J. P. McNally, J. Smallridge, *Adv. Organomet. Chem.*, 30 (1991) 1; (b). B. M. Trost, J. A. Marting, R. J. Kulawiec, A. F. Indolese, *J. Am. Chem. Soc.*, 115 (1993) 10402; (c). P. Pertici, V. Ballantini, P. Salvadori, M. A. Bennett, *Organometallics.* 14 (1995) 2565; (d) D. L. Davies, J. Fawcett, R. Krafczyk, D. R. Russell, *J. Organomet. Chem.*, 545- 546 (1997) 581.
3. (a) B. M. Trost, M. U, Frederiksen, M. T. Rudd. *Angew. Chem. Int. Ed., Eng.* 44 (2005) 6630 (and references cited therein); (b) W. Baratta, A. D. Zotto, P. Rigo, *Chem. Commun.*, (1997) 2163; (c) A. D. Zotto, W. Baratta, G. Verardo, P. Rigo, *Eur. J. Org. Chem.*, (2000) 2795.
4. M. A. Esteruelas, E. G. Puebla, A. M. López, E. Oñate, J. I. Tolosa. *Organometallics.* 19 (2000) 275.
5. (a) R. Lalrempuia, H. Yennawar, Y. A. Mozharivskyj, K. Mohan Rao, *J. Organomet. Chem.*, 689 (2004) 539; (b) T. Wilczewski, *J. Organomet. Chem.*,

317 (1986) 307; (c) T. Wilczewski, *J. Organomet. Chem.*, 297 (1985) 331; (d) M. I. Bruce, G. A. Koutsantonis, M. J. Liddel, B. K. Nicholson, *J. Organomet. Chem.*, 320 (1987) 217 (and references cited therein).

6. (a) P. Govindaswamy, K. Mohan Rao, *J. Coord. Chem.*, 59 (2006) 663; (b) P. Govindaswamy, Y. A. Mozharivskyj, K. Mohan Rao, *Polyhedron.* 24 (2005) 1710; (c) H. Aneetha, P. S. Zacharias, B. Srinivas, G. H. Lee, Y. Wang, *Polyhedron.* 18 (1999) 299.

7. (a) T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc.*, A 1971, 2376; (b). G. S. Ashby, M. I. Bruce, I. B. Tomkins, R. C. Wallis, *Aust. J. Chem.*, 1979, 32, 1003; (c). S. G. Davies, S. J. Simpson, H. Felkin, T. Fillebeen-Khan, *Organometallics.* 1983, 2, 539; (d). S. G. Davies, S. J. Simpson, H. Felkin, T. Fillebeen-Khan, F. Tadjand, O. Watts, *J. Chem. Soc., Chem. Commun.*, 1981, 341; (e) M. I. Bruce, S. F. Wong, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans. 1981*, 1398.

8. (a) J. P. Selegue, *Organometallics* 1 (1982) 217; (b) J. P. Selegue, *J. Am. Chem. Soc.*, 105 (1983) 5921.

9. (a) R. Lalrempuia, P. Govindaswamy, Y. A. Mozharivskyj, K. Mohan Rao, *Polyhedron.* 23 (2004) 1069; (b) K. Mohan Rao, E. K. Rymmai, *Polyhedron.* 22 (2003) 307; (c) K. Sarjit Singh, P. J. Carroll, K. Mohan Rao, *Polyhedron.* 24 (2005) 391; (d) K. Sarjit Singh, Y. A. Mozharivskyj, C. Thone, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 3720.

10. B. Chiswell, F. Lions, B. S. Morris, *Inorg. Chem.*, 31 (1964) 110.

11. (a). M. I. Bruce, N. J. Windsor, *Aust. J. Chem.*, 30 (1977) 1601; (b) M. I. Bruce, P. J. Low, B. W. Skelton, E. R. T. Tiekink, A. Werth, A. H. White, *Aust. J. Chem.*, 48 (1995) 1887.

12. (a). J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.*, 91 (1969) 5970; (b). C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.*, 29 (1992) 228.

13. M. Sheldrick, *Acta Cryst.*, A 46 (1990) 467.

14. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany (1999).

15. L. J. Farrugia, *J. Appl. Cryst.*, 30 (1997) 565.

16. I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. Mc Cabe, J. Pearson, R. Taylor, *Acta Cryst.*, B58 (2002) 389.

17. A. Singh, N. Singh, D. S. Pandey, *J. Organomet. Chem.*, 642 (2002) 48.

18. (a) H. Mishra, R. Mukherjee, *J. Organomet. Chem.*, 691 (2006) 3545; (b) R. Lalrempuia, K. Mohan Rao, *Polyhedron* 22 (2003) 3155.

19. P. Govindaswamy, C. Sinha, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 3465.

20. H. Brunner, A. Köllnberger, T. Burgemeister, M. Zabel, *Polyhedron.* 19 (2000) 1519.

21. S. Tsuzuki, K. Honda, T. Uchimura, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.*, 124 (2002) 104.

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CHAPTER 6

Syntheses of Benzene Ruthenium Triazolato Complexes by [3+2] Cycloaddition Reactions of Activated Alkynes and Fumaronitrile to Benzene Ruthenium Azido Complexes.

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Syntheses of benzene ruthenium triazolato complexes by [3+2] cycloaddition reactions of activated alkynes and fumaronitrile to benzene ruthenium azido complexes.

Abstract:

The dinuclear complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl]_2$ (**1**) is obtained by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with sodium azide in ethanol. The benzene ruthenium β-diketonato complexes of the general formula $[(\eta^6\text{-}C_6H_6)Ru(L\cap L)Cl]$ {L∩L = *O,O'*-acac (**2**); *O,O'*-bzac (**3**); *O,O'*-dbzm (**4**)} are obtained in methanol by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the corresponding *β*-diketonates. These complexes further react with sodium azide in ethanol to yield complexes of the type $[(\eta^6\text{-}C_6H_6)Ru(L\cap L)N_3]$ [L∩L = *O,O'*-acac (**5**); L∩L = *O,O'*-bzac (**6**); L∩L = *O,O'*-dbzm (**7**)]. The complexes **5** to **7** are obtained as well by treating **1** with sodium salts of *β*-diketonates. These neutral benzene ruthenium azido complexes undergo [3+2] dipolar cycloaddition reaction with activated alkynes ($MeO_2CC{\equiv}CCO_2Me$, $EtO_2CC{\equiv}CCO_2Et$) or fumaronitrile (NCHC=CHCN) to yield the corresponding benzene ruthenium triazolato complexes; $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2(CO_2Me)_2\}]$ (**8**), $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2(CO_2Et)_2\}]$ (**9**), $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2HCN\}]$ (**10**), $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-bzac})\{N_3C_2HCN\}]$ (**11**) and $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-dbzm})\{N_3C_2HCN\}]$ (**12**). These complexes are fully characterized on the basis of microanalyses, FT-IR and FT-NMR spectroscopy. The molecular structure of $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2(CO_2C_2H_5)_2\}]$ (**9**) is confirmed by single crystal X-ray diffraction study.

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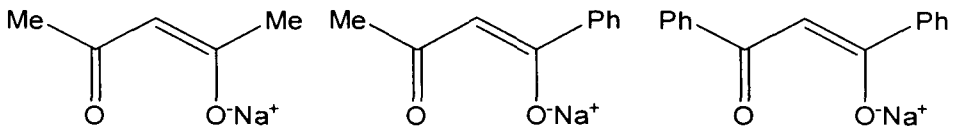
6.1. Introduction

Arene ruthenium compounds belong to a well-established family of robust metal-organic molecules that have played an important role in the development of organometallic chemistry [1]. Our interest in such systems arises due their catalytic potential in a wide range of organic reactions [2] and very promising anticancer activity [3]. The arene ruthenium halide compounds obtained by Winkhaus *et al.* [4] are key starting materials for the formation of a wide range of neutral and cationic derivatives [5]. Reaction of chloro bridged dimeric arene ruthenium complexes with Lewis bases and a variety of ligands have been reported. Azide chemistry has attracted the attention of many chemists, as these compounds play an important role in organic chemistry [6]. The 1,3-dipolar cycloaddition reactions between substituted acetylenes and azides is a very important reaction and the most efficient route to synthesize 1,2,2-triazoles. Among the various 1,3-dipolar cycloaddition reactions, organic azides have been particularly important for synthesizing heterocyclic compounds [7]. Similarly coordinated azides in metal complexes can also undergo cycloaddition reaction [8]. We have recently reported the triazolato complexes $[(\eta^6\text{-}p\text{-cymene})Ru(L\cap L)\{N_3C_2(CO_2R)_2\}]$ and $[(\eta^5\text{-indenyl})Ru(L\cap L)\{N_3C_2(CO_2R)_2\}]$ ($L\cap L$ = β-diketonates, dppe, dppm) from the reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ and $[(\eta^5\text{-indenyl})Ru(L\cap L)(N_3)]$, respectively with various substituted acetylenes [9]. However, to the best of our knowledge, there is no report in the literature on structurally characterized benzene ruthenium triazolato complexes. Our continuing interest in chloro bridged dimeric arene ruthenium involves the substitution of chloride with azide group and the synthesis of the corresponding

azido complexes. We had already reported that complete substitution of chloride by azido groups in the *p*-cymene ruthenium dimer is not achieved, whereas in the case of the hexamethylbenzene ruthenium dimer, the complete chloride substitution reaction is successfully carried out [10]. Keeping this in mind, the reaction of sodium azide with benzene ruthenium dimer is studied in this work. The substitution of all the chlorides in benzene ruthenium dimer with azide was incomplete as observed for the *p*-cymene analogue. This work presents a comparison between the 1,3–dipolar cycloaddition reactions of *p*-cymene ruthenium dimer and benzene ruthenium dimer in relation to azide bonding and activated acetylene groups. The benzene ruthenium triazolato complexes thus generated were characterized on the basis of microanalyses and spectroscopic data. The molecular structure of the representative complex (**9**) was established by single crystal X-ray structure analysis.



Na[acac] Na[bzac] Na[dbzm]

Chart 6.1. L∩L ligands used in this study

6.2. Experimental:

Caution- *Reactions with azide salts and their complexes should be perform with extreme care.*

All solvents were dried in appropriate drying agents and distilled prior to use [11]. Dimethylacetylenedicarboxylate (Aldrich), diethylacetylenedicarboxylate (Across),

fumaronitrile (Aldrich) and $RuCl_3 \cdot 3H_2O$ (Arora Matthey Limited) were used as received. NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 (^1H), or 100.61 MHz (^{13}C) with $SiMe_4$ as internal reference and coupling constants are given in Hz. The starting material $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was synthesized according to the literature procedure [12]. Sodium salts of acetylacetone, benzoylacetone and diphenylmethane were prepared by treating the appropriate β-diketonates with NaOH in ethanol.

6.2.1 *Preparation of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl]_2$ (1)*

A mixture of the starting complex $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}]_2$ (0.1 g, 0.20 mmol) and sodium azide (0.03 g, 0.50 mmol) in ethanol (20 ml) was stirred at room temperature for 5 hrs; a yellow colored compound was precipitated. The precipitate was filtered and washed with methanol (3 x 10 ml) and then dried in vacuo. The additional complex was isolated by concentration of the filtrate and washing with methanol (3 x 10 ml), and then dried in vacuum to give a yellow powdered compound.

Yield: 50.5 mg, 48.3 %.

IR (KBr, cm^{-1}): 2044 (ν_{N3}), 1639 ($\nu_{C=C}$).

^1H NMR ($CDCl_3$,δ): 5.81 (s, 6H, C_6H_6).

6.2.2 *Preparation of $[(\eta^6\text{-}C_6H_6)Ru(L\cap L)Cl]$ [$L\cap L$ = O,O'-acac (2), O,O'-bzac (3), O,O"-dbzm (4)]*

General method of preparation of these complexes:

A mixture of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}]_2$ (0.1 g, 0.20 mmol) and the L∩L sodium salt (0.06 g, 0.40 mmol) in dry methanol (20 ml) was stirred at room temperature for 3 hrs. The color of the solution turns a brick-red and the reaction mixture is evaporated to dryness under

reduced pressure. The solid residue is dissolved in dichloromethane and filtered to remove NaCl. The solution is concentrated to *ca.* 5 ml and addition of hexane precipitates an orange powdered solid which is filtered and dried under vacuum.

Complex [(η^6-C_6H_6)Ru(O,O'-acac)Cl] (2)

Yield: 35 mg, 51.0 %

IR (KBr, cm^{-1}): 1570, 1533 ($\nu_{C=O+C=C}$)

^{1}H NMR ($CDCl_3$, δ): 2.05 (s, 6H, CH_3), 5.65 (s, 6H, C_6H_6), 5.21 (s, 1H, γH).

Complex [(η^6-C_6H_6)Ru(O,O'-bzac)Cl] (3)

Yield: 37 mg, 46.3 %.

IR (KBr, cm^{-1}): 1520, 1447 ($\nu_{C=O+C=C}$)

^{1}H NMR ($CDCl_3$,δ): 2.14 (s, 3H, CH_3), 5.60 (s, 1H, γH), 5.80 (s, 6H, C_6H_6), 7.52-7.61 (m, 5H, Ph)

Complex [(η^6-C_6H_6)Ru(O,O'-dbzm)Cl] (4)

Yield: 34 mg, 38.7 %.

IR (KBr, cm^{-1}): 1533, 1525 ($\nu_{C=O+C=C}$)

^{1}H NMR ($CDCl_3$,δ): 5.70 (s, 1H, γH), 6.04 (s, 6H, C_6H_6), 7.32-7.59 (m, 10H, Ph).

6.2.3 Preparation of [(η^6-C_6H_6)Ru(L∩L)N_3] [*(L∩L = O,O'-acac* (5), *O,O'-bzac* (6), *O,O"-dbzm* (7)]

Two routes were used to prepare these complexes:

Route (a): A mixture of [(η^6-C_6H_6)Ru(L∩L)Cl] (0.1 g, 0.29 mmol) and NaN_3 (0.06 g, 0.73 mmol) in ethanol (20 ml) was stirred at room temperature for 8 hrs. The mixture solution turned a brick-red color. The reaction mixture was evaporated to dryness under reduced pressure; the solid residue was dissolved in dichloromethane and filtered to remove NaCl.

The filtrate on evaporation at room temperature afforded orange-yellow powder complexes **5-7**, which were separated and dried under vacuum.

Route (b): The above complexes **5-7** can also be synthesized by the reaction of azide dimer [{(η^6-C_6H_6)Ru(μ-N_3)Cl}$_2$] (**1**) (0.1 g, 0.20 mmols) and the appropriate sodium salts of β-diketonates (0.07 g, 0.48 mmol) in ethanol (20 ml). The mixture was stirred at room temperature for 7 hrs. The solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (5 ml) and filtered to remove sodium chloride. The filtrate upon concentration to a minimum volume *ca.* 5 ml and addition of excess hexane gave the orange-yellow complexes **5-7**, which were separated and dried under vacuum.

(***Caution***: *This complex should be handled with extreme care and usage of spatula is avoided*)

Complex [(η^6-C_6H_6)Ru(O, O'-acac)N_3] (5)

Yield: 42 mg, 41 %.

IR (KBr, cm^{-1}): 2026 (ν_{N3}); 1568, 1387 ($\nu_{C=O + C=C}$)

^{1}H NMR ($CDCl_3$,δ): 2.20 (s, 6H, CH_3), 5.69 (s, 1H, γH), 5.81 (s, 6H, C_6H_6), 7.37-7.42 (m, Ph)

Complex [(η^6-C_6H_6)Ru(O, O'-bzac)N_3] (6)

This complex was prepared by following a similar method employed in the preparation of [(η^6-C_6H_6)Ru(O,O'-acac)N_3] (**5**), using Na(O,O'-bzac).H_2O instead of Na(O,O'-acac). H_2O.

Yield: 49 mg, 51 %.

IR (KBr, cm^{-1}): 2025 (ν_{N3}), 1553, 520 ($\nu_{C=O}$ +$\nu_{C=C}$)

^{1}H NMR ($CDCl_3$,δ): 2.02 (s, 3H, CH_3), 5.59 (s, 1H, γH), 5.91 (s, 6H, C_6H_6), 7.02-7.28 (m, 5H, Ph)

***Complex [(η^6-C_6H_6)Ru(O,O'-dbzm)N_3]* (7)**

This complex was prepared by following the similar procedure as described in the preparation of complex [(η^6-C_6H_6)Ru(O,O'-acac)N_3] (**5**) using Na(O,O'-dbzm).H_2O instead of Na (O,O'-acac).H_2O.

Yield: 56 mg, 58 %

IR (KBr, cm^{-1}): 2022 (ν_{N3}), 1646, 1573 ($\nu_{C=O,\ C=C}$)

^{1}H NMR ($CDCl_3$,δ): 5.47 (s, 1H, γH), 5.89 (s, 6H, C_6H_6), 7.30-7.62 (m, 10H, Ph).

6.2.4 *Preparation of triazolato complex [(η^6-C_6H_6)Ru(O,O'-acac){$N_3C_2(CO_2CH_3)_2$}]* (8)

To a round-bottom flask charged with the corresponding azido complex [(η^6-C_6H_6)Ru(*O,O'*-acac)N_3] (0.1 g, 0.31 mmol) was added a five-fold excess of dimethylacetylenedicarboxylate and CH_2Cl_2 (20 ml). The mixture was stirred at room temperature for 14 to 15 hrs. The solution was evaporated to *ca.* 5 ml. To this solution was added 30 ml of hexane, whereby the compound was precipitated out as a yellow solid. The solid compound was collected by filtration and washed

with (2 x 20 ml) of hexane and dried under vacuum to gave the triazolato complexes [(η^6-C_6H_6)Ru(L∩L){$N_3C_2(CO_2CH_3)_2$}].

Yield: 52 mg, 34 %.

IR (KBr, cm^{-1}): 1437-1446 ($\nu_{N=N}$), 1580, 1529 ($\nu c_{=O}$ + $c_{=}c$).

^{1}H NMR ($CDCl_3$,δ): 1.91(s, 6H, acac-Me); 2.87 (s, 6H, OCH_3); 5.47 (s, 1H, acac-γH); 5.69 (s, 6H, C_6H_6).

6.2.5 *Preparation of triazolato complexes[(η^6-C_6H_6)Ru(O,O'-acac) {$N_3C_2(CO_2C_2H_5)_2$}] (9)*

The complex is prepared by following the same procedure for the preparation of [(η^6-C_6H_6)Ru(O,O'-acac){$N_3C_2(CO_2CH_3)_2$}] (**8**), where diethylacetylenedicarboxylate is used instead of dimethylacetylenedicarboxylate.

Yield: 55 mg, 39 %.

IR (KBr, cm^{-1}): 1437-1446 ($\nu_{N=N}$), 1533 ($\nu c{=}o + c{=}c$).

^1H NMR ($CDCl_3$,δ): 1.93 (s, 6H, (acac-Me), 2.21 (s, 6H, {$OCH_2(CH_3)_2$}, 2.35 (t, 4H, -CH_2 of OCH_2 $(CH_3)_2$); 5.85 (s, 1H, (acac-γH), 5.94 (s, 6H, C_6H_6)

6.2.6. *Preparation of complexes [(η^6-C_6H_6)Ru(L∩L){N_3C_2HCN}] L∩L = O,O'-acac (10); O,O'-bzac (11); O,O'-dbzm (12)*

To a round-bottom flask charged with the azido complex [**5**] (0.1 g, 0.31 mmol) was added fumaronitrile (0.05 g, 0.63 mmol) and 20 ml of dichloromethane–methanol mixture. The solution was stirred at room temperature for 10 hrs. The solvent was reduced to *ca.* 5 ml and an excess of n-pentane added to give a chocolate color precipitate. The powder compound was collected and washed with n-pentane (3 x 10 ml) and dried under vacuum.

Complex [(η^6-C_6H_6)Ru(O, O'-acac){N_3C_2HCN}] (10)

Yield: 50 mg, 43.14 %.

IR (KBr, cm^{-1}): 2236 ($\nu_{C\equiv N}$), 1580, 1520 ($\nu_{C=N} + \nu_{C=C}$).

^1H NMR ($CDCl_3$,δ): 2.25 (s, 6H, CH_3), 5.59 (s, 1H, γH), 6.02 (s, 6H, C_6H_6); 6.82 (s, 1H, CH).

Complex [(η^6-C_6H_6)Ru(O,O'-bzac){N_3C_2HCN}] (11)

Yield: 54 mg, 47.64 %.

Elemental Anal (%), Calc for $C_{19}H_{16}N_4O_2Ru$: C, 52.66; H, 3.69; N, 12.93; found: C, 52.03; H, 3.96; N, 13.15

IR (KBr, cm^{-1}): 2234 ($\nu_{C\equiv N}$), 1572, 1520 ($\nu_{C=N} + \nu_{C=C}$)

^{1}H NMR ($CDCl_3$,δ): 2.12 (s, 3H, (bzac-CH_3), 5.75 (s, 1H, γH), 5.79 (s, 6H, C_6H_6); 6.86 (s, 1H, CH); 7.24-7.52 (m, 5H)

Complex [(η^6-C_6H_6)Ru(O,O'-dbzm){N_3C_2HCN}] (12)

Yield: 56 mg, 50.3 %.

IR (KBr, cm^{-1}): 2225 ($\nu_{C\equiv N}$), 1571, 1520 ($\nu_{C=N} + \nu_{C=C}$)

^{1}H NMR ($CDCl_3$,δ): 5.81 (s, 1H, γH), 5.94 (s, 6H, C_6H_6), 6.83 (s, 1H, CH); 7.28-7.42 (m, 10H, Ph).

6.2.7. *Single-crystal X-ray structures analysis*

A crystal suitable for X-ray diffraction study for compound (**9**) was grown by slow diffusion of diethylether into a dichloromethane solution of the complex. The orange reddish crystal of compound (**9**) was mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, with ϕ range 0-200°, D_{max}-D_{min} = 12.45-0.81 Å. X-ray intensity data were collected with Mo-Kα graphite monochromated radiation (α = 0.71073 Å) at 173 (2) K, having increment of 1.0° and 3 minutes per frame. The intensity data were corrected for Lorenz and polarization effects. The structure was solved by direct methods using the program SHELXS-97 [13]. Refinement and all further calculations were carried out using SHELXL-97 [14]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default

parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1. Figure 1 was drawn with ORTEP 32 [15].

6.3. Results and discussion

6.3.1 *Syntheses of benzene ruthenium azide dimer complex.*

Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2)_2]$ with an excess of sodium azide in ethanol after stirring for 5 hrs affords a yellow colored complex $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl\}_2]$ (**1**). *Safety measure should be taken while handling the solid in dry condition, scratching with a spatula should be avoided since it can explode.* The formation of this compound can be readily confirmed from the appearance of a strong adsorption peak at 2044 cm^{-1} which corresponds to the stretching frequency of the bridging ν_{N3} group and compares well with analogous compounds [10]. The ^1H NMR spectrum shows a singlet peak at 5.86 ppm corresponding to the protons of the benzene ligand. However, attempts to substitute all the chlorides in the starting benzene dimer with azide group was incomplete, possibly due to less electron density on the ruthenium metal atom in comparison to hexamethylbenzene ruthenium dimer where we reported the substitution of all the chlorides with azide group [10].

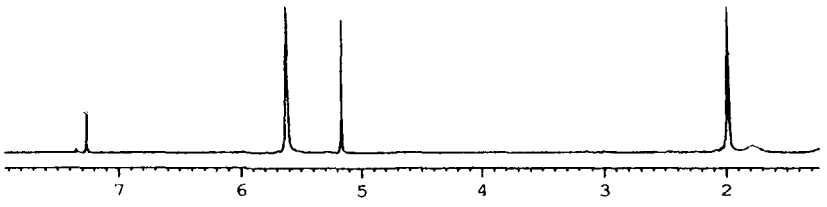


Figure 6.1: ^1H {NMR} spectrum of $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-}acac)Cl]$ (**2**)

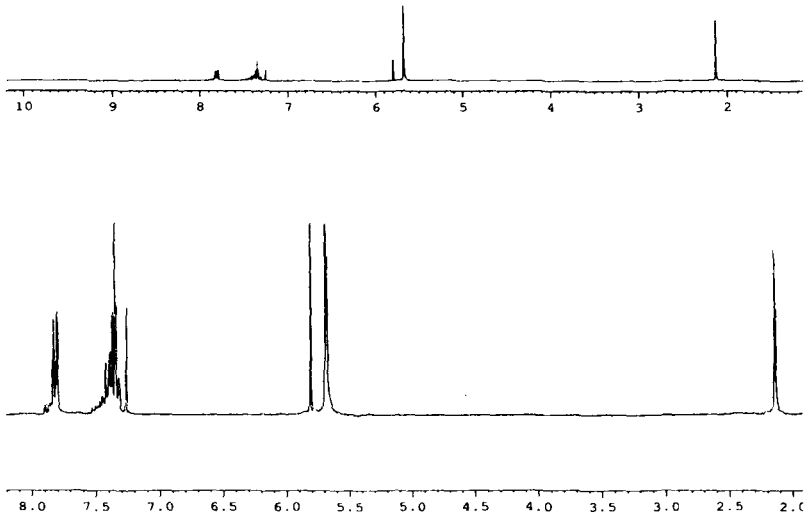


Figure 6.2: ^{1}H {NMR} spectrum of $[(\eta^{6}\text{-}C_6H_6)Ru(O,O'\text{-}bzac)Cl]$ (**3**)

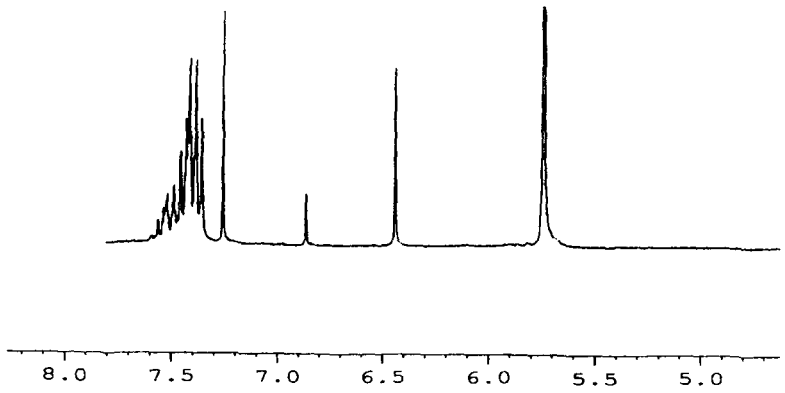


Figure 6.3: ^{1}H {NMR} spectrum of $[(\eta^{6}\text{-}C_6H_6)Ru(O,O'\text{-}dbzm)Cl]$ (**4**)

6.3.2 *Syntheses of benzene ruthenium β-diketonato complexes.*

Reaction of $[(\eta^{6}\text{-}C_6H_6)RuCl_2)_2]$ with sodium salt of the appropriate β-diketonate in dry methanol for 5 hrs results in orange colored complexes of the general formula $[(\eta^{6}\text{-}C_6H_6)Ru(L\cap L)Cl]$ [L∩L = *O,O'*-acac (**2**); *O,O'*-bzac (**3**); *O,O'*-dbzm (**4**)]. The infrared spectrum of these complexes shows strong bands within the range of 1570-1447 cm^{-1} corresponding to the stretching frequency of C=O and C=C groups. The ^{1}H NMR

spectra of these complexes (**2**, **3** and **4**) shows a characteristic singlet resonance within the range of 5.80-6.04 ppm assignable to the protons of the benzene ligand. Singlet peaks observed within the range of 2.14 - 2.35 ppm and 5.68-5.72 ppm are assigned to the $-CH_3$ group and to the γ-H proton of the β-diketonate ligand respectively. Phenyl protons of β-diketonate ligand show characteristic multiplet resonance at the aromatic region.

6.3.3 *Syntheses of benzene ruthenium azido complexes.*

Treatment of complexes **2** to **4** with sodium azide forms the corresponding azido complexes: $[(\eta^6\text{-}C_6H_6)Ru(L\cap L)N_3]$ [L∩L = *O,O'*-acac (**5**); *O,O'*-bzac (**6**); *O,O'*-dbzm (**7**)] (Scheme 6.1). The formation of these complexes is readily confirmed by the observation of a sharp absorption peak in the range 2020-2035 cm^{-1} which is characteristic to terminal azido group [10](Figure 6.4). Accordingly, complexes **5**, **6** and **7** can also be prepared by reacting the azido dimer $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl)\}_2]$ (**1**) with sodium salts of β-diketonates in methanol at room temperature (scheme 1). The formation of azido complexes is confirmed by the disappearance of the bridging azide stretching frequency at 2044 cm^{-1} and the appearance of a new band at 2020-2035 cm^{-1}

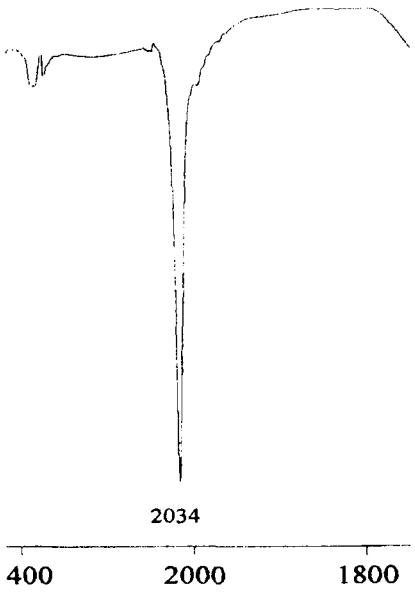
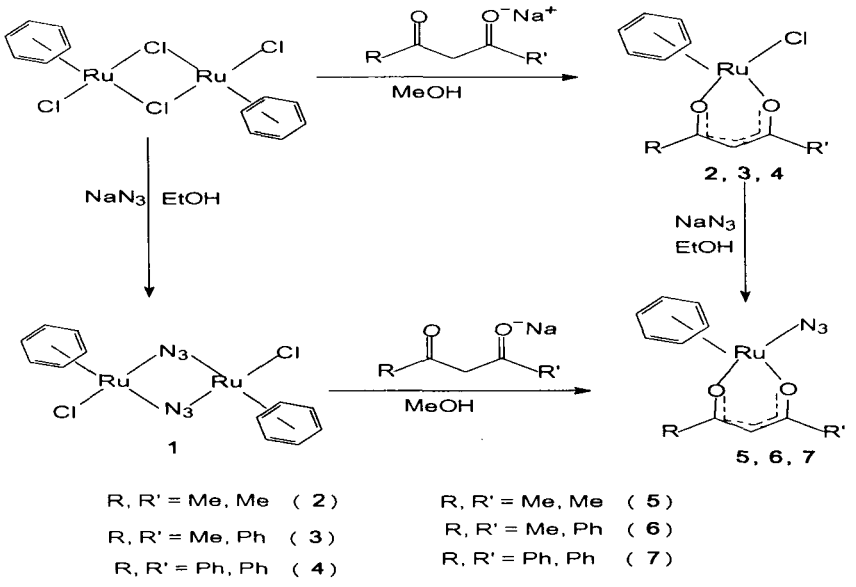


Figure 6.4: IR spectrum of $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})N_3]$ (**5**)

corresponding to stretching frequencies of terminal $\nu_{(N3)}$. The infrared spectra also showed a pair of strong to medium absorption bands in the range 1571-1520 cm^{-1} which is assigned to $\nu_{(C=O)} + \nu_{(C=C)}$ stretching frequencies of β-diketonate ligands [16].

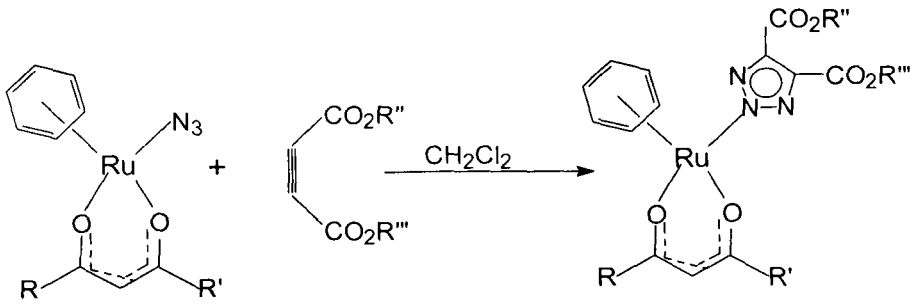


Scheme 6.1: Reaction pathways

The ^{1}H NMR spectra of these complexes exhibit a characteristic peaks in the range 5.80-6.00 ppm which corresponding to the protons of the benzene ligand. A singlet peak observed at 2.70-2.85 ppm is assigned to the methyl group of the β-diketonate ligand. In **4**, 5, **7** and **8** multiplets are observed in the aromatic region corresponding to the protons of the phenyl groups of the chelating ligands. A singlet at 5.60-5.78 ppm may be attributed to the *γ*-H proton of the *β*-diketonate ligands.

6.3.4. *Reaction of benzene ruthenium azido complexes with dimethylacetylene-dicarboxylate and diethylacetylenedicarboxylate*

Treatment of complex [(η^6-C_6H_6)Ru(*O,O'*-acac)N_3] (**5**) with a five-fold excess of a substituted acetylenes *viz.*, dimethylacetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$) and diethylacetylenedicarboxylate ($EtO_2CC{\equiv}CCO_2Et$) in dichloromethane or acetone and stirring at room temperature for 14-15 hrs affords in low yield the yellow-colored benzene ruthenium triazolato complexes: [(η^6-C_6H_6)Ru(*O,O'*-acac){N_3C_2-(CO_2CH_3)$_2$}] (**8**) and [(η^6-C_6H_6)Ru(O,O'-acac){N_3C_2($CO_2C_2H_5$)$_2$}] (**9**), respectively (Scheme 2).



R, R' = Me, Me (5)

R, R', R", R'" = Me, Me, Me, Me (8)

R, R' = Me, Me R", R'" = Et, Et (9)

Scheme 6.2: Reaction of carboxylate with ruthenium azide complex (**5**)

The formation of the yellow triazolato complexes (**8** and **9**) is confirmed by observing

the disappearance of the azido stretching frequency and appearance of a carbonyl ($\nu_{C=O}$) stretch at 1580 cm^{-1} for complex **8** and 1533 cm^{-1} for complex **9**. Apart from $\nu_{C=O}$, the infrared spectra show medium bands in the region 1580-1437 cm^{-1} due to ($\nu_{C=C}$) and ($\nu_{N=N}$), respectively (Figure 6.5). The ^1H NMR spectra of complexes **8** and **9** show a singlet resonance at 5.80-6.00 ppm corresponding to the protons of the benzene ligand.

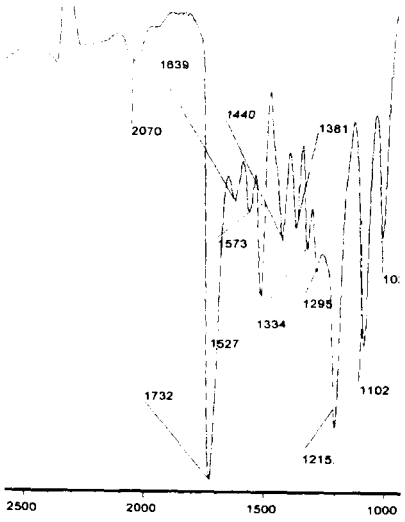


Figure 6.5: IR spectra of $[(\eta^6\text{-}C_6H_6)Ru(O,O'\text{-acac})\{N_3C_2(CO_2C_2H_5)_2\}]$ (**9**)

Singlet peak observed around 2.14 - 2.35 ppm is assigned to the methylene protons of the β-diketonate ligand. The protons of the methoxy group of the triazole ring appear as singlet at 1.91-2.21 ppm. In the case of **9**, the ^1H NMR spectrum exhibits a quartet at 3.65 ppm and a triplet at 2.35 ppm due to the methylene and methyl protons of the ethyl groups. We had recently reported the *p*-cymene ruthenium triazolato complex $[(\eta^6\text{-}p\text{-cymene})Ru(O,O'\text{-bzac})\{N_3C_2(CO_2C_2H_5)_2\}]$ where a terminal nitrogen of the triazolato group bonds to the metal [9]. In the case of benzene ruthenium triazolato complexes, the ruthenium metal binds with the middle nitrogen atom, which is a (N1)-bound isomer, as confirmed from the single crystal X-ray analysis of complex **9** (Figure 6.5). The bond

formation of ethoxy substituted complexes of *p*-cymene ruthenium and benzene ruthenium indicates that steric factors play an important role. The bulkier organic fragment of *p*-cymene ruthenium could cause steric hindrance for the incoming diethylacetylenedicarboxylate ligand which leads to bond formation with the terminal nitrogen. In the case of the benzene derivative **6**, the organic fragment does not encountered steric hindrance for the incoming ligands which results in metal bonding to the middle nitrogen (N1). Similarly, indenyl ruthenium bis(triphenylphosphine) azido complexes did not yield the triazolato complexes due to steric factor [9]. Study of the molecular models of the linkage isomer indicates that this congestion would be totally relieved in the isomer involving the middle nitrogen atom (N2) bonding. It should be noted that the triazole anion may be coordinated to a metal either through the N(1) atom or the N(2) atom [17]. Evidence obtained to date indicates that both the N(1) and N(2)-bonded products may be formed simultaneously [18]. In our study, the ethoxy substituted complex exclusively produces the isomer with the metal bonded to the middle nitrogen atom (N1).It has been reported that the initial formation of the N(1)-bonded complex *via* azide attack on the coordinated nitrile carbon of the pentamethylamine cobalt complexes is followed by slow isomerization to the N(2)-bonded complex [19]. In case of complexes **5** and **6**, our efforts to prepare the corresponding triazole complexes were unsuccessful. This may be due to lower electron density on the metal center (i) no methyl groups on aromatic ring and (ii) the substituents on the *β*-diketonate ligand, *viz.*, phenyl and methyl in (*O,O'*-bzac) and phenyl and phenyl in (*O,O'*-dbzm). At the same time, solubility problems are also encountered throughout the whole reaction process. The complexes **8** and **9** are soluble

in chlorinated solvents but insoluble in non-polar solvents and stable in air. The complexes **1** to **7** are partially soluble in methanol, dichloromethane, acetone and acetonitrile, but insoluble in non-polar solvents. Solubility problem with starting compounds have been faced throughout this study, which results in low yields.

The molecular structure of the complex [(η^6-C_6H_6)Ru(O,O'-acac) -{$N_3C_2(CO_2C_2H_5)_2$}] (**9**) is presented in Figure 1 and selected bond lengths and angles are given as well. The complex shows typical piano-stool geometry with the metal center being coordinated by a benzene ligand, a chelating β-diketonate and triazolate ligands. The Ru(1)-O(1) and Ru(1)-O(2) bond distances [2.062(3) and 2.063(3)] of the acetylacetato complex are similar to reported Ru-O bond lengths of other ruthenium β-diketonate systems [3b, 9, 20]. The Ru(1)-N(1) bond distance [2.078(3)] Å in complex **9** is comparable to those in [(η^6-*p*-cymene)Ru(*O,O'*-acac){$N_3C_2(CO_2C_2H_5)_2$}] [9a] and other ruthenium triazolato complexes [21]. The N-N bond distances of the triazole ring are 1.331(4) and 1.343(4) Å which is comparable to reported triazolato N-N bond lengths [9a, 21] (Figure 6.6). The O(1)-Ru(1)-O(2) [88.21(10)] bond angles of the complex are also comparable to other related systems [3b, 9, 20].

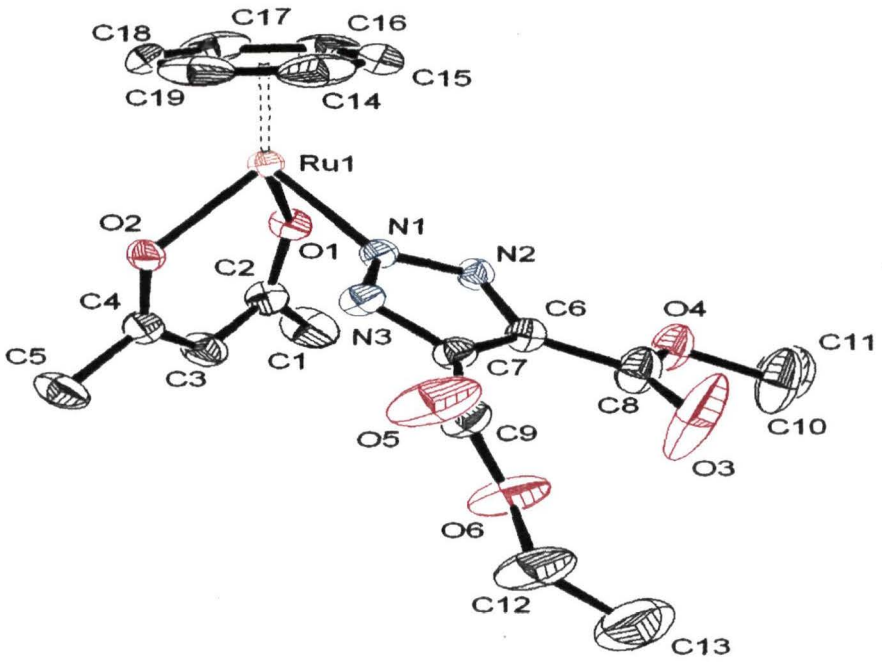


Figure 6.6: ORTEP diagram of **9** with labeling scheme at 50% probability level and H atoms being omitted for clarity. Selected bond distances (Å) and angles (°): C(2)-C(3) 1.386(6), C(3)-C(4) 1.388(6), N(1)-N(2) 1.331(4), N(1)-N(3) 1.343(4), N(1)-Ru(1) 2.078(3), O(2)-Ru(1) 2.063(3), O(1)-Ru(1) 2.062(3); N(2)-N(1)-N(3) 112.8(3), N(2)-N(1)-Ru(1) 125.1(2), N(3)-N(1)-Ru(1) 122.2(2), C(2)-O(1)-Ru(1) 124.4(2), C(4)-O(2)-Ru(1) 124.6(2), O(1)-Ru(1)-O(2) 88.21(10), O(1)-Ru(1)-N(1) 83.95(12), O(2)-Ru(1)-N(1) 83.27(12).

6.3.5. *Reaction of ruthenium azido complexes with fumaronitrile*

The reaction of azido complexes (**5**, **6** and **7**) with an excess of fumaronitrile at room temperature for 24 hrs affords the chocolate-colored triazolato complexes (**10, 11,** and **12**). The complexes are readily soluble in polar solvents like dichloromethane, chloroform, acetone and methanol but insoluble in non-polar solvents. The formation of the triazolato complexes is readily confirmed by the absence of the starting azide stretching frequency and the appearance of a strong peak in the range of 2225-2236 cm^{-1}

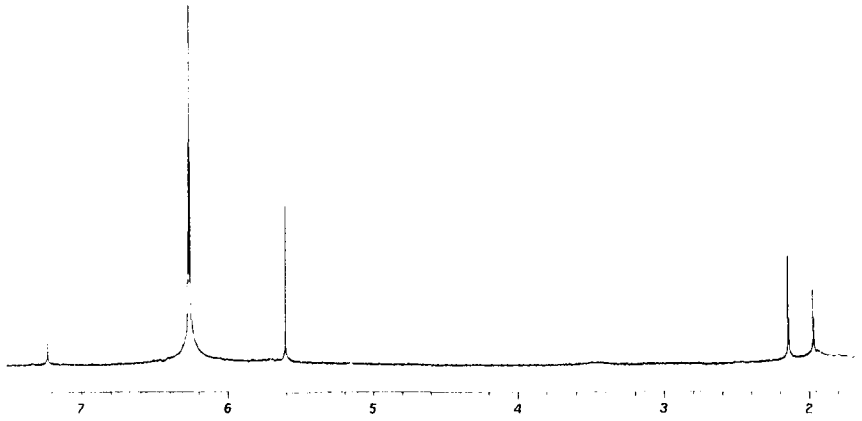
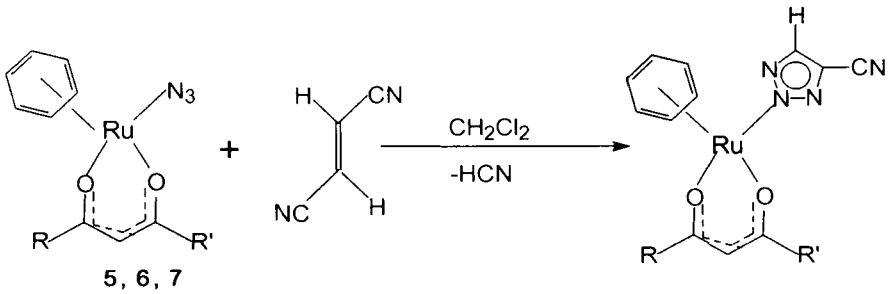


Figure 6.7: ^{1}H {NMR} spectrum of [(η^6-C_6H_6)Ru(O, O'-acac){N_3C_2HCN}] (**10**)

which corresponds to the stretching frequency of the C≡N group of the coordinated triazolato ligands. The ^{1}H NMR spectrum of the complexes shows characteristic singlet resonance at 6.86 ppm assignable to the CH proton of the triazolato group. A singlet in the region 5.59-5.81 ppm is attributed to the γH proton of the β-diketonate group (Figure 6.7).



R, R' = Me, Me (5)
R, R' = Me, Ph (6)
R, R' = Ph, Ph (7)

R, R' = Me, Me (10)
R, R' = Me, Ph (11)
R, R' = Ph, Ph (12)

Scheme 6.3: Reaction of fumaronitrile with ruthenium azide complexes

In addition, the aromatic protons of the benzene ligand give a signal at 5.92 ppm. In principle, cycloaddition of fumaronitrile to coordinated azide can take place through the C≡N or the C=C bond.

6.4. Conclusions

The syntheses of benzene ruthenium azido complexes of β-diketonates are described. These complexes undergo [3+2] cycloaddition reaction with substituted alkynes or fumaronitrile leading to the formation of substituted triazolato complexes. The cycloaddition of diethylacetylenedicarboxylate produces triazolato complexes with the middle atom of the triazole group bonded to the metal. In the case of the *p*-cymene ruthenium triazolato analogue, the same reaction produces terminal nitrogen-bonded triazalato complexes.

Table 6.1. Crystal data and experimental details for [(η^6-C_6H_6)Ru(*O,O'*-acac) - {$N_3C_2(CO_2C_2H_5)_2$}] (**9**).

Chemical formula	$C_{19}H_{24}N_3O_6Ru$
Formula weight	491.48
Crystal system	Monoclinic
Space group	P 2_1/c (no. 14)
Crystal colour and shape	red block
Crystal size	0.42 x 0.22 x 0.10
a (Å)	11.265(2)
b (Å)	7.2910(10)
c (Å)	24.976(5)
β (°)	98.36(3)
V (Å^3)	2029.6(6)
Z	4
T (K)	173(2)
D_c (g.cm^{-3})	1.608
μ (mm^{-1})	0.813
Scan range (°)	$2.28 < \theta < 25.97$
Unique reflections	3941
Reflections used [I>2σ(I)]	2772
R_{int}	0.0481
Final R indices [I>2σ(I)]*	0.0364, wR_2 0.0894

R indices (all data)	0.0574, wR_2 0.0951
Goodness-of-fit	1.038
Max. Min $\Delta\rho/e$ ($Å^{-3}$)	0.794, -0.549

* Structures were refined on F_0^2: $wR_2 = [\sum[w(F_0^2 - F_c^2)^2] / \sum w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$

References

1. (a) H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.*, 29 (1989) 163; (b) M. A. Bennett, *Coord. Chem. Rev.*, 166 (1997) 225.
2. (a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.*, 30 (1997) 97; (b) T. Naota, H. Takaya, S. I. Murahashi, *Chem. Rev.*, 98 (1998) 2599; (c) M. J. Palmer, M. Wills, *Tetrahedron Asym.*, 10 (1999) 2045; (d) D. Carmona, M. P. Lamata, L. A. Oro, *Eur. J. Inorg. Chem.*, (2002) 2239; (e) R. K. Rath, M. Nethaji, A. R. Chakravarty, *Polyhedron* 20 (2001) 2735; (f) D. L. Davies, J. Fawcett, S. A. Garratt, D. R. Russell, *Organometallics* 20 (2001) 3029; (g) H. Brunner, T. Zwack, M. Zabel, W. Beck, A. Böhm, *Organometallics* 22 (2003) 1741; (h) S. B. Wendicke, E. Burri, R. Scopelliti, K. Severin, *Organometallics* 22 (2003) 1894; (i) V. Cadierno, J. Diez, J. Carcía-Álvarez, J. Gimeno, *Organometallics* 22 (2004) 3425.
3. (a) Y. K. Yan, M. Melchart, A. Habtemariam, P. J. Sadler, *Chem. Commun.*, (2005) 4764 5; (b) R. Fernandez, M. Melchart, A. Habtemariam, S. Parsons, P. J. Sadler. *Chem. Eur. J.*, 10 (2004) 5173; (c) H. Chen, J. A. Parkinson, S. Parsons, R.

A. Coxall, R. O. Gould, P. J. Sadler, J. *Am. Chem. Soc.* 124 (2002) 3064; (d) P. J. Dyson, G. Sava, *Dalton Trans.*, (2006) 1929.

4. G. Winkhaus, H. Singer, *J. Organomet. Chem.*, 7 (1967) 487.

5. (a) I. de Los Rios, M. J. Tenerio, M. A. J. Tenerio, M. C. Puerta, P. Valerga, J. *Organomet. Chem.*, 525 (1996) 57; (b) A. Schluter, K. Bieber, W. S. Sheldrick, *Inorg. Chim. Acta.*, 340 (2002) 35; (c) Y. Chen, M. Valentini, P. S. Pregosin, A. Albinati, *Inorg. Chim. Acta.*, 327 (2002) 4.

6. (a) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, 2 (1963) 565; (b) R. Huisgen, *J. Org. Chem.*, 41 (1976) 403; (c) S. Patai, "*The chemistry of azides Groups*" Interscience publishers: New York, (1971) 331.

7. (a) R. Huisgen, in : A. Padwa (Ed.), *1, 3-dipolar cycloaddition chemistry*, John Wiley : New York; Vol. A. pp 1-176 (1984); (b) T. L. Gilchrist, G. E. Gymer, A. R. Katritzky, J. A. Button, *Adv. Heterocyl. Chem.*, 16 (1974) 33.

8. H.-W. Frühauf, Chem. Rev. 97 (1997) 523; (b) Z. Dori, R. F. Ziolo, *Chem. Rev.*, 73 (1973) 247.

9. (a) K. Sarjit Singh, K. A. Kreisel, G. P. A. Yap, K. Mohan Rao, *J. Organomet. Chem.*, 691 (2006) 3509; (b) K. Sarjit Singh, C. Thöne, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 4222; (c) P. Govindaswamy, S. M. Mobin, C. Thöne, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 1218.

P. Govindaswamy, P. J. Carroll, Y. A. Mozharivskyj, K. Mohan Rao, *J. Organomet. Chem.*, 690 (2005) 885.

10. A. I. Vogel, "*A. I. Vogel text book of practical organic chemistry*" ELBS, Fourth Edition (1984) 264.

11. M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 21 (1982) 74.

12. M. Sheldrick, *Acta Cryst.*, A46 (1990) 467.

13. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany (1999).

14. L. J. Farrugia, *J. Appl. Cryst.*, 30 (1997) 565.

15. S. Kawaguchi, *Coord. Chem. Rev.*, 70 (1986) 51.

16. (a) J. H. Nelson, D. L. Schmitt, R. A. Hendry, D. W. Moore, H. B. Jonassen, *Inorg. Chem.*, 9 (1970) 2678; (b) D. A. Redfield, J. H. Nelson, R. A. Hendry, D. W. Moore, H. B. Jonassen, *J. Am. Chem. Soc.*, 96 (1974) 6298.

17. Jr W. R. Ellis, W. L. Purcell, *Inorg. Chem.*, 21 (1982) 834.

18. T. Kemmerich, J. H. Nelson, N. E. Takach, H. Boebme. B. Jablonski, W. Beck, *Inorg. Chem.*, 21 (1982) 1226.

19. F. Kuhlwein, K. Polborn, W. Beck, *Z. Anorg. Allg. Chem.*, 623 (1997) 1211.

20. C.-W- Chang, G.-H. Lee, *Organometallics.* 22 (2003) 3107.

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CHAPTER 7

Syntheses of mono, di and trinuclear η^6-arene ruthenium carboxylato complexes: their reactions towards azide and acetate anions and some neutral ligands.

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Syntheses of mono, di and trinuclear η^6-arene ruthenium carboxylato complexes: their reactions towards azide and acetate anions and some neutral ligands.

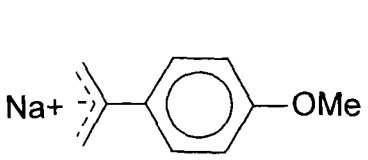
Abstract

Arene ruthenium complexes containing carboxylato groups can be readily prepared by reacting $[(\eta^6\text{-arene})RuCl_2]_2$ with the corresponding sodium salts of the carboxylic acids. The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ [arene = benzene (**1**), *p*-cymene (**2**)] with sodium salts of carboxylic acids *viz.* sodium anisiate (pa), in methanol yields complexes of formulations $[(\eta^6\text{-arene})RuCl(O_2CC_6H_4\text{-}p\text{-}OMe)]$ (**3** and **4**). In similar manner the reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with sodium oxlate $Na_2C_2O_4$, sodium malonate $Na_2CH_2(CO_2)_2$, sodium salt of benzene 1, 4 dicarboxylic acid (terephthalic acid) $Na_2\ C_6H_4(CO_2)_2$ and sodium salt of benzene tricaboxylic acid $Na_3C_6H_3(CO_2)_3$ to yield complexes of the type $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}\eta^4\text{-}C_2O_4)]$ (**5** and **6**), $[\{(\eta^6\text{-arene})RuCl\}_2\{\mu\text{-}\eta^4\text{-}CH_2(CO_2)_2\}]$ (**7** and **8**), $[\{(\eta^6\text{-arene})RuCl\}_2\{\mu\text{-}\eta^4\text{-}1,4\text{-}C_6H_4(CO_2)_2\}]$ (**9** and **10**) and $[\{(\eta^6\text{-arene})RuCl\}_3\{\mu\text{-}\eta^6\text{-}1,3,5\text{-}C_6H_3(CO_2)_3\}]$ (**11** and **12**) respectively. These complexes (**5**) to (**10**) reacts with NaN_3 in ethanol to give known azide dimers $[(\eta^6\text{-arene})Ru(\mu\text{-}N_3)Cl]_2$ by the displacement of the carboxylate ligand. Whereas complexes **11** and **12** with sodium azide yielded triazido complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}N_3)Cl]_3$ (**13** and **14**) respectively. This is the first time trimers which were isolated.

Keywords: *Ruthenium, cymene, benzene tricaboxylic acid, terephthalic acid, oxalic acid.*

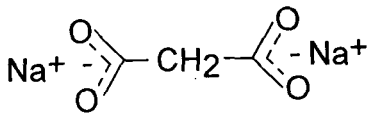
7.1 Introduction

The reactivity of arene ruthenium(II) dimers with various ligands have been reported [1-3]. In contrast, the chemistry of arene ruthenium dimer with oxygen donor ligands is relatively unexplored. A few reports are available on these complexes of β-diketonate and a few carboxylato ligands [4-6]. It is well known that carboxylato complexes of the platinum-group metals are useful synthetic precursors owing to the lability of the carboxylato ligands, which allows, for example, the generation of hydrido-complexes under mild conditions [7, 8]. Carboxylato group can be displaced by other anions in the complexes. The labile nature of carboxylato group towards anions leads to generate a lot of interesting chemistry of arene ruthenium carboxylato complexes. We reinvestigated the preparation of mono and di-nuclear arene ruthenium complexes [5, 6] and reported an improved method for the preparation of $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(\mu\text{-}\eta^4\text{-}C_2O_4)]$ and its reaction with various ligands. This chapter describes the synthesis of mono, di and tri-nuclear arene ruthenium complexes containing carboxylato groups and the facile displacement of the carboxylate ligands with another anions such as azide and acetate and various neutral ligands. The formation of carboxylato complexes from the versatile starting complexes $[(\eta^6\text{-}arene)Ru(\mu\text{-}N_3)Cl]_2$ are also described. The complexes were characterized on the basis of microanalysis, Infrared and NMR spectroscopic data. The following ligands are used in this study (Scheme 7.1).



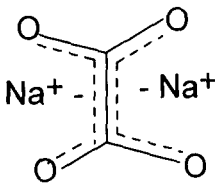
p-anisiate(pa)

L_1



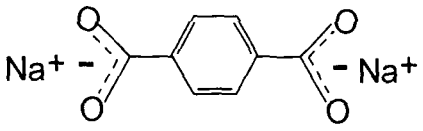
malonate (ma)

L_3



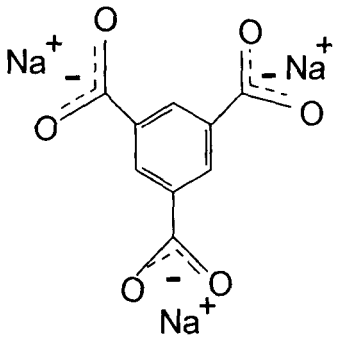
oxalate (ox)

L_2



Sodium salt of benzene 1, 4 dicarboxylate

L_4



Sodium salt of benzene 1,3, 5 tricarboxylate

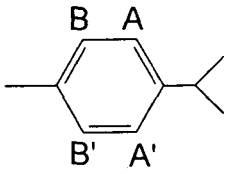
L_5

Scheme 7.1: Ligands are used in this study

7.2 Experimental

All solvents were dried in appropriate drying agents and distilled prior to use [9]. $RuCl_3$. $3H_2O$ (Arora Matthey Limited) Oxalic acid (SD Fine), Malonic acid (SD Fine) and *p*-Anisic acid (SRL), terephthalic acid (SRL), benzene 1, 3, 5 tricarboxylic acid (Alfa Aesar) were used as received. ^1H NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 (^1H), or 100.61 MHz (^{13}C) with $SiMe_4$ as internal references and coupling constants are given in hertz. The precursor complexes [(η^6-

benzene)$RuCl_2]_2$ (**1**) and $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (**2**) were prepared according to the literature method [10].



7.2.1 *Preparation of sodium salts of carboxylic acids*

Sodium salts of carboxylic acids were prepared by reacting corresponding carboxylic acids with 2 equiv. of NaOH in ethanol as delineated here. 2 equivalents of NaOH in 100 ml of ethanol were stirred until NaOH is completely dissolved. To this stirring solution was added 1 equiv. of the corresponding carboxylic acid and stirred for 24 hr. The white precipitate was filtered and washed with cold ethanol and dried.

7.2.2. Preparation of $[(\eta^6$-arene)$Ru(L_1)Cl]$ (3 and 4)

The complex $[(\eta^6$-*arene*)$RuCl_2]_2$ (100 mg, 0.163 mmol) and the ligand L_1 (56 mg, 0.326 mmol) were stirred in 40 ml of methanol for 6 hr. The red solution changed to orange red as the reaction proceeded. The solvent was evaporated in vacuum and the residue was dissolved in dichloromethane. The solution was concentrated to *ca.* 5 ml followed by excess of hexane was added. The yellow orange solid was collected and washed with (2 x 20 ml) hexane and dried under vacuum.

Complex $[(\eta^6$-$C_6H_6)RuCl(O_2CC_6H_4$-p-OMe)] (3)

Yield: 140 mg (67.7%)

Complex $[(\eta^6$-p-cymene)$RuCl(O_2CC_6H_4$-p-OMe)] (4)

Yield: 46 mg (76%).

7.2.3 Preparation of [{(η^6-arene)RuCl}$_2$(μ-L_2)] (L_2 = μ-η^4-C_2O_4) (5, 6)

To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (200 mg, 0.326 mmol) in MeOH (30 ml) was added $Na_2C_2O_4.H_2O$ (43 mg, 0.326 mmol). The mixture was stirred for 1 hr at room temperature. The yellow orange precipitate was collected by centrifuged and washed with methanol and finally with diethyl ether and dried under vacuum. Additional product can be obtained from the liquid by evaporating the liquid to dryness and filtered to remove NaCl and precipitated out with hexane.

Complex [{(η^6-C_6H_6)RuCl}$_2$(μ-η^4-C_2O_4)] (5)

Yield: 75 mg (72.4%)

Complex [{η^6-p-cymene)RuCl}$_2$(μ-η^4-C_2O_4)] (6)

Yield: 143 mg (92%)

7.2.4. *Preparation of [{(η^6-arene)RuCl}$_2$ (μ-L_3)] (L_3 = η^4-$CH_2(CO_2)_2$) (7, 8)*

A round bottom flask was charged with [{(η^6-*p*-arene)$RuCl_2$}$_2$] (120 mg, 0.196 mmol), $Na_2CH_2(CO_2)_2$ (ma) (28 mg, 0.196 mmol) and methanol (40 ml). The mixture was stirred at room temperature for 6 hrs. The red solution turned into orange yellow solution as the reaction proceeded. The solvent was removed under reduced pressure then the solid residue was extracted with dichloromethane. After which the solution was filtered to remove insoluble materials. The filtrate on subsequent concentration to *ca.* 5 ml and addition of excess hexane induced a yellow solid of the complex. The solid was collected and washed with hexane (2 x 10 ml) and dried under vacuum.

Complex [{(η^6-C_6H_6)RuCl}$_2${μ-η^4-$CH_2(CO_2)_2$}] (7).

Yield: 138 mg (87%).

Complex [{η^6-p-cymene)RuCl}$_2${μ-η^4-$CH_2(CO_2)_2$}] (8).

Yield: 120 mg (98%).

7.2.5 *Preparation of [{(η^6-arene)RuCl}$_2$(μ-L_4)] (L_4 = η^4-$C_6H_4(CO_2)_2$) (9, 10)*

A round bottom flask was charged with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (100 mg, 0.163 mmol), $Na_2C_6H_4(CO_2)_2$ (bd) (34 mg, 0.163 mmol) and methanol (30 ml). The mixture was stirred at room temperature for 8 hrs. The brick-red solution turned into orange yellow solution as the reaction proceeded. The solvent were removed under reduce pressure then the solid residue was extracted with dichloromethane. After that the solution was filtered to remove insoluble materials. The filtrate on subsequent concentration to *ca.* 5 ml and addition of hexane induced a yellow solid of the complex. The solid was collected and washed with (2 x 20 ml) of hexane and dried under vacuum.

Complex [{(η^6-C_6H_6)RuCl}$_2${μ-η^4-1,4-$C_6H_4(CO_2)_2$}] (9)

Yield: 65 mg (60.3%).

Complex [{η^6-p-cymene)RuCl}$_2${μ-η^4-1,4-$C_6H_4(CO_2)_2$}] (10)

120 mg (75%).

7.2.6 *Preparation of [{(η^6-C_6H_6)RuCl}$_3$(μ_3-$C_6H_3(CO_2)_3$] (11)*

A round bottom flask was charged with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (100 mg, 0.19 mmol), $NaC_6H_3(CO_2)_3$ (bt) (16 mg, 0.59 mmol) and methanol (30 ml). The mixture was stirred at room temperature for 8 hrs. The brick-red solution turned into orange color solution as the reaction proceeded. The solvent were removed under reduce pressure then the solid residue was extracted with dichloromethane. After that the solution was filtered to remove insoluble materials. The filtrate on subsequent concentration to *ca.* 5 ml and

addition of hexane induced a yellow solid of the complex. The solid was collected and washed with (2 x 20 ml) of hexane and dried under vacuum.

Yield: 65 mg (39.3%)

7.2.7 *Preparation of [{(η^6-p-cymene)RuCl}$_3$(μ_3-L_5)] (L_5 = (η^6-$C_6H_3(CO_2)_3$) (12)*

A round bottom flask was charged with [(η^6-*p*-cymene)$RuCl_2$]$_2$ (100 mg, 0.163 mmol), $Na_3C_6H_3(CO_2)_3$ (bt) (22 mg, 0.082 mmol) and methanol (30 ml). The mixture was stirred at room temperature for 10 hrs. The wine-red solution turned into deep orange color solution as the reaction proceeded. The solvent were removed under reduce pressure then the solid residue was extracted with dichloromethane. After that the solution was filtered to remove insoluble materials. The filtrate on subsequent concentration to *ca.* 5 ml and addition of hexane induced a yellow solid of the complex. The solid was collected and washed with (2 x 20 ml) of hexane and dried under vacuum. Yield: 79 mg (51.33%).

7.2.8 *Preparation of [(η^6-arene)Ru(μ-N_3)Cl]$_3$ (13 and 14)*

This complex is prepared by the reaction of [{(η^6-arene)RuCl}$_3${μ-$C_6H_3(CO_2)_3$}] (100 mg, 0.19 mmol) with five fold of sodium azides (60 mg, 0.98 mmol) in 20 ml of ethanol. The reddish mixture solution was stirred at room temperature for 8hrs. The solution turned into a yellow solution. The insoluble materials were filtered off and the solvent were removed by rotary evaporator to *ca.*5 ml. The residue was extracted with dichloromethane followed by addition of an excess of hexane which afforded a yellow solid compound.

Complex [(η^6-C_6H_6)Ru(μ-N_3)Cl]$_3$ (13).

Yield: 68 mg (44.1%).

Complex [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_3$ (14).

Yield: 119 mg (78%).

7.3. *Results and discussion*

The reaction of [(η^6-arene)$RuCl_2$]$_2$ with sodium salts of the ligand (pa) in methanol yielded an orange yellow mononuclear complexes of formulation [(η^6-arene)RuCl(L_1)] (L_1 = pa; **3** and **4**) in good yield (Scheme 7.2). The infrared spectra of these complexes (**3** and **4**) shows a strong peak corresponding to the $\nu_{C=O}$ around 1626 cm^{-1} (Figure 7.1). The proton NMR spectra of the complexes exhibited a characteristic peaks for benzene and p-cymene groups where as methoxy group of the coordinated ligand appeared as singlet at δ 3.80 (IR and ^{1}H NMR details data are given in table 7.1).

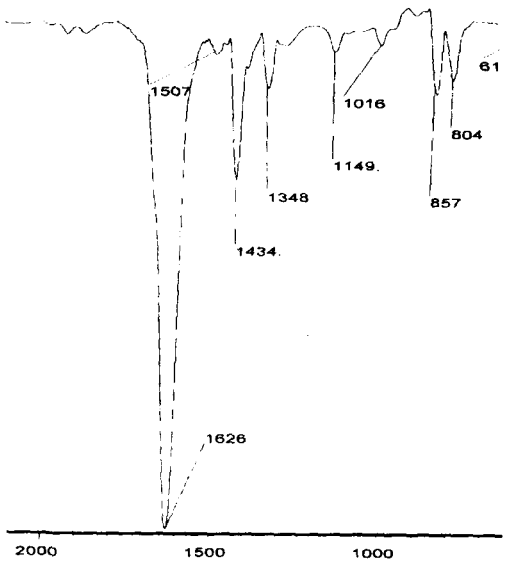
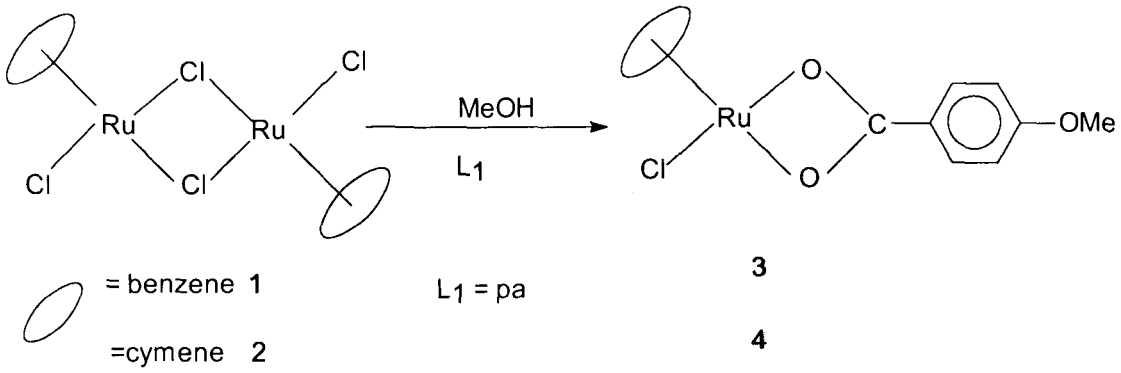


Figure 7.1: IR spectrum of [η^6-*p*-cymene)RuCl(pa)]



Scheme 7.2: Syntheses of mono nuclear complexes

7.3.2 *Reactions of sodium oxlate, sodium malonate and sodium salt of benzene dicarboxylate:*

We reinvestigated and report an improved method for the preparation of this complex **6** in good yield by two methods. (a) Treatment of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with $Na_2C_2O_4.H_2O$ in methanol stirring for 1 hr afforded yellow complex of (**6**) in good yield. (b) Treatment of complex $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ with sodium oxalate gave the complex in fairly good yield. The complex **6** has been fully characterized by analytical, spectroscopic data (^1H, ^{13}C $\{^1H\}$ NMR data, details are given in table 7.1) and confirmed by X-ray crystallography. Since the single crystal data matched well to the one reported by G. S. Fink and co-workers [5], so data is not reported here. The IR spectrum showed a strong single peak at around 1619 cm^{-1} characteristic of $\nu_{(C=O)}$ which is slightly lower than that reported in copper oxalato system [11]. The single absorption peak indicates the delocalization of electron in oxalato group. The ^{13}C $\{^1H\}$ NMR data of the complex exhibits signal in addition to signal for the carbons of arene ring at 171 ppm assignable to the carbon of CO_2 group (spectroscopic analytical data, details are given in table 7.1).

This complex can also be obtained by azide displacement of complex [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ with oxalato group. Thus, treatment of azide dimer [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ with sodium oxalate in ethanol gave a yellow solid of the complex [{(η^6-*p*-cymene)RuCl}$_2$(η^2-C_2O_4)]. The formation of this complex was confirmed by the absence of azide stretching frequency and appearance of new peak at 1619 cm^{-1} for $\nu_{(C=O)}$ in the IR spectrum. This indicates that the reaction is reversible. In an attempt to synthesis [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ by treating the complex [{(η^6-*p*-cymene)Ru(η^2-C_2O_4)Cl}$_2$] with sodium azide in ethanol afforded a red compound appears to be same complex obtained from [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ with trimethylsilyl azide by Bates *et al* [12] and reported by us [12a]. The IR spectrum of this complex showed strong absorption at 2057 cm^{-1} characteristic of bridging azide ligands [13]. The complex is believed to be resulted by the displacement of *oxalato* group with azido group giving a well known azide dimer [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ which had already been synthesized and structurally characterized by previous workers (Scheme 7.3) [12]. The formation of this compound is supported by analytical and spectroscopic data. Further, single crystal X-ray analysis confirmed the formation this compound [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$. These reactions we extended to benzene dimer and observed similar results. The IR spectrum complex **5** showed a strong single peak at around 1633 cm^{-1} characteristic of $\nu_{(C=O)}$ which is higher than that of *p*-cymene dimer, which is understood easily by low electron density on metal as compared to p-cymene dimer due to benzene ring. The proton NMR spectrum has exhibited single sharp peak at δ 5.97 due to benzene ring protons.

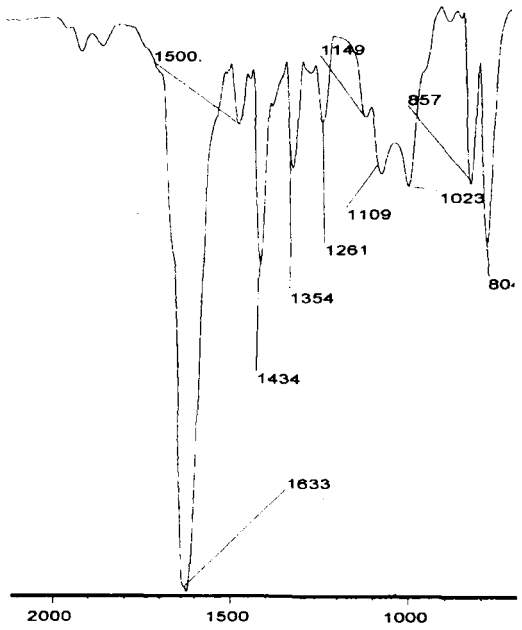
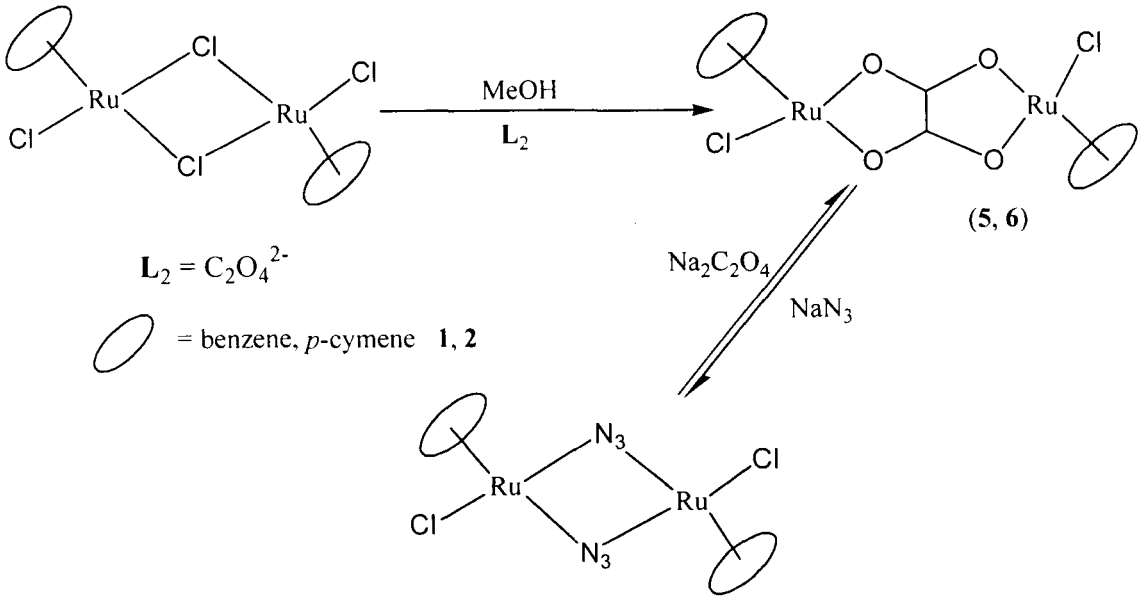
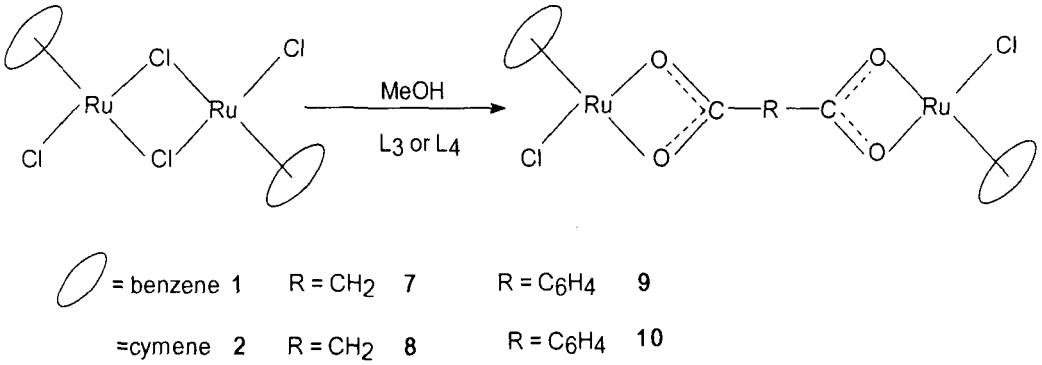


Figure 7.2: IR spectrum of $[\{(\eta^6\text{-}C_6H_6)RuCl\}_2(\mu\text{-}\eta^4\text{-}C_6H_4(CO_2)_2)]$ (**9**)



Scheme 7.3: Syntheses of dinuclear complexes

In similar manner dinuclear complex [{(η^6-*p-arene*)RuCl}$_2$(μ-η^2-$(CO_2)_2CH_2$)] can be prepared by the treatment of complex [(η^6-*p*-arene)$RuCl_2]_2$ with sodium malonate in methanol at room temperature (Scheme 7.4). The infrared spectra of these complexes exhibited a strong band due to $\nu_{(C=O)}$ around 1630 cm^{-1}. Treatment of dimers [{(η^6-*p*-arene)RuCl}$_2$(μ-η^2-$(CO_2)_2CH_2$)] with sodium azide gave azide dimer [(η^6-*p*-cym)Ru(μ-N_3)$Cl]_2$ by the displacement of malanato group which has been observed in the case of oxalato complexes.



Scheme 7.4: Syntheses of dinuclear complexes

The proton NMR spectra of these complexes exhibited bridging CH_2 group at 3.5 ppm as a singlet and bridging benzene protons at 5.98 ppm as a singlet respectively along with benzene and *p*-cymene peaks.

3.3 Reaction with benzene tricarboxylate (L_5)

Arene dimers **1** and **2** reacted with sodium salt of benzene tricarboxylate in ethanol and yielded trimeric complexes. These complexes exhibited sharp single band in the infrared spectra around 1619 for $\nu_{(C=O)}$ indicating the symmetric complexes (**11** and **12**) and also exhibited single sharp peak at δ 5.14-5.94 for protons of benzene ring apart from which an usual peaks for cymene ring and single peak for benzene in the ratio 1:3. We are

unable to get single crystals of these complexes. However on the basis dimeric structures of dicarboxylates, these complexes are proposed trimeric structures (Scheme 7.5). Like complexes **7-10**, these complexes also reacted with Sodium azide and yielded trimeric azido complexes (**13** and **14**) (Scheme 7.5). These are the first complexes of this nature. These complexes conformed by mass spectral analyses. The infrared spectra also shows the absence of $\nu_{(C=O)}$ band and the presence of 2057 cm^{-1} due to azido group which conforms the formation of azido complexes (Figure 7.6). However, efforts to make single crystals of these compounds not yielded fruitful results. So, we proposed the following structures which are mentioned in scheme 7.5.

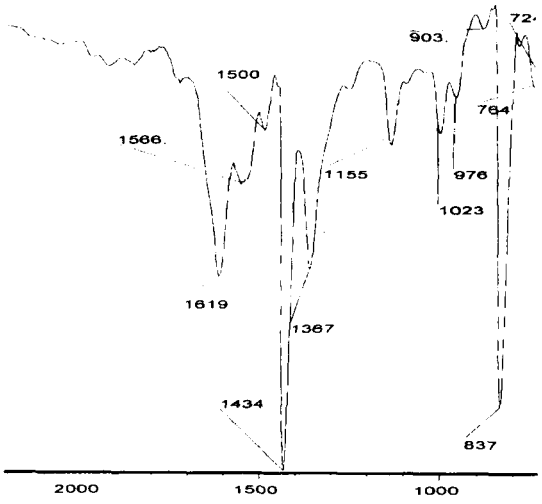


Figure 7.5: IR spectrum of $[\{(\eta^6\text{-}C_6H_6)RuCl\}_3(\mu_3\text{-}C_6H_3(CO_2)_3]$ (**11**)

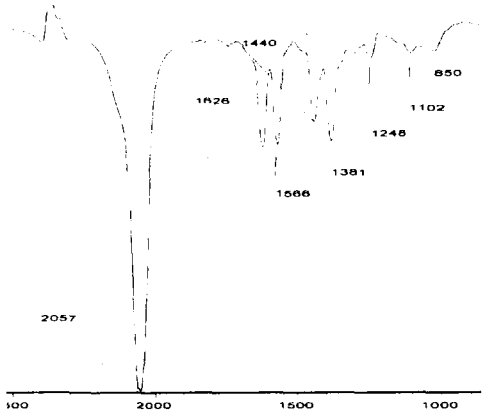
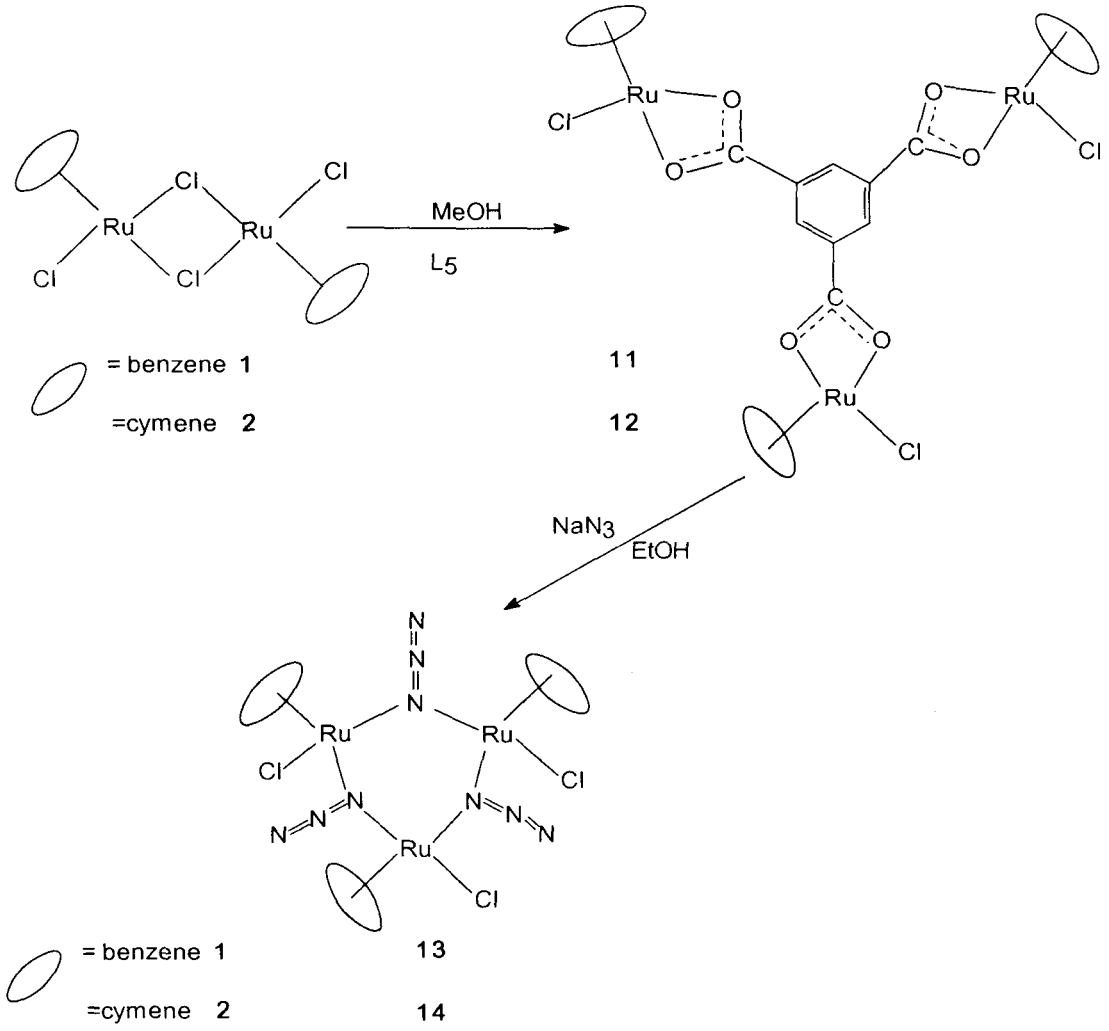


Figure 7.6: IR spectrum of complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl]_3$



$\mathbf{L_5} = Na_3C_6H_3(CO_2)_3$

Scheme 7.5: Syntheses of trinuclear complexes

Table 7.1; IR and NMR data of the complexes (**3-14**)

Complex No.	IR (KBr, cm-1, $\nu_{(C=O)}$	^{1}H NMR ($CDCl_3$, δ)	^{13}C NMR ($CDCl_3$, δ)
3	1624	3.80 (s, 3H, OCH_3); 5.89 (s, 6H, C_6H_6); 7.12 (d, J_{H-H} = 7.00Hz, 1H); 8.00 (d, J_{H-H} = 7.7Hz, 1H)	
4	1626	1.39 (d, 6H, $CH(CH_3)_2$, J_{H-H} = 6.92 Hz), 2.32 (s, 3H, (CH_3)), 2.98 (m, 1H, $CH(CH_3)_2$)), 3.80 (s, OMe), 5.44 (d, 2H, J_{H-H} = 6.96 Hz), 5.67 (d, 2H, J_{H-H} = 6.0 Hz), 6.79 (d, 2H, J_{H-H} = 8.76 Hz), 7.81 (d, 2H, J_{H-H} = 8.76 Hz).	18.81 (s, CH_3), 22.40 (s, CH_3, $CH(CH_3)_2$), 31.59 (s, CH, $CH(CH_3)_2$), 55.35 (s, CH_3 (OCH_3)), 78.56 (s, $C_{AA'}$), 79.12 (s, $C_{BB'}$), 94.20 (s, CMe), 100.44 (CPr^i), 113.23 (s), 124.16 (s), 130.60 (s), 163.29 (s, $C(CO_2)$), 184.38 (s, (CO_2).
5	1633	5.97 (s, 6H, C_6H_6)	120(s),159.07(s,CO_2)

6	1619	^{1}H NMR ($CDCl_3$, δ): 1.30 (d, 6H, J_{H-H} = 6.86), 2.22 (s, 3H), 2.63 (m, 1H), 5.33 (d, 2H, J_{H-H} = 6.08), 5.56 (d, 2H, J_{H-H} = 6.02).	18.64 (s, CH_3), 22.55 (s, CH_3, $CH(CH_3)_2$), 31.23 (s, CH, $CH(CH_3)_2$), 78.52, 80.53, 95.60, 99.95 (C_6H_4), 171.80 (s, CO).
7	1633	5.88 (s, 6H, C_6H_6); 3.62 (s, 2H, (CH_2)).	
8	1633.	1.26 (d, 12H, J_{H-H} = 6.9), 2.08 (s, 6H), 2.82 (m, 2H, $CH(CH_3)_2$), 3.47 (s, 2H, (CH_2)), 5.32 (d, 4H, J_{H-H} = 5.8), 5.46 (d, 4H, J_{H-H} = 5.7).	18.39 (s, Me), 22.07 (s, CH_3, $CH(CH_3)_2$), 30.76 (s, CH, $CH(CH_3)_2$), 40.76 (s, -CH_2-), 77.33-101.20 (C_6H_4), 172.43 (s, CO_2).
9	1633.	5.87 (s, 6H, C_6H_6); 5.98 (s, 4H)	122.45 (s, C_6H_6), 160.65 (s, CO_2).
10	1606.	1.26 (d, 12H, J_{H-H} = 6.9), 2.08 (s, 6H), 2.82 (m, 2H, $CH(CH_3)_2$), 3.47 (s, 4H, (C_6H_4)), 5.32 (d, 4H, J_{H-H} =6.02).	
11	1619.	5.71 (s, 6H, C_6H_6), 5.95 (s, 3H,	125 (s, C_6H_6),

		$C_6H_3(CO_2)_3$)	158.95 (s, CO_2)
12	1624.	1.32 (d, 12H, J_{H-H} = 6.9), 2.25(s, 6H), 2.92 (sept., 2H), 5.20 (d, 4H, J_{H-H} = 6.2 Hz), 5.14 (s, 3H, $C_6H_3(CO_2)_3$), 5.46 (d, 4H, J_{H-H} = 6.4 Hz), 5.12 (s, 3H, $C_6H_3(CO_2)_3$)	
13	2057	5.82 (s, 6H, C_6H_6);	
14	2057	1.34 (d, 12H, J_{H-H} = 6.4), 2.10 (s, 6H), 2.78 (sept., 2H), 3.80 (s, 6H, OMe), 5.26 (d, 4H, J_{H-H} = 5.9), 5.48 (d, 4H, J_{H-H} = 6.2), 6.78 (d, 4H, J_{H-H} = 5.7), 7.72 (d, 2H, J_{H-H} = 6.8), 7.88 (d, 4H, J_{H-H} = 6.0), 8.69 (d, 2H, J_{H-H} = 6.7).	

4 *Conclusions*

The present chapter described the synthesis of a series of arene ruthenium(II) complexes incorporating carboxylato groups. Mono, di and trinuclear complexes of arene ruthenium complexes were prepared and their reaction towards anions and neutral

ligands has been discussed. It also highlighted that the facile displacement of carboxylato group in the dinuclear complexes 5, 6, 9, 10, 11 and 12 by azide anion resulting in the formation of arene ruthenium azide dimer $[(\eta^6\text{-arene})Ru(\mu\text{-}N_3)Cl_2]_2$ and $[\{(\eta^6\text{-arene})Ru(\mu\text{-}N_3)Cl\}_3]$.

References

[1] H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.*, 29 (1989) 165.

[2] (a) R. Lalrempuia, P. J. Carroll, M. R. Kollipara *J. Chem. Sci.*, 116 (2004) 21; (b) R. Lalrempuia, M. R. Kollipara, *Polyhedron* 22 (2003) 3155.

[3] I. Moldes, E. de la Encarnacion, J. Ros, A. Alvarez-Larena, Joan F. Piniella, *J. Organomet. Chem.*, 566 (1998) 165.

[4] (a) M. A. Bennett, T. R. B Mitchell, M. R. Stevens, A. C. Willis, *Can. J. Chem.*, 79 (2001) 655; (b) Daniel Carmona, J. Ferrer, Luis A. Oro, *J. Chem. Soc. Dalton Trans.*, (1990) 1463.

[5] H. Yan, G. Süss-Fink, Antonia Neels, H. Stoeckli-Evans, *J. Chem. Soc. Dalton Trans.* (1997) 4345.

[6] Derek A. Tocher, Robert O. Gould, T. A. Stephenson, *J. Chem. Soc. Dalton Trans.* (1983) 1571.

[7] Part 32, A. Nutton, P. M. Maitlis, *Preceding paper.*

[8] (a) P. M. Maitlis, *Chem. Soc. Rev.*, 10 (1981) 1; (b) P. M. Maitlis, *Acc. Chem. Res.*, 11 (1978) 301.

[9] A. I. Vogel, "*A. I. Vogel's Text Book of Practical Organic Chemistry*" ELBS, Fourth Edition (1984) 264.

[10] (a) M. A Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 21 (1985) 75; (b) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem.*, 10 (1980) 1014; (c) M. A. Bennett, A. K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.

[11] Katrin Köhler, J. Eichhorn, Franc Meyer, Denis Vodovic, *Organometallics*, 22 (2003) 4426.

[12] R. S. Bates, M. J. Begley, A. H. Wright, *Polyhedron*, 9 (1990) 1113.

[13] (a) Z. Dori, R. F. Ziolo, *Chem. Rev.*, 73 (1973) 247; (b) W. Beck, W. P. Fehlhammer, P. Pöllman, E. Schuierer, K. Feldl, *Chem. Ber.*, 100 (1967) 2325; (c) R. Mason, G. A. Rusholme, H. Engelman, *J. Chem. Soc. Chem. Commun.*, (1971) 496.

[14] H. Nunez, J. -J. Timor, J. Server-Carrio, L. Soto, E. Escriva, Inorg. *Chim. Acta.*, 318 (2001) 8.

[15] (a) R. Lalrempuia, M. R. Kollipara, P. J. Carroll, *Polyhedron* 22 (2003) 605; (b) S. K. Mandal, A. R. Chakravarty, *Polyhedron* 11 (1992) 823.

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Bsc	Chemistry	NEHU	1989-1991	54.8
PU(sc)	Chemistry	PUC(NEHU)	1987-1988	49.8
HSLC	Maths, Science, English	Mizoram Board of School Education	1986	58.9

List of Publications

K. Pachhunga, Bruno Therien, K. Mohan Rao, *Polyhedron* 00 (2007) 000, "Reactivity studies of cyclopentadienyl ruthenium(II), osmium(II) and pentamethylcyclopentadienyl iridium(III) complexes towards 2-(2'-pyridyl)imidazole derivatives"

2. **K. Pachhunga**, Bruno Therien, K.Mohan Rao, *Inorganic Chim Acta.*, 00 (2008) 000. "Synthesis of benzene ruthenium triazolato complexes by [3+2] cycloaddition reactions of activated alkynes and fumaronitrile to benzene ruthenium azido complexes'

3. **K.Pachhunga**, Patrick. J. Carrol, K.Mohan Rao, *Inorganic Chim Acta.*, communicated "Reactivity study of cyclopentadienyl osmium (II) bisphosphine azido complexes with activated alkynes and nitriles: isolation of osmium triazole and tetrazole complexes by 1,3 dipolar addition"(communicated).

4. **K. Pachhunga**, Gajendra Gupta, Bruno Therien, K. Mohan Rao, "Syntheses and characterization of η^5-pentamethylcyclopentadienyl and η^5-cyclopentadienyl ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes of 3,5-bis(2-pyridyl)pyrazole (Hbpp). The molecular structure of the complexes $[(\eta^5\text{-}C_5H_5)Ru(Hbpp)PPh_3]^+$ and $[(\eta^5\text{-}C_5Me_5)Ir(Hbpp)Cl]^+$" (under preparation)

5. **K. Pachhunga**, Y. A. Mozharivskyl, K. Mohan Rao, "Di-tri- and tetra-nuclear arene ruthenium (II) complexes containing oxalato and azide ligands" (under preparation).

6. **K. Pachhunga**, Bruno Therien, K. Mohan Rao, "Syntheses, characterization and molecular structure of *p*-cymene ruthenium (II) complexes of N,N'-donor base ligands" (under preparation).

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