SYNTHESES AND STRUCTURAL STUDIES OF MONO AND BINUCLEAR COMPLEXES OF SOME TRANSITION METALS WITH N-BASED TETRADENTATE LIGANDS

A THESIS SUBMITTED IN FULFILMENT OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

BY

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DEDICATED

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DECLARATION

I, Mr. GAJENDRA GUPTA, hereby declare that the thesis entitled "*Syntheses and Structural Studies of Mono and Binuclear Complexes of Some Transition Metals with N-based Tetradentate Ligands*" is the result of the work carried out by me under the supervision of Professor K. Mohan Rao, Department of Chemistry, School of Physical Sciences, North Eastern Hill University, Shillong, for the award of Doctor of Philosophy in Chemistry. The contents of this thesis did not form the basis of the award of any previous degree to me or anybody else. The work presented in this thesis is original and the outcome of the interesting results has been published in the international journals.

To the best of my knowledge the thesis has not been submitted for any degree to this university or any other university.

Date: 09-03-2010
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CERTIFICATE

This is to certify that the thesis entitled "*Syntheses and Structural Studies of Mono and Binuclear Complexes of some Transition Metals with N-based Tetradentate Ligands*" is based on the original work done by Mr. Gajendra Gupta, 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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Doing research and earning a degree is not just a simple race but it's a heptathlon wherein you have to go through various trials and tribulations before you touch the finishing line. It is an exhilarating experience after touching the ribbon on completing a race and in the race of life nothing can be demarcated as being purely of sports or academic, the same experience applies to all acts of life. As in sports we need a coach who hones the skill, brings forth the hidden talent, guides and takes care of the minutest aspects leading to the road to perfection, in research we have guides who perform the same encore and well who else but Prof. K. Mohan Rao, who represent the highest echelons of this fast dwindling fraternity of sincere, enthusiastic and energetic supervisor, is a role model for me as a coach-cum-guide in my brief career of research of around three and half years. His constructive criticism, valuable comments, constant encouragement, and sometimes, soothing scolding, are some of the memories to be cherished the whole life. I cannot express my gratitude and acknowledgement in words since he is not part of vocabulary of any world renowned dictionaries, so I would like to be a bit moderate and pay him the highest tributes and regards and wish him all the very best for all his future endeavors. I hope this is not the end but just the beginning of a lifelong collaboration and I would like to be a part of his brilliant team of researchers forever.

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GAJENDRA GUPTA

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Abbreviations

bpp-H	*3,5-bis(2-pyridyl)pyrazole*
Cp	*Cyclopentadienyl*
*Cp**	*Pentamethylcyclopentadienyl*
C_6Me_6	*Hexamethylbenzene*
Cym	*P-cymene*
d	*doublet*
dd	*doublet of doublet*
dt	*doublet of triplet*
dpt-NH_2	*4-amino-3,5-di-pyridyltriazole*
Hz	*Hertz*
m	*multiplet*
NaClO4	*sodium perchlorate*
NMR	*Nuclear Magnetic Resonance*
NH_4PF_6	*Ammonium hexafluorophosphate*
NH_4BF_4	*Ammonium tetrafluoroborate*
PPh_3	*triphenylphosphine*
ppm	*parts per million*
qt	*quartet*
s	*singlet*
sept	*septet*
t	*triplet*
TMS	*Tetramethylsilane*
UV-vis	*Ultra violet-visible*

Preface

The 1950s were crucial for the emergence of organometallic chemistry as an independent field of research. Major discoveries such as the Wittig reaction, the Ziegler–Natta process or the preparation of π-allyl palladium complexes were achieved during that prolific time. Moreover, the early 1950s saw the synthesis of the first sandwich complexes, ferrocene $(\eta^5\text{-}C_5H_5)_2Fe$, by Pauson in 1951.The structure, erroneously assigned by Pauson, was correctly addressed a year later by Wilkinson and Woodward. It was soon after the preparation of ferrocene that Wilkinson synthesised the corresponding ruthenocene derivative. Since this pioneering work, a multitude of π-systems incorporating cyclopentadienyl ligands with different transition metals were synthesised. Other than sandwich complexes, half-sandwich, multidecker and tilted sandwich complexes were prepared as well.

Organic and organometallic chemists have extensively investigated arene metal complexes for around 50 years. Arene ruthenium complexes play an increasingly important role in organometallic chemistry. They appear to be good starting materials for access to reactive arene metal hydrides or 16-electron metal (d^6) intermediates that have been used recently for carbon-hydrogen bond activation. Various methods of access to cyclopentadienyl, borane and carborane arene ruthenium complexes have been reported. Recently, from classic organometallic arene ruthenium has grown an area making significant contributions to the chemistry of cyclophanes. These compounds are potential precursors of organometallic polymers that show interesting electrical properties and conductivity. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic "piano stool" structure offers the possibility to vary the additional donors *via* substitution of halide(s) with a variety of σ-donors ranging from tertiary phosphines to β-diketones to aliphatic as well as aromatic amines.

The primary objective of the thesis is to explore the chemistry of η^5- and η^6-cyclic hydrocarbon platinum group metal (Ru, Rh, Os and Ir) complexes and give reader a synthetic methodology for these classes of complexes.

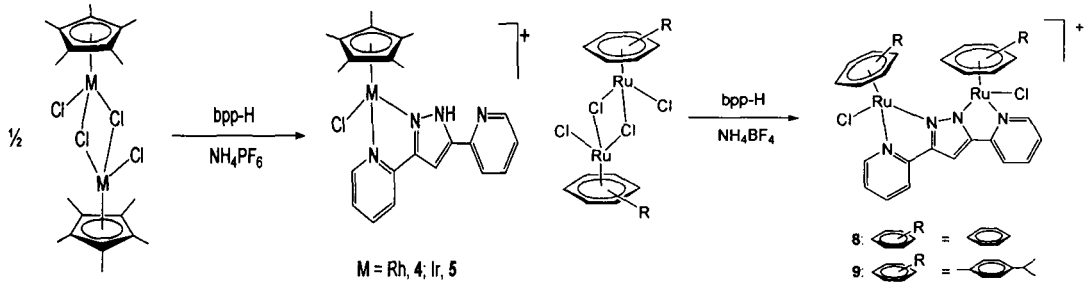
The sequence of chapters reflects preparation of η^5- and η^6-cyclic hydrocarbon platinum group metal (Ru, Rh, Os and Ir) complexes and their characterization with the help of analytical and spectroscopic data. The solid-state structures of representative complexes were determined by single crystal X-ray crystallographic studies. The work of this thesis has been studied in six chapters.

Chapter 1

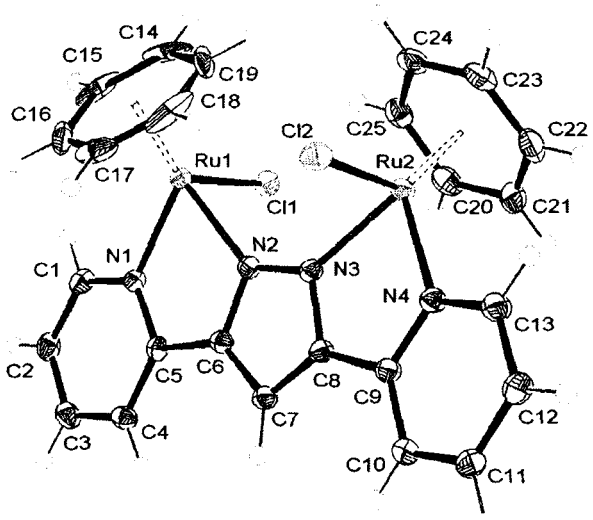
This is general introductory chapter and highlights a brief account on the chemistry of arene, cyclopentadienyl, pentamethylcyclopentadienyl and indenyl ruthenium complexes, cyclopentadienyl osmium and pentamethylcyclopentadienyl rhodium and iridium complexes. The concluding part of this chapter gives a brief account on the various physical method used in the study and preparation of some starting materials involved in the study.

Chapter 2

This chapter deals with the reaction of η^5- and η^6-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the N_4 type ligand 3,5-bis(2-pyridyl)pyrazole (bpp-H), which posses two contiguous binding sites for metal ions forming both mono- and binuclear complexes. However, arene ruthenium complexes yielded bimetallic complexes with bpp-H, whereas $(\eta^5\text{-}C_5Me_5)M$ dimers and mononuclear triphenylphosphine complexes did not yield bimetallic complexes with bpp-H, this could be due to the steric effect of $\eta^5\text{-}C_5Me_5$ and PPh_3 ligands (Scheme 1). These compounds have been characterized by IR, NMR and mass spectrometry as well as by elemental analyses. The molecular structures of representative complexes have been established by single crystal X-ray diffraction studies and some representative examples have been studied by UV-visible spectroscopy.



Scheme 1

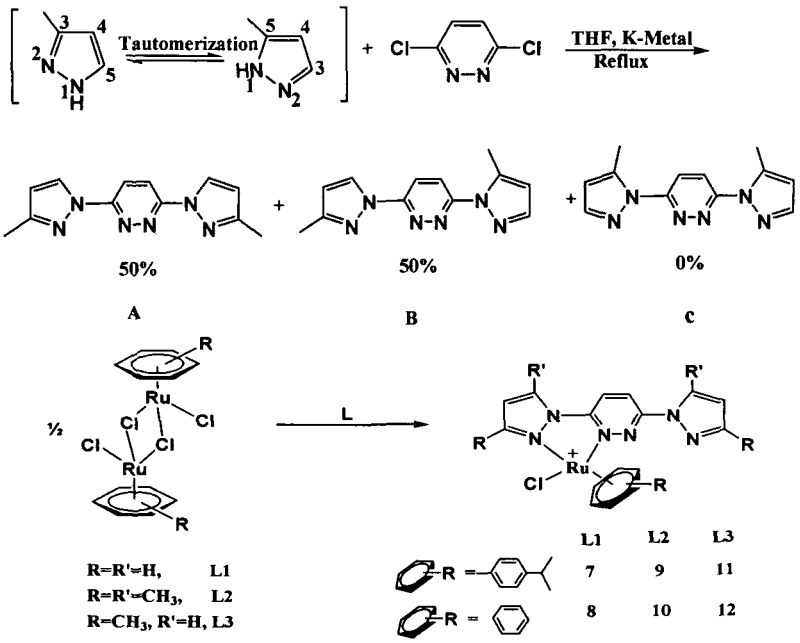


Complex **8**

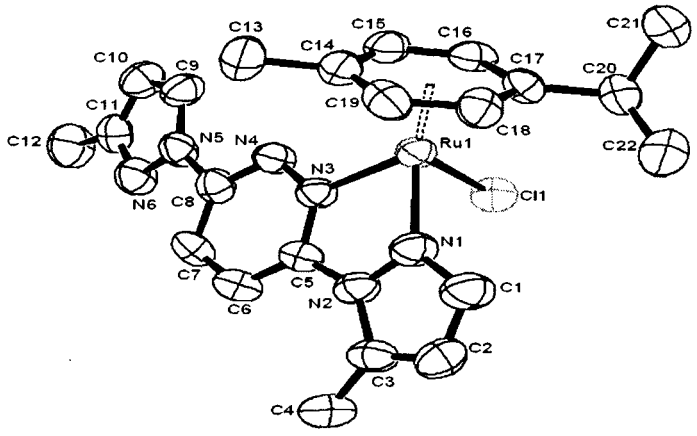
Chapter 3

This chapter describes the reaction of ruthenium half-sandwich complexes with tautomerized pyrazolyl-pyridazine ligands. Here, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methlypyrazole moiety and the existence of both the tautomers in a single compound is described in this chapter which are the first of its kind known in the literature. The tautomerized products were supported by ^{1}H NMR and ^{13}C NMR as well as single crystal X-ray structure. The reactions of η^6-areneruthenium complexes in methanol with the above mentioned pyrazolyl pyridazine ligands form mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(Cl\text{-}L)(Cl)]^+$ and $[(\eta^6\text{-arene})Ru(L)(Cl)]^+$; (arene = benzene and *p*-cymene;

Cl-L= Cl-L1, Cl-L2, Cl-L3; L = L1, L2, L3) (Scheme 2). All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.



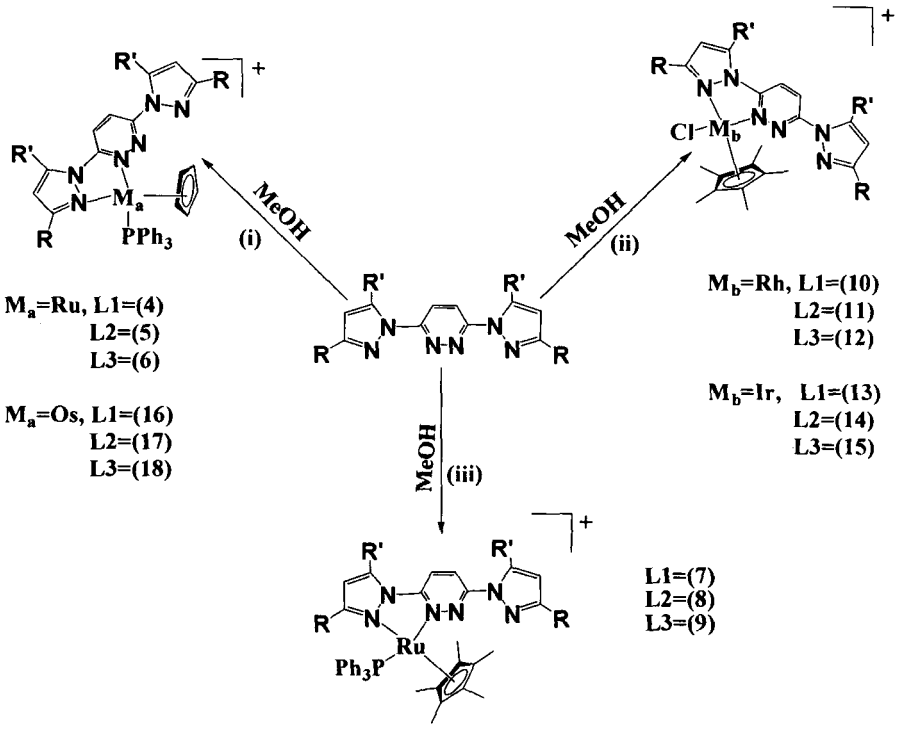
Scheme 2



Complex **11**

Chapter 4

This chapter emphasise the formation of mononuclear η^5-pentamethyl-cyclopentadienyl complexes of platinum group metals with different pyrazolyl-pyridazine ligands (Scheme 3). All these pyrazolyl-pyridazine complexes are interesting in their own right from a synthetic, structural and electrochemical point of view. However, attempts to make di-nuclear complexes with these metals have not been successful. The reason could be the large size of the pentamethylcyclopentadienyl and triphenylphosphine ligands. These complexes are fully characterized by IR, NMR and mass spectrometry. The molecular structures of some of the representative complexes are described as well.

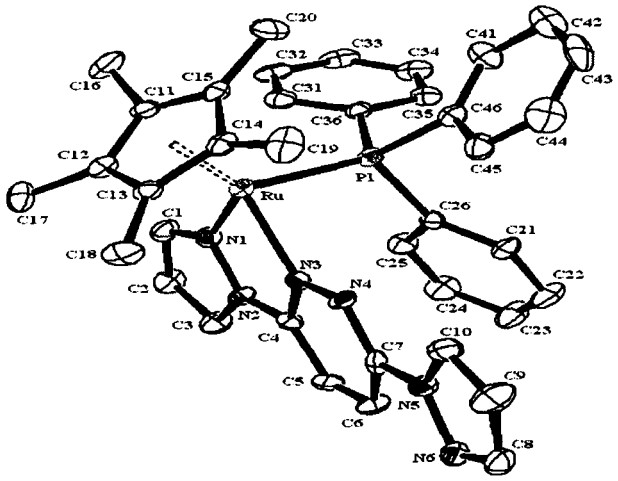


(i) = $[(\eta^5\text{-Cp})M_aCl(PPh_3)]_2$; M_a=Ru, Os

(ii) = $[(\eta^5\text{-Cp}^*)M_bCl(\mu\text{-Cl})]_2$; M_b=Rh, Ir

(iii) = $[(\eta^5\text{-Cp}^*)RuCl(PPh_3)_2]$

Scheme 3

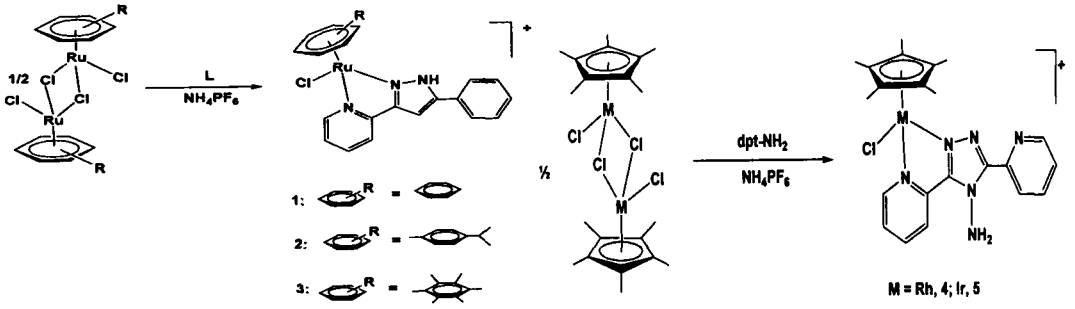


Complex 7

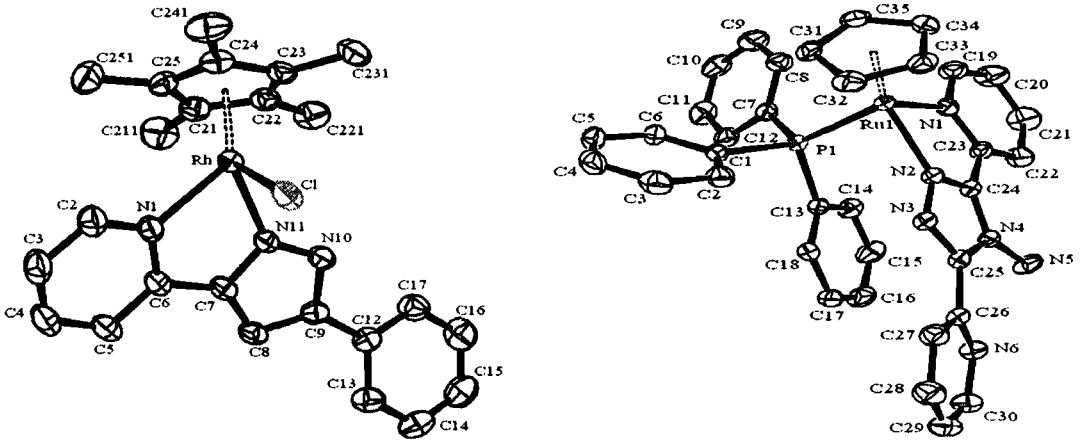
Chapter 5

This chapter has been divided into two sections, i) Chapter 5A and ii) Chapter 5B. Chapter 5A described the syntheses and characterization of the complexes resulting from the reaction of η^5- and η^6-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the N, N'-donar phenyl substituted pyridyl pyrazolyl ligand 2-(5-phenyl-1H-pyrazol-3-yl)pyridine. 2-(5-phenyl-1H-pyrazol-3-yl)pyridine is a tridentate ligand. Our main aim in choosing this phenyl substituted ligand was to synthesize a series of mononuclear and dinuclear compounds by activating the carbon atom of the phenyl ring. But attempts to prepare a dimetallic derivative by addition of a second organometallic anion by activation of the carbon atom were unsuccessful and we ended up with a series of mononuclear compounds only with metal binded to two nitrogen atoms of the ligand.

Chapter 5B deals with the syntheses and characterization of the complexes resulting from the reaction of η^5- and η^6-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the N, N'-donar tetradentate ligand 4-amino-3,5-di-pyridyltriazole (*dpt-NH_2*). Here we have synthesized a series of mononuclear complexes, metal binding to two nitrogen atoms only. Our effort to make dinuclear complexes by allowing metals to bind with all the four nitrogen atoms was not successful. All these compounds are fully characterized by IR, NMR and mass spectrometry. The molecular structures of representative complexes have been established by single crystal X-ray diffraction studies and some representatives have been studied by UV-visible spectroscopy.



Scheme 4

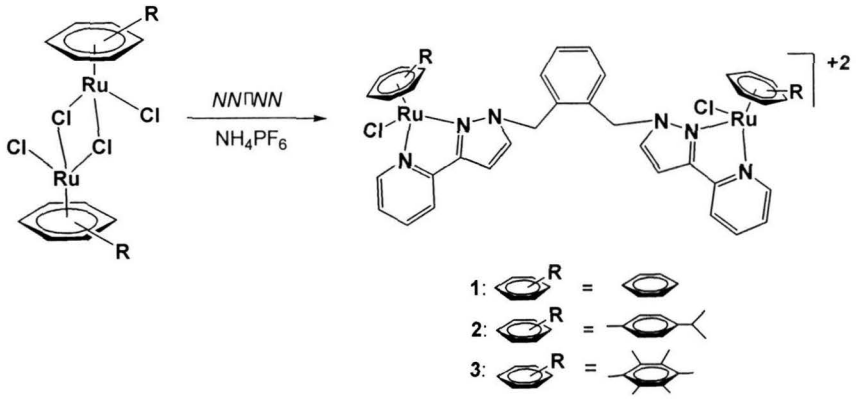


Complexes **4** and **6**

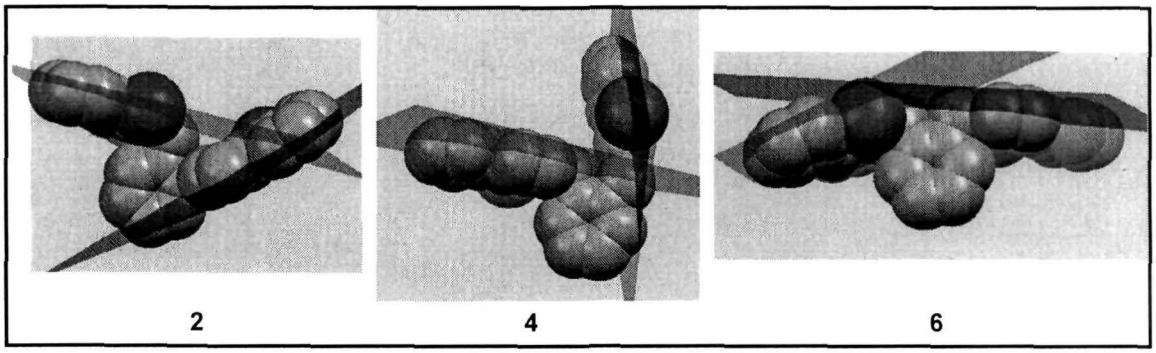
Chapter 6

The concluding chapter describes the syntheses of various dinuclear complexes arising from the reaction of η^5- and η^6-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the tetradentate nitrogen donor ligand, 1,3-bis((3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene (*NN*∩*NN*), in which the two pyrazolyl-pyridine units are connected by an aromatic spacer. This ligand has the ability to form both mono and dinuclear complexes with metals like Cu and Ag, but surprisingly in the case of arene ruthenium and Cp*rhodium and Cp*iridium systems, it only forms dinuclear complexes. The complexes are characterized by a combination of NMR spectroscopy, IR spectroscopy, mass spectrometry and UV-visible spectroscopy. The solid state structures

of representative complexes are determined by single crystal X-ray crystallographic studies. Despite the presence of two chiral centers in all the X-ray structures, only racemic mixtures were obtained, and all compounds crystallize in centrosymmetric space groups.

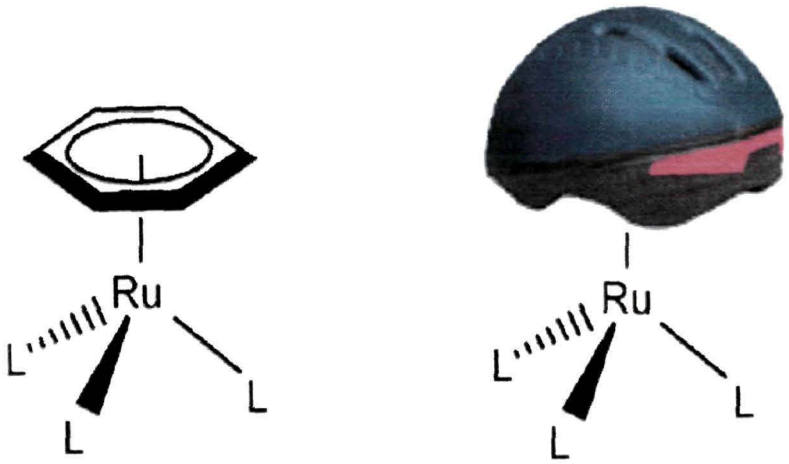


Scheme 5



CHAPTER 1

GENERAL INTRODUCTION



3 remaining coordination sites for ligands L.

GENERAL INTRODUCTION

Organometallic Chemistry is concerned with molecular compounds that contain organic groups bound to metal atom through one or more carbon atoms. The chemistry of such compounds provides a bridge between that of purely organic compounds on one hand and that of coordination complexes on the other. The first organometallic compound is believed to be Cacodyl, $[(CH_3)_4As_2]$ reported in 1760. Organic and organometallic chemists have extensively investigated arene metal complexes for over 45 years. However, immense studies had started after Zeise prepared the first olefin compound in 1827, and Frankland developed the chemistry of alkyl zinc compounds in the mid- and late nineteen century [1]. Organometallic compounds have wide applications in catalysis [2-11] and their electrochemical behavior [12-18], as well as in the development of new biological active agents [19-25]. Arene ruthenium complexes have been found to perform all three of these functions. 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 [26, 27]. As depicted in Figure **1.1**, coordination of a metal fragment (ML_n) to an arene ring dramatically increases the electrophilic character of the ligand. Thus, processes such as nucleophillic aromatic addition and substitution, arene deprotonation, and benzylic deprotonation are greatly facilitated. Additionally, the presence of a transition metal center (and ancillary ligands) on one face of the coordinated arene can serve as 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 [28-31]. Few years ago, 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 [32-36]. 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 center afforded by incorporation of an arene ligand.

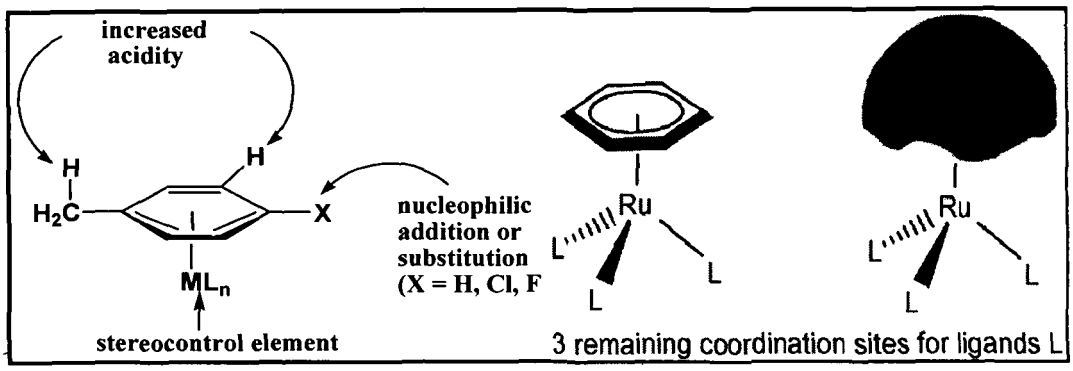


Figure **1.1** Important features of arene metal complexes

Comprehensive review concerning the syntheses of complexes based on these systems, $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = *p*-cymene, C_6H_6, C_6Me_6), $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) and $[(Cp)M(PPh_3)_2Cl]$ (M = Ru, Os; Cp = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_9H_7$, $\eta^5\text{-}C_5Me_5$) would be too vast a subject to cover in one's thesis, the purpose of this introductory chapter is primarily to give the reader a taste of the diverse range of the complexes that have been prepared, and the diverse range of chemistry that results in these complexes.

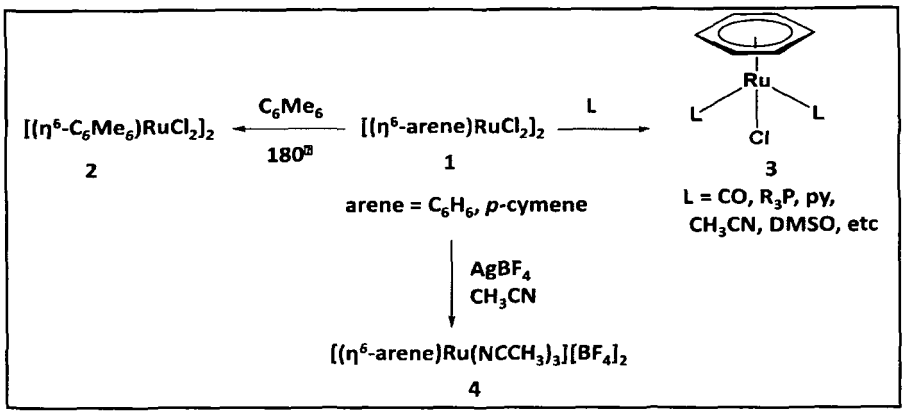
1.1 Half-Sandwich η^6-arene (Piano Stool) complexes

The chemistry of organoruthenium compounds is dominated by the +2 oxidation state. Since the first reports on chloro-bridged arene complexes of ruthenium in the oxidation state +2 more than 30 years ago [37, 38], compounds of this kind had a tremendous impact on organometallic synthesis and catalysis. Dimeric complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ constitute the most important entry point to (arene)Ru chemistry. This field has continuously gained in importance since various (arene)Ru complexes turned out to be highly active catalysts or precatalysts, performing a large number of organic transformations in many different areas.

The bis arene ruthenium complexes were first reported by Fischer and Böttcher in 1957 [39]. The bis(arene) complexes $[Ru(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2]^{2+}$ and $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ were prepared by heating the $RuCl_3$, $AlCl_3$ and aluminum powder in arene solvent under slight pressure for several hours.

Winkhaus and Singer [40] described in 1967 the first mono (arene) ruthenium complexes. They found that refluxing of 1,3-cyclohexadiene with ruthenium trichloride in ethanol formed a benzene complex which they formulated as the polymer $[RuCl_2(\eta^4\text{-}$

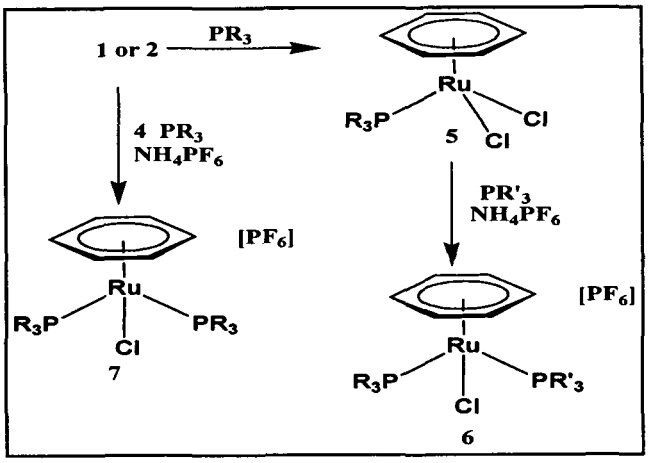
$C_6H_6)]_n$. Treatment of this "polymer" with tri-n-butlyphosphine formed a derivative which they formulated as the dimer $[RuCl_2(\eta^4\text{-}C_6H_6)(PBu_3^n)]_2$.



Scheme **1.1**

Zelonka and Baird have shown that, on the basis of spectroscopic and molecular weight data, that these complexes in fact contained η^6-arene ligand, and were dimeric and monomeric respectively [41]. This was further confirmed by X-ray crystal structures of $[(\eta^6\text{-}C_6H_6)\ RuCl_2\ (PMePh_2)]$ (Scheme **1.1**) and $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PMePh_2)]$, which showed that the phosphine complexes had a "piano-stool" type of structure (Scheme **1.1**) [42]. Since then, the chemistry of arene ruthenium compounds has been extensively developed.

In these compounds the chloro bridges are very labile and stirring these dimeric complexes in coordinating solvents such as CH_3CN, DMSO leads to the formation of solvated monomeric derivatives (Scheme 1.1). Compounds **1** and **2** with suitable monodentate ligands (such as CO, pyridines, triaryphosphines, triarylphosphates, triarylarsines and amines) generate isolable monomeric air-stable arene ruthenium complexes **3** [37, 40, 43]. 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 second monodentate phosphines in the presence of NH_4PF_6 afforded complex **6** with two different phosphines ligated to the Ru(II) center (Scheme **1.2**) [44].



Scheme **1.2**

Interest in the reactions of arene-ruthenium (II), has led to a large number of publications from 1980 to 2009. Severe page constraints on this chapter, it is not possible to provide a fully survey of this area. However, it is hoped that the discussion that follows will give some important entry into the literature. In 2004, Gimeno *et al.* found that catalytic efficiency of compounds $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ is strongly dependent on the arene ligand. The rate order observed, i. e. C_6H_6 (TOF = 500 h^{-1}) > *p*-cymene (TOF = 333 h^{-1}) > C_6Me_6 (TOF = 125 h^{-1}), indicates clearly that the less sterically demanding and electron-rich arene the higher performances, also found that these arene ruthenium complexes are much more active than the classical ruthenium(II) catalysts $[RuCl_2(PPh_3)_3]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ [45], furthermore, Finke *et. al.*, reported that arene-ruthenium monometallic complexes are heterogeneous catalysts and pentamethylcyclopentadienyl-rhodium compounds are homogeneous catalysts [46, 47].

1.1.1 $[(\eta^6\text{-arene})RuCl_2]_2$

The versatile starting materials $[(\eta^6\text{-arene})RuCl_2]_2$ are usually made by heating the appropriate 1,3 or 1,4-cyclohexadiene with $RuCl_3.3H_2O$ in ethanol. Detailed procedures are available for the syntheses of benzene, *p*-cymene (cymene = $1,4\text{-}MeC_6H_4CHMe_2$) complexes and for the hexamethylbenzene analogue made by fusion of C_6Me_6 and *p*-cymene ruthenium dimer. The $[(\eta^6\text{-arene})RuCl_2]_2$ complexes of mesitylene, 1,2,3,4-tetramethylbenzene, 1,3,5-trimethyl-benzene, 1,3,5-triisopropylbenzene and tetramethylthiophene have been made similarly from $[(\eta^6\text{-cymene})RuCl_2]_2$. The syntheses of benzene and *p*-cymene ruthenium complexes were carried out from ethanol, $RuCl_3$.

xH_2O, cyclohexadiene and α–phellandrene, respectively, are markedly accelerated by microwave heating (Figure **1.2**) [48-52].

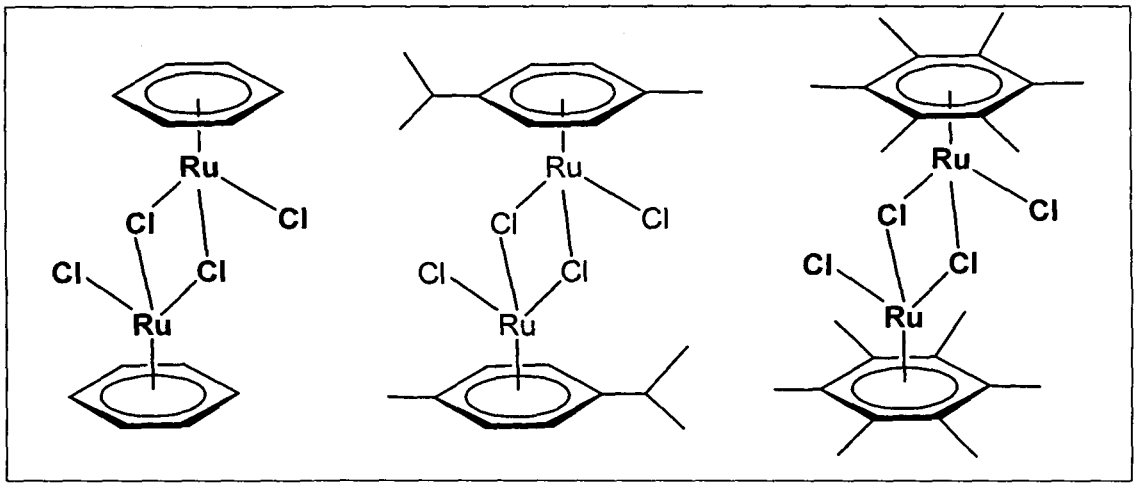
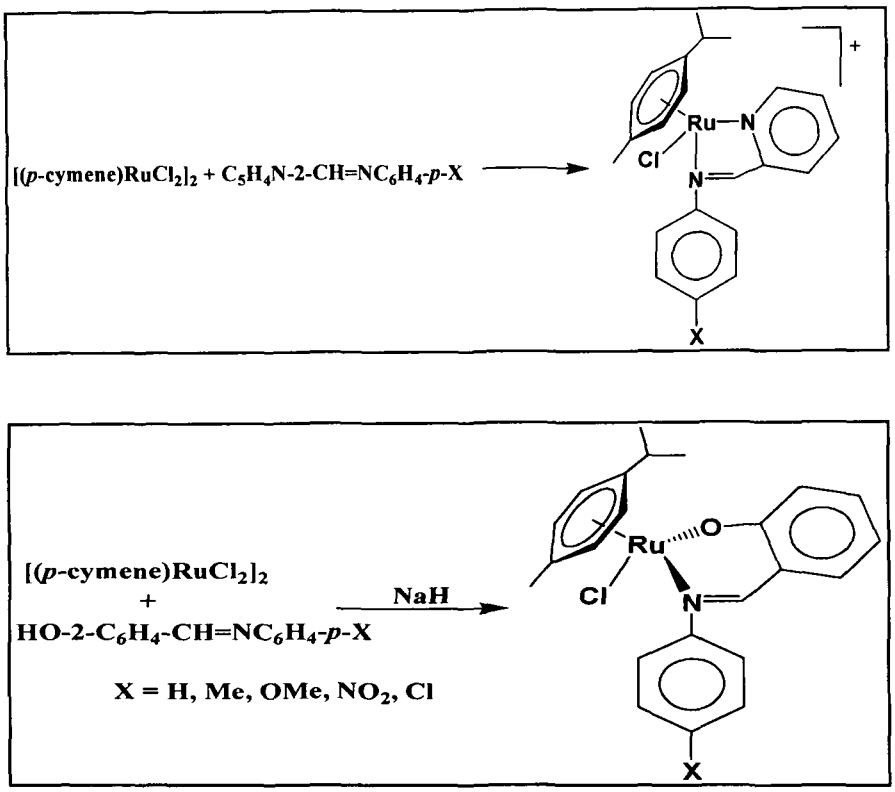


Figure **1.2**

1.1.2 Complexes with Nitrogen, Phosphorous and Oxygen donor ligands

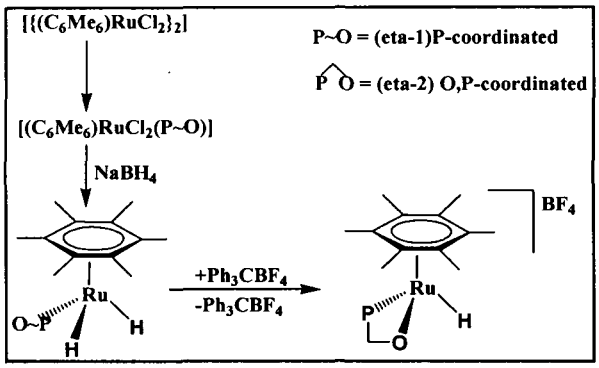
A variety of complexes of arene ruthenium fragment containing N,N'; P,N and N,O donor ligands can be generated by the reaction of well known $[(\eta^6\text{-arene})RuCl_2]_2$ with the appropriate ligands [53-55]. The $[(\eta^6\text{-arene})RuCl_2]_2$ complex react with NaOR/ROH [56, 57] or TlOPh [58] to give $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-OR})_3]^+$ which can be isolated with usual large anions (R=Me, Et, Ph, arene = C_6H_6, *p*-cymene). The complexes $[(\eta^6\text{-arene})RuCl_2]_2$ reacts with a range of primary and secondary amines, either at room temperature with sonication [59] or on heating in non-polar solvents, to give $[(\eta^6\text{-arene})RuCl_2(L)]$ (arene = 1,3,5-$C_6H_3Me_3$; L = $C_5H_{10}NHPy$) [60]. Similar complexes were obtained with amino pyridines, for example, $[(\eta^6\text{-arene})RuCl_2NC_5H_4NH_2\text{-}o]$ (arene = *p*-cymene), where only pyridyl nitrogen atom is coordinated [61]. Reaction of *p*-cymene dimer, $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with bi-dentate N-donor ligands such as Polypyridyl resulted in cationic complexes of formulation $[(p\text{-cymene})RuCl(L_2)]^+$ (L_2 = Polypyridyl ligands) [62]. Reaction of *p*-cymene dimer with N,N' and N,O-donor Schiff's base ligand generated cationic and neutral chelated complexes $[(\eta^6\text{-}p\text{-cymene})Ru(NN')Cl]^+$ and $[(\eta^6\text{-}p\text{-cymene})Ru(NO)Cl]$ (Scheme **1.3**) [53].



Scheme **1.3**

Arene ruthenium complexes with chiral Schiff's base ligands are also known [63]. The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with sodium salts of chiral Schiff's base ligand (S)-α-methylbenzylsalicylaldimine (HL*) in THF at -70°C, gives two diasteromers in a ratio of 85:15. The reactivity of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with various aromatic amines, pyridine derivatives [64] and amino acid ligands [65] have been reported. Amino acids such as L-Alaninine and L-proline displace *acac* from $[(\eta^6\text{-}p\text{-cymene})RuCl(acac)]$ to give the diasteriomers of $[(\eta^6\text{-}p\text{-cymene})RuCl(aa)]$ in the ratio 7:3 and 9:1 respectively. The diasteriomers in the derived cations $[(\eta^6\text{-}p\text{-cymene})Ru(MeOH)(aa)]^+$ epimerize rapidly owing to exchange of methanol, whereas those of $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)(aa)]^+$ are configurationally stable [66]. Arene ruthenium complexes containing bulky phosphines were also known [67]. Bates *et al.* described a versatile complex $[(\eta^6\text{-}p\text{-cymene})Ru(\mu N_3)Cl]_2$ by treatment of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with trimethlysilyl azide in which nitrogen atoms of the bridging azide groups are, surprisingly pyramidal coordinated [59]. Unlike the chloride precursor, the azide complex readily loses coordinated arene on heating in toluene. The reaction of the complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with PN donor ligand such as diphenylpyridylphosphine afforded both neutral and chelated complexes.

Neutral complex [(η^6-*p*-cymene)Ru(PPh_2Py)Cl_2] was isolated when the reaction is carried out in less polar solventssuch as dichloromethane while polar solventssuch as methanol in the presence of NH_4PF_6 isolated chelated complex [(η^6-*p*-cymene) -Ru(PPh_2Py)Cl_2] [55]. The reaction [(η^6-arene)$RuCl_2$]$_2$ with pyrazole in acetonitrile in the presence of NH_4BF_4 gives amidine complexes [68, 69], which are resulted by the transfer of hydrogen from pyrazole to the nitrile carbon. Arene ruthenium dihydrido complexes [(η^6-arene)Ru(PO)(H_2)] were obtained upon replacing both chlorides by hydrides in the intermediates with $NaBH_4$ [70] which results from the reaction of [(η^6-C_6Me_6)$RuCl_2$]$_2$ with the ligands (Scheme **1.4**) [71]. Treatment of dihydrido complexes [(η^6-arene)RuH_2(P~O)] with Ph_3CBF_4 in THF, leads to the bi-functionalized complexes [(η^6-C_6Me_6)RuH(P^O)]BF_4 (Scheme **1.4**), which have wide applications in ring-opening metathesis polymerization [72].

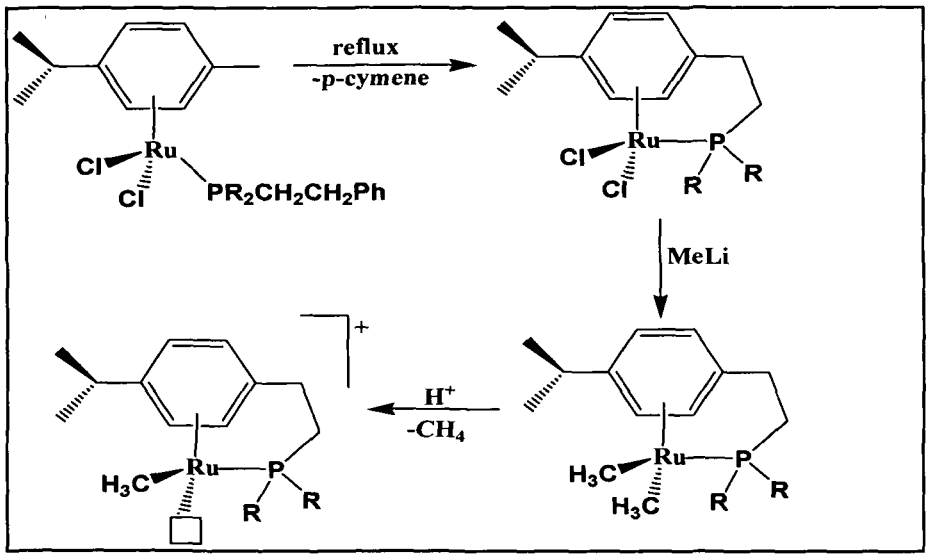


Scheme **1.4**

1.1.3 Half sandwich complexes of ruthenium with tethered arene ligands

Transition metals with half-sandwich complexes with potentially coordinating groups appended to the cyclic perimeter are receiving increasing attention as a special class of complexes bearing hemilabile ligands. These so-called tethered ligands are a class of mixed donor ligands that involve an arene or cyclopentadienyl (Cp) ring to which a pendant donor atom is linked. The dangling coordinating functionality may serve to stabilize otherwise elusive and coordinatively unsaturated species by forming an additional coordinate bond to the metal, thus rendering the respective arene a tetradentate chelate ligand. Examples of tethered η^6: η^1-arene ruthenium (II) complexes have been reported with nitrogen, oxygen [73, 74], phosphorus [74-82] and arsenic donors [79].

Almost those entire examples center around arene phosphine derivatives with the phosphine donor linked to the arene *via* a flexible hydrocarbyl spacer. Such an appended phosphine group may even serve as a "Trojan horse" by anchoring the functionalized arene to the metal prior to π-coordination. Arene displacement of complexes $[(\eta^6\text{-arene})\text{-}RuCl_2\{PR_2(CH_2)_naryl\}]$ is then achieved in an either thermally [75, 77, 81] or oxidatively [75] induced substitution step. These studies have also disclosed that such tethers may endow the complexes with reactivities that differ significantly from their non-tethered analogues [83, 84]. They can considerably contribute to the stability of a complex or a performing catalyst by making use of the chelate effect or enrich them with other favorable properties such as enhanced solubilities in polar or protic media and thermal stabilities. As an example, *Lee and others* presented a family of ruthenium (II) complexes containing arene-phosphine ligands $C_6H_5CH_2CH_2PR_2$ where R = Cy, Ph, Et. Their synthesis follows the sequence shown in Scheme **1.5** Abstraction of a single methyl group from $[(\eta^6\text{: }\eta^1\text{-}C_6H_5CH_2CH_2PR_2)Ru(CH_3)_2]$ affords a vacant site *cis* to the residual methyl group [81].

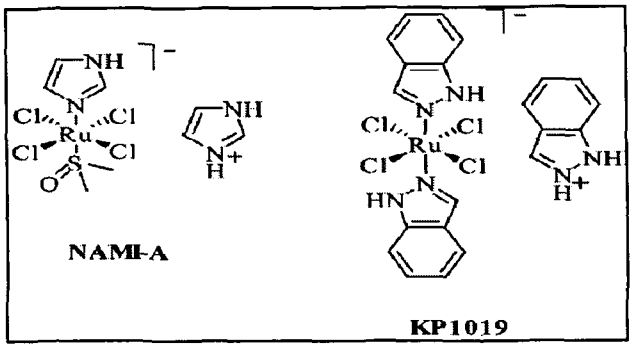


Scheme **1.5**

1.1.4 Biologically active ruthenium and arene ruthenium complexes

Recently it was shown that ruthenium possesses several favourable chemical properties, suggesting that it may be a strong candidate to replace platinum and to form a basis for rational anticancer drug design [85-89]. A number of ruthenium complexes show high *in vitro* and *in vivo* antitumor activity and two of them have successfully completed

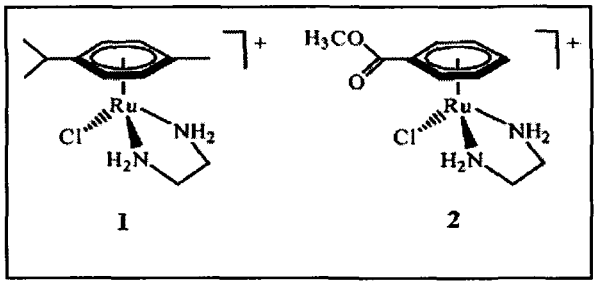
phase I of clinical trials, NAMI-A [90] and KP1019 [91]. The synthesis of ruthenium complexes is relatively easy and the metal possesses the ability under physiological conditions to adopt a large range of oxidation states (Ru^{II}, Ru^{III} and Ru^{IV}), an important feature for metal-based anticancer drugs. In addition, ruthenium is less toxic than platinum and it is believed that the remarkable anticancer activity of ruthenium resides in its ability to mimic iron in binding to several biomolecules, including serum transferrin and albumin.



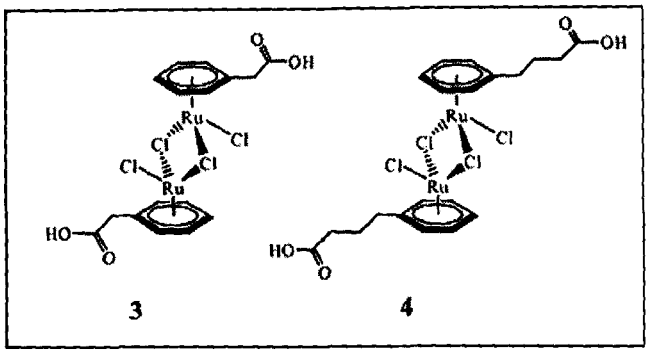
Like other classes of ruthenium compounds, organometallic ruthenium complexes bearing η^6-arene ligands have been intensively studied as potential anticancer drug candidates. The arene ligand not only provides a lipophilic side to the complex but also stabilises the ruthenium atom in the oxidation state II. Several studies revealed that this type of complex binds covalently to DNA *via* the N atom of purines and causes cytoxicity by inhibiting cellular DNA synthesis [92]. So far, the arene ligands seem to play only a minor role in the cytotoxicity effect of arene ruthenium drugs. However, it is obvious from the number of recent publications that functionalised arene ruthenium complexes possessing a biological active substituent is an emerging field of research. The attached bio-sensor can act as carriers, active agents, bio-markers or recognition sites and therefore pave the way for a multitude of potentially new research projects with interesting applications. While DNA interactions cannot be ruled out as the principal target and principal mechanism to focus on for the development of new arene ruthenium anticancer agents, other potential targets, involving different mechanisms, clearly need to be investigated to produce a new generation of metal-based drugs with higher selectivity and cytotoxicity.

One of the earliest example of an arene ruthenium complex investigated as anticancer drug candidates was $[(\eta^6\text{-}\ C_6H_6)Ru(dmso)Cl_2]$ [93]. It has been suggested by the authors that the DMSO derivative strongly inhibit topoisomerase II activity by

cleavage complex formation *via* interaction with DNA and crosslink formation with topoisomerase II. Arene ruthenium complexes containing ethylenediamine ligand (en) or its derivatives $[(\eta^6\text{-arene})Ru(en)Cl]^+$ showed high *in vitro* cytotoxicity, comparable to that of cisplatin [94]. It appears that extended arene ligands, such as biphenyl and tetrahydroanthracene, improve the cytotoxicity of the drug, while the introduction of an electron withdrawing group at the arene moieties such as $COOCH_3$ result in complexes with poor cytotoxicity. Indeed, the cationic complex $[(\eta^6\text{-}C_6H_5COOCH_3)RuCl(en)]^+$ **1**, isolated as its hexafluorophosphate salt, showed a moderate activity on A2780 ovarian cancer cells (IC50 =55 μM), because the presence of an electron withdrawing group at the arene ligand reduces the activity of the complex, as compared to the *p*-cymene analogue $[(\eta^6\text{-}$ *p*-cymene$)RuCl(en)]PF_6$ ([**2**]PF_6) (IC50 =9 μM) [94].

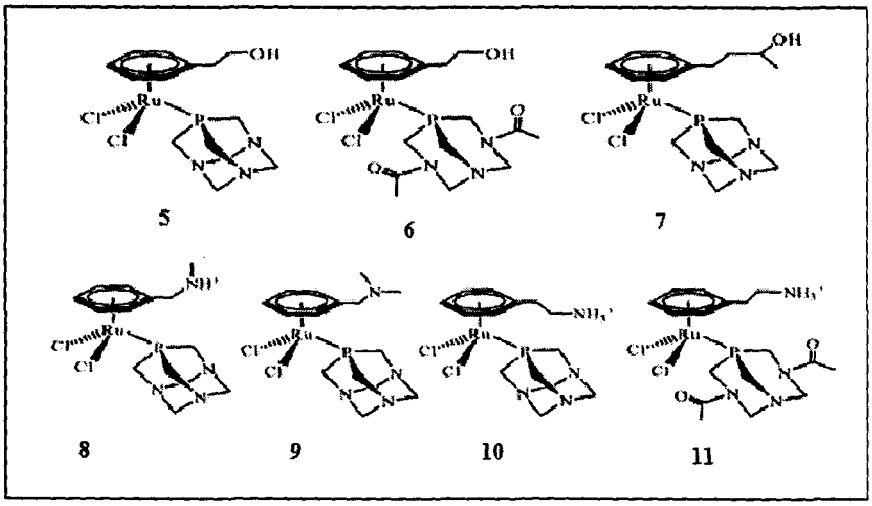


The introduction of carboxylato groups into a pendant arm tethered to the arene ligand has been used for N-terminal labelling of α-amino acids and peptides [95]. The dinuclear complexes $[\{\eta^6\text{-}C_6H_5(CH_2)_nCOOH\}Ru(\mu\text{-}Cl)Cl]_2$ {n=1 (**3**) and n = 3 (**4**)} were prepared by dehydrogenation of the appropriate cyclohexadiene with $RuCl_3{\cdot}nH_2O$, and their reactivity was studied, which demonstrated that the pendant arm fragment $\{\eta^6\text{-}C_6H_5(CH_2)_3COOH\}Ru^{2+}$ is suitable for both η^6- and *N*-terminal labelling of amino acids and peptides. Moreover, it was suggested that the formation of chelate κ*O*-coordinated species through the tethered carboxylate function was a key aspect in the stronger affinity of $\{(\eta^6\text{-}C_6H_5)\text{-}(CH_2)_3COOH\}Ru^{2+}$ with *N*-acetyltryptophan, as compared to the analogous *para*-cymene fragment.



3 4

Recently, a new series of organometallic arene ruthenium complexes with potential hydrogen-bonding groups attached to the pendant arm of the arene ligand have been prepared and studied for their antitumor activity [96]. The *pta* and *dapta* ligands (dapta = 3,7-diacetyl-1,3,5-triaza-5-phosphabicyclo[3.3.1]nonane) were used to obtain the neutral and cationic mononuclear arene ruthenium complexes **5–11**. The cytotoxicity of these functionalised arene ruthenium complexes showed no enhancement of the cytotoxicity toward the cancer cell lines screened, as compared to the analogous arene ruthenium complexes without hydrogen-bonding substituent, namely toluene, *para*-cymene and hexamethlybenzene [96]. While the presence of substituents that can potentially hydrogen bond to DNA at the aromatic rings in titatocene-type drugs increase markedly their cytotoxicity [97], it is striking to note that in the case of these arene ruthenium complexes the effect of the hydrogen-bonding function is actually the opposite. The origins of this unexpected effect were not clearly identified.

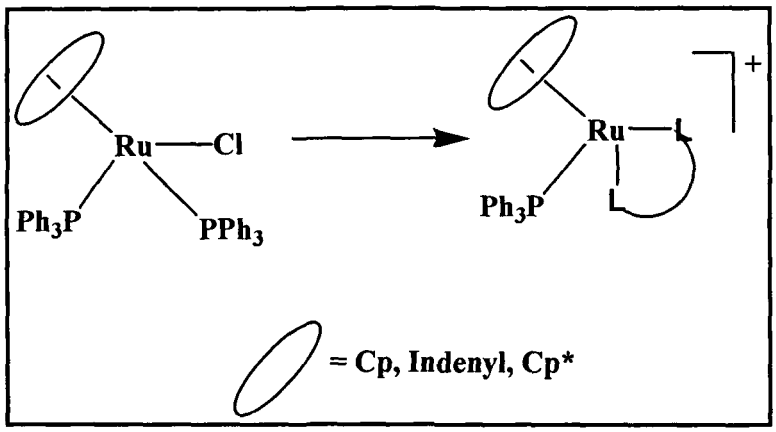


5 6 7

8 9 10 11

1.2 η^5- cyclic hydrocarbons ruthenium (II) complexes

The compound $[CpRu(PPh_3)_2Cl]$, first prepared by Wilkinson (1969) and later developed by Bruce *et al*, has shown that it is one of the most attractive molecule for synthetic manipulation. In the past several years, extensive efforts have been done towards the development of cyclopentadienyl ruthenium complexes and its analogue *viz*, Cp* and indenyl complexes owing to their high reactivity [98] and catalytic activity [99, 100]. Particularly, the chemistry of cyclopentadienyl ruthenium biphosphine auxiliary has been exploited considerably [101-103]. The spectrum of reactivity and chemical properties to date for this cyclopentadienyl ruthenium system is remarkable, especially considering the limited number of synthetic precursors, *viz.* $[CpRu(PPh_3)_2Cl]$ and $[CpRu(CO)_2Cl]$ [104].



The primary motivation of our study is to synthesis cyclopentadienyl, indenyl and pentamethylcyclopentadienyl ruthenium(II) complexes. A wide range of reactions of these classes of complexes with N-base ligands such as N, N' donor Schiff's base, azines and polypyridyl ligands were carried out. During the past few decades half sandwich complexes *viz.*, cyclopentadienyl and arene ruthenium complexes have been immensely studied owing to their high reactivity towards various ligands. In the organometallic chemistry, the compound $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$, has shown many unusual reactions. The pronounced steric interaction and the presence of high electron density on the metal center resulting from two bulky tertiary phosphine ligands have possibly been responsible for its much of unusual chemistry. Replacement of Cp by bulky electron releasing group such as C_5Me_5 (Cp*) ligand leads to many novel discoveries in ruthenium chemistry. Thus Cp* ligands are believed to induce dissociation by bulky PR_3 ligand in great extent compared to the analogous Cp ligand. Furthermore, the indenyl ruthenium complex is well known

towards enhance substitution reaction and having intermediate *haptacity* generally associated with the ligand. The complexes $[\eta^5\text{-Cp'})Ru(PPh_3)_2Cl]$ are characterized by ready substitution of one of the PPh_3 molecule by other donor group/or the ease of scission of Ru-Cl bond has engendered an intense interest in their potential synthetic utility for the preparation of their large number of cationic and neutral substituted derivatives, thus making the $[\eta^5\text{-Cp'})Ru(PPh_3)_2Cl]$ as one of the most versatile organoruthenium complexes of contemporary interest. Although the chemistry of Cp* and indenyl ruthenium complexes show similar behavior towards substitution reaction to that of analogous Cp complexes they differ in certain aspects such as higher reactivity and labile nature of the *organic moieties.* The higher reactivity of indenyl complexes is due to the well known indenyl effect *i.e.*, slippage of η^5 to η^3 - and back to η^5 of the indenyl ligand whereas steric nature of the five methyl group associated with Cp* ligand is solely responsible for their reactivity [105-107]. The Cp* complexes differ from Cp analog in three respects.

1) More organic property

2) More electrons donating ability

3) More steric nature

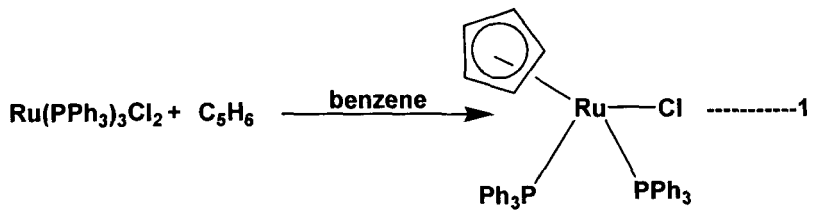
Indenyl complexes differ from the cyclopentadienyl analogues in having *intermediate haptacity, i.e., η^5 and η^3-coordination.*

The high reactivity and labile nature of these complexes prompted us to explore their chemistry. Literature survey reveals that most of the reaction of cyclopentadienyl and its analogous complexes in particular indenyl and Cp* complexes were concerned with the reaction towards terminal alkynes. However, substitution reaction of Cp* and indenyl ruthenium complexes were virtually unknown although reports are available in the case of cyclopentadienyl ruthenium cases.

1.2.1 Cyclopentadienyl ruthenium(II) complexes

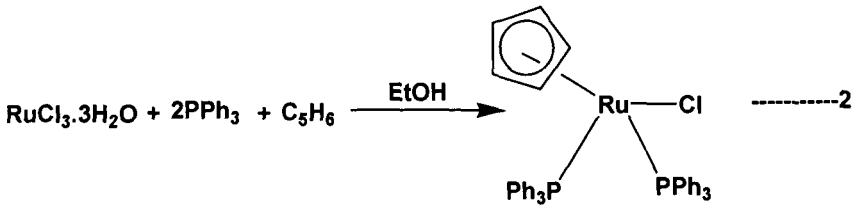
The cyclopentadienyl ruthenium bisphosphine complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ was first prepared by Gilbert and Wilkinson in 1969, by reacting cyclopentadiene and tris(triphenylphosphine) ruthenium dichloride $[Ru(PPh_3)_3Cl_2]$ over a period of 2 days (Equ. 1) [108]. This preparation, however, suffers from a competing dimerization reaction to form the unreactive $[Ru(PPh_3)_3Cl_2]$. Later this complex was synthesized by using

thallium cyclopentadiene [109] and $[Ru(PPh_3)_3Cl_2]$ but the toxicity of thallium and the mass of the reagent needed render this procedure unsuitable for large-scale preparations.



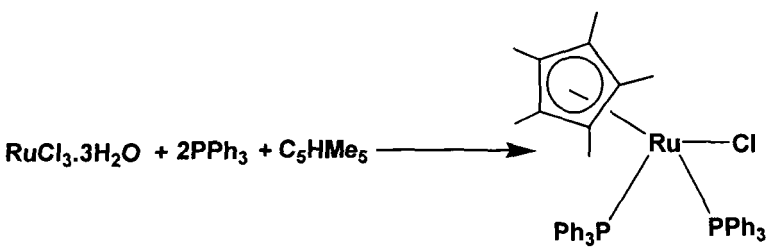
yield 60%

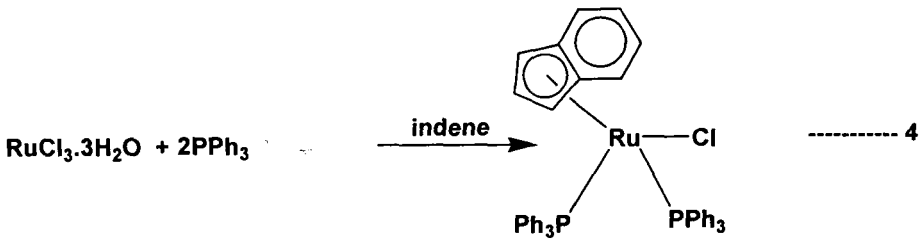
An improved method was reported by Bruce *et al.*, [110, 111], using cyclopentadiene, ruthenium trichloride trihydrate ($RuCl_3.3H_2O$), and triphenylphosphine, which gave the desired complex in high yield (Equ. 2). The primary advantage of this method is the formation of the complex in high yield in single step.



yield 90-95%

The pentamethylcyclopentadienyl analog $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ can be prepared in good yield (77%) using a similar procedure, although considerably longer reaction times are required (60 hours) [112]. The complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ can be prepared using less strenuous conditions if ruthenium trichloride hydrate and pentamethylcyclopentadiene are first reacted to give polymeric pentamethylcyclopentadienyl-ruthenium dichloride, which is then treated with excess triphenylphosphine to generate the required ruthenium product $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl)]$ (Equ. 3) [113, 114]. The corresponding indenyl-ruthenium complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl)]$ can be prepared from $[RuCl_2(PPh_3)_3]$ with indene and potassium hydroxide in ethanol (Equ. 4) [115].





Among all the substitution reactions carried out now, one type has been centered around the reactions of Ru-Cl resulting in the replacement of chloride either by other anions or by neutral ligands to yield neutral or cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(L)]$ or $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(L)]^+$. These are possibly based on the following equilibrium [116-118] that lies largely to the right in polar solvents like methanol, DMSO, etc.

$$[(\eta^5\text{-Cp})RuCl(PPh_3)_2] + MeOH \rightarrow [(\eta^5\text{-Cp})Ru(MeOH)(PPh_3)_2]^+Cl^- \text{ ------- 5}$$

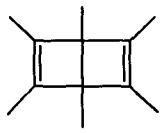
Another type has been the substitution of the PPh_3 and chloride ligands or by both the phosphines with various ligands like heterocyclic molecules such as bipyridine etc. and other tertiary phosphines to yield cationic or neutral compounds. In addition, a third possibility of reaction , though very little studied, is to activate C_5H_5- group in order to determine the nature of the aromaticity of the C_5H_5 ring in the complex. We believe that there should be a relationship between the aromatic character of C_5H_5 ring and the degree of electron density on the metal center, which, in turn should be a function of the attached ligands.

1.3 Pentamethylcyclopentadienyl rhodium and iridium complexes

The cyclopentadienyl ligand has played a central role in organometallic chemistry ever since the discovery of ferrocene $[(\eta^5\text{-}C_5H_5)_2Fe]$ in 1952 [119-121]. Following the synthesis of ferrocene, alkali cyclopentadienides were reacted with a wide variety of metal halides in order to synthesize new organometallics with π-bonded cyclopentadienyl ligands. Interest in pentamethylcyclopentadienyl metal complexes started in the early 1980's with the development of convenient synthetic methods.

1.3.1 The pentamethylcyclopentadienyl as a ligand

In view of the significant activity in this area over the past two and half decades these compounds have been dealt with in a separate section from their unsubstituted analogs. The chemistry of Cp* complexes of rhodium and iridium has been reviewed [122] and the use of these compounds as homogeneous catalysts for the generation of alkenes and arenes [123, 124]. It has been pointed out [122] that, while the η^5-C_5H_5 ligand is easily displaced from rhodium under acidic conditions, or in the presence of H_2, the corresponding Cp* ligand survives such conditions. Furthermore, the electron donating inductive effect of five methyl groups appears to help stabilize cationic species and the steric bulk of the Cp* ligand probably adds some kinetic stability to reactive rhodium centers.



$$+ \ RhCl_3.3H_2O \longrightarrow [Cp^*RhCl_2]_2 \text{---------- 1}$$

$$C_5Me_5H + MCl_3.xH_2O \xrightarrow[M = Rh \text{ or } Ir]{MeOH} [(C_5Me_5)MCl_2]_2] \text{ ---------- 2}$$

The first Cp* complex of rhodium was prepare serendipitously in the reaction of [$RhCl_3$. $3H_2O$] with hexamethyl bicyclo [2.2.0] hexa-2,5-diene [125, 126] (Equ. 1). After initial incorrect formulations as a complex of this diene, the red crystalline compound obtained in this reaction was correctly formulated [(η^5-C_5Me_5)$RhCl_2$]$_2$ [125, 126] and was shown crystallographically to have structure (Figure **1.3**) [125-127]. Notably the Rh_2Cl_2 bridge is planar, and not folded, and Rh-Rh distance of 3.719 Å demonstrates the absence of a Rh-Rh bond [127].

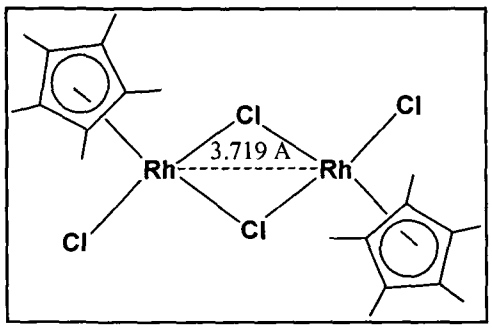


Figure **1.3**

The same compound can be prepared directly from [$RhCl_3$. $3H_2O$] and pentamethylcyclopentadiene [126], or 1-(1-chloroethyl) pentamethylcyclopentadiene [125] (Equ. 2) in methanol over refluxing 36 h. These compounds are crystalline dimers, soluble in organic solvents, in contrast to their amorphous, polymeric Cp analogs.

The pentamethylcyclopentadienyl ligand and its stabilizing effect on transition metal complexes are well known. The stability effect arises from two complementary factors. First, the electron-releasing effect of five methyl substituents increases the electron density on the pentamethylcyclopentadienyl ligand, leading to stronger ring-metal bonding. The extra electron density on the metal also causes increased back donation to other π-acceptor ligands, leading to further stabilization. The second factor is the size of the pentamethylcyclopentadienyl ligand, which effectively shields one side of the metal. The stability of the pentamethylcyclopentadienyl makes them interesting as potential homogeneous catalysts, since ring loss during the catalytic cycle should be less of a problem.

Other benefits of pentamethylcyclopentadienyl complexes are that they are generally crystalline and readily soluble in non polar organic solvents. The fifteen equivalent hydrogens of the ring methyls also give a strong signal in the ^1H NMR spectrum (normally a singlet), which is sensitive to the electron density at the metal, thus enabling the ligand to act as a useful NMR probe.

The reactions of Cp* Rh and Ir complexes with N donor ligands with a series of bidentate ligands with sp^2 N-donors such as bis(pyrazolyl)-methane (L_1), bis(1-methylimidazolyl)methane (L_2), bis(3,5-dimethylpyrazolyl)methane (L_3), bis(1-methylimidazolyl)ketone (L_4), bis(2,4,6-trimethylphenylimino)-acenapthene (L_5) (Chart 1.1) resulted a series of complexes of the formulations [Cp*MCl(N–N)][X] (M = Rh and Ir), where N–N (L_1-L_7) [128] (Chart 1.1).

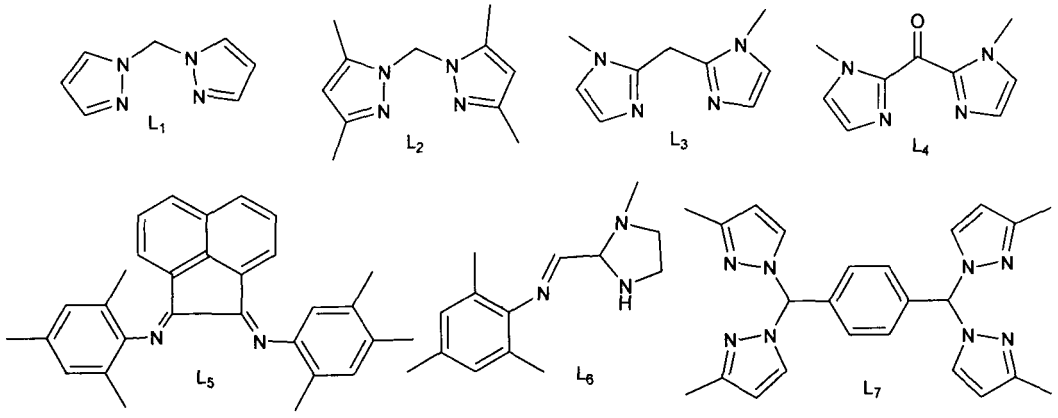
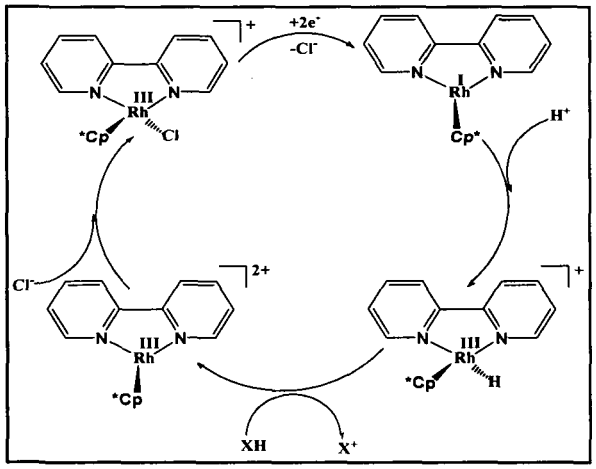


Chart 1.1

The complex $[(\eta^5\text{-}C_5Me_5)RhCl(N\text{-}N)]^+$ (N-N = 2,2'-bipyridine), was shown to occur as a crucial intermediate [129-131] in hydride transfer catalysis schemes aimed at H_2 production [129-131] or NADH regeneration (Scheme 1.6). Related compounds could be generated from photolysis of olefin-containing precursors [132]. Treatment of hydroquinone with $[Cp^*M(solvent)_3][OTf]_2$ (M = Rh, Ir) in acetone afforded the π-bonded complexes $\{[Cp^*M(\eta^5\text{-semiquinone})][OTf]_n\}$ (M = Rh, Ir) [133].



$Cp^* = \eta^5\text{-}C_5Me_5$

Scheme **1.6**

1.4 Physical Measurements

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

FT-NMR: The NMR spectroscopic data (^1H, ^{13}C $\{^1H\}$ and ^{31}P $\{^1H\}$) were recorded in deuterated solvents using Bruker Advance II 400 spectrometer using TMS as an internal

standard while chemical shift for $^{31}P\{^{1}H\}$ resonance were referred to 85% H_3PO_4. The coupling constants were given in hertz.

UV-visible: Electronic spectra were recorded on a Hitachi-U-2300 spectrophotometer in acetonitrile (*ca.* 10^{-4} M).

Mass spectra: Mass spectra were obtained from a Waters ZQ-4000 mass spectrometer by the ESI method.

Elemental analyses: Micro analytical data were obtained using a Perkin-Elmer 2400 CHN/S analyzer.

1.5 Materials

All reagents were purchased either from Aldrich or Fluka and used as received. All reactions were carried out in distilled and dried solvents. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, *p*-$^{i}PrC_6H_4Me$ and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [48, 134-137], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [110, 138-140, 115].

Supplementary material

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 at the end of the respective chapters. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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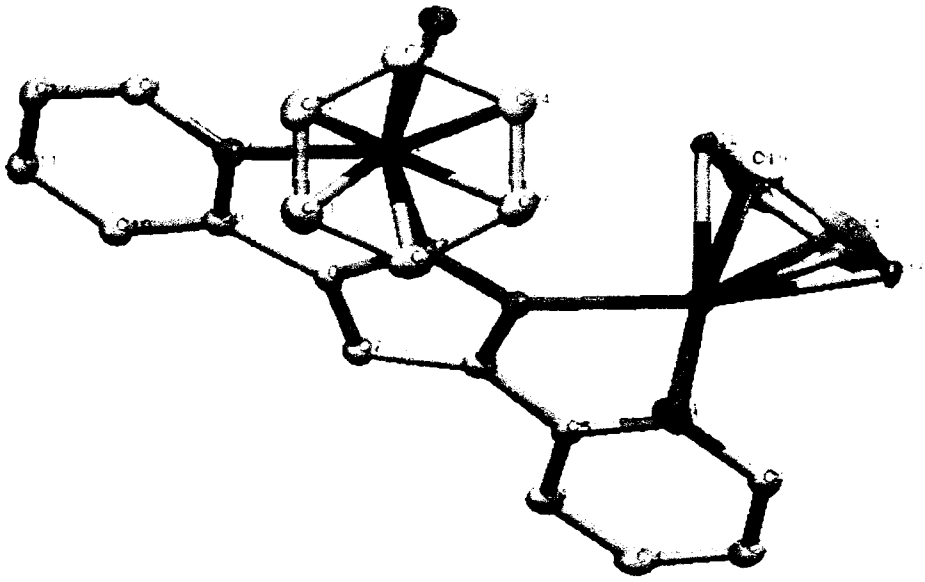
CHAPTER 2

Study of novel η^5-cyclopentadienyl and η^6 –arene platinum group metal complexes containing N_4-type ligand and their structural characterization



Study of novel η^5-cyclopentadienyl and η^6 –arene platinum group metal complexes containing N_4-type ligand and their structural characterization*

2.1 Abstract

The mononuclear η^5-cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)\text{-}Os(PPh_3)_2Br]$ and pentamethylcyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ react in the presence of 1 equivalent of the tetradentate N,N'-chelating ligand, 3,5-bis(2-pyridyl)pyrazole (bpp-H), and 1 equivalent of NH_4PF_6 in methanol to afford the mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ ([**1**]PF_6), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(bpp\text{-}H)]PF_6$ ([**2**]PF_6) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ ([**3**]PF_6), respectively. The dinuclear η^5- pentamethyl-cyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ as well as the dinuclear η^6-arene ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ react with 2 equivalents of bpp-H in the presence of NH_4PF_6 or NH_4BF_4 to afford the corresponding mononuclear complexes $[(\eta^5\text{-}C_5Me_5)Rh(bpp\text{-}H)Cl]PF_6$ ([**4**]PF_6), $[(\eta^5\text{-}C_5Me_5)Ir(bpp\text{-}H)Cl]PF_6$ ([**5**]PF_6), $[(\eta^6\text{-}C_6H_6)Ru(bpp\text{-}H)Cl]BF_4$ ([**6**]BF_4) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(bpp\text{-}H)Cl]BF_4$ ([**7**]BF_4). However, in the presence of 1 equivalent of bpp-H and NH_4BF_4 the reaction with the same η^6-arene ruthenium complexes affords the dinuclear salts $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]BF_4$ ([**8**]BF_4) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)_2Ru_2\text{-}(bpp)Cl_2]BF_4$ ([**9**]BF_4), respectively. These compounds have been characterized by IR, NMR and mass spectrometry as well as by elemental analysis. The molecular structures of [**1**]PF_6, [**5**]PF_6 and [**8**]BF_4 have been established by single crystal X-ray diffraction studies and some representatives have been studied by UV-visible spectroscopy.

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2.2 Introduction

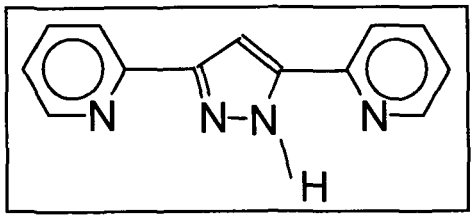
Within the large family of η^5- and η^6-cyclichydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer activities. These three-legged piano stool complexes possess a pseudo-octahedral geometry at the metal centre, the arene ligand occupying three coordinating sites (the seat) with three other ligands (the legs). Therefore, the octahedral geometry can be viewed as pseudo-tetrahedral, thus limiting the number of possible isomers.

Transition metal complexes containing polypyridyl ligands are associated with interesting photochemical and electrochemical properties [1-8], and they are used as catalysts [9, 10], multi-electron storage systems [11-13], in the designing of new materials [14-17] and as molecular devices [18-22]. Complexes with these ligands are also potential DNA intercalates with an ability to inhibit nucleic acid synthesis [23]. More recently, metal polypyridyl complexes have been widely used as building blocks [24-27]. The occurrence of isomers by the synthetic assembly of mononuclear building blocks is a major problem in the design of supramolecular systems.

Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted lot of attention [28-31]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal centre [32]. Many studies of cyclopentadienyl and arene ruthenium(II) complexes with bidentate ligands have shown that substitution reactions occur predominantly with retention of configuration at the metal centre [33]. Few studies have been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with polypyridyl ligands [34]. The reactivity of ruthenium(II), osmium(II), rhodium(III) and iridium(III) with various polypyridyl ligands have been reported [35-37].

In this chapter, we report a series of η^5-cyclopentadienyl ruthenium, osmium, η^5-pentamethylcyclopentadienyl ruthenium, rhodium and iridium and η^6-arene ruthenium complexes with tetradentate N,N'-donor ligand *viz.*, 3,5-bis(2-pyridyl)pyrazole (bpp-H) (see below). The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ruthenium metal complexes are associated with being an extremely interesting water oxidation catalyst [38, 39]. This ligand has

been acting as a bidentate as well as tetradentate ligand depending on the ratio of metal to ligand used. The molecular structures of representative compounds are presented as well.



Ligand used in this study

2.3 Experimental

2.3.1 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 ^{1}H NMR spectra were recorded on a Bruker ACF-400 (400 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 trihydrate, rhodium trichloride, iridium trichloride and osmium tetraoxide (OsO_4) were purchased from Arora Matthey Ltd. The 3,5-bis(2-pyridyl)pyrazole (bpp-H) was prepared by following a literature procedure [40, 41]. The precursor's complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ [42-44], $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ [45, 46], $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$, $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ [47], $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ [48] and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ [49-51], were prepared by following the reported literature methods.

2.3.2 Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for compound **[1]**PF_6 and **[5]**PF_6 were grown by slow diffusion of wet diethylether into dichloromethane solution of **[1]**PF_6, and **[5]**PF_6, respectively. Whereas in the case of compound **[8]**BF_4, crystals were grown by slow diffusion of wet diethylether in acetonitrile solution of **[8]**BF_4. A bright red crystal of **[1]**$PF_6 \cdot H_2O$ and a pale green crystal of **[5]**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 a crystal of **[8]**$BF_4 \cdot H_2O$ 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 [52]. Refinement and all further calculations were carried out using SHELXL-97 [53]. 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. The data collection parameters and bond lengths and angles are presented in Tables **2.1** and **2.2**, respectively.

2.3.3 Preparation of $[(\eta^5\text{-}C_5H_5)M(bpp\text{-}H)(PPh_3)]PF_6$ {M = Ru [1]PF_6, Os [2]PF_6}

A mixture of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X = Cl and M = Os, X = Br} (100 mg, 0.11 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (50 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 color of the solution changed from pale yellow to orange. The solvent was 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 and upon addition of diethyl ether the orange-yellow complex precipitated which was separated and dried under vacuum.

Complex $[(\eta^5\text{-}C_5H_5)Ru(bpp\text{-}H)(PPh_3)]PF_6$ [1]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 ($\nu_{C=N}$); 850 ($\nu_{P\text{-}F}$). ^1H NMR ($CDCl_3$, δ): 9.31 (d, 1H); 8.55 (d, 1H); 8.06 (s, 1H); 7.8 (td, 1H); 7.75 (d, 2H); 7.62 (m, 2H); 7.45 (m, 2H); 4.75 (s, 5H, C_5H_5); 7.32 - 7.2 (m, 15H, PPh_3).

^{31}P {^1H} NMR ($CDCl_3$, δ): 50.83 (s, PPh_3).

ESI-MS (m/z): 651.1 [M- PF_6], 650.1 [M-PF_6-H], 389.0 [M-PF_6-PPh_3].

UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 329 (24000)

Complex $[(\eta^5\text{-}C_5H_5)Os(bpp\text{-}H)(PPh_3)]PF_6$ [2]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): 9.2 (d, 1H); 8.55 (d, 1H); 8.45 (s, 1H); 7.81 (td, 1H); 7.78 (d, 1H); 7.7 (m, 2H); 7.38 (m, 1H); 6.9 (t, 2H); 4.69 (s, 5H, C_5H_5); 7.3 - 7.25 (m, 15H, PPh_3).

ESI-MS (m/z): 740.3 [M- PF_6], 739.2 [M- PF_6-H], 478.3 [M- PF_6-PPh_3].

2.3.4 Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(bpp\text{-}H)(PPh_3)]PF_6$ [3]PF_6

A mixture of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (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 color of the solution changed from pale yellow to orange. The solvent were removed in rotary evaporator under reduced pressure, the residue was 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($\nu_{N\text{-}H}$); 1613 ($\nu_{C=N}$); 850 ($\nu_{P\text{-}F}$). ^1H NMR ($CDCl_3$, δ): 11.92 (s,1H); 8.7 (d, 1H); 8.5 (s, 1H); 7.8 (td, 1H); 7.6 (d, 1H); 7.28 (t, 2H); 7.1 (m, 1H); 6.89 (t, 2H); 1.45 (s, 15H); 7.33 - 7.18 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 49.72 (s, PPh_3). ESI-MS (m/z): 722.3 [M- PF_6], 460.3 [M-PF_6-PPh_3];

UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 358 (17000)

2.3.5 Preparation of $[(\eta^5\text{-}C_5Me_5)M(bpp\text{-}H)Cl]PF_6$ {M = Rh [4]PF_6, Ir [5]PF_6}

A mixture of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) (Rh dimer = 100 mg, 0.16 mmol and Ir dimer = 125 mg, 0.16 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (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 color 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 [4]PF_6: 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 ($\nu_{N\text{-}H}$); 1612 ($\nu_{C=N}$); 850 ($\nu_{P\text{-}F}$). ^1H NMR ($CDCl_3$, δ): 11.80 (s, 1H); 8.9 (d, 1H); 8.6 (d, 1H); 8.2 (td, 1H); 8.0 (s,1H); 7.5 (t, 2H); 7.4 (t, 1H); 7.2 (t, 2H); 1.48 (s, 15H). ESI-MS (m/z): 494.2 [M- PF_6], 459.2 [M-PF_6-Cl].

UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 308 (26000)

Complex [5]PF_6: 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 ($\nu_{N\text{-}H}$); 1613

($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR ($CDCl_3$, δ): 11.86 (s,1H); 8.75 (d,1H); 8.58 (d, 1H); 8.45 (td, 1H); 8.24 (s, 1H); 7.5 (t, 2H); 7.4 (t, 2H); 7.2 (t, 1H); 1.45 (s, 15H).
ESI-MS (m/z): 583.2[M- PF_6], 548.2 [M-PF_6-Cl]

2.3.6 *Preparation of [(η^6-C_6H_6)Ru(bpp-H)Cl]BF_4 [6]BF_4*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.1 mmol), 3,5-bis(2-pyridyl) pyrazole (bpp-H) (88 mg, 0.395 mmol) and NH_4BF_4 (52 mg, 0.496 mmol) was stirred in dry methanol (15 ml) for 4hrs. at room temperature. The solvent was rotary evaporated. The solid was dissolved in dichloromethane and then filtered to remove ammonium chloride. The solution was concentrated to 2 ml and excess of diethyl ether was added for precipitation. The light brown color product was separated out, washed with ether and dried in vacuum. Yield: 70 mg, 67.3%. Elemental Anal (%) Calc. for $C_{19}H_{16}N_4BClF_4Ru$: C 42.75; H 4.91; N 10.50; found: C 42.6; H 5.0; N 10.41. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR ($CDCl_3$, δ): 9.2 (d,1H), 8.79 (d, 1H), 8.65 (s, 1H), 7.98 (t, 2H), 7.84 (d, 2H), 7.45 (m, 2H), 7.38 (m, 1H), 6.25 (s, 6H). ESI-MS (m/z): 437 [M- BF_4], 435.9[M- BF_4-H].
UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 318 (14000)

2.3.7 *Preparation of [(η^6-p-cymene)Ru(bpp-H)Cl]BF_4 [7]BF_4*

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.163 mmol), 3,5-bis(2-pyridyl) pyrazole (bpp-H) (144 mg, 0.65 mmol) and NH_4BF_4 (85 mg, 0.81 mmol) was stirred in dry methanol (15 ml) for 4hrs at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum. Yield: 140 mg, 74%. Elemental Anal (%) Calc. for $C_{23}H_{24}N_4BClF_4Ru$: C 47.65; H 4.17; N 9.66; found: C 47.5; H 4.1; N 9.61. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR ($CDCl_3$, δ): 9.2 (d, 1H), 8.64 (d, 1H), 8.53 (d, 1H), 7.95 (t, 2H), 7.84 (d, 2H), 7.8 (m, 2H), 7.36 (t, 1H), 6.51 (d, 1H, Ar_{p-cy}), 6.1 (d, 1H, Ar_{p-cy}), 5.88 (d, 1H, Ar_{p-cy}), 5.78 (d, 1H, Ar_{p-cy}), 2.63 (sep, 1H), 2.32 (s, 3H), 1.03 (d, 6H). ESI-MS (m/z): 492.1 [M- BF_4], 491.1[M-BF_4-H], 457.1[M- BF_4-Cl].
UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 430 (10000)

2.3.8 Preparation of $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]BF_4$ [8]BF_4

A mixture of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (50 mg, 0.10 mmol), 3,5-bis(2-pyridyl) pyrazole (bpp-H) (22 mg, 0.10 mmol) and NH_4BF_4 (51 mg, 0.49 mmol) was stirred in dry methanol (15 ml) for 4 hrs at room temperature. The brown compound which formed was filtered, washed with methanol and diethyl ether and dried under vacuum. Yield: 50 mg, 67.9%. Elemental Anal (%) Calc. for $C_{25}H_{23}N_4BCl_2F_4ORu_2$: C 39.75; H 3.07; N 7.42; found: C 39.6; H 3.0; N 7.38. IR (KBr pellets, cm^{-1}): 3416 ($\nu_{N\text{-}H}$); 1613 ($\nu_{C=N}$); 1082 ($\nu_{B\text{-}F}$). ^1H NMR ($CDCl_3$, δ): 8.91 (d, 1H), 8.5 (d, 1H), 8.35 (t, 2H), 8.12 (s, 1H), 7.92 (m, 2H), 7.7 (d, 1H), 7.55 (d, 1H), 6.35 (s, 6H), 6.1 (s, 6H). ESI-MS (m/z): 650.9 [M- BF_4], 649.9[M-BF_4-H]; UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 328 (18000), 424 (3000).

2.3.9 Preparation of $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)_2Ru_2(bpp)Cl_2]BF_4$ [9]BF_4

A mixture of $[(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}Cl)Cl]_2$ (100 mg, 0.163 mmol), 3,5-bis(2-pyridyl) pyrazole (bpp-H) (36 mg, 0.16 mmol) and NH_4BF_4 (85 mg, 0.81 mmol) was stirred in dry methanol (15 ml) for 4hrs at room temperature. The pale yellow compound which formed was filtered, washed with methanol and diethyl ether and dried under vacuum. Yield: 95 mg, 68.44%. Elemental Anal (%) Calc. for $C_{33}H_{37}N_4BCl_2F_4Ru_2$: C 46.66; H 4.39; N 6.60; found: C 46.5; H 4.4; N 6.7. IR (KBr pellets, cm^{-1}): 3416 ($\nu_{N\text{-}H}$); 1613 ($\nu_{C=N}$); 1082 ($\nu_{B\text{-}F}$). ^1H NMR ($CDCl_3$, δ): 9.1 (s,1H); 8.8 (d, 1H); 8.77 (d, 1H); 8.37 (t, 1H); 7.95 (t, 2H); 7.93 (s, 1H); 7.68 (t, 1H); 6.46 (d, 1H); 6.09 (d, 1H, $Ar_{p\text{-}cy}$), 6.01 (d, 1H, $Ar_{p\text{-}cy}$), 5.99 (d, 2H, $Ar_{p\text{-}cy}$); 2.67 (sep, 1H), 2.17 (s, 3H), 1.04 (d, 6H). ESI-MS (m/z): 763 [M- BF_4], 762.0[M-BF_4-H].

UV-vis. [(CH_3CN; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 322 (19000), 425 (3000).

2.4 Results and discussion

The mononuclear η^5-cyclic hydrocarbon complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ reacts with 3,5-bis(2pyridyl)pyrazole (bpp-H) in the presence of ammonium hexafluorophosphate in methanol to form the mononuclear cationic cyclopentadienyl ruthenium and cyclopentadienyl osmium complexes having the general formula $[(\eta^5\text{-}C_5H_5)M(bpp\text{-}H)PPh_3]^+$ (M = Ru [**1**]PF_6; M = Os [**2**]PF_6) and pentamethylcyclopentadienyl ruthenium complex having the general formula $[(\eta^5\text{-}C_5Me_5)Ru(bpp\text{-}H)PPh_3]^+$ ([**3**]PF_6) (Chart **2.1**). The complexes are orange

yellow, non-hygroscopic, air stable, crystalline solids. They are soluble in polar solvents such as methanol, dichloromethane, chloroform, acetone, but insoluble in hexane, petroleum ether or diethyl-ether.

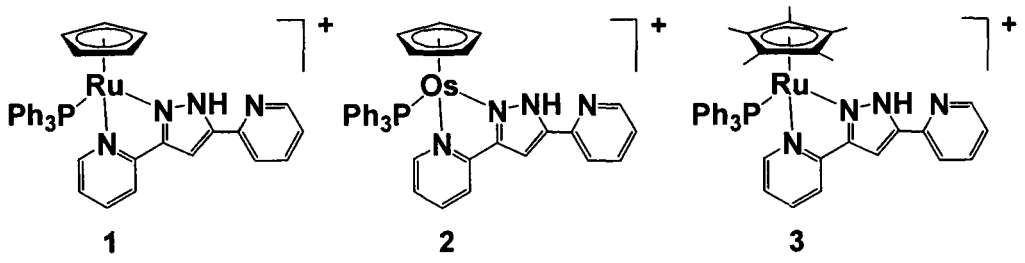


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Chart **2.1**

2.4.1 Cyclopentadienyl ruthenium [1]PF_6 and osmium complexes [2]PF_6

The analytical data of these compounds are consistent with the formulations (Chart **2.1**). These complexes are formed by reaction of metal complexes with bpp-H ligand irrespective of the metal to ligand ratio, yielding only mononuclear compounds. However, attempts to make dinuclear complexes by increasing the metal complex ratio was unsuccessful, it might be due to the steric bulkiness of the complex due to the presence of triphenylphosphine. The infrared spectra of the complexes [**1**]PF_6 and [**2**]PF_6 exhibit a chelated N,N'-bidentate ligand with 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 of PF_6 for both the complexes. The proton NMR spectra of these complexes [**1**]PF_6 and [**2**]PF_6 exhibit a singlet at 4.75 and 4.69 ppm for the cyclopentadienyl ring protons, indicating a downfield shift from the starting complex [(η^5-C_5H_5)$Ru(PPh_3)_2Cl$] and [(η^5-C_5H_5)$Os(PPh_3)_2Br$] [42, 46]. 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 (bpp-H) ligand through two nitrogen atoms. In addition to the other ligand peaks as mentioned in the experimental section, a multiplet in the range of 7.3–7.2 ppm which corresponds to the phenyl protons of triphenylphosphine of these complexes is observed.

The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ligand reacts with the pentamethylcyclopentadienyl ruthenium(II) complexes in the presence of NH_4PF_6 in

methanol, to yield the mononuclear cationic complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ ([**3**]PF_6) (Chart **2.1**). The complex is an orange crystalline solid, 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. In addition to the proton peaks of the ligand as mentioned in the experimental section the proton NMR spectrum also displays singlet peak at 1.45 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ring and a multiplet in the range of 7.3–7.2 ppm which corresponds to the phenyl protons of triphenylphosphine. The ^{31}P $\{^1H\}$ NMR spectra of the complexes [**1**]PF_6 and [**3**]PF_6 exhibit a single sharp resonance for triphenylphosphine at 50.8 and 49.7 ppm respectively, whereas for the starting complexes $[(\eta^5\text{-}C_5H_5)$ - $Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ the signals appear at 42.0 and 38.5 ppm, respectively [42-44, 48]. The structure of representative complex [1]PF_6 is solved by single crystal X ray diffraction study (Figure **2.3**).

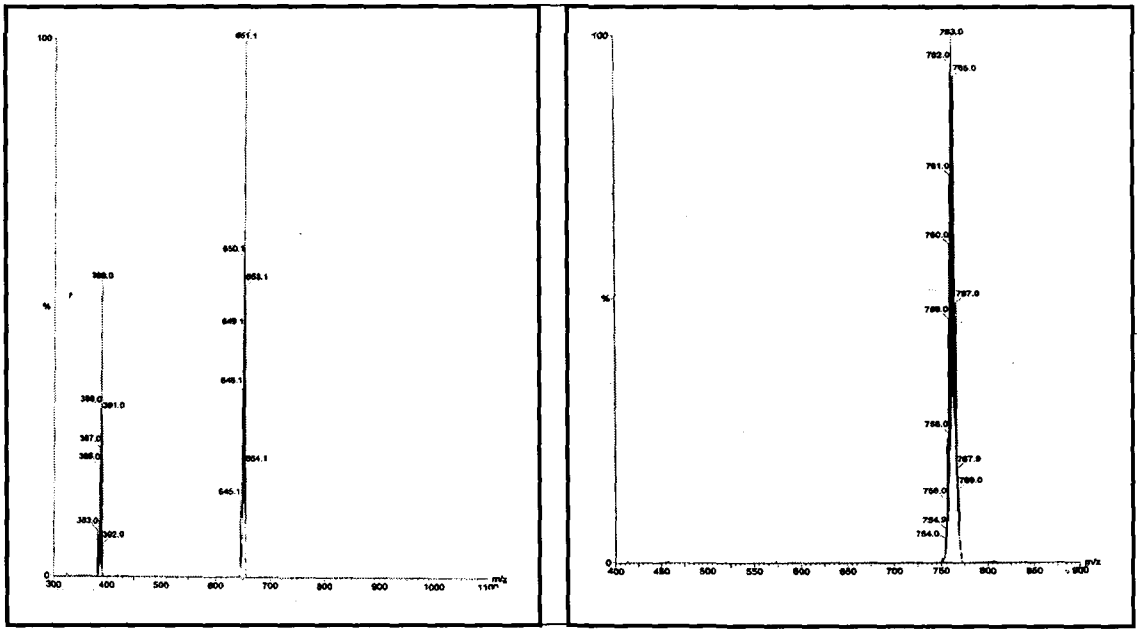


Figure **2.1:** Mass spectra of complexes **1** and **9**

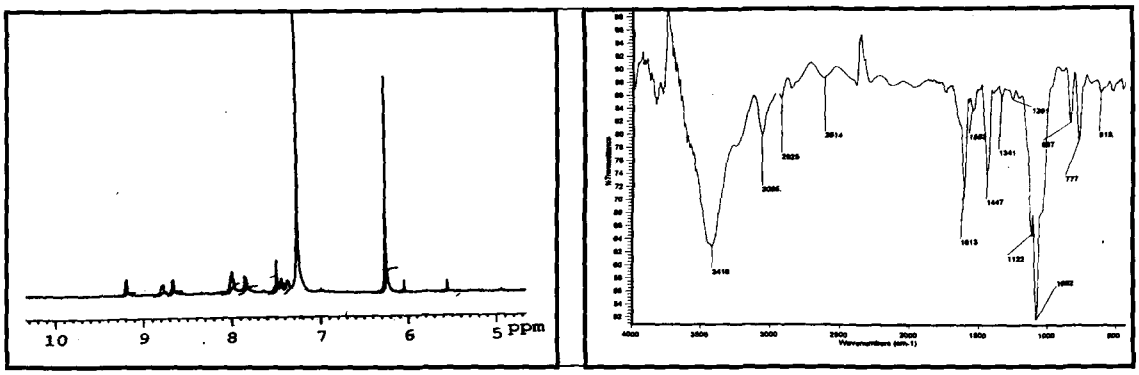


Figure **2.2:** ^{1}H NMR spectra of complex **6** and IR spectrum of complex **7**

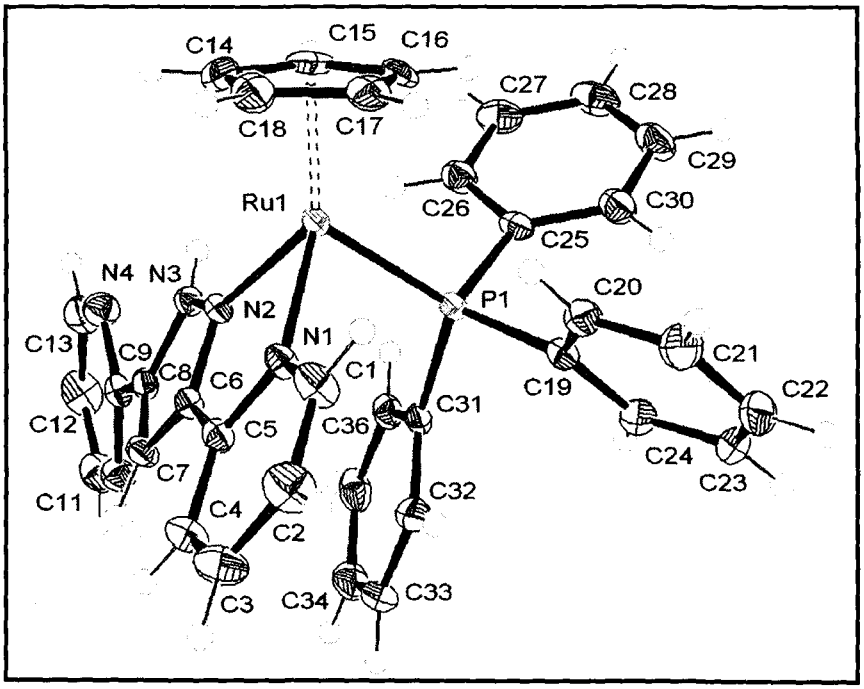
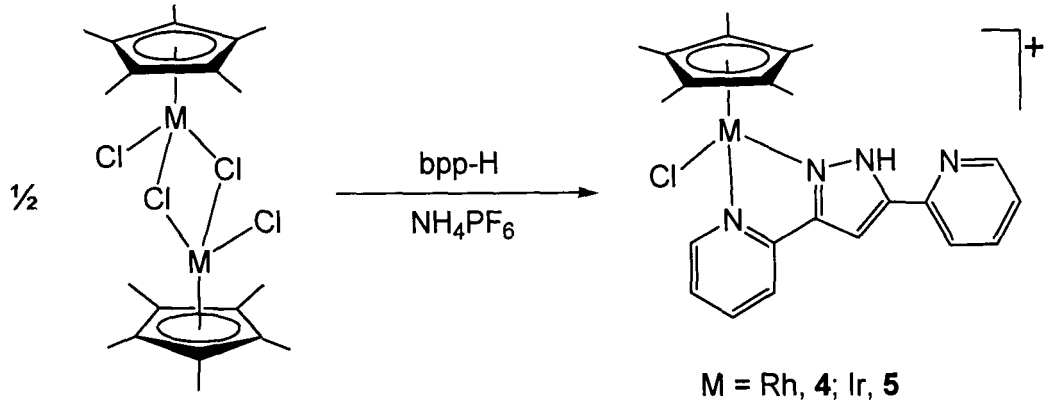


Figure **2.3:** ORTEP diagram with labelling scheme for $[(\eta^5\text{-Cp})Ru(bpp\text{-}H)(PPh_3)]^+$ ([**1**]PF_6), at 50% probability level, PF_6 anion omitted for clarity.

3.4.2 Pentamethylcyclopentadienyl rhodium [4]PF_6 and iridium complexes [5]PF_6

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with N,N'-bidentate nitrogen base (bpp-H) ligand in methanol at room temperature leads to the formation of chloride displaced complexes [**4**]PF_6 and [**5**]PF_6, respectively (Scheme **2.1**).



Scheme **2.1**

These complexes were isolated as their hexafluorophosphate salts. Here also we are able to isolate only the mononuclear complexes despite the lack of triphenylphosphine groups. Change in concentration and longer reaction times do not change the reaction pathways. The orange-yellow complexes are air stable, soluble in polar solvents but insoluble in hexane, petroleum ether and diethylether. Complex [**4**]PF_6 exhibits a pale green color when it dissolves in solution. The infrared spectra of the complexes [**4**]PF_6 and [**5**]PF_6 exhibit for a chelated N,N'-bidentate ligand, 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. In addition, the infrared spectra contain a strong band at 850 cm^{-1} due to the ν_{P-F} stretching frequency of PF_6. The proton NMR spectra of compounds [**4**]PF_6 and [**5**]PF_6 displays a singlet at 1.48 and 1.45 ppm corresponding to the protons of the pentamethylcyclopentadienyl group. The molecular structure of the complex [5]PF_6 is solved by single crystal X ray crystallography and the structure is presented as Figure **2.4**.

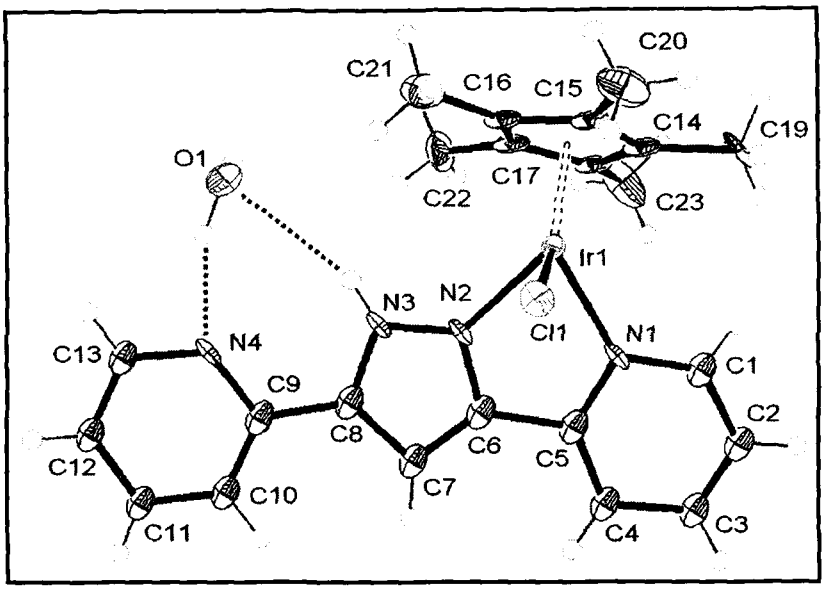
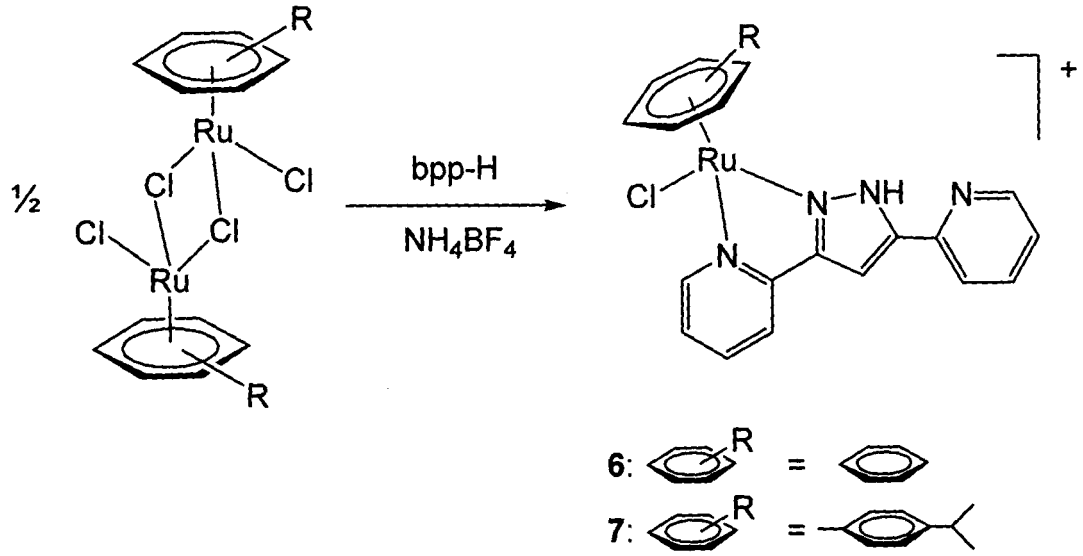


Figure **2.4:** ORTEP diagram with labelling scheme for $[(\eta^5\text{-}C_5Me_5)Ir(bpp\text{-}H)Cl]^+$ ([**5**]$PF_6.H_2O$), at 50% probability level, PF_6 anion omitted for clarity.

2.4.3 Mononuclear arene ruthenium complexes [6]BF_4 and [7]BF_4 and dinuclear complexes [8]BF_4 and [9]BF_4

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene and *p*-cymene) react with N,N'-based ligand (bpp-H) in methanol to produce the mononuclear cationic complexes [**6**]BF_4 and [**7**]BF_4 (Scheme 2) and the dinuclear cationic complexes [**8**]BF_4 and [**9**]BF_4 (Scheme 3). The complexes [**6**]BF_4 and [**7**]BF_4 are brown in color while in solution the color turns yellow, non-hygroscopic, air stable solids. However the complexes [**8**]BF_4 and [**9**]BF_4 are yellow in color, non-hygroscopic, air stable solids. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile, while they are insoluble in non-polar solvents like hexane, diethyl ether or petroleum ether.

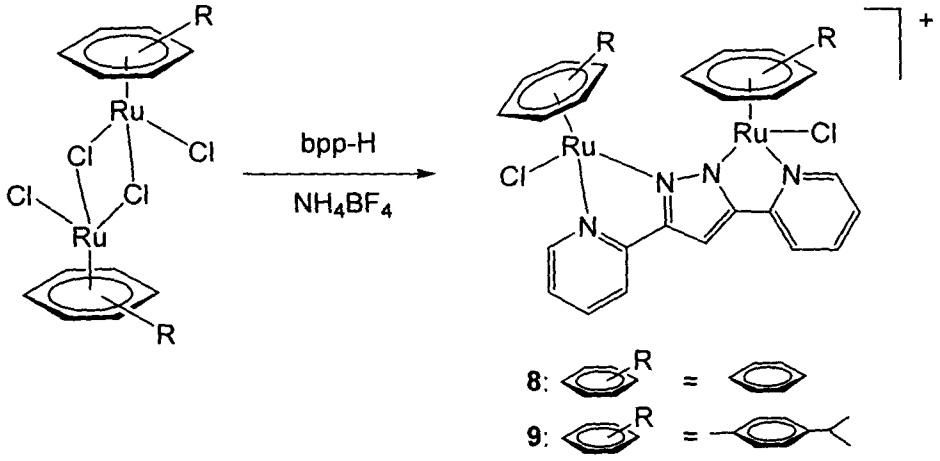


Scheme **2.2**

These complexes display strong bands at 3416 cm^{-1} and 1613 cm^{-1} corresponding to the stretching frequencies of the N-H bond of the pyrazole ring and C-N bond of the pyridine ring. In addition, the IR spectra of all these complexes contained a strong band at 1082 cm^{-1} due to the stretching frequency of B-F bond of the counter ion of these complexes. In complex [**6**]BF_4, in addition to the proton peaks of the ligand, the NMR spectra also displays a singlet at around 6.25 ppm which corresponds to the six protons of the benzene ring. Whereas in the case of the dinuclear complex [**8**]BF_4, in addition to the ligand peaks, the spectra displays two singlet in the range of 6.3–6.1 ppm which corresponds to the protons of the two benzene rings. The formations of these compounds are also confirmed by ESI-MS spectroscopy. The presence of peaks at m/z = 651.1, 740.3, 722.3, 658.5, 748.2, 437.2, 650.9, 492.1 and 763, which coincides with the molecular mass of the cationic complexes [**1**]PF_6 to [**9**]BF_4 also confirms the formation of these compounds.

An interesting point to make here is when starting dimers $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, *p*-cymene and hexamethylbenzene) is treated with terpyridine in methanol, rapid displacement of the arene group with terpyridine to form ruthenium terpyridine complex. Whereas, when [**8**]BF_4 or [**9**]BF_4 is treated with terpyridine, the reaction does not occur, i.e., the displacement of arene group by terpyridine is directly not possible [54, 55]. This could be due to the following reasons: i) The formation of complex as a solvated cationic complex in the case of $[(\eta^6\text{-arene})RuCl_2]_2$; which is not possible in the case of

[8]BF_4 or [9]BF_4. ii) In these complexes arene binds to the metal with *fac-* coordination, it is difficult them to replace with *mer-* coordination ligands such as terpyridine due to frozen free rotation of ligands unlike in the starting dimers. These complexes are prepared with different methods [38, 39]. The dinuclear structure of representative complex [8]BF_4 is further confirmed by the molecular structure determination by single crystal X ray study (Figure **2.5**).



Scheme **2.3**

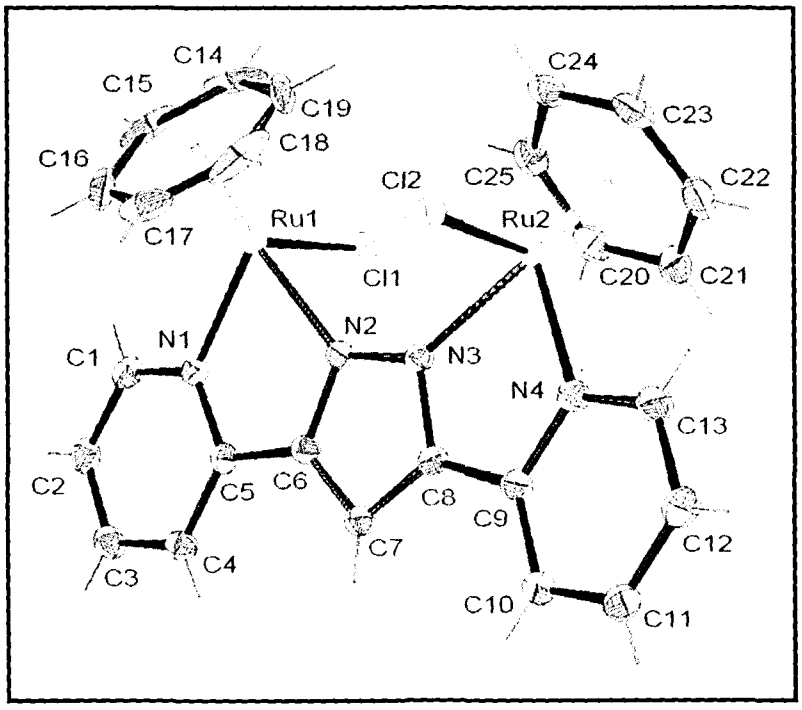


Figure **2.5**: ORTEP diagram with labelling scheme for $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]^+$ ([8]BF_4 H_2O), at 50% probability level, water and BF_4 anion omitted for clarity.

2.5 UV-visible spectroscopy

UV-vis spectra of the representative complexes [1]PF_6, [3]PF_6, [4]PF_6, [6]BF_4, [7]BF_4, [8]BF_4 and [9]BF_4 were acquired in acetonitrile, and spectral data are summarized in the experimental section. Mononuclear complexes [1]PF_6, [3]PF_6, [4]PF_6 and [6]BF_4 displayed intense transition in the UV region. The high energy absorption bands in the electronic spectra of [1]PF_6, [3]PF_6, [4]PF_6, [6]PF_6 in the UV region at ~308-358 nm have been assigned to ligand-centered $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions [56], whereas, in the case of [7]BF_4, it shows a low energy absorption band in the visible region at ~ 430 nm and can be assigned to MLCT transition. The dinuclear complexes [8]BF_4 and [9]BF_4 exhibited similar trends, with an additional band at ~ 425 nm that can be assigned to the MLCT band due to $d\pi$M-arene$\rightarrow \pi^*_{bpp}$ transition [56] and can be assigned to exhibit significant red shift . In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen bonded metal complexes, which display a ligand band based $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions in the UV region and metal-to-ligand charge transfer transitions in the visible region. The electronic spectra of these complexes are shown in Figure **2.6**.

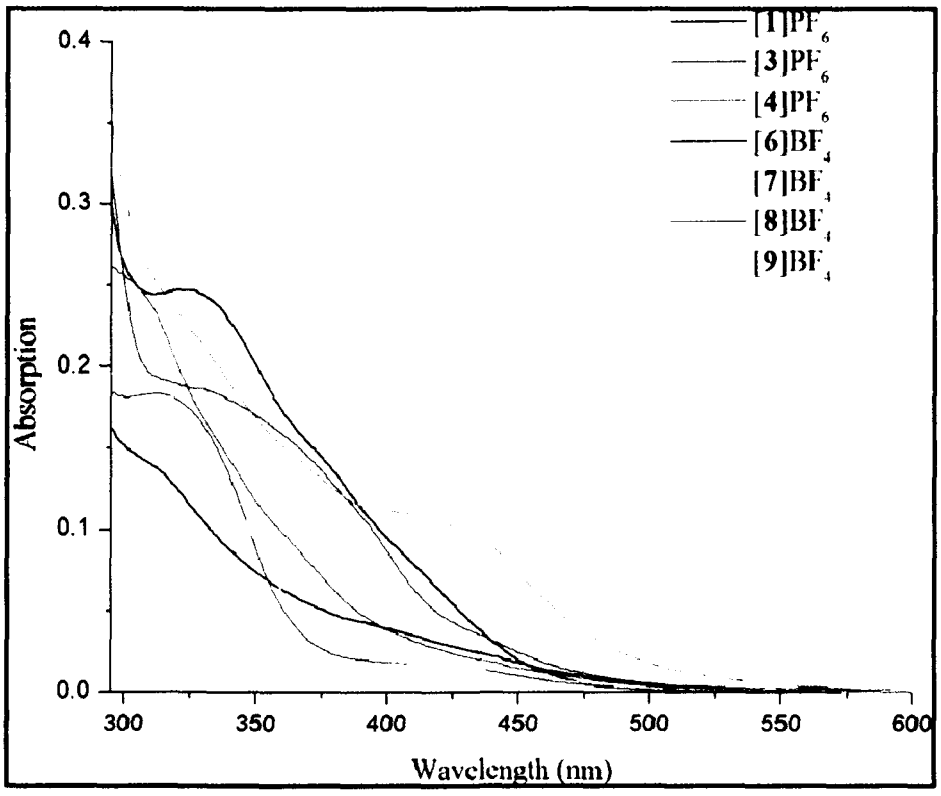


Figure **2.6:** UV-visible spectra of complexes [1]PF_6, [3]PF_6, [4]PF_6, [6]BF_4, [7]BF_4, [8]BF_4 and [9]BF_4 in acetonitrile at 298 K.

2.6 Molecular structure

The molecular structures of $[(\eta^5\text{-}C_5H_5)Ru(bpp\text{-}H)PPh_3]PF_6$ ([**1**]PF_6) $[(\eta^5\text{-}C_5Me_5)Ir(bpp\text{-}H)Cl]PF_6{\cdot}H_2O$ ([**5**]PF_6) and $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]BF_4{\cdot}H_2O$ ([**8**]BF_4) have been established by single-crystal X-ray analysis of their hexafluorophosphate and tetrafluoroborate salts. The complexes show typical piano-stool geometry with the metal centre coordinated by the cyclopentadienyl or arene ligand, a terminal chloride in complexes [**5**]PF_6 and [**8**]BF_4, triphenylphosphine in complex [**1**]PF_6 and the chelating bpp-H ligand. The metal atom is in octahedral arrangement with two *cis*-nitrogen atoms of the bpp-H ligand acting as a bidentate chelating ligand through neighbouring pyridyl and pyrazolyl nitrogen atoms. In this study, mononuclear complexes [**1**]PF_6 and [**5**]PF_6 were found to be coordinated to N1, N2 and dinuclear complex [**8**]BF_4 was found to be first metal center coordinated to N1 and N2 and second metal center coordinated to N3 and N4 in a five-membered ring chelating fashion involving nitrogen atoms of the pyridine and the pyrazolyl moiety respectively. The aromatic ring occupies three coordinate sites in these complexes to complete octahedral geometry around the metal centre. The molecular structures of complexes [**1**]PF_6, [**5**]PF_6 and [**8**]BF_4 are shown in Figures **2.3**, **2.4** and **2.5**, respectively. Selected bond lengths and angles are presented in Table **2.2**.

The distances between the iridium atom and the centroid of the $\eta^5\text{-}C_5Me_5$ ring is 1.786 Å in complex [**5**]PF_6, whereas the distance betwen the ruthenium atom and centroid of $\eta^5\text{-}C_5H_5$ ring is 1.830 Å in complex [**1**]PF_6. These bond distances are comparable to those in the related complex cations $[(\eta^5\text{-}C_5Me_5)IrCl(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)]^+$, where X = NO_2, and Cl [57] and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(\kappa^2\text{-}paa)]^+$ and $[Ru(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}dppm)(\kappa^2\text{-}paa)]^+$ [58]. Whereas in the complex [**8**]BF_4, the distances between the metal and the centeriod of the arene rings are 1.685 Å and 1.681 Å which are in accordance with the values reported in other related complexes [59].

All these complexes crystallizes in monoclinic space groups. The complexes [**5**]PF_6 and [**8**]BF_4 crystallizes with a molecule of water per asymmetric unit. The M-N distance in complex [**5**]PF_6 appears to be significantly shorter than the M-N distances in complexes [**1**]PF_6 and [**8**]BF_4. There are no significant differences in the C-C bond lengths in the pentamethylcyclopentadienyl ring, all being about 1.337 Å and pointing to uniform π-electron delocalization in the ring. Furthermore; the five membered ring is planar as evident in the nearly equal bond distances between metal atom and the ring carbons. The Ir-Cl bond distance is 2.398 Å, which is close to related two-coordinated chelating N,N'-

base ligands iridium and rhodium complexes [57]. An interesting structural feature of the homodinuclear complex **[8]**BF_4 is the presence of an orientation disorder at the location of the benzene ring C14-C19 (occupancy factors 75). The ring C14-C19 is the major contribution of the disordered system, whereas; the corresponding minor contribution is the orientation disorder ring C26-C31 (occupancy factors 25) (not shown in Figure 3). The refined site distribution of C14-19 to C26-31 is 75/25. The Ru(1)---Cl(1) 2.403(13) Å and Ru(2)---Cl(2) 2.4339(14) Å are comparable to mononuclear complexes. However the bond length of Ru(2)---Cl(2) is much longer than other metal to chloride Ru(1)---Cl(1) distance but there was no significant change in environment.

2.7 Conclusions:

The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ligand which posses two contiguous binding sites for metal ions, has been found to form mononuclear and binuclear complexes with metal precursors. However, arene ruthenium complexes yielded bimetallic complexes with bpp-H, whereas (η^5-C_5Me_5)M dimers and mononuclear triphenylphosphine complexes did not yield bimetallic complexes with bpp-H and this could be due to the steric effect of η^5-C_5Me_5 and PPh_3 ligands. The mononuclear complexes can be made available to bind with other less steric metal precursors to form homo or hetero bimetallic complexes through the other two nitrogen atoms of bpp-H ligand.

Supplementary material

CCDC- **700916** **[1]**$(PF_6)_2$, **702728** **[5]**$(PF_6)_2 \cdot H_2O$ and **702729** **[8]**$(BF_4) \cdot H_2O$ contain the supplementary crystallographic data for this chapter.

Table **2.1**: Crystallographic and structure refinement parameters for complexes [**1**]PF_6 · H_2O, [**5**]PF_6 and [**8**]BF_4 · H_2O

	[**1**]PF_6	[**5**]$PF_6 \cdot H_2O$	[**8**]$BF_4 \cdot H_2O$
Chemical formula	$C_{36}H_{30}F_6N_4P_2Ru$	$C_{23}H_{27}ClF_6IrN_4OP$	$C_{25}H_{23}BCl_2F_4N_4ORu_2$
Formula weight	795.65	748.11	755.32
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P* $2_1/n$ (no. 14)	*P c* (no. 7)	*P* $2_1/c$ (no. 14)
Crystal color and shape	green block	red block	Orange plate
Crystal size	0.32 x 0.20 x 0.20	0.25 x 0.24 x 0.21	0.22 x 0.13 x 0.04
a (Å)	13.663(1)	8.760(1)	14.229(7)
b (Å)	14.426(1)	13.903(2)	11.265(6)
c (Å)	17.172(1)	13.706(2)	16.008(8)
β(°)	104.284(8)	129.18(1)	95.750(5)
V ($Å^3$)	3280.1(4)	1293.8(3)	2553(2)
Z	4	2	4
T (K)	173(2)	173(2)	120(2)
D_c ($g.cm^{-3}$)	1.611	1.920	1.965
μ (mm^{-1})	0.644	5.393	1.451
Scan range (°)	$2.09 < \theta < 26.00$	$2.41 < \theta < 26.02$	$2.21 < \theta < 28.21$
Unique reflections	6310	4670	5885
Reflections used [$I>2\sigma(I)$]	5334	3109	5452
R_{int}	0.0542	0.1067	0.0230
Flack parameter	-0.06(3)		
Final R indices [$I>2\sigma(I)$]*	0.0324, *w*R_2 0.0854	0.0715, *w*R_2 0.1780	0.0252, *w*R_2 0.0622
R indices (all data)	0.0414, *w*R_2 0.0940	0.0942, *w*R_2 0.1872	0.0282, *w*R_2 0.0647
Goodness-of-fit	1.008	0.932	1.026
Max, Min $\Delta\rho$/e ($Å^{-3}$)	0.662, -1.640	4.068, -4.524	0.758, -0.415

* 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 **2.2**: Selected bond lengths and angles for complexes [**1**]PF_6, [**5**]$PF_6.H_2O$ and [**8**]$BF_4 \cdot H_2O$.

Distances (Å)	[**1**]PF_6	[**5**]$PF_6 \cdot H_2O$	[**8**]$BF_4 \cdot H_2O$
N(1)-M(1)	2.188(2)	2.07(8)	2.103(2)
N(2)-M(1)	2.085(2)	2.01(5)	2.096(2)
Cl(1)-M(1)		2.398(17)	2.403(13)
N(2)-N(3)	1.342(3)	1.37(8)	1.350(3)
M(1)--CNT(1)	1.830	1.786	1.685
N(3)--M(2)			2.090(2)
N(4)--M(2)			2.090(2)
Cl(2)--M(2)			2.4339(14)
M(2)--CNT(2)			1.681
Angles (°)			
N(3)-N(2)-M(1)	135.60(15)	135(4)	135.49(14)
N(2)-M(1)-N(1)	75.75(8)	77(2)	76.63(8)
N(2)-M(1)-Cl(1)		83.1(15)	87.4
N(1)-M(1)-Cl(1)		87.9(15)	87.1
N(2)-N(3)-M(2)			136.49(15)
N(3)-M(2)-N(4)			76.83(8)
N(4)-M(2)-Cl(2)			82.77(6)
N(3)-Ru(2)-Cl(2)			87.43(5)

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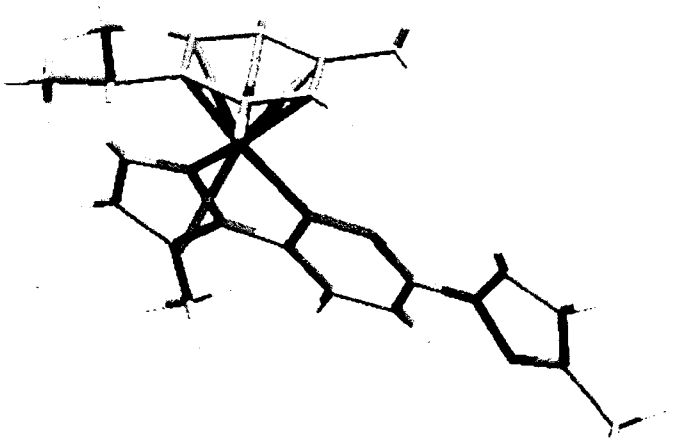
CHAPTER 3

Ruthenium half-sandwich complexes with tautomerized pyrazolyl pyridazine ligands: Syntheses, spectroscopic and molecular structural studies



Ruthenium half-sandwich complexes with tautomerized pyrazolyl pyridazine ligands: Syntheses, spectroscopic and molecular structural studies*

3.1 Abstract

Condensation of 1,4-dichloropyridazine with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole yielded two types of pyrazolyl pyridazine ligands, *viz.*, (i) products of substitution on one side of the pyridazine as 3-chloro-6-(pyrazolyl)pyridazine (Cl-L1), 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (Cl-L2) and 3-chloro-6-(3-methylpyrazolyl)-pyridazine (Cl-L3), and (ii) products of substitution on both sides such as 3,6-bis(pyrazolyl)pyridazine (L1), 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (L2) and *tautomers* of 3,6-bis(3-methylpyrazolyl)pyridazine (L3). The reactions of η^6-areneruthenium complexes in methanol with the above mentioned pyrazolyl pyridazine ligands form mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(Cl\text{-}L)(Cl)]^+$ and $[(\eta^6\text{-arene})Ru(L)(Cl)]^+$; (arene = benzene and *p*-cymene; Cl-L= Cl-L1, Cl-L2, Cl-L3; L = L1, L2, L3). All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

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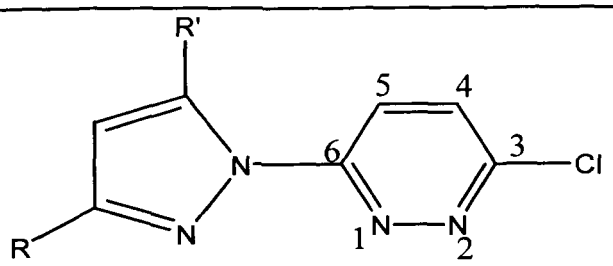
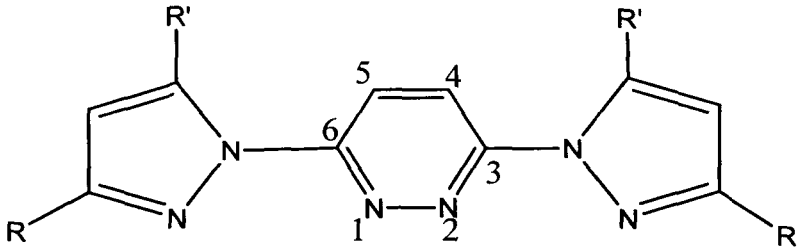
3.2 Introduction

Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 40 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1, 2]. Coordination of a metal fragment to an arene ring dramatically facilitates electrophilic aromatic addition and substitution, arene deprotonation and benzylic deprotonation. Arene metal complexes have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis and Diels-Alder cycloaddition [3-6]. In recent years, we have been carrying out reactions of arene ruthenium dimers with a variety of nitrogen-based ligands [7-12] including pyridyl-pyridazine and pyrazolyl-pyradazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [13, 14]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing annular tautomerized pyrazolyl-pyradazine ligands have not yet been investigated.

Herein, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methylpyrazole moiety [15]; the existence of both tautomers in a single compound is reported here. The syntheses of 12 mononuclear arene ruthenium complexes incorporating these as well as some other pyrazolyl-pyridazine ligands are also reported. Given below are the structures of the ligands used in this study. All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The molecular structures of the ligand (L3) and four representative complexes are also presented in this chapter.



R=R'=H, Cl-L1 (3-chloro-6-(pyrazolyl)pyridazine)
R=R'=CH_3, Cl-L2 (3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, Cl-L3 (3-chloro-6-(3-methylpyrazolyl)pyridazine)



R=R'=H, L1 (3,6-Bis(pyrazolyl)pyridazine)
R=R'=CH_3, L2 (3,6-Bis(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, L3 (3,6-Bis(3-methylpyrazolyl)pyridazine)

Ligands used in this study

3.3 Experimental

All solvents were dried and distilled prior to use. Ruthenium trichloride trihydrate (Arora Matthey Ltd.), pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole and 3,6-dichloropyridazine (Aldrich) were purchased and used as received. The ligands were prepared by following a literature procedure [16]. The precursor complexes $[(\eta^6\text{-arene})Ru\ (\mu\text{-}Cl)Cl]_2$ (arene = benzene and *p*-cymene) were prepared by following the literature methods [17-19]. NMR spectra were recorded on an AMX 400 MHz. spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Mass spectra were obtained from a Waters ZQ 4000 mass spectrometer by the ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV-visible spectrophotometer. All the new complexes gave satisfactory CHN results.

3.3.1 Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4 were grown by slow diffusion of diethylether into dichloromethane solution of the respective complexes. For the ligand **L3**, crystals were grown by slow evaporation of chloroform solution of **L3**. The intensity data of the white crystal of **L3**, the bright orange crystal of compound [**1**]PF_6 , the red color crystal of [**10**]PF_6 and the yellow crystals of compound [**3**]PF_6 and [**11**]ClO_4 were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoKα radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with the SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [20] and refined with full-matrix least squares on F2 using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [22] for Windows. The ORTEP presentations of the representative complexes are shown in Figures **3.5** to **3.9** respectively. The bond lengths and angles and data collection parameters are presented in Tables **3.2** and **3.3**.

3.3.2 Preparation of cationic complexes [**1**]PF_6 to [**6**]PF_6

3.3.2.1 Synthesis of [(η^6- p-cymene)Ru(Cl-L1)Cl]PF_6 ([**1**]PF_6)

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl-L1 (28 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a color change from light red to deep red. The solvents were removed using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 69 mg, 70.9%

Elemental Anal (%) Calc. for $C_{17}H_{19}N_4RuCl_2PF_6$: C 34.24; H 3.21; N 9.40; found: C 33.92; H 3.33; N 9.49

^{1}H NMR (400MHz, $CDCl_3$, 25 °C, TMS): δ = 8.02 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 7.85 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 6.39 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 5.90 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.84 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.76 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.69 (d, $^3J_{H,H}$ = 6.0 Hz ,1H, $Ar_{p\text{-}cy}$), 2.99 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.19 (s, 3H), 1.32 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 3H). ESI-MS (m/z): 451.2 [M- PF_6], 415.1 [M-PF_6-Cl].

3.3.2.2 Synthesis of [(η^6-C_6H_6)Ru(Cl-L1)Cl]PF_6 ([2]PF_6)

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl-L1 (36 mg, 0.020 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 65 mg, 60.2%

Elemental Anal (%) Calc. for $C_{13}H_{11}N_4RuCl_2PF_6$: C 28.90; H 2.05; N 10.37; found: C 29.05; H 1.98; N 10.55

^{1}H NMR (400MHz, CD_3CN, 25 °C, TMS): δ = 8.20 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 7.91 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 6.44 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.12 (s, 6H, C_6H_6). ESI-MS (m/z): 395.1 [M- PF_6].

3.3.2.3 Synthesis of [(η^6-p-cymene)Ru(Cl-L2)Cl]PF_6 ([3]PF_6)

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl-L2 (34 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were reduced using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum

Yield: 65 mg, 63.9%

Elemental Anal (%) Calc. for $C_{19}H_{23}N_4RuCl_2PF_6$: C 36.55; H 3.71; N 8.97; found: C 36.43; H 3.79; N 9.01

^{1}H NMR (400MHz, $CDCl_3$, 25 °C, TMS): δ = 8.05 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 7.85 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 6.40 (s, 1H), 5.96 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.85 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.80 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.75 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 2.91 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.20 (s, 6H, CH_3), 2.1 (s, 3H), 1.35 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 3H). ESI-MS (m/z): 479.2 [M- PF6].

*3.3.2.4 Synthesis of [(η^6-C_6H_6)Ru(Cl-L2)Cl]PF_6 ([**4**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl-L2 (41 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 67 mg, 59.0%.

Elemental Anal (%) Calc. for $C_{15}H_{15}N_4RuCl_2PF_6$: C 31.70; H 2.66; N 9.86; found: C 32.37; H 2.45; N 9.72.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.44 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.22 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 6.53 (s, 1H), 6.04 (s, 6H, C_6H_6), 2.71 (s, 6H.CH_3). ESI-MS (m/z): 422.7 [M-PF6].

*3.3.2.5 Synthesis of [(η^6- p-cymene)Ru(Cl-L3)Cl]PF_6 ([**5**]PF_6)*

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl-L3 (31 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 66 mg, 66.3%.

Elemental Anal (%) Calc. for $C_{18}H_{21}N_4RuCl_2PF_6$: C 35.42; H 3.47; N 9.18; found: C 35.61; H 3.11; N 9.34

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.58 (d, $^3J_{H,H}$ = 5.6 Hz, 1H), 8.32 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 8.21 (d, $^3J_{H,H}$ = 5.6 Hz, 1H), 7.92 (d, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.12 (d, $^3J_{H,H}$ = 6.4 Hz,

1H, $Ar_{p\text{-}cy}$), 5.98 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.86 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.79 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $Ar_{p\text{-}cy}$), 3.22 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.41 (s, 3H, CH_3), 2.31 (s, 3H), 1.53 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.49 (d, $^3J_{H,H}$ = 5.6 Hz, 3H). ESI-MS (m/z): 465.2 [M- PF_6], 430.1 [M- PF_6-Cl].

*3.3.2.6 Synthesis of [(η^6-C_6H_6)Ru(Cl-L3)Cl]PF_6 ([**6**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl-L3 (39 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 70 mg, 63.3%.

Elemental Anal (%) Calc. for $C_{14}H_{13}N_4RuCl_2PF_6$: C 30.34; H 2.36; N 10.11; found: C 29.97; H 2.55; N 10.32.

^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 8.52 (d, $^3J_{H,H}$ = 2.0 Hz, 1H), 8.39 (d, $^3J_{H,H}$ = 3.6 Hz, 1H), 8.19 (d, $^3J_{H,H}$ = 4.8 Hz, 1H), 7.98 (d, $^3J_{H,H}$ = 7.2 Hz, 1H), 6.25 (s, 6H, C_6H_6), 2.65 (s, 3H, CH_3). ESI-MS (m/z): 408.9 [M- PF_6].

3.3.3 Preparation of the cationic complexes [**7**]PF_6 to [**10**]PF_6, [**11**]ClO_4 and [**12**]PF_6

3.3.3.1 Synthesis of [(η^6- p-cymene)Ru(L1)Cl]PF_6 ([7]PF_6)

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L1 (35 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a light red to deep red color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 65 mg, 63.4%

Elemental Anal (%) Calc. for $C_{20}H_{22}N_6RuClPF_6$: C 38.26; H 3.53; N 13.38; found: C 37.92; H 3.77; N 12.95.

1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.61 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.59 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.55 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.23 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 7.90 (d, $^3J_{H,H}$ = 6.4 Hz,

1H), 7.72 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.87 (t, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.48 (t, $^3J_{H,H}$ = 5.6 Hz, 1H), 6.20 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 6.07 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.91 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.82 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 2.72 (sep, $^3J_{H,H}$ = 6.2 Hz, 1H), 2.20 (s, 3H), 1.22 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.18 (d, $^3J_{H,H}$ = 7.6 Hz, 3H). ESI-MS (m/z): 483.1 [M- PF_6].

*3.3.3.2 Synthesis of [(η^6-C_6H_6)Ru(L1)Cl]PF_6 ([**8**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L1 (42 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 66 mg, 57.8%

Elemental Anal (%) Calc. for $C_{16}H_{14}N_6RuClPF_6$: C 33.61; H 2.47; N 14.70; found: C 33.73; H 2.65; N 13.98.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.72 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.63 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.54 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.44 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.02 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 7.91 (d, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.92 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.53 (t, $^3J_{H,H}$ = 6.4 Hz, 1H), 5.90 (s, 6H, C_6H_6). ESI-MS (m/z): 427.2 [M- PF_6].

*3.3.3.3 Synthesis of [(η^6- p-cymene)Ru(L2)Cl]PF_6 ([**9**]PF_6)*

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L2 (43 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvent was reduced using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 67 mg, 65.6%

Elemental Anal (%) Calc. for $C_{24}H_{30}N_6RuClPF_6$: C 46.06; H 4.83; N 13.43; found: C 46.73; H 4.25; N 13.07

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.36 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.11 (d, $^3J_{H,H}$ = 9.2 Hz, 1H), 6.54 (s, 2H), 6.05 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.92 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}}$

$_{cy}$), 5.84 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.77 (d, $^3J_{H,H}$ = 6.4 Hz, H, $Ar_{p\text{-}cy}$), 2.71 (s, 12H, CH_3), 2.69 (sep, $^3J_{H,H}$ = 6.0 Hz, 1H), 2.18 (s, 3H), 1.09 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.06 (d, $^3J_{H,H}$ = 6.8 Hz, H).ESI-MS (m/z): 538.8 [M- PF_6].

*3.3.3.4 Synthesis of [(η^6-C_6H_6)Ru(L2)Cl]PF_6 ([**10**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L2 (53 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 64 mg, 56.3%.

Elemental Anal (%) Calc. for $C_{20}H_{22}N_6RuClPF_6$: C 42.16; H 3.89; N 14.75; found: C 41.90; H 4.05; N 14.33.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.50 (d, $^3J_{H,H}$ = 9.6 Hz, H), 8.48 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 7.76 (s, 2H), 5.87 (s, 6H, C_6H_6), 2.78 (s, 12H, CH_3). ESI-MS (m/z): 483.3 [M- PF_6].

*3.3.3.5 Synthesis of [(η^6- p-cymene)Ru(L3)Cl]ClO_4 ([**11**]ClO_4)*

A mixture of [(η^6- *p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L3 (39 mg, 0.16 mmol) and 2.5 equivalents of $NaClO_4$ in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml), and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 73 mg, 73.4%

Elemental Anal (%) Calc. for $C_{22}H_{26}N_6RuCl_2O_4$: C 43.28; H 4.29; N 13.77; found: C 43.78; H 3.94; N 13.92

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.53 (d, $^3J_{H,H}$ = 10.0 Hz, 1H), 8.45 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.27 (s, 1H), 8.19 (d, $^3J_{H,H}$ = 9.6 Hz, H), 6.44 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 6.34 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 5.93 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.87 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.76 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.68 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 3.1 (sep, $^3J_{H,H}$ = 6.8

Hz, 1H), 2.39 (s, 6H, CH_3), 2.26 (s, 3H), 1.42 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.38 (d, $^3J_{H,H}$ = 7.2 Hz, 3H).ESI-MS (m/z): 511.3 [M- ClO_4].

*3.3.3.6 Synthesis of [(η^6-C_6H_6)Ru(L3)Cl]PF_6 ([**12**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L3 (48 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 56 mg, 51.78%.

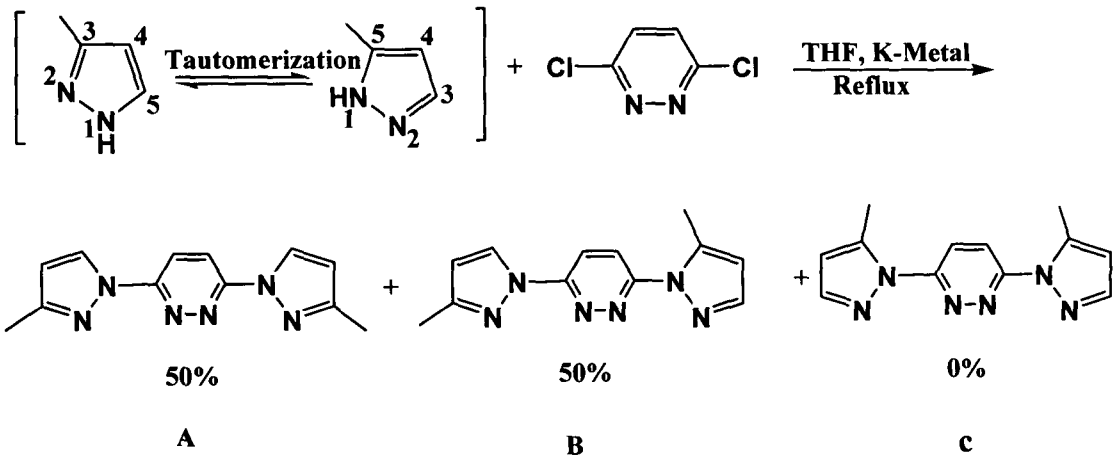
Elemental Anal (%) Calc. for $C_{18}H_{18}N_6RuClPF_6$: C 39.91; H 3.35; N 15.51; found: C 40.22; H 3.08; N 14.92

^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 8.53 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.46 (d, $^3J_{H,H}$ = 10.4 Hz, H), 8.42 (s, 1H), 8.31 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.21 (d, $^3J_{H,H}$ = 9.6 Hz, H), 6.76 (d, $^3J_{H,H}$ = 2.8 Hz, 1H), 6.09 (s, 6H, C_6H_6), 2.76 (s, 6H,CH_3). ESI-MS (m/z):455.2 [M- PF_6], 419.2 [M-PF_6-Cl].

3.4 Results and Discussion

3.4.1 Pyrazolyl pyridazine ligands

The ligands were synthesized by a known procedure [16] involving the condensation of 3,6-dichloropyridazine with substituted pyrazoles by refluxing in THF for around 8 hours. These starting materials in 1:1 ratio yielded one-side condensation products *viz.* pyrazolylchloropyridazines, while in 1:2 ratios they yielded both-side condensation products such as bis-pyrazolylpyridazines. In the case of both-side condensation, a small fraction of the one-side condensed product is also formed which is easily separated. An interesting phenomenon observed here is that, in the preparation of the ligand 3,6-bis(3-methylpyrazolyl)pyridazine (L3), a 1:1 mixture of two isomers, *viz.*, 3,6-bis(3-methylpyrazolyl)pyridazine and 6-(3-methylpyrazolyl)-3-(5-methylpyrazolyl) -pyridazine is formed. The presence of both isomers was confirmed by ^{13}C NMR spectroscopy. Apparently the starting 3-methylpyrazole under the reaction conditions undergoes tautomerization as shown in Scheme **3.1**.



Scheme **3.1**

The existence of the two annular tautomers is reported herein. The numbering of the pyrazole carbons depends on the concerned tautomer, since the protonated nitrogen (N-H) is always N1. In the tautomer A (Scheme **3.1**) [23], C3 is the carbon bearing the methyl substituent, while in B it is C5. The isomer ratios are determined tentatively by taking the ^{13}C NMR spectrum of a concentrated solution of the synthesized ligand (L3) in $CDCl_3$ (see Figure **3.1**). The isomers are not easily separable by TLC or column chromatography. Crystallization yielded single crystals of the 3,3-isomer of the pyrazolyl pyridazine ligand (L3) whose crystal structure is presented herein. However, after metallation, the presence of both the 3,3- and 3,5-pyrazolyl pyridazine tautomers is confirmed from the combination of single crystal X-ray structure of the complex [**11**]ClO_4, as well as from the ^{13}C NMR spectrum of the ligand and the complex. We were able to isolate single crystals of the 3,3 isomer of the ligand and of the complex containing the 3,5-isomer of the ligand, indicating both isomers exist in the pure ligand as well as in the complex. The ^{13}C NMR spectrum of the ligand in $CDCl_3$ reveals that the signal at 13.8 ppm corresponds to 3-methylpyrazole (≈50%), whereas the signal at 14.8 ppm is for 5-methylpyrazole (≈50%) (Figure **3.1**). Although the formation of another isomer, *viz.*, 3,6-bis(5-methylpyrazolyl)-pyridazine is also hypothetically possible (C in Scheme **3.1**), its formation here was not observed from these NMR studies.

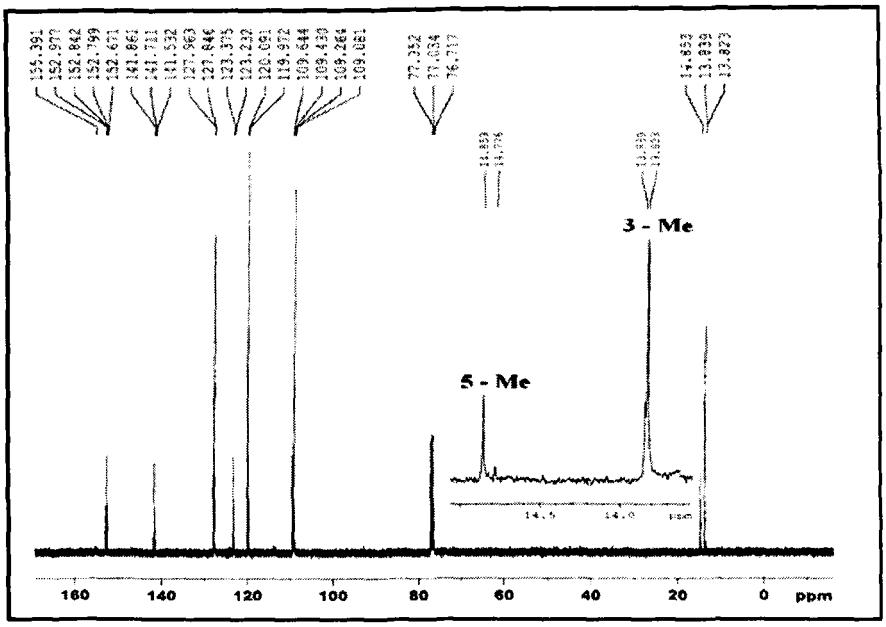


Figure **3.1:** ^{13}C NMR spectrum of the ligand mixture of 3,3 and 3,5 (L3) in $CDCl_3$

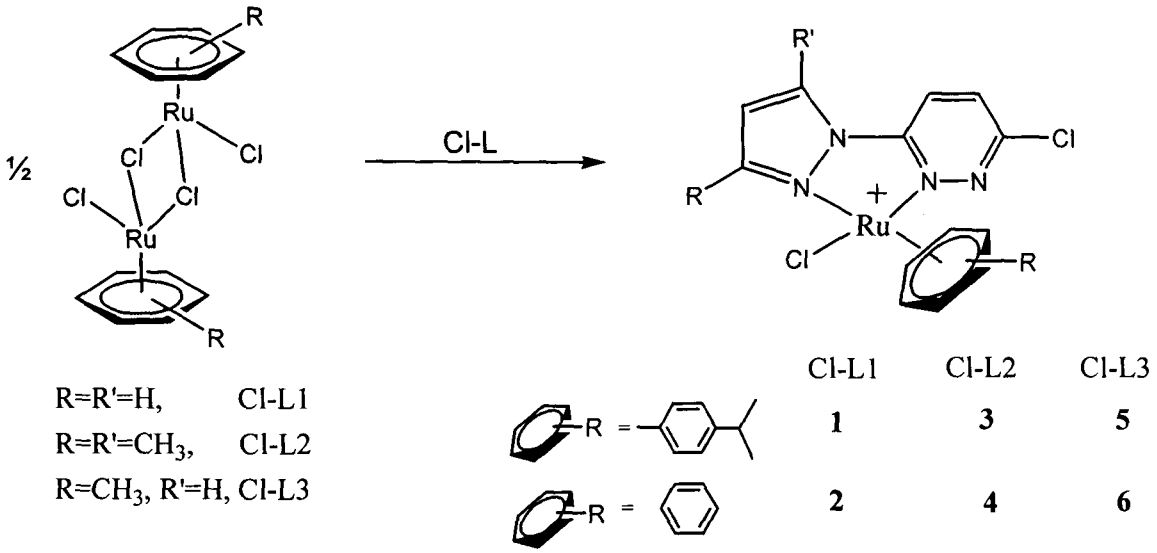
3.4.2 Arene ruthenium complexes

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, *p*-cymene) reacted in methanol with the ligands (Cl-L1), (Cl-L2), (Cl-L3), L1, L2 and L3 to give the mononuclear cationic complexes $[(\eta^6\text{-}p\text{-cymene})Ru(L)Cl]^+$ {L = Cl-L1 ([**1**]PF_6); Cl-L2 ([**3**]PF_6); Cl-L3 ([**5**]PF_6); L1 ([**7**]PF_6); L2 ([**9**]PF_6); L3 ([**11**]ClO_4) and $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ {L= Cl-L1 ([**2**]PF_6); Cl-L2 ([**4**]PF_6); Cl-L3 ([**6**]PF_6); L1 ([**8**]PF_6); L2 ([**10**]PF_6); L3 ([**12**]PF_6)} (Schemes **3.2** and **3.3**). The cationic ruthenium complexes ([**1**]PF_6) to ([**10**]PF_6) and ([**12**]PF_6) are obtained as their hexafluorophosphate salts, while complex ([**11**]ClO_4) is obtained as its perchlorate salt.

The complexes ([**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**] PF_6 and [**11**]ClO_4) are yellow in color, while the complexes ([**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6, [**12**]PF_6) are yellowish brown in color. They are non-hygroscopic, air-stable solids. The complexes ([**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**]PF_6 and [**11**]ClO_4) are soluble in solvents like acetonitrile, methanol, dichloromethane, chloroform, acetone *etc.*, but insoluble in hexane, petroleum ether and diethyl ether. The complexes {[**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6 and [**12**]PF_6} are

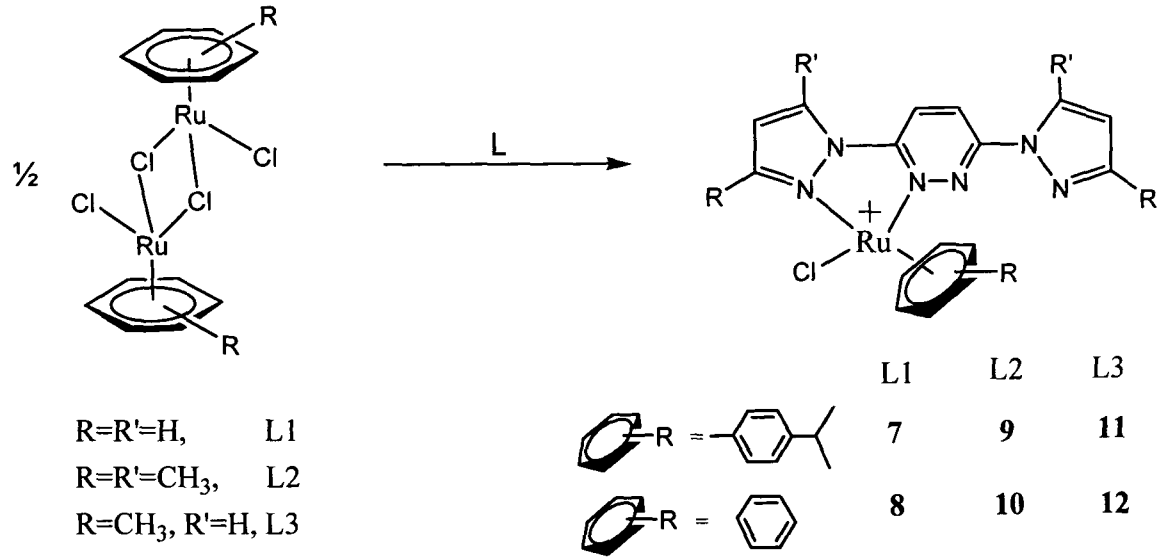
soluble in acetonitrile and partially soluble in dichloromethane, chloroform, methanol and acetone.

The infrared spectra of these complexes exhibit a strong $\nu_{C=N}$ band in the range of 1543 to 1583 cm^{-1} and a $\nu_{C=C}$ band in the range of 1437 to 1450 cm^{-1} which are the characteristic bands of the ligands. Besides these, the complexes ([**1**]PF_6 to [**10**]PF_6 and [**12**]PF_6) also exhibit a strong band at around 836-845 cm^{-1} due to the stretching ν_{P-F} mode of the counter ion of these complexes. However, in the case of the complex [**11**]ClO_4, a strong absorption at 1100 cm^{-1} is observed due to the perchlorate ion [24]. The *m/z* values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section, are in good agreement with the theoretically expected values.



	Cl-L1	Cl-L2	Cl-L3
R =	**1**	**3**	**5**
R =	**2**	**4**	**6**

Scheme **3.2**



	L1	L2	L3
	7	9	11
	8	10	12

Scheme **3.3**

3.4.3 NMR spectroscopy

The ^{1}H NMR spectra of the *p*-cymene and benzene derivatives which have Cl-L1, Cl-L2, Cl-L3, L1, L2 and L3 as ligands exhibit three resonances in the region δ = 8.02–6.39 for Cl-L1 ([**1**]PF_6, [**2**]PF_6), three resonances in the region δ = 8.05–6.40 for Cl-L2 ([**3**]PF_6, [**4**]PF_6), four resonances in the region δ = 8.58–7.92 for Cl-L3 ([**5**]PF_6, [**6**]PF_6), eight resonances at around δ = 8.72–6.48 for L1 ([**7**]PF_6, [**8**]PF_6), three resonances at around δ = 8.50–6.54 for L2 ([9]PF_6, [**10**]PF_6) and six resonances in the region δ = 8.53–6.34 for L3 ([**11**]ClO_4, [**12**]PF_6) in the aromatic region corresponding to the pyrazole and pyridazine protons which are clearly assigned as shown later. Besides these, all ligands other than Cl-L1 and L1 show a singlet in the region δ = 2.70 – 2.20 which corresponds to the methyl protons of these ligands.

The ^{13}C NMR spectrum of the complex [**11**]ClO_4 (Figure **3.3**) indicates a mixture of the two tautomers of the ligand. We were unable to separate these isomers. However, we were able to provide assignments of the resonances for both isomers. Crystallization yields the tautomer of the 3,5 complex (see molecular structure). The peaks assigned at around 13.6 and 14.3 ppm correspond respectively to the methyl carbons of the 3,3-isomer and of the 3,5-isomer of the ligand, which are also in accordance with the methyl peaks of the isomers as shown in ^{13}C NMR spectrum of the free ligands (Figure **3.1**). This also confirms the presence of both the tautomers in the complex as well.

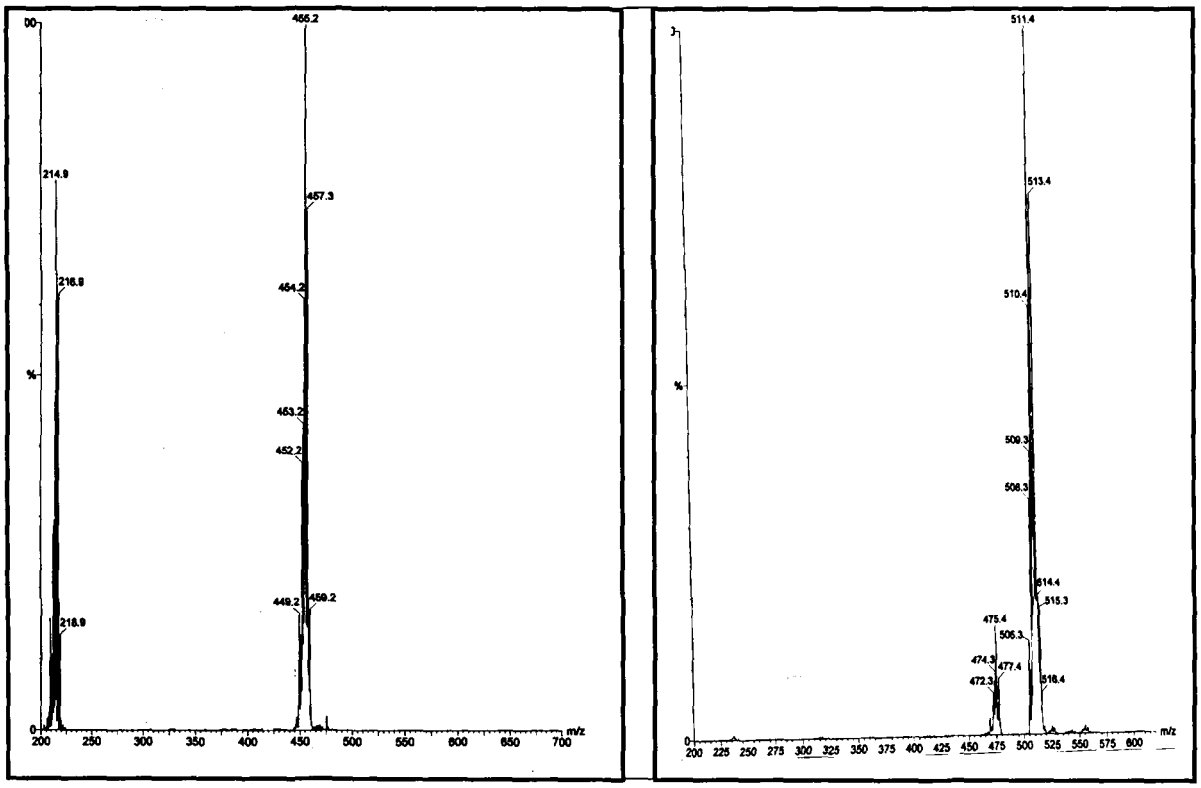


Figure **3.2:** Mass spectra of complexes **11** and **12**

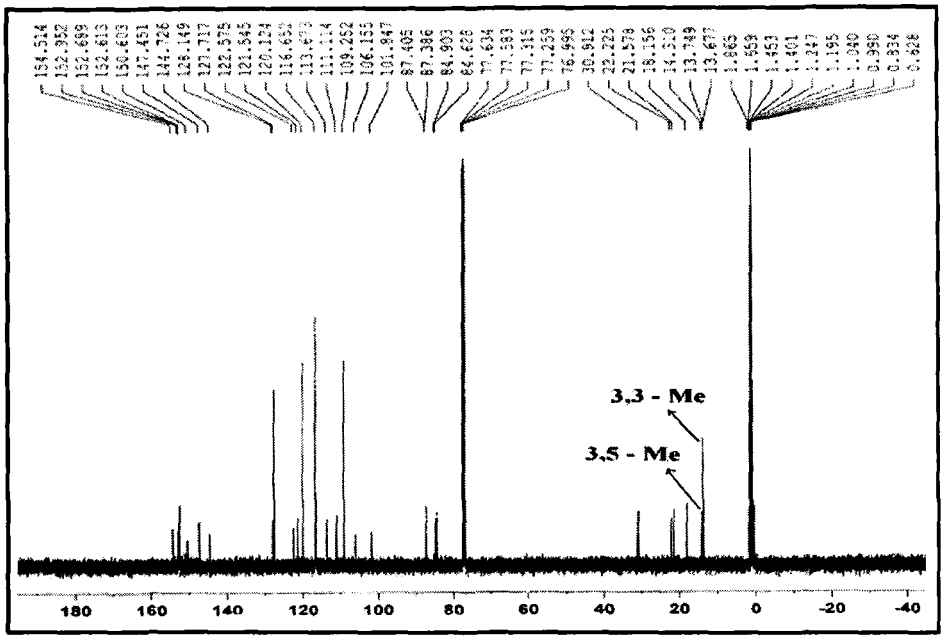


Figure **3.3:** ^{13}C NMR spectrum of the complex mixture of 3,3 and 3,5 [**11**]ClO_4 in $CDCl_3$+CD_3CN.

In addition to these signals, complexes [**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6, [**12**]PF_6 exhibit a singlet for the benzene ring protons at δ = 6.25–6.04. The complexes [**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**]PF_6 and [**11**]ClO_4 exhibit an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group display two doublets at *ca.* δ = 1.53–1.08 instead of one doublet as in the starting precursor. The aromatic protons of the *p*-cymene ligand for these complexes also display four doublets at *ca.* δ = 6.20–5.68, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behavior of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [25]. In other words we can say the different signals are entirely due to the chiral nature of the metal [26, 27].

3.5 UV-visible spectroscopy

UV-visible spectra of the complexes [**1**]PF_6 to [**4**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6 were acquired in acetonitrile and spectral data are summarized in Table **3.1**. Electronic spectra

of representative complexes are depicted in Figure **3.4**. The low spin d^6 configuration of these mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centers which can interact with the low lying π^* orbital of the ligands. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) $t_{2g}\rightarrow\pi^*$ transition in their electronic spectra [28-33]. The electronic spectra of these complexes display a medium intensity band in the UV-visible region. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~ 420–410 and ~ 368–335 nm have been tentatively assigned on the basis of their intensity and position to $\pi\rightarrow\pi^*$ MLCT transitions. The bands on the high energy side at ~ 305–292 nm for the complexes [**2**]PF_6, [**3**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6, have been assigned to ligand-centered $\pi\rightarrow\pi^*/n\rightarrow\pi^*$ transitions [34, 35]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi\rightarrow\pi^*$ transition for pyrazolyl pyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

Table **3.1**: UV-Vis absorption data in acetonitrile at 298 K

Complex	λ_{max}/nm ($\varepsilon/10^{-4}M^{-1}cm^{-1}$)		
[**1**]PF_6	335(0.25)	412(0.14)	
[**2**]PF_6	302(0.20)	340(0.07)	410(0.04)
[**3**]PF_6	292(0.60)	365(0.17)	420(0.14)
[**4**]PF_6	360(0.09)	415(0.06)	
[**9**]PF_6	305(0.90)	368(0.14)	418(0.07)
[**11**]ClO_4	293(0.99)	366(0.05)	413(0.04)
[**12**]PF_6	302(0.46)	365(0.05)	414(0.04)

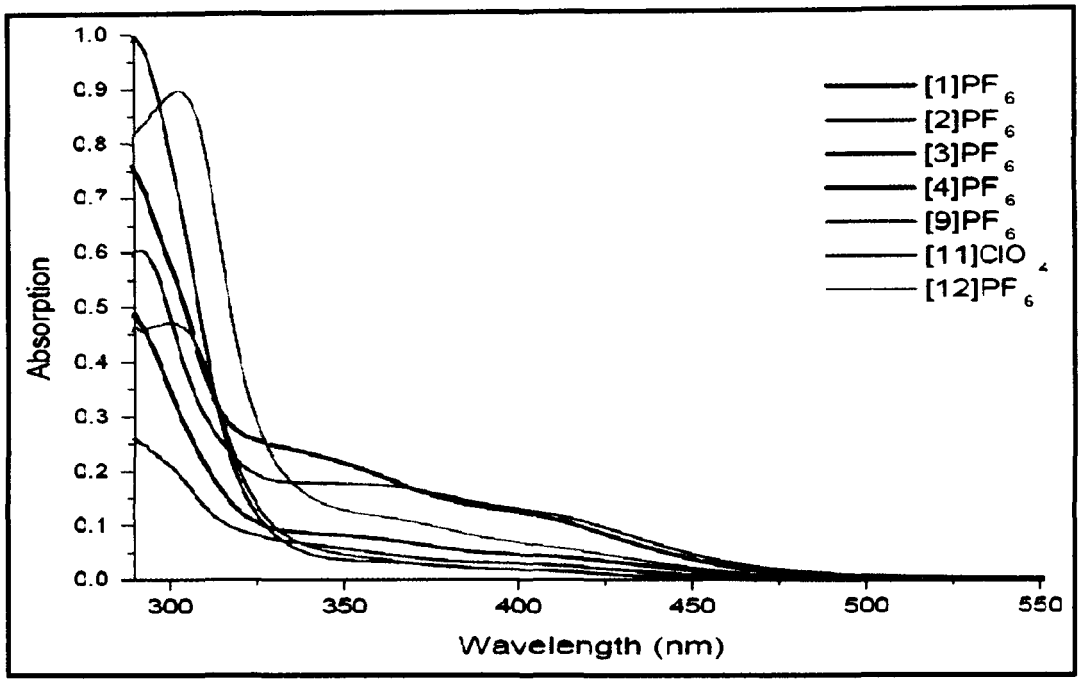


Figure **3.4:** UV- visible spectra of complexes [**1**]PF_6 to [**4**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6 in acetonitrile at 298 K.

3.6 Molecular structures

The crystal structures of the ligand **L3** and the complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4 are shown in Figures **3.5** to **3.9** respectively. Selected inter-atomic distances and angles are listed in Table **3.2**. The overall geometry of all these structures [except **L3**] corresponds to the characteristic piano-stool configuration. For all these compounds, the aromatic ring is planar as observed in related structures [36, 37]. The aromatic C-H bonds are bent umbrella-like towards the metal. We also observe a significant alternation in the aromatic C-C distances. The N1-Ru bond length in complex [**11**]ClO_4 is shorter by 0.029 Å than the N1-Ru average bond distance in complexes [**1**]PF_6 and [**3**]PF_6. The Ru-Cl bond distance of all these complexes are almost similar to those of other Ru-Cl complexes reported [38-46]. The N-N bond distances in all the complexes and in the ligand are comparable to each other, *i.e.*, not much variation is observed. The average P-F bond distance is 1.553(4) Å. The average metal-centroid distance is 1.685 Å, which appears to be close to the average distance of 1.69 Å in other Ru(II)-Cl complexes [47].

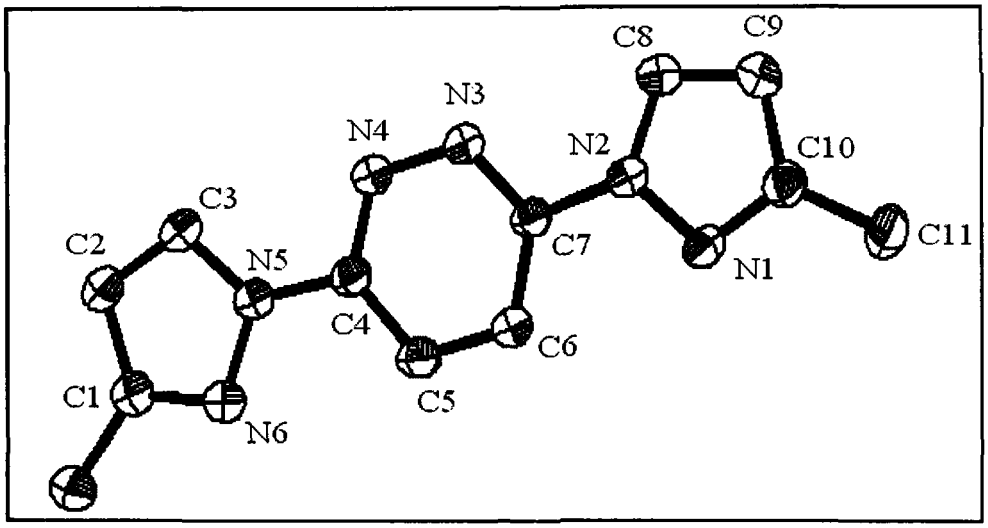


Figure **3.5:** Molecular structure of the ligand L3 with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

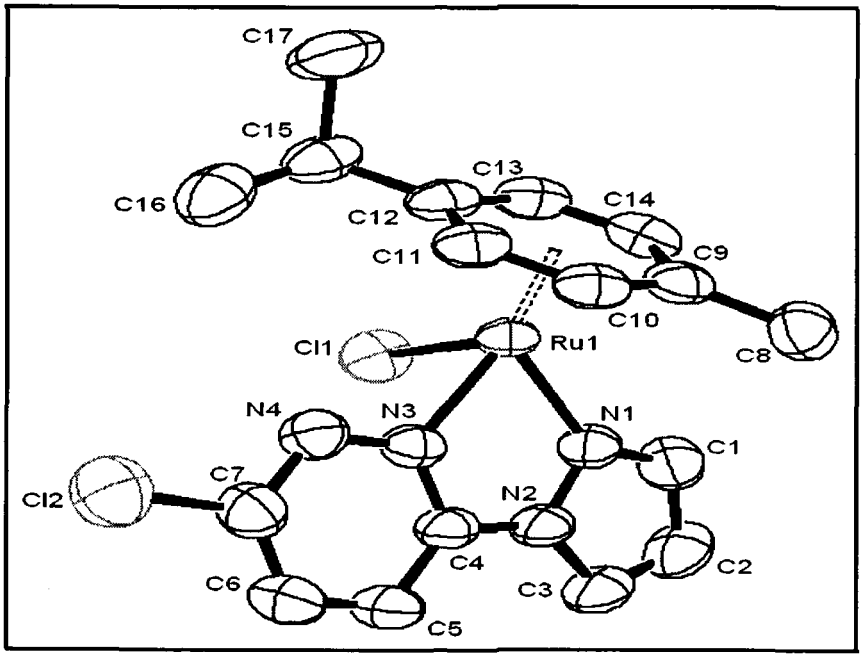


Figure **3.6:** Molecular structure of complex $[(\eta^6\text{-}C_{10}H_{14})Ru(Cl\text{-}L1)Cl]PF_6$ **[1]**PF_6 with 50% probability thermal ellipsoids.

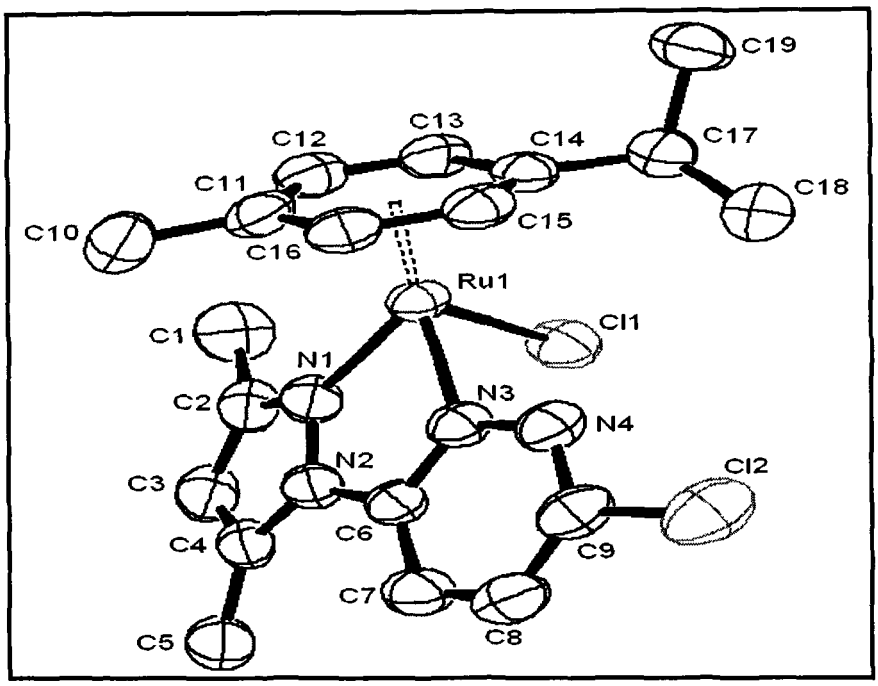


Figure **3.7:** Molecular structure of complex $[(\eta^6\text{-}C_{10}H_{14})Ru(Cl\text{-}L2)Cl]PF_6$ **[3]**PF_6 with 50% probability thermal ellipsoids.

Values of the angle N1-Ru-N3 in the *p*-cymene complexes **[3]**PF_6, **[10]**PF_6 and **[11]**ClO_4 are respectively 75.38(14), 75.50(9) and 75.9(2)°, while in the benzene complex **[1]**PF_6 the value is 76.09(14)°, larger than for the *p*-cymene complexes. In contrast, the angle Ru-N(1)-N(2) for the benzene complex **[1]**PF_6 is smaller than for the *p*-cymene complexes **[3]**PF_6, **[10]**PF_6 and **[11]**ClO_4. The *p*-cymene hydrogens and the pyrazole hydrogen of one molecule and the pyrazole hydrogens of another molecule are involved in an intermolecular C-H....O interaction with oxygen atoms of the ClO_4 counter ion (Figure **3.10**). The matrices for these interactions are as follows: H1.....O2 (2.503 Å), H4A....O4 (2.594 Å), H22A....O2 (2.705 Å), and ∠H1-O2-H22A (76.25°).

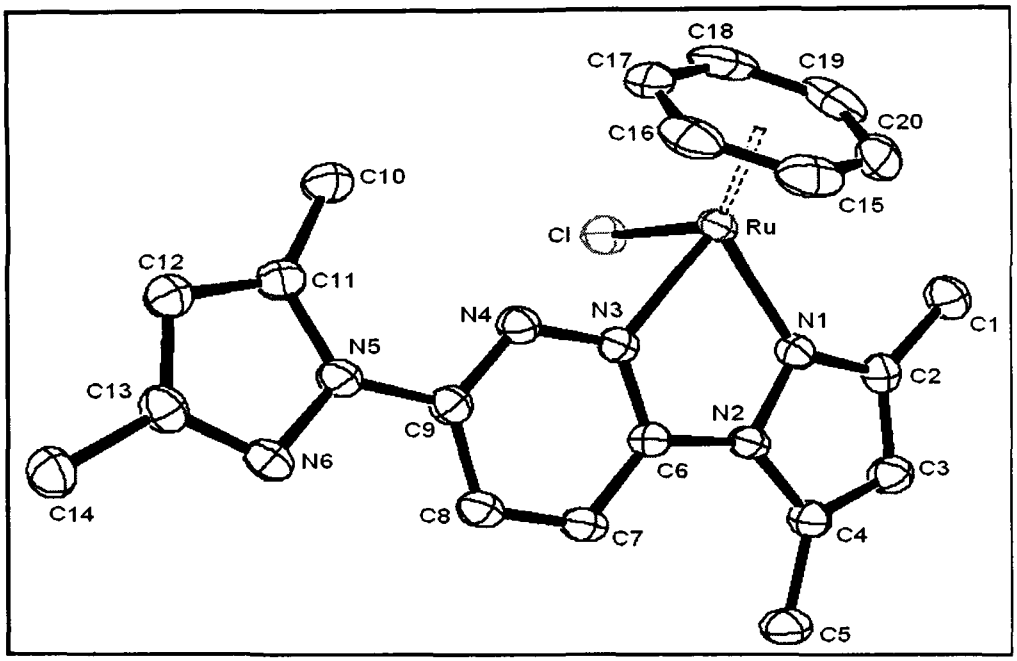


Figure **3.8:** Molecular structure of complex $[(\eta^6\text{-}C_6H_6)Ru(L2)Cl]PF_6$ [**10**]PF_6 with 50% probability thermal ellipsoids.

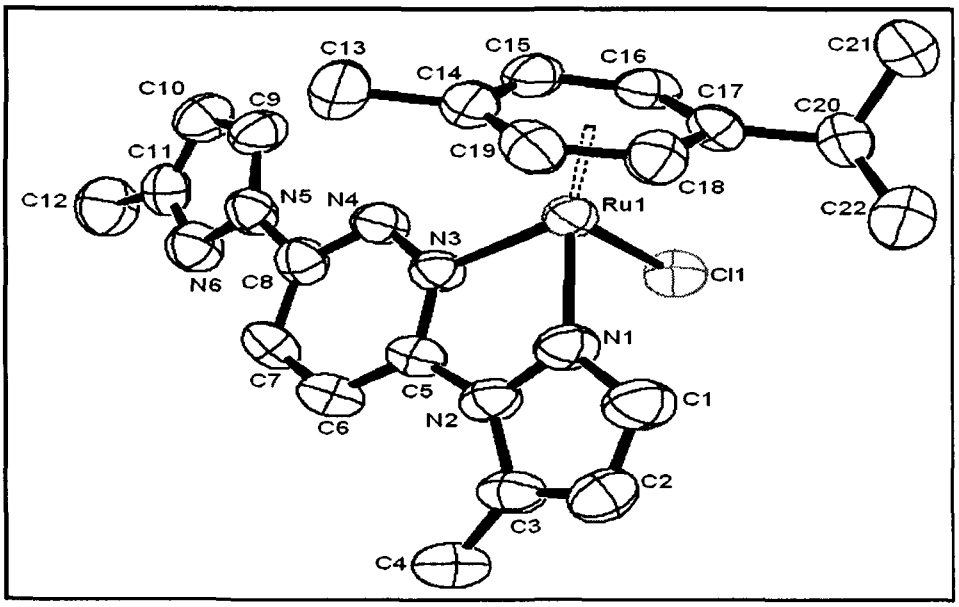


Figure **3.9:** Molecular structure of complex $[(\eta^6\text{-}C_{10}H_{14})Ru(L3)Cl]ClO_4$ [**11**]ClO_4 with 50% probability thermal ellipsoids.

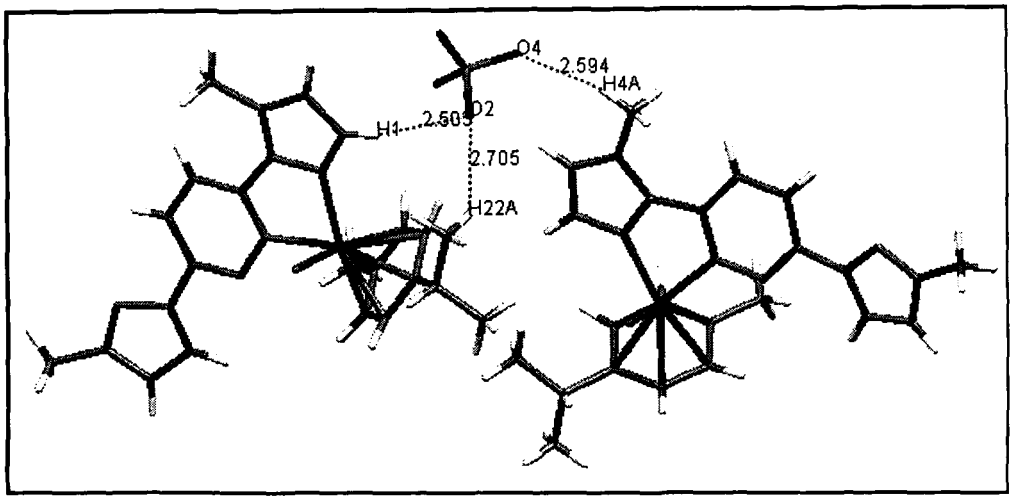


Figure **3.10:** Diagram showing hydrogen bonding between two adjacent molecular units in **[11]**ClO_4.

3.7 Conclusion

In summary, a series of η^6-arene ruthenium pyrazolyl pyridazine complexes which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. The titled complexes represent a new structural moiety related to the existence of two tautomers in the same compound which are not easily separable by TLC or column chromatography but are easily confirmed by ^{13}C NMR and single crystal X ray diffraction studies.

Supplementary material

CCDC- **710387** (**L3**), **710388** **[1]**(PF_6), **710389** **[3]**(PF_6), **710390** **[10]**(PF_6) and **710391** **[11]**(ClO_4) contain the supplementary crystallographic data for this chapter.

Table **3.2:** Selected bond lengths and angles for ligand **L3** and complexes [**1**]PF_6 , [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4

Distances (Å)	**L3**	**[1]PF_6**	**[3]PF_6**	**[10]PF_6**	**[11]ClO_4**
N(1)-Ru		2.082(3)	2.084(4)	2.073(2)	2.054(5)
N(3)-Ru		2.071(3)	2.070(3)	2.062(3)	2.075(5)
N(1)-N(2)	1.374(3)	1.365(5)	1.380(5)	1.391(3)	1.358(7)
N(3)-N(4)	1.347(4)	1.335(5)	1.346(5)	1.341(3)	1.346(7)
N(5)-N(6)	1.370(3)			1.377(3)	1.362(7)
Ru-Cl(1)		2.3932(11)	2.4048(12)	2.3974(13)	2.4059(19)
Ru-centroid		1.681	1.689	1.686	1.685
Angles (°)					
N(1)-Ru-N(3)		76.09(14)	75.38(14)	75.50(9)	75.9(2)
Ru-N(1)-N(2)		114.0(3)	115.1(3)	115.15(16)	115.9(4)
N(1)-Ru-Cl(1)		84.80(10)	83.62(11)	86.74(6)	84.32(17)
N(3)-Ru-Cl(1)		83.62(10)	88.62(10)	85.41(7)	84.89(16)

Table **3.3:** Crystallographic and structure refinement parameters for the ligand (**L3**) and complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4.

Compound	**L3**	[**1**]PF_6	[**3**]PF_6	[**10**]PF_6	[**11**]ClO_4
Empirical formula	$C_{12}H_{12}N_6$	$C_{17}H_{19}Cl_2F_6RuN_4P$	$C_{19}H_{23}Cl_2F_6N_4PRu$	$C_{20}H_{22}ClF_6N_6PRu$	$C_{22}H_{26}Cl_2N_6Ru$
Formula weight	240.28	596.30	624.35	627.93	610.46
Temperature	296(2)K	296(2) K	296(2) K	170(2)K	296(2) K
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, P-1	Monoclinic, $P2_1/c$	Monoclinic, C2/c	Triclinic, P-1	Monoclinic, P 2(1)/c
Unit cell dimensions					
a (Å)	5.9546(6)	13.7823(2)	15.3266(3)	7.823(4)	14.8458(9)
b (Å)	9.2459(9)	11.0438(2)	12.1360(3)	12.081(7)	16.0246(10)
c (Å)	11.1289(11)	14.7558(2)	25.5224(6)	13.352(7)	11.3289(7)
∝ (°)	85.832(7)			72.463(8)	
β (°)	87.678(7)	96.8950(10)	94.988(2)	73.762(8)	112.201(3)
γ (°)	73.043(6)			79.764(9)	
Volume (A^3)	584.40(10)	2229.72(6)	4729.28(19)	1149.2(11)	2496.9(3)
Z, Calculated density (Mg/m^3)	2, 1.365	4, 1.776	8, 1.754	2, 1.815	4, 1.624
Absorption coefficient (mm^{-1})	0.090	1.077	1.019	0.940	0.883
F(000)	252	1184	2496	628	1240
Crystal size (mm)	0.48 x 0.24 x 0.18	0.48 x 0.16 x 0.12	0.45 x 0.20 x 0.11	0.28 x 0.17 x 0.15	0.35 x 0.20 x 0.15

θ range for data collection (°).	1.84 to 28.28	1.49 to 28.29	2.14 to 28.32	1.78 to 28.32	1.95 to 28.37
Index ranges	-7<=h<=7,	-16<=h<=18,	-20<=h<=20,	-10<=h<=10,	-19<=h<=19,
	-12<=k<=12,	-14<=k<=14,	-15<=k<=16,	-16<=k<=16	-14<=k<=21,
	-14<=1<=14	-19<=1<=19	-33<=1<=33	-17<=1<=17	-15<=1<=10
Reflections collected / unique	7613/2722	26791/5432	36312/5813	15829/5711	22034/6211
[R_{int} = 0.2224]	[R_{int} = 0.0277]	[R_{int} = 0.0312]	[R_{int} = 0.0378]	[R_{int} = 0.0400]	[R_{int}= 0.0511]
Refinement method(F^2)		Full-matrix least-squares on			
Completeness to θ (°)	28.28, 94.2	28.29, 98.0	28.32, 98.5	25.00, 100.0	28.37, 99.4
Data/restraints/parameters	2722/0/166	5432/0/283	5813/0/303	5711/0/320	6211/0/321
Goodness-of-fit on (F^2)	1.015	1.064	1.046	1.021	1.029
Final R indices [I>2σ(I)]	R_1=0.0731,	R_1=0.0478,	R_1=0.0517,	R_1=0.0384,	R_1=0.0757,
	wR_2=0.2040	wR_2=0.1287	wR_2=0.1348	wR_2=0.0940	wR_2=0.1879
R indices (all data)	R_1=0.1003	R_1=0.0673,	R_1=0.0765,	R_1=0.0459,	R_1=0.1363,
	wR_2=0.2146	wR_2=0.1403	wR_2=0.1477	wR_2=0.0986	wR_2=0.2172
Largest diff. peak and hole (A^{-3})	0.245 and -0.213	0.597 and -0.583	0.725 and -0.677	1.029 and –0.632	0.574 and -0.475

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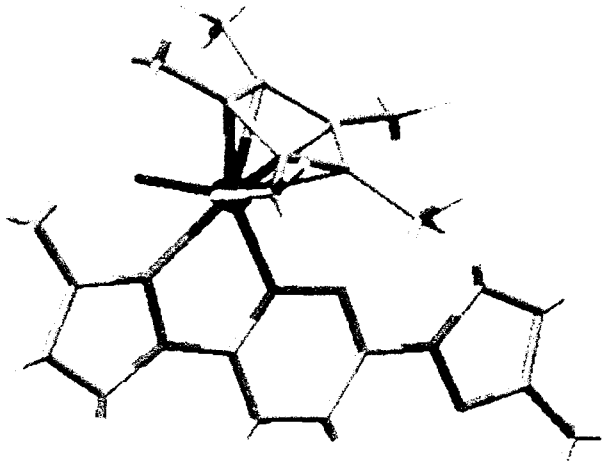
CHAPTER 4

Novel mononuclear η^5-pentamethylcyclopentadienyl complexes of platinum group metals bearing pyrazolyl-pyridazine ligands: Syntheses and spectral studies



Novel mononuclear η^5-pentamethylcyclopentadienyl complexes of platinum group metals bearing pyrazolyl-pyridazine ligands: Syntheses and spectral studies*

4.1 Abstract

Condensation of 3,6-dichloropyridazine with 3,5-dimethylpyrazole in 1:1 ratio yielded one side substituted pyrazolylpyridazine ligand 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (**L**) while condensation of 3,6-dichloropyridazine with substituted pyrazoles in 1:2 ratio yielded both side substituted pyrazolylpyridazine ligands such as 3,6-bis(pyrazolyl)pyridazine (**L1**), 3,6-bis(3-methylpyrazolyl)pyridazine (**L2**) and 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (**L3**). A new series of cationic mononuclear complexes of the type *$[(\eta^5\text{-}Cp)M_a(L)(PPh_3)]PF_6$*, *$[(\eta^5\text{-}Cp^*)M_b(L)Cl]PF_6$*, *$[(\eta^5\text{-}Cp^*)Ru(L')(PPh_3)]PF_6$ and $[(\eta^5\text{-}Cp^*)M_b(L')Cl]^+$ (where M_a=Ru, Os; M_b=Rh, Ir and L'=L1, L2, L3)* bearing pyrazolylpyridazine and η^5-cyclopentadienyl ligands are reported. The complexes have been completely characterized by spectral studies. The molecular structures of representative complexes have been determined by single crystal X-ray crystallography.

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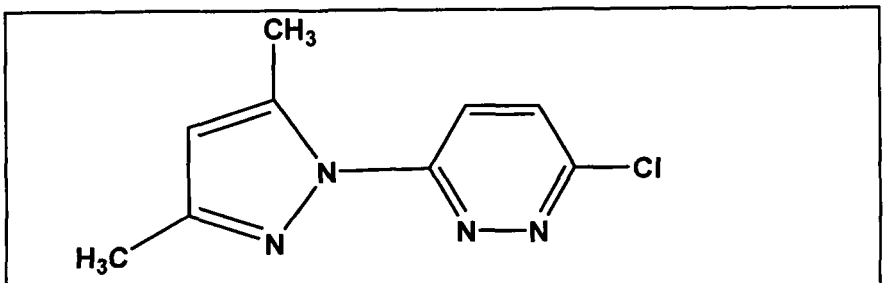
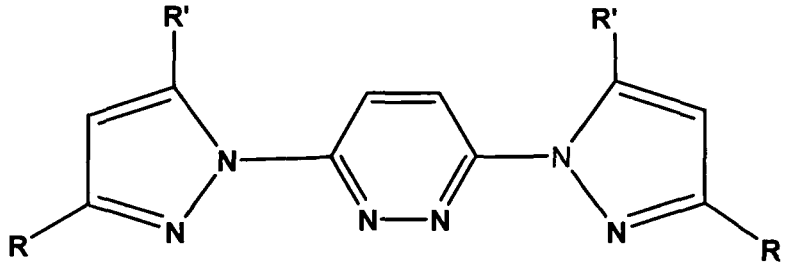
4.2 Introduction

Mononuclear complexes of platinum group metals containing nitrogen based ligands have received considerable attention owing to their photochemical properties [1-9], catalytic activities [10-19], electrochemical behavior [20-26], as well as in the development of new biological active agents [27-33]. In particular, the chemistry of cyclopentadienyl and pentamethylcyclopentadienyl ruthenium, osmium, rhodium and iridium complexes are the family of an area of active research [34, 35] due to their high reactivity and catalytic activities [36-42]. These properties have prompted wide spread interest regarding both the synthetic and the mechanistic features of cyclopentadienyl and pentamethylcyclopentadienyl complexes for a large number of transition metals. The chemistry of $[(\eta^5\text{-Cp})RuCl(PPh_3)_2]$, $[(\eta^5\text{-Cp*})RuCl(PPh_3)_2]$ or $[(\eta^5\text{-Cp})OsBr(PPh_3)_2]$ is characterized by facile displacement of either chloride or one or both triphenylphosphine ligands depending on the solvent and reaction conditions [43-47]. The reactivity of these pyrazolylpyridazine ligands with different metals has also been reported [48]. However, no reports are available for cyclopentadienyl and pentamethylcyclopentadienyl platinum group metals (Ru, Os, Rh and Ir) in connectivity with these ligands. Recently [49], we described a series of arene ruthenium complexes of these ligands which have exhibited interesting chemistry. In continuation of our studies, here we describe the syntheses of eighteen mononuclear cyclopentadienyl and pentamethylcyclopentadienyl Ru, Os, Rh and Ir complexes bearing substituted pyrazolyl-pyridazine ligands. All these pyrazolyl-pyridazine complexes are interesting in their own right from a synthetic, structural and electrochemical point of view. However, attempts to make di-nuclear complexes with these metals have not been successful. The reason could be the large size of the pentamethylcyclopentadienyl and triphenylphosphine ligands. These complexes are fully characterized by IR, NMR and mass spectrometry. The molecular structures of some of the representative complexes are described as well. The following pyrazolyl-pyridazine ligands were used in this study.



L 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine



R=R'=H,	**L1**	(3,6-Bis(pyrazolyl)pyridazine)
$R=CH_3$, R'=H,	**L2**	(3,6-Bis(3-methylpyrazolyl)pyridazine)
$R=R'=CH_3$,	**L3**	(3,6-Bis(3,5-dimethylpyrazolyl)pyridazine)

Ligands used in this study

4.3 Experimental

All solvents were dried and distilled prior to use. Pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole and 3,6-dichloropyridazine (Aldrich) were purchased and used as received. The ligands were prepared by following a literature procedure [48]. The precursor complexes $[(\eta^5\text{-Cp})RuCl(PPh_3)_2]$, $[(\eta^5\text{-Cp*})RuCl(PPh_3)_2]$, $[(\eta^5\text{-Cp})OsBr(PPh_3)_2]$, $[(\eta^5\text{-Cp*})RhCl(\mu\text{-Cl})]_2$ and $[(\eta^5\text{-Cp*})IrCl(\mu\text{-Cl})]_2$ were prepared following literature methods [50-56]. NMR spectra were recorded on Bruker AMX - 400 MHz spectrometer. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. All the complexes have given satisfactory C, H and N analysis. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Mass spectra were obtained from Waters ZQ-4000 mass spectrometer by ESI method.

4.3.1 Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for compound **2, 10** and **11** were grown by slow diffusion of petroleum ether into acetone solution of the said complexes while crystals of compound **7** were grown by slow diffusion of hexane into chloroform solution of complex **7**. The intensity data of all these crystals were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoKα radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [57] and refined with full-matrix least squares on F^2 using SHELXL-97 [58]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows. The ORTEP presentations of the representative complexes are shown in figures **4.4** to **4.7** respectively. The data collection parameters and bond lengths and angles are presented in tables **4.2** and **4.3**.

4.3.2 Synthesis and characterization of $[(\eta^5\text{-Cp})Ru(L)(PPh_3)]PF_6$ (1)

A mixture of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (100 mg, 0.137 mmol), **L** (29 mg, 0.137 mmol) and two equivalents of NH_4PF_6 in dry methanol (30 ml) was refluxed under dry nitrogen for 12 h. The solvent was removed under vacuum, the residue obtained was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 2 ml, and upon addition of hexane the reddish-brown complex precipitated, which was separated and dried under vacuum.

Yield: 73 mg, 67.9%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, 1H), 7.86 (d, 1H), 6.41 (d, 1H), 7.516-7.124 (m, 15H, PPh_3), 2.20 (s, 3H, CH_3); ESI-MS (m/z): 679.4 [M- PF_6] $^+$, 418.4 [M- PF_6-PPh_3]. ^{31}P $\{^1$H$\}$ NMR ($CDCl_3$, δ): 50.10 (s, PPh_3).

4.3.3 Synthesis and characterization of $[(\eta^5\text{-Cp}^*)Rh(L)Cl]PF_6$ (2)

A mixture of $[(\eta^5\text{-Cp}^*)Rh(\mu\text{-Cl})Cl]_2$ (50 mg, 0.08 mmol), **L** (34 mg, 0.16 mmol) and two equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature

for around 6 h. The yellow compound formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 75 mg, 74.03%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, 1H), 8.24 (d, 1H), 6.55 (s, 1H), 2.72 (s, 6H, CH_3) 1.86 (s, 15H, Cp*); ESI-MS (m/z): 481.8 [M-PF_6], 445.4 [M-PF_6-Cl]$^+$.

4.3.4 Synthesis and characterization of $[(\eta^5$-Cp)Ir(L)Cl]PF_6* (**3**)

A mixture of $[(\eta^5$-Cp*)Ir(μ-Cl)Cl]$_2$ (50 mg, 0.062 mmol), **L** (26 mg, 0.124 mmol) and two equivalents of NH_4PF_6 in dry methanol (15 ml) was refluxed under dry nitrogen for 12 h. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The orange solution was concentrated to 2 ml, and upon addition of diethylether the orange–yellow complex precipitated, which was separated by filtration, washed with diethylether and dried under vacuum.

Yield: 62 mg, 69.04%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, 1H), 7.98 (d, 1H), 6.63 (s, 1H), 2.68 (s, 6H, CH_3), 1.79 (s, 15H, Cp*); ESI-MS (m/z): 571 [M-PF_6], 534.6 [M-PF_6-Cl]$^+$.

4.3.5 Syntheses and characterization of complexes ***4-6***

A mixture of $[(\eta^5$-Cp)Ru(PPh_3)$_2$Cl] (100 mg, 0.137 mmol), corresponding ligand (0.137 mmol) and two equivalents of NH_4PF_6 in dry methanol (15 ml) was refluxed under dry nitrogen for 12 h. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 2 ml, and upon addition of hexane the reddish-brown complex precipitated, which was separated and dried under vacuum.

*4.3.5.1 $[(\eta^5$-Cp)Ru(L1)(PPh_3)$]PF_6$ (**4**)*

Yield: 65 mg, 60.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.822 (d, 1H), 8.765 (d, 1H), 8.649 (d, 1H), 8.543 (d, 1H), 8.304 (d, 1H), 8.092 (d, 1H), 7.634-7.262 (m, 15H, PPh_3), 7.006 (t, 1H), 6.716 (t, 1H), 4.785 (s, 5H, Cp); ESI-MS (m/z): 641.21 [M-PF_6]$^+$, 379.21 [M-PF_6-PPh_3].

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 49.70 (s, PPh_3).

4.3.5.2 [(η^5-Cp)Ru(L2)(PPh_3)]PF_6 (5)

Yield: 67 mg, 59.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.478 (d, 1H), 8.311 (d, 1H), 8.129 (d, 1H), 7.817 (d, 1H), 7.428-7.062 (m, 15H, PPh_3), 6.499 (dd, 2H), 4.773 (s, 5H, Cp), 2.620 (s, 3H, CH_3), 2.404 (s, 3H, CH_3); ESI-MS (m/z): 669.3 [M- PF_6] $^+$. ^{31}P {^{1}H} NMR ($CDCl_3$, δ): 49.90 (s, PPh_3).

4.3.5.3 [(η^5-Cp)Ru(L3)(PPh_3)]PF_6 (6)

Yield: 68 mg, 58.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.554 (d, 1H), 7.721 (d, 1H), 7.563-7.208 (m, 15H, PPh_3), 6.294 (s, 2H), 4.761 (s, 5H, Cp), 2.741 (s, 6H, CH_3), 2.618 (s, 6H, CH_3); ESI-MS (m/z): 697.2 [M- PF_6] $^+$, 434.2 [M- PF_6-PPh_3].

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 50.09 (s, PPh_3).

4.3.6 Syntheses and characterization of complexes 7-9

A mixture of [(η^5-Cp*)Ru(PPh_3)$_2$Cl] (100 mg, 0.125 mmol), corresponding ligand (0.125 mmol) and two equivalents of NH_4PF_6 in dry methanol (15 ml) was refluxed under dry nitrogen for 12 h producing a color change in solution from yellow to orange. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 2 ml, and upon addition of excess hexane the reddish-brown complex precipitated, which was separated and dried under vacuum.

4.3.6.1 [(η^5-Cp)Ru(L1)(PPh_3)]PF_6 (7)*

Yield: 65 mg, 60.4%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.081 (d, 1H), 8.763 (d, 1H), 8.550 (d, 1H), 8.202 (d, 1H), 8.015 (d, 1H), 7.838 (d, 1H), 7.464-7.218 (m, 15H, PPh_3),7.006 (t, 1H), 6.821 (t, 1H), 1.855 (s, 15H, Cp*); ESI-MS (m/z): 710.2 [M- PF_6]: 448.2 [M- PF_6-PPh_3].

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 50.29 (s, PPh_3).

4.3.6.2 [(η^5-Cp)Ru(L2)PPh_3)]PF_6 (8)*

Yield: 67 mg, 60.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.461 (d, 1H), 8.610 (d, 1H), 8.166 (d, 1H), 7.743 (d, 1H), 7.377-7.111 (m, 15H, PPh_3), 6.543 (d, 1H), 6.354 (d, 1H), 2.459 (s, 3H, CH_3), 2.408 (s, 3H, CH_3), 1.586 (s, 15H, Cp*); ESI-MS (m/z): 738.2 [M-PF_6]: 476.2 [M-PF_6-PPh_3]. ^{31}P {1H} NMR ($CDCl_3$, δ): 50.41 (s, PPh_3).

4.3.6.3 [(η^5-Cp)Ru(L3)PPh_3)]PF_6 (**9**)*

Yield: 70 mg, 61.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.736 (d, 1H), 7.928 (d, 1H), 7.431-7.107 (m, 15H, PPh_3), 6.432 (s, 2H), 2.938 (s, 6H, CH_3), 2.714 (s, 6H, CH_3), 1.632 (s, 15H, Cp*); ESI-MS (m/z): 766.2 [M- PF_6]: 504.2 [M- PF_6-PPh_3].

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 50.37 (s, PPh_3).

*4.3.7 Syntheses and characterization of complexes **10-12***

A mixture of [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), corresponding ligand (0.16 mmol) and two equivalents of counter ion in dry methanol (15 ml) was stirred at room temperature for around 6 h. The yellow compound formed was filtered, washed with methanol and diethylether and dried under vacuum.

4.3.7.1 [(η^5-Cp)Rh(L1)Cl]BF_4 (**10**)*

Yield: 70 mg, 75.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.754 (d, 1H), 8.696 (d, 1H), 8.549 (d, 1H), 8.444 (d, 1H), 8.204 (d, 1H), 8.082 (d, 1H), 6.922 (t, 1H), 6.656 (t, 1H), 1.861 (s, 15H, Cp*); ESI-MS (m/z): 485.55 [M-BF_4], 449.2 [M-BF_4-Cl]$^+$

4.3.7.2 [(η^5-Cp)Rh(L2)Cl]ClO_4 (**11**)*

Yield: 72 mg, 72.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.651 (d, 1H), 8.418 (d, 1H), 8.302 (d, 1H), 8.136 (d, 1H), 6.672 (d, 1H), 6.432 (d, 1H), 2.693 (s, 3H, CH_3), 2.408 (s, 3H, CH_3), 1.809 (s, 15H, Cp*); ESI-MS (m/z): 513.2 [M- ClO_4], 477.2 [M- ClO_4-Cl]$^+$

4.3.7.3 [(η^5-Cp)Rh(L3)Cl]PF_6 (**12**)*

Yield: 77 mg, 69.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.160 (d, 1H), 8.696 (d, 1H), 7.909 (d, 1H), 6.394 (s, 2H), 2.745 (s, 6H, CH_3), 2.622 (s, 6H, CH_3), 2.176 (s, 15H, Cp*). ESI-MS (m/z): 533.97 [M-PF_6], 504.52 [M-PF_6-Cl]

*4.3.8 Syntheses and characterization of complexes **13-15***

A mixture of [(η^5-Cp*)Ir(μ-Cl)Cl]$_2$ (50 mg, 0.062 mmol), corresponding ligand (0.124 mmol) and two equivalents of NH_4PF_6 in dry methanol (15 ml) was refluxed under dry nitrogen for 12 h. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The orange solution was concentrated to 2 ml, and upon addition of diethylether the orange–

yellow complex precipitated, which was separated by filtration, washed with diethylether and dried under vacuum.

4.3.8.1 [(η^5-Cp)Ir(L1)Cl]PF_6 (13)*

Yield: 62 mg, 65.9%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.180 (d, 1H), 9.066 (d, 1H), 8.778 (d, 1H), 8.556 (d, 1H), 8.206 (d, 1H), 7.936 (d, 1H), 7.012 (t, 1H), 6.720 (t, 1H), 1.873 (s, 15H, Cp*); ESI-MS (m/z): 575.01 [M- PF_6], 539.56 [M- PF_6-Cl]

4.3.8.2 [(η^5-Cp)Ir(L2)Cl]PF_6 (14)*

Yield: 60 mg, 63.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.596 (d, 1H), 8.505 (d, 1H), 8.472 (d, 1H), 8.338 (d, 1H), 8.050 (d, 1H), 6.822 (d, 1H), 2.706 (s, 3H, CH_3), 2.378(s, 3H, CH_3), 2.136 (s, 15H, Cp*); ESI-MS (m/z): 603.05 [M-PF_6], 567.60 [M-PF_6-Cl]

4.3.8.3 [(η^5-Cp)Ir(L3)Cl]PF_6 (15)*

Yield: 66 mg, 67.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.273 (d, 1H), 7.918 (d, 1H), 6.444 (s, 2H), 2.855 (s, 6H, CH_3), 2.675 (s, 6H, CH_3), 1.739 (s, 15H, Cp*); ESI-MS (m/z): 631.11 [M-PF_6], 595.65 [M-PF_6-Cl]

4.3.9 Syntheses and characterization of complexes 16-18

A mixture of [(η^5-Cp)Os(PPh_3)$_2$$CH_3CN$]$BF_4$ (100 mg, 0.110 mmol), corresponding ligand (0.110 mmol) and one equivalent of NH_4BF_4 in dry methanol (35 ml) was refluxed under dry nitrogen for 12 h whereby the colorless suspension gradually changed to dark red solution. The solvent was removed under vacuum, the residue was dissolved in acetone (2 ml) and upon addition of excess hexane the reddish-brown complex precipitated, which was separated and dried under vacuum.

4.3.9.1 [(η^5-Cp)Os(L1)(PPh_3)]BF_4 (16)

Yield: 60 mg, 67.9%. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.722 (d, 1H), 8.745 (d, 1H), 8.608 (d, 1H), 8.516 (d, 1H), 8.330 (d, 1H), 8.106 (d, 1H), 7.324-7.232 (m, 15H, PPh_3), 7.018 (t, 1H), 6.626 (t, 1H), 4.758 (s, 5H, Cp); ESI-MS (m/z): 730.2 [M-BF_4] $^+$, 468.2 [M-BF_4-PPh_3].

4.3.9.2 [(η^5-Cp)Os(L2)(PPh_3)]BF_4 (17)

Yield: 56 mg, 60.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.518 (d, 1H), 8.432 (d, 1H), 8.339 (d, 1H), 7.987 (d, 1H), 7.408-7.162 (m, 15H, PPh_3), 6.529 (dd, 2H), 4.753 (s, 5H, Cp), 2.618 (s, 3H, CH_3), 2.420 (s, 3H, CH_3); ESI-MS (m/z): 758.2 [M- BF_4]$^+$, 496.3 [M-BF_4-PPh_3].

4.3.9.3 [(η^5-Cp)Os(L3)(PPh_3)]BF_4 (18)

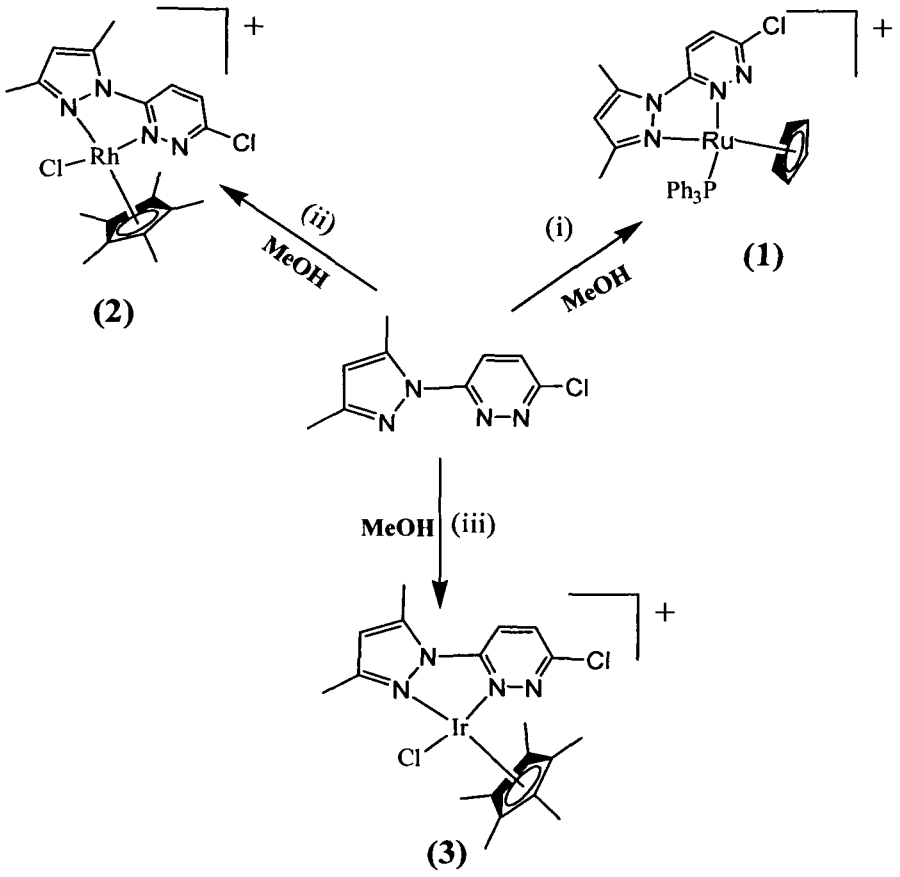
Yield: 59 mg, 61.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.632 (d, 1H), 7.921 (d, 1H), 7.363-7.204 (m, 15H, PPh_3), 6.334 (s, 2H), 4.765 (s, 5H, Cp), 2.731 (s, 6H, CH_3), 2.642 (s, 6H, CH_3). ESI-MS (m/z): 786.3 [M- BF_4]$^+$, 524.3 [M- BF_4-PPh_3].

4.4 Results and discussion

The synthetic route for the mononuclear η^5-cyclopentadienyl and pentamethylcyclopentadienyl complexes of Ru, Os, Rh and Ir are presented in Schemes **4.1** and **4.2** respectively. All these complexes were obtained in good yield from the reaction of starting precursors and pyrazolylpyridazine ligands in methanol. Attempts to make dinuclear complexes by increasing the metal to ligand ratio were unsuccessful. The reason could be the steric bulkiness of the complex because of the presence of bulky triphenylphosphine ligand and methyl groups of pentamethylcyclopentadienyl ligand. The complexes **1** and **4** to **9** are reddish-brown in color whereas complexes **2**, **3** and **10** to **15** are yellow in color, while the complexes **16** to **18** are of cream color. They are non-hygroscopic crystalline solids soluble in common polar solvents and are very much stable in solid state as well as in solution. Information about the complexes was also obtained from ESI-MS spectrometry. The molecular structures of **2**, **7**, **10** and **11** have been authenticated by single crystal X-ray diffraction analyses.

Recently, we have reported [49] a series of arene ruthenium complexes using these pyrazolylpyridazine ligands, where we observed that in the ligand **L2**, the starting 3-methyl- pyrazole was tautomerized to 5-methylpyrazole and the existence of both these isomers was also observed in the same reaction products. The formation of both the tautomers in the same reaction is the first of its kind known in the literature. The tautomerized products were supported by ^{1}H NMR and ^{13}C NMR as well as single crystal structure (previous chapter). But surprisingly, here in this work, although we used the

same pyrazolylpyridazine ligands, we did not observe any tautomerized product with the pentamethylcyclopentadienyl complexes of Ru, Os, Rh and Ir metals.

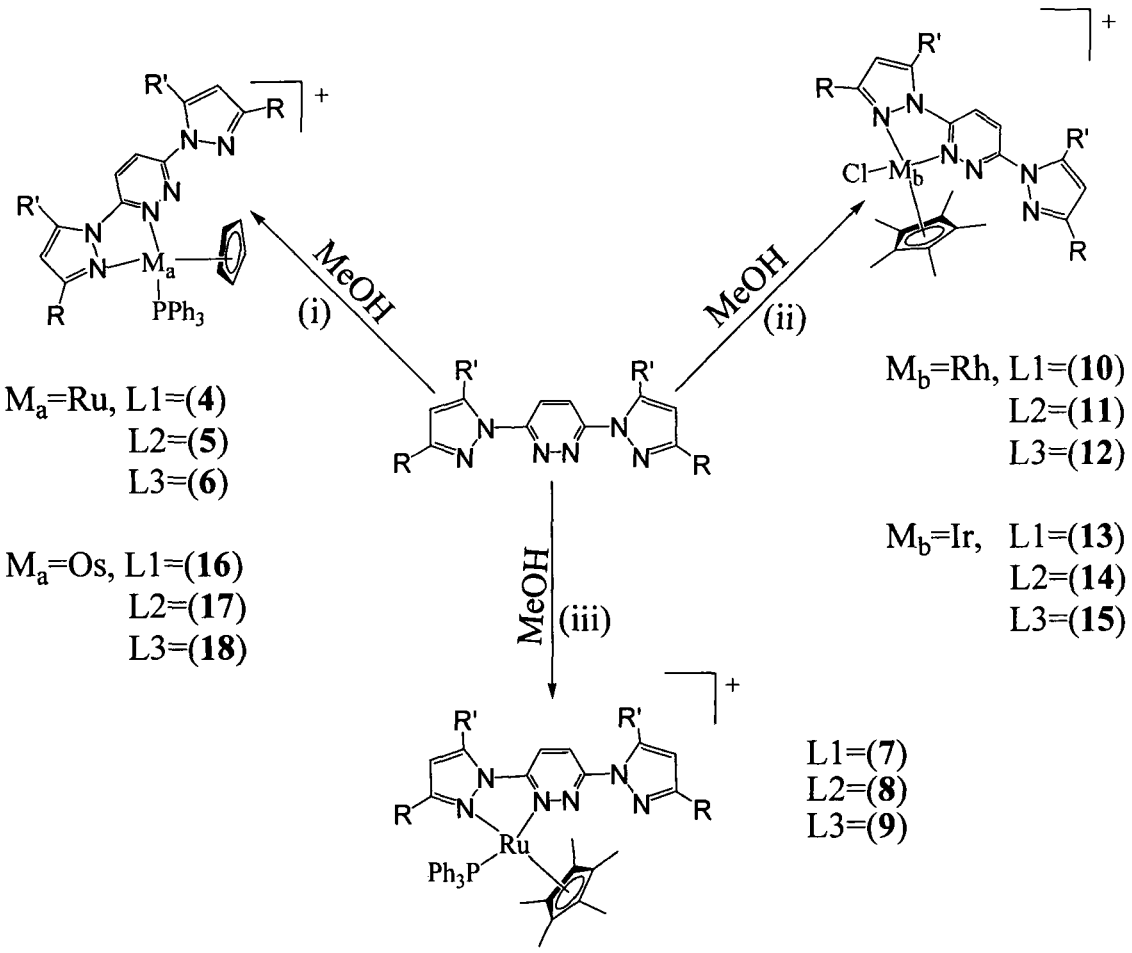


(i) = $[\{(\eta^5\text{-Cp})RuCl(PPh_3)_2\}]$

(ii) = $[\{(\eta^5\text{-Cp*})RhCl(\mu\text{–}Cl)\}_2]$

(iii) = $[\{(\eta^5\text{-Cp*})IrCl(\mu\text{–}Cl)\}_2]$

Scheme **4.1**



(i) = $[\{(\eta^5\text{-Cp})M_aCl(PPh_3)_2\}]$; M_a=Ru, Os

(ii) = $[\{(\eta^5\text{-Cp*})M_bCl(\mu\text{-Cl})\}_2]$; M_b=Rh, Ir

(iii) = $[\{(\eta^5\text{-Cp*})RuCl(PPh_3)_2\}]$

Scheme **4.2**

The infrared spectra of these complexes exhibit a strong $\nu_{C=N}$ band in the range of 1543 to 1583 cm^{-1} and $\nu_{C=C}$ in the range of 1437 to 1450 cm^{-1} which are the characteristic bands of the ligands. Besides these, for the complexes **1** to **9** and **12** to **15**, a strong band in the range of 841-844 cm^{-1} is observed due to the stretching frequency of $\nu_{P\text{-}F}$ band of the counter ions of these complexes. Whereas, the complex **10** displays a strong band at 1098 cm^{-1} which is due to the stretching frequency of the perchlorate ion [59] and complexes **11**, **16** to **18** exhibit a strong band at around 1082 to 1084 cm^{-1} corresponding to the stretching frequency of the $\nu_{B\text{-}F}$ band of the counter ions of these complexes. The m/z

values of all these complexes and their stable ion peaks, as given in the experimental section, are in good agreement with the theoretical values, in its ZQ mass spectra. ESI mass spectra of the complexes also displayed prominent peaks corresponding to the molecular ion fragment. Complexes **1**, **4** to **9** and **16** to **18** displayed the loss of the coordinated triphenylphosphine in the first step, whereas **2**, **3** and **10** to **15** displayed the loss of the chloride ions. In these complexes, the metal to cyclopentadiene and pentamethylcyclopentadiene bond is stronger and remains intact.

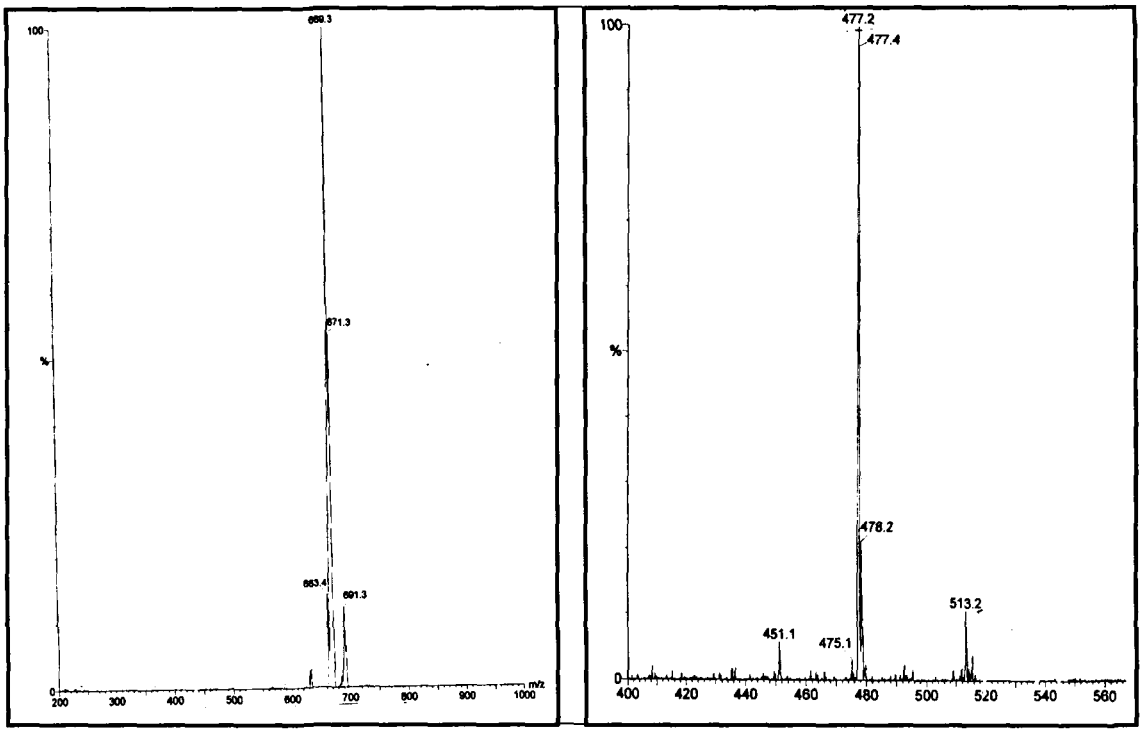


Figure **4.1:** Mass spectra of complexes **5** and **11**

^{1}H NMR spectral data of the complexes, along with their assignments, are well formulated in the experimental section. The NMR spectra of the Cp and Cp* derivatives, which have ligands **L**, **L1**, **L2** and **L3** exhibit three resonances for **L**, eight resonances for **L1**, six resonances for **L2** and three resonances for **L3** in the aromatic region corresponding to the pyrazole and pyridazine protons which are clearly assigned in the experimental section. Besides, all the ligands other than **L1** show singlet in the region δ=2.93-2.20 ppm which corresponds to the methyl protons of the ligands. ^{1}H NMR spectra of the complexes bearing **L2** as ligand give very informative NMR spectra with peaks spread over a quiet wide range as compared to that of the free ligand. The metal

complexes of the ligand **L2** (Figure **4.2**) show two signals, a singlet at around δ=2.378-2.408 ppm and another singlet at around δ=2.459-2.706 ppm as compared to that of the free ligand which gives only one singlet at δ=2.377 ppm. The singlet at around 2.378-2.408 ppm is arising from the methyl protons of free pyrazole ring containing methyl group while the second singlet comes from the methyl protons of the bonded pyrazole ring. But we do not find much variation with the methyl protons in case of the ligand **L3** and its complexes. In the case of the free ligand **L3**, we observe two signals, a singlet at around 2.418 ppm which is assigned to the **R'R'** protons and another singlet at 2.731ppm which corresponds to the **RR** protons. Likewise the complexes bearing this ligand also show two singlets at almost the same range. Apart from the ligands signals, the methyl protons associated to the Cp* of the complexes **2**, **3** and **10** to **15** (Figure **4.2**) displayed a downfield shift, a singlet, in the range of 2.17 to 1.73 ppm as compared to that in the precursor complexes which show at around 1.59 ppm. The downfield shift in the position of the Cp* protons and the methyl protons of the complexes bearing ligand **L2** might result from a change in the electron density on the metal center due to chelation of the ligands through the two nitrogen atoms. These indicate that there is a significant deshielding after substituting one chlorine with chelating N,N'-donor ligands. Further, the protons associated with the η^5-Cp ring in complexes **1**, **4** to **9** and **16** to **18** resonated at almost same the position as singlets, *i.e.*, at around ~ 4.78 ppm. Beside this, the complexes also displayed a multiplet in the range of 7.563-7.062 ppm corresponding to the phenyl protons of the triphenylphosphine group of these complexes.

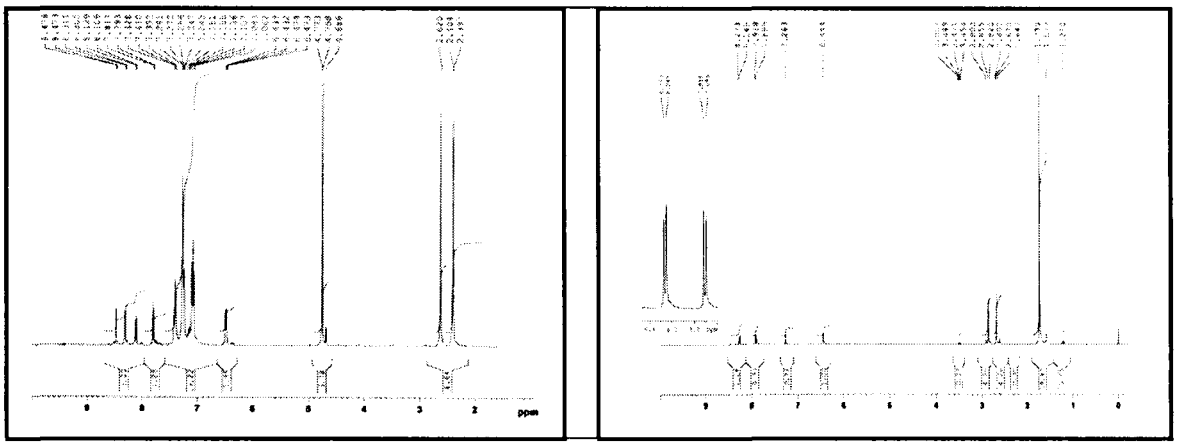


Figure **4.2:** ^{1}H NMR spectra of complexs **5** and **15**

The ^{31}P $\{^1H\}$ NMR spectra of the complexes **1** and **4** to **9** exhibit a single sharp resonance for triphenylphosphine in the range of 50.41 and 49.70 ppm, indicating the presence of triphenylphosphine group in these complexes whereas for the starting complexes $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ the signals appear at 38.5 and 42.0 ppm respectively [52-55].

4.5 UV-visible spectroscopy

UV-visible spectra of the complexes **2**, **5**, **6**, **7**, **8**, **10**, **11**, **14** and **15** were acquired in acetonitrile and spectral data are summarized in Table **4.1**. Electronic spectra of representative complexes are depicted in Figure **4.3**. The low spin d^6 configuration of these dinuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centers which can interact with the low lying π^* orbital of the ligands. One should therefore expect a band attributable to the metal-ligand charge transfer (MLCT) $t_{2g}\rightarrow\pi^*$ transition in their electronic spectra. The electronic spectra of these complexes display a medium intensity bands in the UV-visible region. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~ 428–364 nm have been tentatively assigned on the basis of their intensity and position to $t_{2g}\rightarrow\pi^*$ MLCT transitions. The bands on the high energy side at ~ 300.3–224.9 nm for the complexes **2**, **5**, **6**, **7**, **8**, **10**, **11**, **14** and **15**, have been assigned to ligand-centered $\pi\rightarrow\pi^*/n\rightarrow\pi^*$ transitions. In general, these complexes follow the normal trend observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi\rightarrow\pi^*$ transition for pyrazolylpyridazine ligand in the UV region and metal-ligand charge transfer transitions in the visible region.

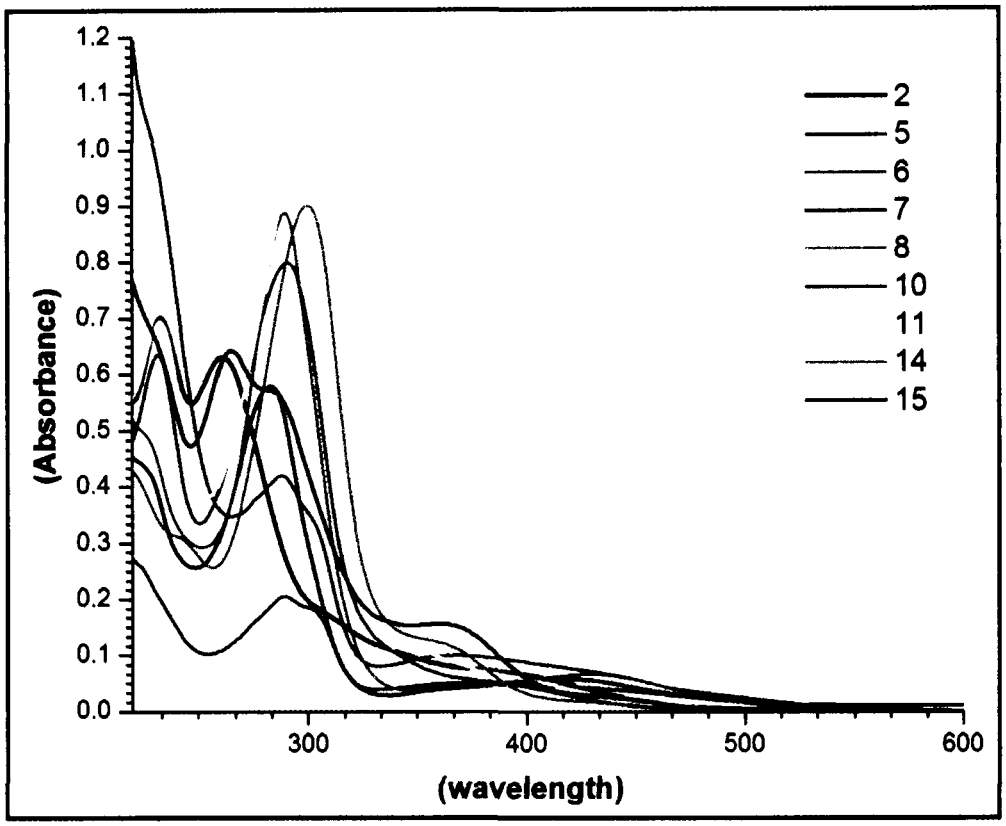


Figure **4.3**: UV-vis. absorption spectra of mononuclear complexes **2**, **5**, **6**, **7**, **8**, **10**, **11**, **14** and **15** in acetonitrile at 298 K.

Table **4.1**: UV-vis. absorption data of the representative complexes in acetonitrile at 298K.

Complex	λ_{max}/nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})		
2	232.8 (0.70)	260.7 (0.63)	383.9 (0.07)
5	224.9 (0.25)	289.5 (0.21)	374.9 (0.05)
6	231.7 (0.97)	287.9 (0.42)	364.0 (0.10)
7	226.6 (0.43)	283.2 (0.58)	417.0 (0.06)
8	225.7 (0.49)	289.5 (0.89)	428.0 (0.07)
10	231.7 (0.64)	290.4 (0.80)	393.0 (0.05)
11	232.5 (0.70)	298.3 (1.02)	393.9 (0.06)
14	244.4 (0.30)	300.3 (0.90)	368.6 (0.11)
15	264.8 (0.64)	286.6 (0.56)	366.9 (0.15)

4.6 Molecular structures

Molecular structures of **2**, **7**, **10** and **11** have been determined crystallographically. The complexes crystallize in Pca2 (1), $P2_1/c$ (1), $P2_1/c$ (2) and $P2_1/n$ (10) space groups. Details about data collection, refinement and structure solution are recorded in Table **4.2**, and selected bond lengths and angles are presented in Table **4.3**. Crystal structures of **2**, **7**, **10** and **11** with atom-numbering schemes are shown in Figures **4.4 to 4.7**. In complexes **2**, **10** and **11**, the metal is bonded with the major coordinating sites N1 and N3 in a k^2 manner, one chloro group, and the pentamethylcyclopentadienyl (Cp*) ring in a η^5 manner. Similarly, Ru1 in **7** is also coordinated through pyrazole nitrogen N1, pyridazine nitrogen N3 in a k^2 manner, one phosphorus P1 of PPh_3, and the pentamethylcyclopentadienyl (Cp*) ring in a η^5 manner. Typical piano-stool geometry about the metal in all these complexes is maintained. The Cp* ring in **2, 10** and **11** is planar with an average Rh-C distance of 2.155 Å and the Rh center is displaced by 1.785 Å, 1.776 Å and 1.788 Å from the centroid of the Cp* ring, which are comparable to the distances in other rhodium pentamethylcyclopentadienyl complexes. The C-C bond lengths within the Cp* ring and C-Me distances are normal. Rh-N and Rh-Cl bond lengths are consistent with the values reported in the literature [60-63]. The Cp* ring in complex **7** is also planer, the average Ru-C distance is 2.203 Å, and the Ru to centroid bond distance is 1.840 Å, which is comparable to the distances reported in other ruthenium pentamethylcyclopentadienyl complexes [64-66]. The Ru-P and Ru-Cl distances are normal and consistent with the values reported in other related complexes [64-66]. The chelating N-Rh-N bite for the coordination of the pyrazole nitrogen and the pyridazine nitrogen of the ligand in the complexes **2, 10** and **11** are 74.40, 75.25 and 75.0°, while in the case of the complex **7** the N-Ru-N angle is 75.4° which is comparable to other reported [64-66] similar ruthenium complexes. The N(4)-N(3)-M(1) angles in complexes **7**, **10** and **11** are close to each other and are in the range of around ~121.28-121.70°, whreas in complex **2** the N(4)- N(3)- M(1) angle is much lower than that in the other above mentioned complexes.The N-Rh-Cl angles in complexes **2, 10** and **11** are normal [63].

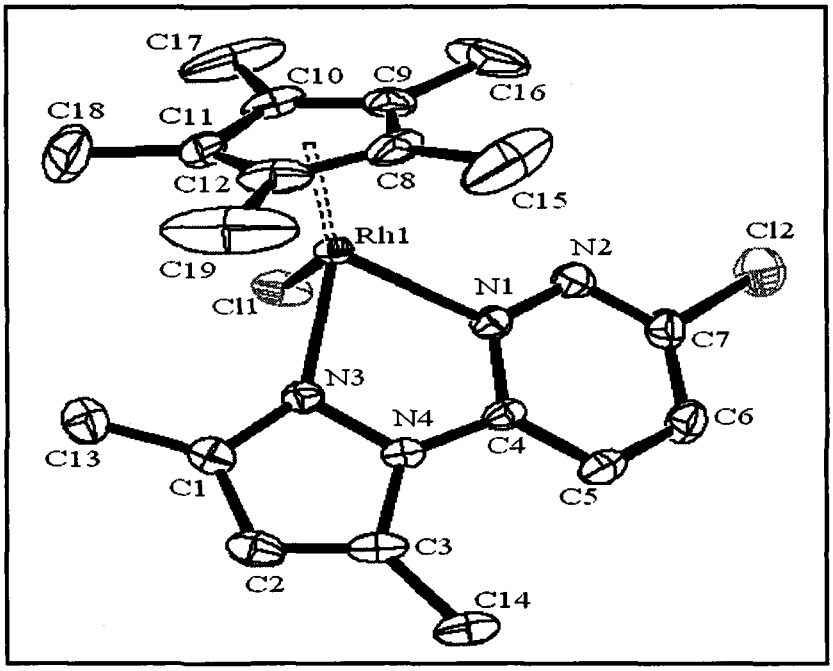


Figure **4.4:** Molecular structure of complex **2** with 50% probability thermal ellipsoids. Hydrogen atoms and PF_6 anion are omitted for clarity.

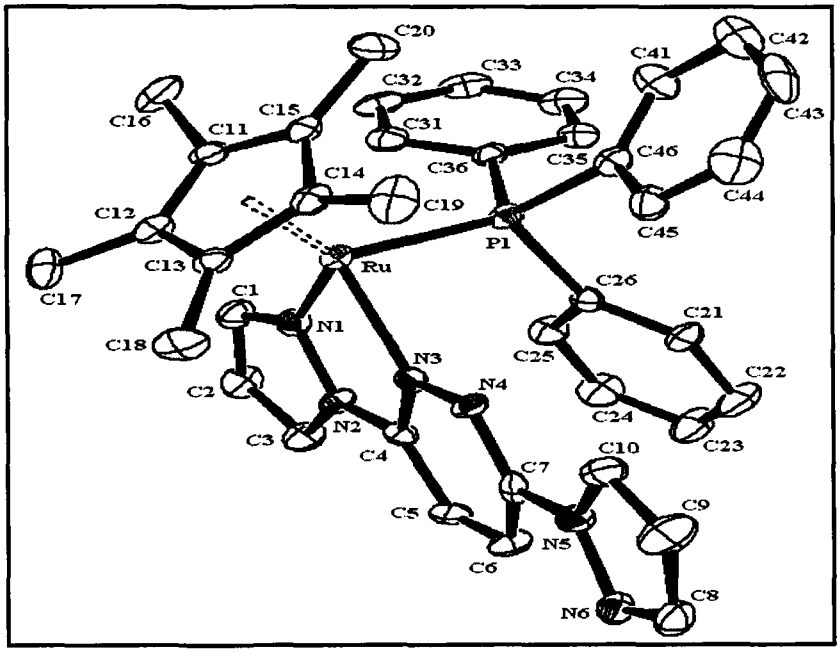


Figure **4.5:** Molecular structure of complex **7** with 50% probability thermal ellipsoids. Hydrogen atoms and PF_6 anion are omitted for clarity.

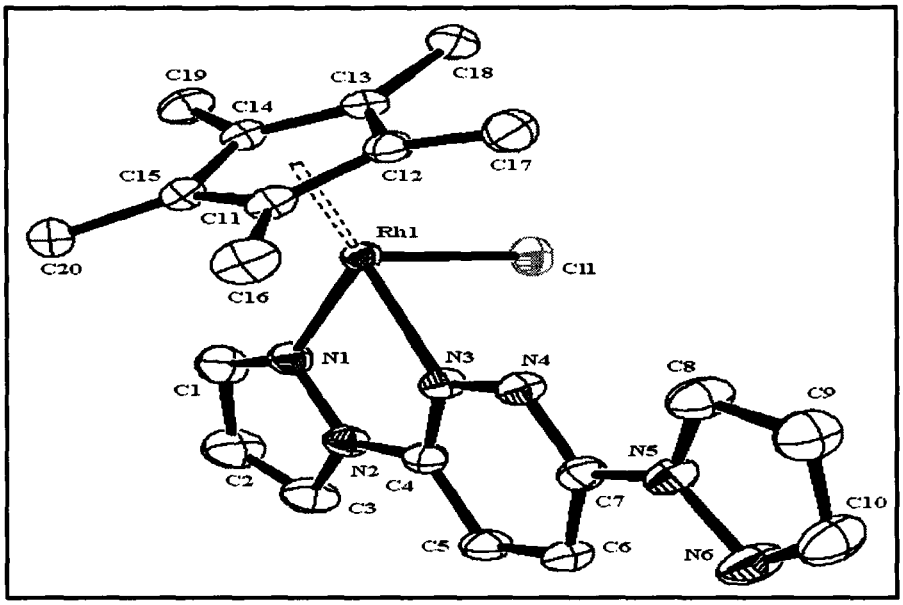


Figure **4.6:** Molecular structure of complex **10** with 50% probability thermal ellipsoids. Hydrogen atoms and BF_4 anion are omitted for clarity.

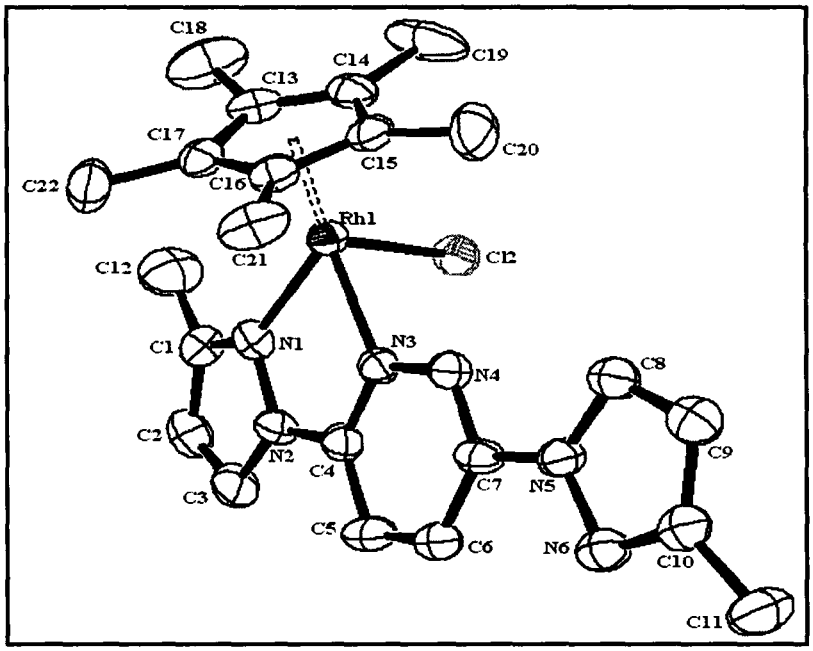


Figure **4.7:** Molecular structure of complex **11** with 50% probability thermal ellipsoids. Hydrogen atoms and ClO_4 anion are omitted for clarity.

Table **4.2**: Crystallographic and structure refinement parameters for complexes **2**, **7**, **10** and **11**

Compound	**2**	**7**	**10**	**11**
Emperical formula	$C_{19}H_{24}Cl_2F_6N_4PRh$	$C_{38}H_{38}F_6N_6P_2Ru$	$C_{20}H_{23}BClF_4N_6Rh$	$C_{22}H_{27}Cl_2N_6O_4Rh$
Formula weight	627.20	855.75	572.61	629.31
Temperature	296(2) K	203(2) K	296(2) K	296(2) K
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pca2(1)	P2(1)/n	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a (Å)	14.2891(3)	11.843(4)	12.4751(3)	11.1784(17)
b (Å)	10.1246(3)	19.694(7)	11.8730(3)	7.7033(11)
c (Å)	17.0868(4)	16.668(6)	15.3094(4)	32.731(5)
β(°)		103.547(10)	91.8840(10)	95.392(11)
Volume (A^3)	2471.97(11)	3779(2)	2266.35(10)	2806.1(7)
Z, Calculated density (mg/m^3)	4, 1.685	4, 1.504	4, 1.678	4, 1.490
Absorption coefficient (mm^{-1})	1.032	1.451	0.925	0.840
F(000)	1256	1488	1152	1280
Crystal size(mm)	0.40 x 0.25 x 0.12	0.22 x 0.13 x 0.04	0.50 x 0.30 x 0.18	0.25 x 0.15 x 0.10
θ range for data collection (deg)	2.01 to 28.51	2.21 to 28.21	1.63 to 28.74	1.25 to 28.76
Index ranges	-18<=h<=18,-13<=k<=12,-21<=l<=20	-14<=h<=14,-23<=k<=23,-19<=l<=19	-16<=h<=16,-15<=k<=15,-20<=l<=20	-15<=h<=14,-17<10=k<=10,-44<=l<=44
Reflections collected / unique	25506/5618	29788/6659	25492 / 5622	43864/7274
R_{int}	0.0662	0.2384	0.0251	0.1384
Goodness-of-fit on F^2	0.971	0.821	1.043	1.023

Table **4.3**: Selected bond lengths and angles for complexes **2**, **7**, **10** and **11.**

	2	**7**	**10**	**11**
Distances (Å)				
N(1)-M(1)	2.105(3)	2.072(7)	2.104(2)	2.127(2)
N(3)-M(1)	2.109(3)	2.098(6)	2.105(2)	2.115(6)
N(3)-N(4)	1.387(4)	1.351(8)	1.342(3)	1.349(8)
N(5)-N(6)		1.363(8)	1.361(3)	1.381(9)
Cl(1)-M(1)	2.386(10)		2.3957(7)	2.408(2)
M(1)-CNT(1)	1.785	1.840	1.776	1.788
Angles (°)				
N(4)-N(3)-M(1)	114.2(2)	121.7(5)	121.28(16)	121.4(5)
N(2)-N(1)-M(1)	120.4(2)	115.0(5)	113.58(16)	113.6(5)
N(3)-M(1)-N(1)	74.40(11)	75.4(2)	75.25(8)	75.0(3)
N(1)-M(1)-Cl(1)	88.10(8)		85.32(7)	86.0(2)
N(3)-M(1)-Cl(1)	88.70(8)		84.97(6)	87.07(18)

4.7 Conclusion

In summary, a series of new mononuclear platinum group metal complexes **1** to **18** have been synthesized using pyrazolylpyridazine ligands in good yield, which are remarkably stable in air as well as in solution. In all these complexes, the metal is bonded with the major coordinating sites N1 and N3, whereas an effort to make binuclear complexes or to put another metal at the other binding sites, *i.e.*, N4 and N6, was not fruitful. The reason could be attributed to the presence of large size and steric nature of the triphenylphosphine group.

Supplementary material

CCDC- **738547** (**2**), **727093** (7), **727091** (**10**) and **727092** (**11**) contain the supplementary crystallographic data for this chapter.

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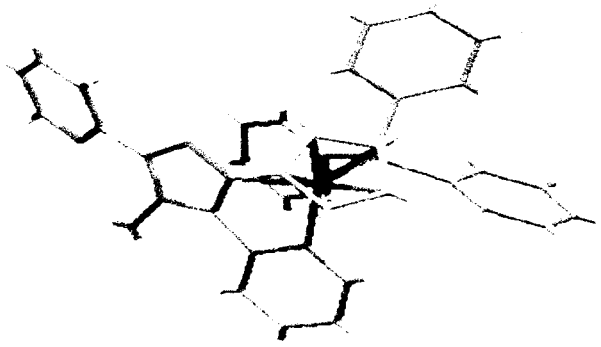
CHAPTER 5

Section A: Mononuclear complexes of platinum group metals containing η^5 and η^6 – cyclic π-perimeter hydrocarbons and pyridyl-pyrazolyl derivatives: syntheses and structural studies

Section B: Study of half–sandwich platinum group metal complexes bearing dpt-NH_2 ligand



Chapter 5A: Mononuclear complexes of platinum group metals containing η^5 and η^6 – cyclic Π-perimeter hydrocarbons and pyridylpyrazolyl derivatives: syntheses and structural studies*.

5A.1 Abstract

Stable piano-stool platinum group metal compounds based on the 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (L) with the formulas $[(\eta^6\text{-arene})Ru(L)Cl]PF_6$ {arene = C_6H_6 (**1**), *p*-cymene (**2**) and C_6Me_6, (**3**)}, $[(\eta^6\text{-}C_5Me_5)M(L)Cl]PF_6$ {M = Rh (**4**), Ir (**5**)} and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(L)]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)]PF_6$ (**8**) and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(L)]PF_6$ (**9**) have been prepared by a general method and characterized by use of a combination of NMR, IR spectroscopy and mass spectrometry. The molecular structures of compounds **4** and **5** were established by single crystal X-ray diffraction studies. In each compound the metal is bonded to N1 and N11 in a k^2 manner.

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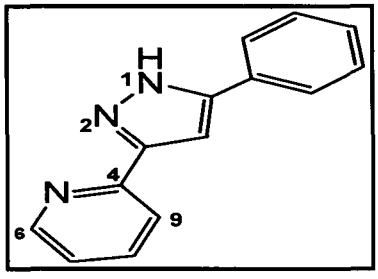
5A.2 Introduction

Mononuclear compounds of platinum group metals containing nitrogen based ligands have received considerable attention owing to their photochemical properties [1-9], catalytic activities [10-19], electrochemical behaviour [20-26], as well as in the development of new biological active agents [27-33]. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the availability of three labile coordinate sites and rigid arene ring occupying another three coordinate sites [34, 35]. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer activities. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted more attention [36-39]. In addition, the four-coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal centre [40]. In recent years we have been carrying out reactions of η^5- and η^6- cyclic Π -perimeter hydrocarbons metal complexes with a variety of nitrogen based ligands [41-48] including various poly-pyridyl ligands. Ruthenium compounds of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [49, 50]. Although extensive studies have been made on η^5- and η^6- transition metal compounds, compounds containing phenyl pyrazolyl pyridine ligand of the type shown below have not yet been investigated.



2-(5-phenyl-1H-pyrazol-3-yl)-pyridine (**L**)

Herein we describe the syntheses of nine mononuclear η^5- and η^6- cyclic Π -perimeter hydrocarbons platinum group metal compounds bearing phenyl pyrazolyl pyridine ligand. Our main aim in choosing this phenyl substituted ligand was to

synthesize a series of mononuclear and dinuclear compounds by activating the carbon atom of the phenyl ring. But attempts to prepare a dimetallic derivative by addition of a second organometallic anion by activation of the carbon atom were unsuccessful and we ended up with a series of mononuclear compounds only with metal bonded to two nitrogen atoms (N1 and N11) of the ligand. All these compounds are fully characterized by IR, NMR and mass spectrometry. Molecular structures of the two representative compounds are also presented in this section.

5A.3 Experimental

All solvents were dried and distilled prior to use. The ligand **L** was synthesized by following a literature method [51]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) [52-55], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [56-61]. NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Mass spectra were obtained from a Waters ZQ-4000 mass spectrometer by the ESI method.

5A.3.1 Single-crystal X-ray structures analyses

Crystals of compound **4** were grown from acetone/hexane as small red plates. Crystals of compound **5** were grown by slow evaporation of methanol solution of the respective compound as deep red blocks. The crystallizations were done at room temperature. The intensity data of **4** and **5** were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo*K*α radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with the SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [62] and refined with full-matrix least squares on F^2 using SHELXL-97 [63]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [64] for Windows. The ORTEP presentations of the representative compounds are shown in Figures **5A.2** and

5A.3 respectively. The data collection parameters and bond lengths and angles are presented in Tables **5A.1** and **5A.2**.

5A.3.2 Preparation of $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]PF_6$ [1]

A mixture of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (100 mg, 0.2 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (90 mg, 0.4 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The brown compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum. Yield: 90 mg, 77%. Calc. for $C_{20}H_{17}ClN_3PF_6Ru$: C 41.34; H 2.97; N 7.25; found: C 41.45; H 3.07; N 7.14. IR (KBr pellets, cm^{-1}): 3436 ($\nu_{N\text{-}H}$); 1625 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 846 ($\nu_{P\text{-}F}$).

^1H NMR (400 MHz, CD_3CN): δ = 9.341 (d, J=5.6 Hz, 1H), 8.132 (dt, J=8.4 Hz, 3H), 8.00 (dd, J=8 Hz, 2H), 7.882 (d, J=7.2 Hz, 2H), 7.600-7.530 (m, 1H), 7.321 (s, 1H), 6.079 (s, 6H, C_6H_6).

ESI-MS (m/z): 436.1 [M- PF_6], 400.2 [M- PF_6-Cl].

5A.3.3 Preparation of $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(L)Cl]PF_6$ [2]

A mixture of $[(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}Cl)Cl]_2$ (100 mg, 0.163 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (72 mg, 0.325 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum. Yield: 87 mg, 84%. Calc. for $C_{24}H_{25}ClN_3PF_6Ru$: C 45.23; H 3.99; N 6.63; found: C 45.33; H 3.84; N 6.48. IR (KBr pellets, cm^{-1}): 3446 ($\nu_{N\text{-}H}$); 1635 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 849 ($\nu_{P\text{-}F}$).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.204 (d, J=5.6 Hz, 1H), 8.006 (t, J=8.8 Hz, 2H), 7.827 (t, J=7.2 Hz, 1H), 7.550- 7.491 (m, 1H), 7.473 (d, J=6.8 Hz, 2H), 6.984 (s, 1H), 6.341(d, J=6 Hz, 2H), 5.941(d, J=6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.868 (d, J=6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.769 (d, J=6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.651(d, J=6 Hz, 1H, $Ar_{p\text{-}cy}$), 2.792 (sep, 1H), 2.234 (s, 3H), 1.055 (dd, J=6.8 Hz, 6H).

ESI-MS (m/z): 492.1 [M- PF_6], 456.3 [M- PF_6-Cl], 458.3 [M- PF_6-Cl]$^{2+}$

5A.3.4 Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(L)Cl]PF_6$ [3]

A mixture of $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ (100 mg, 0.15 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (66 mg, 0.30 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The solvent was removed by using rotary evaporator. The solid was dissolved in dichloromethane and then filtered to remove

ammonium chloride. The solution was concentrated to 2 ml and excess of diethyl ether was added for precipitation. The light brown color product was separated out, washed with ether and dried in vacuum. Yield: 84 mg, 84%. Calc. for $C_{26}H_{29}ClN_3PF_6Ru$: C 46.93; H 4.45; N 6.30; found: C 46.26; H 4.51; N 6.21. IR (KBr pellets, cm^{-1}): 3430 (ν_{N-H}); 1632 ($\nu_{C=C}$); 1452 ($\nu_{C=N}$); 847 (ν_{P-F}).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.432 (d, J=6.8 Hz, 1H), 8.332 (dt, J=8 Hz, 3H), 8.110 (dd, J=7.2 Hz, 2H), 7.972 (d, J=7.6 Hz, 2H), 7.720-7.610 (m, 1H), 7.431 (s, 1H), 2.188 (s, 18H, C_6Me_6).

ESI-MS (m/z): 448.1 [M- PF_6], 413 [M- PF_6-Cl].

5A.3.5 Preparation of [(η^5-C_5Me_5)M(L)Cl]X {M = Rh, X= BF_4 [4], Ir, X= ClO_4 [5]}

A mixture of [(η^5-C_5Me_5)M(μ-Cl)Cl]$_2$ (M = Rh, Ir) (0.16 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (71 mg, 0.32 mmol) and two equivalents of NH_4BF_4 (compound **4**) and $NaClO_4$ (compound **5**) in dry methanol (30 ml) were stirred at room temperature for 6 hrs until the color of the solution changed to dark yellow. The solvent was removed using rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (5 ml), and the solution was filtered to remove ammonium chloride. The light red solution was concentrated to 2 ml, upon addition of excess hexane gave the orange-yellow complex, which was separated and dried under vacuum.

Compound [4]: Yield: 150 80, 85%. Calc. for $C_{24}H_{26}ClN_3BF_4Rh$: C 49.58; H 4.57; N 7.24; found: C 49.67; H 4.63; N 7.13. IR (KBr pellets, cm^{-1}): 3438 (ν_{N-H}); 1628 ($\nu_{C=C}$); 1450 ($\nu_{C=N}$); 1088 (ν_{B-F}).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.708 (d, J=5.6 Hz, 1H), 8.062 (t, J=7.6 Hz, 1H), 7.973 (d, J=7.6 Hz, 2H), 7.713(d, J=7.2 Hz, 2H), 7.587 (t, J=6.8 Hz, 2H), 7.474-7.403 (m, 1H), 7.194 (s, 1H), 1.688 (s, 15H, C_5Me_5).

ESI-MS (m/z): 459.2 [M-BF_4-Cl], 458.3 [M-BF_4-Cl-H]

Compound [5]: Yield: 69 mg, 82%. Calc. for $C_{24}H_{26}ClN_3BF_4Ir$: C 42.99; H 3.95; N 5.53; found: C 43.07; H 4.04; N 5.46. IR (KBr pellets, cm^{-1}): 3460 (ν_{N-H}); 1634 ($\nu_{C=C}$); 1453 ($\nu_{C=N}$); 1099 (ν_{Cl-O}). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.778 (d, J=5.6 Hz, 1H), 8.137 (dt, J=7.6 Hz, 2H), 8.068 (d, J=7.6 Hz, 2H), 7.792 (dd, J=6 Hz, 2H), 7.681 (dt, J=6.4 Hz, 1H), 7.568-7.505 (m, 1H), 7.383 (s, 1H), 1.724 (s, 15H, C_5Me_5).

ESI-MS (m/z): 494.4 [M- BF_4], 459.1 [M- BF_4-Cl].

5A.3.6 Preparation of $[(\eta^5\text{-}C_5H_5)M(L)(PPh_3)]PF_6$ {M = Ru [6], Os [7]}

A mixture of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X = Cl and M = Os, X = Br} (0.137 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (30 mg, 0.137 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed for 12 hrs until the color of the solution changed from pale yellow to orange. The solvent was 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, upon addition of diethylether the orange-yellow compound precipitate, which was separated and dried under vacuum.

Compound [6]: Yield: 74 mg, 68%. Elemental Anal (%) Calc. for $C_{37}H_{31}N_3P_2F_6Ru$: C 55.94; H 3.97; N 5.27; found: C 56.19; H 4.08; N 5.18. IR (KBr pellets, cm^{-1}): 3430 ($\nu_{N\text{-}H}$); 1628 ($\nu_{C=C}$); 1450 ($\nu_{C=N}$); 849 ($\nu_{P\text{-}F}$).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.006 (d, *J*=5.2 Hz, 1H), 8.614 (d, *J*=4.4 Hz, 2H), 8.009 (d, *J*=7.2 Hz, 2H), 7.939 (t, *J*=8 Hz, 2H), 7.672 (t, *J*=7.6 Hz, 1H), 7.591-7.523 (m, 1H), 7.333-7.022 (m, 15H, PPh_3), 7.189 (s, 1H), 4.723 (s, 5H, C_5H_5).

^{31}P {^1H} NMR ($CDCl_3$, δ): 50.82 (s, PPh_3).

ESI-MS (m/z): 583.6 [M- PF_6], 548.2 [M- PF_6-Cl].

Compound [7]: Yield: 75 mg, 69%. Elemental Anal (%) Calc. for $C_{35}H_{30}N_6P_2F_6Os$: C 50.31; H 3.55; N 4.72; found: C 50.42; H 3.63; N 4.66. IR (KBr pellets, cm^{-1}): 3448 ($\nu_{N\text{-}H}$); 1629 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 844 ($\nu_{P\text{-}F}$). ^1H NMR (400 MHz, $CDCl_3$): δ = 12.882 (s, NH, 1H), 9.130 (d, *J*=5.6 Hz, 1H), 8.622 (d, *J*=7.2 Hz, 2H), 7.804 (d, *J*=7.2 Hz, 2H), 7.720 (t, *J*=8 Hz, 3H), 7.573-7.498 (m, 1H), 7.387-7.018 (m, 15H, PPh_3), 6.560 (s, 1H), 4.658 (s, 5H, C_5H_5).

^{31}P {^1H} NMR ($CDCl_3$, δ): -0.254 (s, PPh_3).

ESI-MS (m/z): 740.5 [M- PF_6], 738.3 [M-PF_6-2H], 737.3 [M-PF_6-3H].

5A.3.7 Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(L)(PPh_3)]PF_6$ [8]

A mixture of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (37.7 mg, 0.125 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed for 12 hrs until the color of the solution changed from

pale yellow to orange. The solvent was removed using rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The orange solution was concentrated to 5 ml, when addition of excess hexane gave the orange-yellow compound, which was separated and dried under vacuum. Yield: 72 mg, 66%. Elemental Anal (%) Calc. for $C_{42}H_{41}N_3P_2F_6Ru$: C 58.36; H 4.80; N 4.89; found: C 58.43; H 4.91; N 4.76. IR (KBr pellets, cm^{-1}): 3434 (ν_{N-H}); 1626 ($\nu_{C=C}$); 1445 ($\nu_{C=N}$); 847 (ν_{P-F}).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.807 (d, J=5.6 Hz, 1H), 8.693 (d, J=7.2 Hz, 2H), 7.862 (t, J=7.6 Hz, 1H), 7.815 (t, J=7.6 Hz, 2H), 7.576-7.454 (m, 1H), 7.371-7.263 (m, 15H, PPh_3), 7.002 (d, J=10.8 Hz, 2H), 6.583 (s, 1H), 2.071 (s, 15H, C_5Me_5). ^{31}P {^1H} NMR ($CDCl_3$, δ): 50.430 (s, PPh_3). ESI-MS (m/z): 719.3[M- PF_6], 457.3 [M-PF_6-PPh_3].

5A.3.8 Preparation of [(η^5-C_9H_7)Ru(L)(PPh_3)]PF_6 [9]

A mixture of [(η^5-C_9H_7)Ru(PPh_3)$_2$Cl] (100 mg, 0.128 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (38.4 mg, 0.128 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed for 8 hrs until the color of the solution changed from pale yellow to dark red. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The red solution was concentrated to 5 ml, upon addition of diethylether the orange-red compound precipitate was separated and dried under vacuum.

Yield: 77 mg, 61%. Elemental Anal (%) Calc. for $C_{41}H_{33}N_3P_2F_6Ru$: C 58.33; H 3.97; N 4.00; found: C 58.42; H 4.08; N 3.89. IR (KBr pellets, cm^{-1}): 3432 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1453 ($\nu_{C=N}$); 847 (ν_{P-F}). ^1H NMR (400MHz, $CDCl_3$): δ = 11.924 (s, NH, 1H), 9.296 (d, J=5.2 Hz, 1H), 8.453 (d, J=7.2 Hz, 2H), 7.720 (d, J=7.6 Hz, 2H), 7.575 (t, J=8 Hz, 2H), 7.480 (t, J=7.2 Hz, 1H), 7.389-7.027 (m, 23H), 6.433 (s, 1H), 4.859 (d, J=8 Hz, 1H), 4.320 (t, J=2.4 Hz, 1H), 3.507 (dd, J=7.2 Hz, 1H).

^{31}P {^1H} NMR ($CDCl_3$): δ = 59.441 (s, PPh_3).

ESI-MS (m/z): 20.5 [M- PF_6], 718.4 [M-PF_6-2H], 458.2 [M-PF_6-PPh_3].

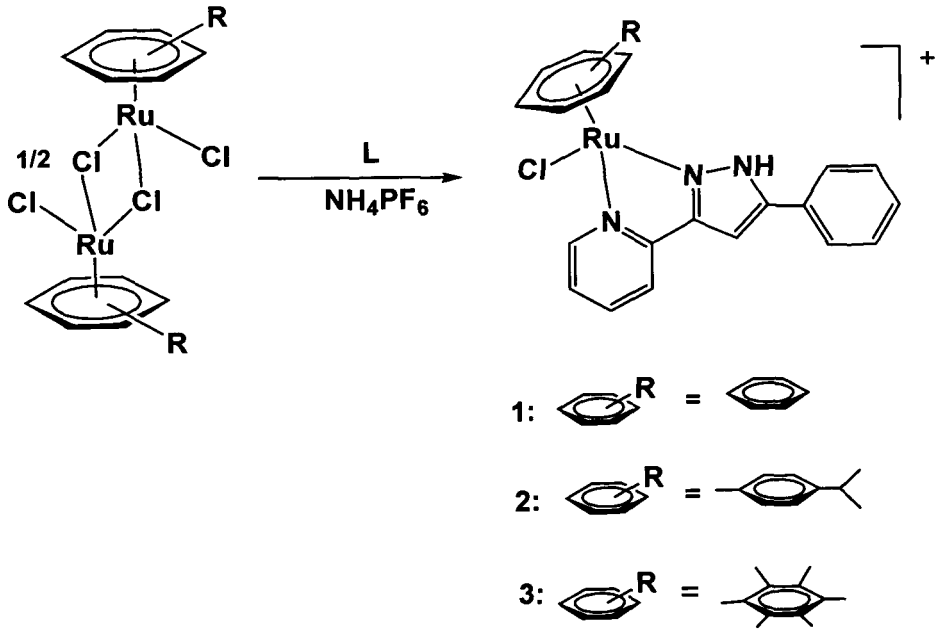
5A.4 Results and discussion

5A.4.1 Arene ruthenium compounds 1, 2 and 3

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, *p*-cymene and C_6Me_6) react with the N,N'-based ligand (**L**) in methanol to produce the mononuclear cationic compounds **1**, **2** and **3** (Scheme **5A.1**). Compound **1** is brown in color while compounds **2** and **3** are yellow in color. These compounds are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethylether and petroleum ether. All these compounds were isolated as their hexafluorophosphate salt.

The infrared spectra of all these compounds exhibit a chelated N,N'-bidentate ligand as broad bands at 3436 cm^{-1}, 3446 cm^{-1}, 3430 cm^{-1}, 1625 cm^{-1}, 1635 cm^{-1}, 1632 cm^{-1}, 1457 cm^{-1}, 1451 cm^{-1} and 1452 cm^{-1} corresponding to the stretching frequencies of N-H bond of pyrazole ring, C=C and C=N bond of the pyridine ring of the ligand respectively. In addition, the IR spectra of all these compounds display a strong band at around 846 cm^{-1} corresponding to the stretching frequency of the P-F bond of the counter ion of these compounds. The ^1H NMR of the free ligand shows seven different sets of signals in the aromatic region. ^1H NMR spectra of the compounds bearing the ligand **L** gives very informative NMR spectra with peaks spread over a quiet wide range as compared to that of the free ligand. Compounds **1** and **3** show a doublet at around 9.204 and 9.341 ppm corresponding to the pyridyl proton adjacent to the nitrogen atom (i.e., H6) where as in the case of the free ligand the same proton comes in the up-field region at around 8.601 ppm. The free ligand also shows two doublets in the range of 7.800-7.704 ppm, two triplets at around 7.426-7.261 ppm, a multiplet and a singlet corresponding to the protons of the pyridyl and phenyl group of the ligand. But in the case of metal compound **1** exhibits a doubly triplet instead of two triplets corresponding to the pyridyl protons of the ligand and it comes in the downfield as compared to the free ligand. In addition to all these peaks, the ^1H NMR spectra of compound **1** also displays a singlet at around 6.079 ppm which corresponds to the six protons of the benzene ring. Whereas in the case of compound **3** it exhibit a singlet at around 2.188 ppm corresponding to the eighteen protons of the hexamethylbenzene ring. Compound **2** exhibits an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group display a doubly doublet at *ca.* δ = 1.055, instead of a doublet as in the starting precursor. The aromatic protons of the *p*-cymene ligand for these compounds also display four doublets at *ca.* δ =

5.941–5.651, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behaviour of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [65]. In other words we can say the different signals are entirely due to the chiral nature of the metal [66, 67].



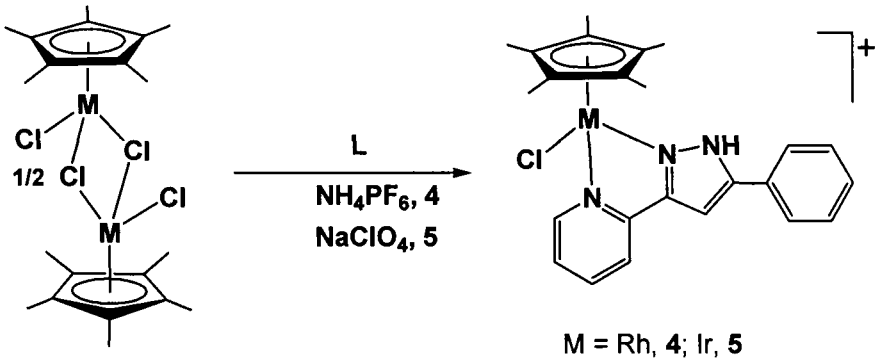
Scheme **5A.1**

5A.4.2 Pentamethylcyclopentadienyl rhodium and iridium compounds 4 and 5

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with N,N'- bidentate nitrogen base (**L**) ligand in methanol at room temperature leads to the formation of chloride substituted compounds **4** and **5**, respectively (Scheme **5A.2**).

The compound **4** was isolated as its tetrafluoroborate salt whereas compound **5** was isolated as perchlorate salt. Both the compounds are orange-yellow in color and are stable in solid state as well as in solution. They are soluble in polar solvents but insoluble in non-polar solvents like hexane, petroleum ether and diethylether. The infrared spectra of both the compounds exhibit a chelated N,N'-bidentate ligand as broad bands at 3438 cm^{-1}, 3460 cm^{-1}, 1628 cm^{-1}, 1634 cm^{-1}, 1450 cm^{-1} and 1453 cm^{-1} corresponding to the stretching frequencies of N-H bond of pyrazole ring, C=C and C-N bond of the pyridine ring of the

ligand respectively. The IR spectrum of compound **4** also exhibits a strong band at 1088 cm^{-1} due to the stretching frequency of the B-F bond of the counter ion. However in the case of compound **5**, a strong absorption at 1099 cm^{-1} is observed due to the perchlorate ion [68]. Compounds **4** and **5** also show a slight downfield shift in the proton NMR as compared to that of the free ligand. They show a doublet at around 8.7 ppm corresponding to the proton next to the nitrogen atom of the pyridyl group of the ligand (*i.e.*, H6) as compared to that of the free ligand which is seen at around 8.6 ppm. It also displays two triplets corresponding to the pyridyl protons at around 8.1 and 7.6 ppm but in case of free ligand it shows two triplets at around 7.4 and 7.3 ppm. Besides these peaks, the other ligand peaks are mentioned in the experimental section. The proton NMR spectra of these compounds also display a singlet at 1.688 ppm for compound **4** and 1.724 ppm for compound **5** respectively, corresponding to the protons of the pentamethyl-cyclopentadienyl group. The molecular structures of compounds **4** and **5** were solved by single crystal X-ray crystallography and the structures are presented in Figures **5A.2** and **5A.3**.



M = Rh, **4**; Ir, **5**

Scheme **5A.2**

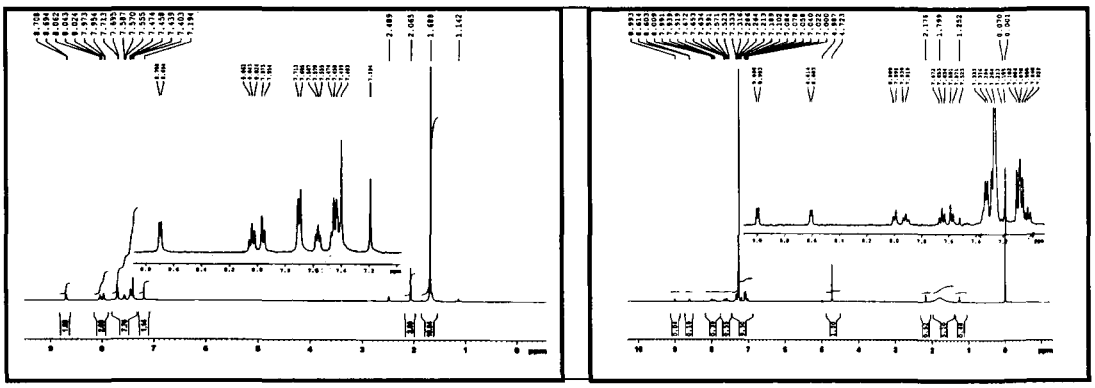


Figure **5A.1**: ^1H NMR spectra of complexes **4** and **6**

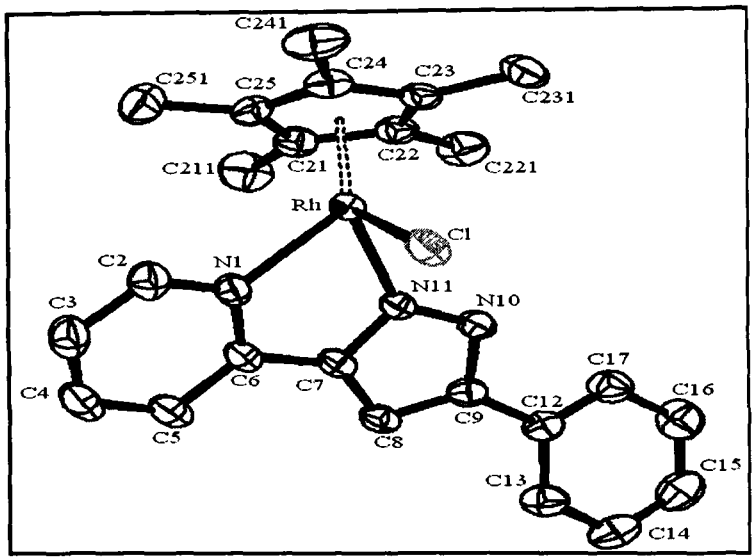


Figure **5A.2**: Molecular structure of a compound **4** with 35 % probability thermal ellipsoids. Hydrogen atoms and BF_4 ion are omitted for clarity.

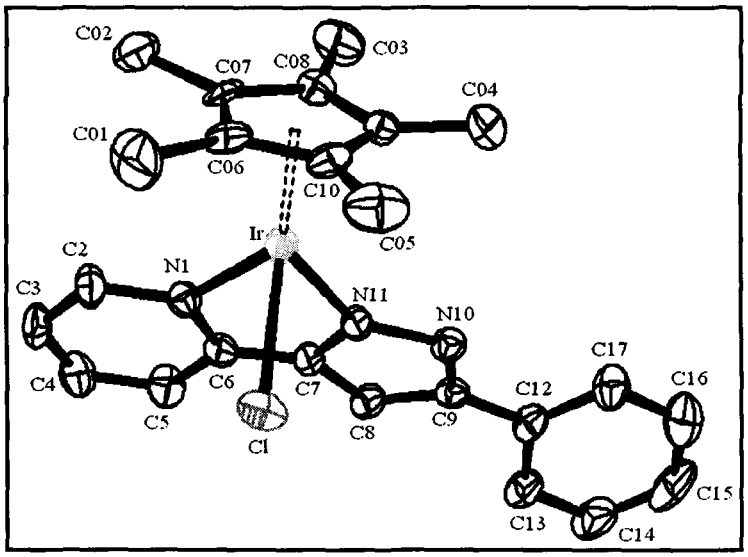


Figure **5A.3**: Molecular structure of a compound **5** with 35 % probability thermal ellipsoids. Hydrogen atoms and perchlorate ion are omitted for clarity.

5A.4.3 Cyclopentadienyl ruthenium and osmium compounds ***6-9***

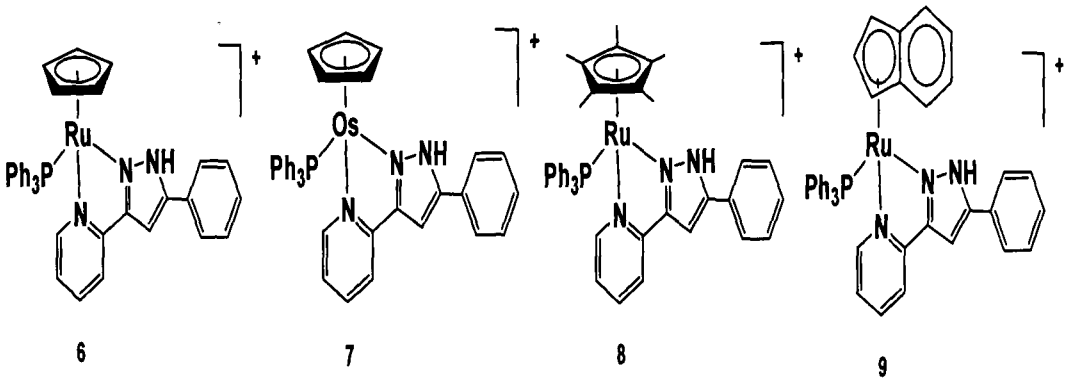
The analytical data of these compounds are consistent with the formulations (Chart **5A.1**). These compounds are formed by the reaction of metal complexes with the ligand **L** yielding only mononuclear compounds. All these compounds are isolated as their

hexafluorophosphate salt. The infrared spectra of all the compounds exhibit a chelated N,N'-bidentate ligand as broad bands between 3430 $cm^{-1}$and 3448 cm^{-1}, 1626 cm^{-1} and 1630 cm^{-1} and between 1445 cm^{-1} and 1453 as mentioned in the experimental section, corresponding to the stretching frequencies of N-H bond of pyrazole ring, C=C and C-N bond of the pyridine ring of the ligand respectively. In addition, the infrared spectra of these compounds also exhibit a strong band between 844 cm^{-1} and 849 cm^{-1}due to the stretching frequency of the P-F bond of the counter ion of these compounds. The proton spectra of compounds **6** and **7** exhibit a singlet at 4.723 and 4.658 ppm for the cyclopentadienyl ring protons, indicating a downfield shift from the starting complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Cl]$ [69, 59]. The downfield shift in the position of the cyclopentadienyl protons might result from a change in the electron density on the metal center due to the chelation of the ligand **L** through two nitrogen atoms. In addition to the other ligand peaks, as mentioned in the experimental section, a multiplet in the range 7.387-7.018 ppm, which corresponds to the phenyl protons of the triphenylphosphine group of these compounds, is observed.

The 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) ligand reacts with the pentamethylcyclopentadienyl ruthenium(II) complexes in the presence of NH_4PF_6 in methanol, to yield the mononuclear cationic compound $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)]PF_6$, **8** (Chart **5A.1**). The compound is an orange crystalline solid, soluble in polar solvents and air stable. The infrared spectrum displays a sharp singlet at 850 cm^{-1} corresponding to the stretching frequency of P-F bond of the counter ion of the compound in addition to the bands due to ligand. In addition to the proton peaks of the ligand, the proton NMR spectrum also display a singlet at 2.071 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ring and a multiplet in the range of 7.371–7.263 ppm which corresponds to the phenyl protons of triphenylphosphine. Compound **9** exhibits a characteristic three sets of signals such as multiplet, triplet and doublet, for the protons of the indenyl group. The protons of the triphenylphosphine ligand exhibit a multiplet at 7.389-7.027 ppm. If we observe carefully the ^1H NMR of all these compounds, we see that the spectra of all the compounds containing ruthenium displays ligand peak at downfield region as compared to that of Rh, Ir and Os compounds. The $^{31}P\ \{^1H\}$ NMR spectra of the compounds **6**, **8** and **9** exhibit a single sharp resonance for triphenylphosphine at 59.441-49.625 ppm respectively whereas in the starting precursors the signals appear in the up

field. In the case of compound **7** the ^{31}P $\{^1H\}$ NMR spectrum display a sharp singlet at -0.254 ppm as compared to the starting complex which show at -6.29 ppm.

The *m/z* values of all these compounds and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section, are in good agreement with the theoretically expected values. ESI mass spectra of the compounds also displayed prominent peaks corresponding to the molecular ion fragment. All the halogenated compounds displayed the prominent peak corresponding to the loss of chloride ion from the molecular ion peak, but the loss of arene or Cp or Cp* group is not observed indicating the stronger bond of metal to these groups and remains intact. Similarly in some of the compounds containing the triphenylphosphine ligand, we can see the loss of triphenylphosphine group from the molecular ion peak and is given in the experimental section.



6 7 8 9

Chart **5A.1**

5A.5 Molecular structures

Molecular structures of **4** and **5** have been determined crystallographically. The compounds crystallize in $P\bar{1}$ and $P2_1/n$ space groups. Compound **5** crystallize with a molecule of methanol per asymmetric unit. In compound **4**, we can see the presence of an oriental disorder for the location of the counter ion BF_4. Details about data collection, refinement and structure solution are recorded in Table **5A.1**, and selected bond lengths and angles are presented in Table **5A.2**. Crystal structures of **4** and **5** with atom-numbering schemes are shown in Figures **5A.2** and **5A.3**. In both the compounds **4** and **5** the metal is bonded with the major coordinated sites N1 and N11 in a k^2 manner, one chloro group, and the pentamethylcyclopentadienyl (Cp*) ring in a η^5 manner. Typical piano-stool geometry around the metal in both the compounds is maintained. The Cp* ring is planar with an average Rh-C and Ir-C distance of 2.149 and 2.159 Å respectively. The bond

distance of Rh metal center to the centroid (CNT) of the Cp* is 1.773 Å in the case of compiound **4**, whereas in the case of compound **5** the Ir center to the centroid (CNT) of the Cp* is 1.791 Å which are comparable to the distances in other rhodium and iridium pentamethylcyclopentadienyl compounds. The Rh-N and Rh-Cl bond lengths are consistent with the values reported in the literature [65, 70-72]. The C-C bond lengths within the Cp* ring and C-Me distances are normal. The B-F lengths and Cl-O lengths are consistent with the values reported previously [41, 43].

5A.6 Conclusion

In summary, a series of new η^5-and η^6- cyclic Π-perimeter hydrocarbons metal compounds bearing 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) ligand, which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. Our main aim of making dimetallic compounds by incorporating a second metal coordinating through the third nitrogen atom and activating a carbon atom of the phenyl group of the ligand **L** was not fruitful.

Supplementary material

CCDC- **749569** (**4**) and **749570** (**5**) contain the supplementary crystallographic data for this chapter.

Table **5A.1**: Crystallographic and structure refinement parameters for compounds **4** and **5**

Compound	**4**	**5**
Emperical formula	C_{24} H_{26} B Cl F_4 N_3 Rh	C_{25} H_{29} Cl_2 Ir N_3 O_5
Formula weight	581.65	714.61
Temperature (K)	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	P2(1)/n
Unit cell dimensions		
a (Å)	10.5688(6)	13.0524(8)
b (Å)	11.4582(7)	10.0571(9)
c (Å)	11.4748(7)	20.7255(14)
α(°)	116.3150(10)	90
β(°)	94.7380(10)	100.251(5)
γ(°)	94.3690(10)	90
Volume (A^3)	1231.40(13)	2677.2(3)
Z	2	4
Calculated density (Mg/m^3)	1.569	1.775
Absorption coefficient (mm^{-1})	0.850	5.227
F(000)	588	1404
Crystal size(mm)	0.20 x 0.10 x 0.02	0.11 x 0.08 x 0.02
Θ range for data collection (deg)	1.95 to 25.00	1.72 to 25.37
Index ranges	-12<=h<=12,	-14<=h<=14,
	-13<=k<=13,	-12<=k<=11,
	-13<=l<=13	-24<=l<=24
Reflections collected / unique	9432/4327	22770/4556
R_{int}	0.0305	0.0609
Final R indices [I>2sigma(I)]	R1 = 0.0471,	R1 = 0.0272,
	wR2 = 0.1049	wR2 = 0.0316
R indices (all data)	R1 = 0.0657,	R1 = 0.0790,
	wR2 = 0.1120	wR2 = 0.0358
Largest diff. peak and hole ($e.Å^{-3}$)	0.761 and -0.643	0.704 and -0.890

Table **5A.2**: Selected bond lengths and angles for compounds **4** and **5**

	4	**5**
Distances (Å)		
N(1)-M(1)	2.139(9)	2.125(3)
N(11)-M(1)	2.090(9)	2.069(2)
N(10)-N(11)	1.378(14)	1.373(3)
Cl(1)-M(1)	2.401(4)	2.399(15)
M(1)-CNT(1)	1.773	1.791
angles (°)		
N(1)-M(1)-N(11)	75.8(4)	75.49(9)
N(10)-N(11)-M(1)	134.0(7)	133.52(17)
N(1)-M(1)-Cl(1)	85.5(3)	86.11(9)
N(11)-M(1)-Cl(1)	88.7(3)	86.74(10)

CNT= Metal to centroid of Cp*

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Chapter 5B: Study of half–sandwich platinum group metal complexes bearing *dpt-NH_2* ligand*.

5B.1 Abstract

A quite general approach for the preparation of η^5-and η^6-cyclic hydrocarbon platinum group metal complexes is presented. The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6) and η^5- pentamethyl-cyclopentadienyl rhodium and iridium complexes $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) react with two equivalents of 4-amino-3,5-di-pyridyltriazole (*dpt-NH_2*) in presence of NH_4PF_6 to afford the corresponding mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(dpt\text{-}NH_2)Cl]PF_6$ {arene = $C_{10}H_{14}$ (**1**), C_6H_6 (**2**) and C_6Me_6, (**3**)} and $[(\eta^6\text{-}C_5Me_5)M(dpt\text{-}NH_2)Cl]PF_6$ {M = Rh (**4**), Ir (**5**)}. However the mononuclear η^5-cyclopentadienyl analogues such as $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ complexes react in presence of one equivalent of *dpt-NH_2* and one equivalent of NH_4PF_6 in methanol yielded mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(dpt\text{-}NH_2)]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(dpt\text{-}NH_2)]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(dpt\text{-}NH_2)]PF_6$ (**8**) and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(dpt\text{-}NH_2)]PF_6$ (**9**) respectively. These compounds have been totally characterized by IR, NMR and mass spectrometry. The molecular structures of **4** and **6** have been established by single crystal X-ray diffraction and some of the representative complexes have also been studied by UV-vis spectroscopy.

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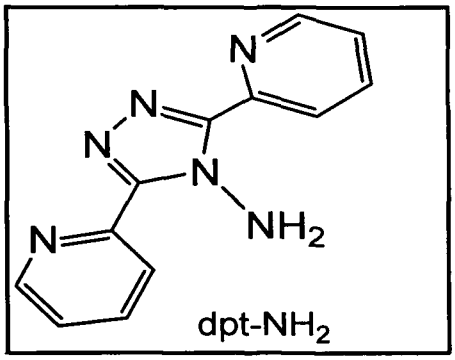
5B.2 Introduction

Within the large family of η^5- and η^6-cyclic hydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 50 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1, 2]. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer activities. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted more attention [3-6]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal centre [7]. In recent years we have been carrying out reactions of η^5- and η^6-cyclichydrocarbon metal complexes with a variety of nitrogen based ligands [8-15] including various poly pyridyl ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [16, 17]. Although comprehensive studies have been made on η^5- and η^6-transition metal complexes, complexes containing NH_2 substituted poly-pyridyl ligand of this type shown below have not yet been reported.



Ligand used in this study

Herein we describe the syntheses of nine mononuclear η^5- and η^6-cyclichydrocarbon platinum group metal complexes bearing dpt-NH_2 ligand. Attempts to prepare dimetallic derivatives by addition of a second organometallic anion were unsuccessful. All these complexes have been fully characterized by IR, NMR, mass

spectrometry and UV-vis spectroscopy. Molecular structures of the two representative complexes are also presented in this section.

5B.3 Experimental

All solvents were dried and distilled prior to use. 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) was prepared using literature method [18]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, *p*-cymene, and C_6Me_6), $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [19-22], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [23-28]. NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Mass spectra were obtained from a Waters ZQ-4000 mass spectrometer by the ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV-visible spectrophotometer. All the new complexes gave satisfactory CHN results.

5B.3.1 Single-crystal X-ray structures analyses

Crystals of **4** were grown from acetone/petroleum ether as small red plates. Crystals of **6** were grown by slow diffusion of petroleum ether into a mixture of acetonitrile and dichloromethane solution of the respective complex as deep red blocks. The crystallizations were done at room temperature. The intensity data of **4** and **6** were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoKα radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART [29] software was used for data acquisition. Data integration and reduction were undertaken with the SAINT [29] and XPREP [30] software. Structures were solved by direct methods using SHELXS-97 [31] and refined with full-matrix least squares on F2 using SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [33] for Windows. The ORTEP presentations of the representative complexes are shown in Figures **5B.1** and **5B.5** respectively. The data collection parameters and bond lengths and angles are presented in Tables **5B.2** and **5B.3**.

5B.3.2 Preparation of [(η^6- p-cymene)Ru(dpt-NH_2)Cl]PF_6 [1]

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.16 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (78 mg, 0.33 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Yield: 193 mg, 90%. Elemental Anal (%) Calc. for $C_{22}H_{24}ClN_6PF_6Ru$: C 40.43; H 3.71; N 12.81; found: C 40.51; H 3.80; N 12.73. IR (KBr pellets, cm^{-1}): 3430 (ν_{N-H}); 1615 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 846 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (d, *J*=8 Hz, 1H), 8.81 (d, *J*=7.2 Hz, 1H), 8.76 (d, *J*=4.4 Hz, 1H), 8.41 (d, *J*=8 Hz, 1H), 8.21 (t, *J*=7.6 Hz, 1H), 8.06 (t, *J*=7.6 Hz, 1H), 7.74 (t, *J*=7.2 Hz, 1H), 7.61 (t, *J*=5.2 Hz, 1H), 7.42 (s, 2H, -NH_2), 5.98 (d, *J*=4 Hz, 1H, Ar_{p-cy}), 5.90 (d, *J*=6 Hz, 1H, Ar_{p-cy}), 5.79 (d, *J*=6 Hz, 1H, Ar_{p-cy}), 5.67 (d, *J*=6 Hz, 1H, Ar_{p-cy}), 2.90 (sep, 1H), 2.24 (s, 3H), 1.24 (d, *J*=6.8 Hz, 3H), 1.19 (d, *J*=6.8 Hz, 3H); ESI-MS (m/z): 496.7 [M- PF_6], 461.7 [M- PF_6-Cl].

5B.3.3 Preparation of [(η^6-C_6H_6)Ru(dpt-NH_2)Cl]PF_6 [2]

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.2 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (96 mg, 0.4 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The brown compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Yield: 180 mg, 75%. Elemental Anal (%) Calc. for $C_{18}H_{16}ClN_6PF_6Ru$: C 36.19; H 2.71; N 14.03; found: C 36.28; H 2.82; N 13.95. IR (KBr pellets, cm^{-1}): 3432 (ν_{N-H}); 1627 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 838 (ν_{P-F}); ^{1}H NMR (400 MHz, CD_3CN): δ = 9.33 (d, *J*=8 Hz, 1H), 8.92 (d, *J*=7.2 Hz, 1H), 8.62 (d, *J*=7.6 Hz, 1H), 8.31 (d, *J*=8 Hz, 1H), 8.22 (t, *J*=5.2 Hz, 1H), 8.09 (t, *J*=7.2 Hz, 1H), 7.69 (t, *J*=6.4 Hz, 1H), 7.54 (t, *J*=5.6 Hz, 1H), 7.43 (s, 2H, -NH_2), 6.29 (s, 6H, C_6H_6); ESI-MS (m/z): 452.8 [M- PF_6].

5B.3.4 Preparation of [(η^6-C_6Me_6)Ru(dpt-NH_2)Cl]PF_6 [3]

A mixture of [(η^6- C_6Me_6)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.14 mmol), 4-amino-3,5-di-pyridyl triazole (dpt-NH_2) (72 mg, 0.29 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The solvent was removed by using rotary evaporator. The solid was dissolved in dichloromethane and then filtered to remove ammonium chloride. The solution was concentrated to 2 ml and excess of diethylether was

added for precipitation. The light brown color product was separated out, washed with diethylether and dried under vacuum.

Yield: 132 mg, 64.7%. Elemental Anal (%) Calc. for $C_{24}H_{28}ClN_6PF_6Ru$: C 42.31; H 4.11; N 12.29; found: C 42.43; H 4.19; N 12.16; IR (KBr pellets, cm^{-1}): 3433 (ν_{N-H}); 1618 ($\nu_{C=C}$); 1474 ($\nu_{C=N}$); 846 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.41 (d, J=7.2 Hz, 1H), 8.96 (d, J=8 Hz, 1H), 8.73 (d, J=8 Hz, 1H), 8.42 (d, J=7.6 Hz, 1H), 8.33 (t, J=6.4 Hz, 1H), 8.16 (t, J=7.6 Hz, 1H), 7.72 (t, J=6.4 Hz, 1H), 7.63 (t, J=5.6 Hz, 1H), 7.51 (s, 2H, -NH_2), 2.10 (s, 18H, C_6Me_6); ESI-MS (m/z): 537.2 [M- PF_6], 502.1 [M- PF_6-Cl].

5B.3.5 Preparation of $[(\eta^5\text{-}C_5Me_5)M(dpt\text{-}NH_2)Cl]PF_6$ {M = Rh [4], Ir [5]}

A mixture of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) (0.16 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (77 mg, 0.32 mmol) and two equivalents of NH_4PF_6 in dry methanol (30 ml) were stirred at room temperature for 6 hrs until the color of the solution changed to dark yellow. The solvent was removed using rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (5 ml), and the solution was filtered to remove ammonium chloride. The light red solution was concentrated to 2 ml, when addition of excess hexane gave the orange-yellow complex, which was separated and dried under vacuum.

Complex [4]: Yield: 150 mg, 75%. Elemental Anal (%) Calc. for $C_{22}H_{25}ClN_6PF_6Rh$: C 40.21; H 3.81; N 12.81; found: C 40.29; H 3.90; N 12.73. IR (KBr pellets, cm^{-1}): 3446 (ν_{N-H}); 1632 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 844 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.95 (d, J=8 Hz, 1H), 8.77 (d, J=5.6 Hz, 1H), 8.70 (d, J=4.8 Hz, 1H), 8.35 (d, J=4 Hz, 1H), 8.14 (t, J=8 Hz, 1H), 7.97 (t, J=6.4 Hz, 1H), 7.67 (t, J=6.4 Hz, 1H), 7.51 (t, J=5.6 Hz, 1H), 7.26 (s, 2H, -NH_2), 1.59 (s, 15H, C_5Me_5); ESI-MS (m/z): 511.3 [M- PF_6], 476.6 [M- PF_6-Cl].

Complex [5]: Yield: 130 mg, 68%. Elemental Anal (%) Calc. for $C_{22}H_{25}ClN_6PF_6Ir$: C 35.44; H 3.39; N 11.24; found: C 35.53; H 3.47; N 11.18. IR (KBr pellets, cm^{-1}): 3434 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 843 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.65 (d, J=7.6 Hz, 1H), 9.31 (d, J=8 Hz, 1H), 9.00 (d, J=5.6 Hz, 1H), 8.93 (d, J=8 Hz, 1H), 8.41 (t, J=7.6 Hz, 1H), 8.27 (t, J=8 Hz, 1H), 7.89 (t, J=9.2 Hz, 1H), 7.83 (t, J=6.4 Hz, 1H), 7.47 (s, 2H, -NH_2), 2.29 (s, 15H, C_5Me_5); ESI-MS (m/z): 600.8 [M- PF_6], 565.8 [M- PF_6-Cl].

5B.3.6 Preparation of $[(\eta^5\text{-}C_5H_5)M(dpt\text{-}NH_2)(PPh_3)]PF_6$ {M = Ru [6], Os [7]}

A mixture of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X = Cl and M = Os, X = Br} (0.137 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (0.137 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 12 hrs until the color of the solution changed from pale yellow to orange. The solvent was 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, upon addition of diethylether the orange-yellow complex was precipitated, which was separated and dried under vacuum.

Complex [6]: Yield: 76 mg, 68%. Elemental Anal (%) Calc. for $C_{35}H_{30}N_6P_2F_6Ru$: C 51.78; H 3.72; N 10.37; found: C 51.89; H 3.79; N 10.28; IR (KBr pellets, cm^{-1}): 3436 ($\nu_{N\text{-}H}$); 1615 ($\nu_{C=C}$); 1440 ($\nu_{C=N}$); 844 ($\nu_{P\text{-}F}$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.37 (d, *J*=8 Hz, 1H), 8.73 (d, *J*=7.6 Hz, 1H), 8.69 (d, *J*=7.2 Hz, 1H), 8.43 (d, *J*=8 Hz, 1H), 8.20 (t, *J*=6.4 Hz, 1H), 8.12 (t, *J*=7.2 Hz, 1H), 7.81 (t, *J*=7.6 Hz, 1H), 7.70 (t, *J*=6.4 Hz, 1H), 7.50 (s, 2H, -NH_2), 7.38-7.21 (m, 15H, PPh_3), 4.91 (s, 5H, C_5H_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): 50.82 (s, PPh_3); ESI-MS (m/z): 696 [M- PF_6].

Complex [7]: Yield: 71 mg, 67.6%. Anal (%) Calc. for $C_{35}H_{30}N_6P_2F_6Os$: C 46.69; H 3.32; N 9.36; found: C 46.78; H 3.39; N 9.28; IR (KBr pellets, cm^{-1}): 3431 ($\nu_{N\text{-}H2}$); 1616 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 843 ($\nu_{P\text{-}F}$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.32 (d, *J*=8 Hz, 1H), 8.88 (d, *J*=7.6 Hz, 1H), 8.71 (d, *J*=6.4 Hz, 1H), 8.49 (d, *J*=8 Hz, 1H), 8.21 (t, *J*=5.6 Hz, 1H), 8.14 (t, *J*=7.2 Hz, 1H), 7.73 (t, *J*=7.6 Hz, 1H), 7.61 (t, *J*=8 Hz, 1H), 7.48 (s, 2H, -NH_2), 7.38-6.80 (m, 15H, PPh_3), 4.59 (s, 5H, C_5H_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): -0.26 (s, PPh_3); ESI-MS (m/z): 781.5 [M- PF_6].

5B.3.7 Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(dpt\text{-}NH_2)(PPh_3)]PF_6$ [8]

A mixture of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), 4-amino-3,5-di-pyridyl triazole (dpt-NH_2) (30 mg, 0.125 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 12 hrs until the color of the solution changed from pale yellow to orange. The solvent was removed using rotary evaporator under reduced pressure, the residue was 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: 73 mg, 65.7%. Anal (%) Calc. for $C_{40}H_{40}N_6P_2F_6Ru$: C 54.47; H 4.56; N 9.55; found: C 54.51; H 4.61; N 9.45; IR (KBr pellets, cm^{-1}): 3435 (ν_{N-H}); 1599 ($\nu_{C=C}$); 1437 ($\nu_{C=N}$); 844 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J=7.6 Hz, 1H), 8.34 (d, J=8 Hz, 1H), 8.27 (d, J=7.2 Hz, 1H), 8.09 (d, J=8 Hz, 1H), 7.84 (t, J=6.4 Hz, 1H), 7.64 (t, J=7.6 Hz, 1H), 7.38 (t, J=8 Hz, 1H), 7.30 (t, J=7.6 Hz, 1H), 7.25 (s, 2H, -NH_2), 7.21-7.09 (m, 15H, PPh_3), 2.03 (s, 15H, C_5Me_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): 49.6 (s, PPh_3); ESI-MS (m/z): 739.8 [M- PF_6].

5B.3.8 Preparation of [(η^5-C_9H_7)Ru(dpt-NH_2)(PPh_3)]PF_6 [9]

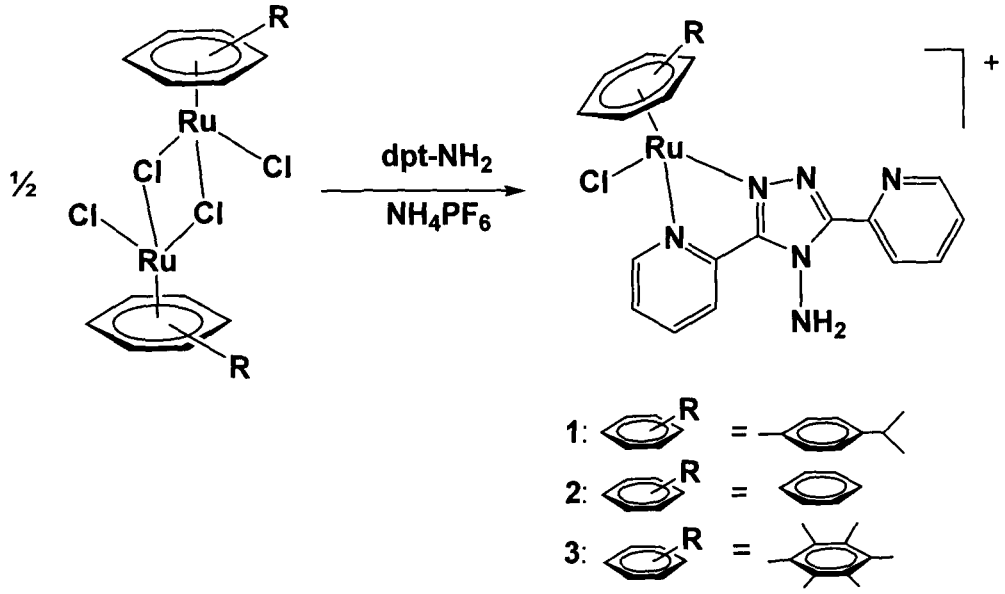
A mixture of [(η^5-C_9H_7)Ru(PPh_3)$_2$Cl] (100 mg, 0.128 mmol), 4-amino-3,5-di-pyridyl triazole (dpt-NH_2) (31 mg, 0.128 mmol) and one equivalent of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 8 hrs until the color of the solution changed from pale yellow to dark red. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The red solution was concentrated to 5 ml, upon addition of diethylether the orange-red complex precipitate, which was separated and dried under vacuum. Yield: 69 mg, 61.9%. Anal (%) Calc. for $C_{39}H_{32}N_6P_2F_6Ru$: C 54.34; H 3.72; N 9.78; found: C 54.40; H 3.81; N 9.66. IR (KBr pellets, cm^{-1}): 3446 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1439 ($\nu_{C=N}$); 843 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.22 (d, J=5.6 Hz, 1H), 8.75 (d, J=8 Hz, 1H), 8.67 (d, J=4.4 Hz, 1H), 8.41 (d, J=8 Hz, 1H), 8.25 (s, 2H, -NH_2), 8.23 (t, J=7.6 Hz, 1H), 8.01 (t, J=6.4 Hz, 1H), 7.96 (t, J=8 Hz, 1H), 7.94 (t, J=9.2 Hz, 1H), 7.55-7.10 (m, 22H), 4.97 (d, J=8 Hz, 1H), 4.85 (d, J=7.6 Hz, 1H), 4.43 (t, J=2.4 Hz, 1H); ^{31}P {^1H} NMR ($CDCl_3$, δ): 57.10 (s, PPh_3); ESI-MS (m/z): 719.1 [M- PF_6].

5B.4 Results and discussion

5B.4.1 Arene ruthenium complexes 1, 2 and 3

The dinuclear arene ruthenium complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6) reacts with the N,N'-based ligand (dpt-NH_2) in methanol to afford the mononuclear cationic complexes **1**, **2** and **3** (Scheme **5B.1**). The complexes **1** and **3** are yellow in color while complex **2** is brown in color. These complexes are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethylether and petroleum ether.

The analytical data of these compounds are consistent with the formulations. These complexes give only mononuclear complexes irrespective of the metal-ligand ratio. The complexes are isolated as their hexafluorophosphate salts. The infrared spectra of all these complexes exhibit a chelated N,N'-bidentate ligand as broad bands around 3430 cm^{-1}, 3432 cm^{-1}, 3433 cm^{-1}, 1615 cm^{-1}, 1627 cm^{-1}, 1618 cm^{-1}, 1457 cm^{-1}, 1451 cm^{-1} and 1474 cm^{-1} corresponding to the stretching frequencies of N-H bond of NH_2 group of triazole ring, C=C and C=N bond of the pyridine ring of the ligand respectively. In addition, the infrared spectra contained a strong band at 846 cm^{-1} due to the stretching frequency of P-F bond of PF_6 for these complexes.



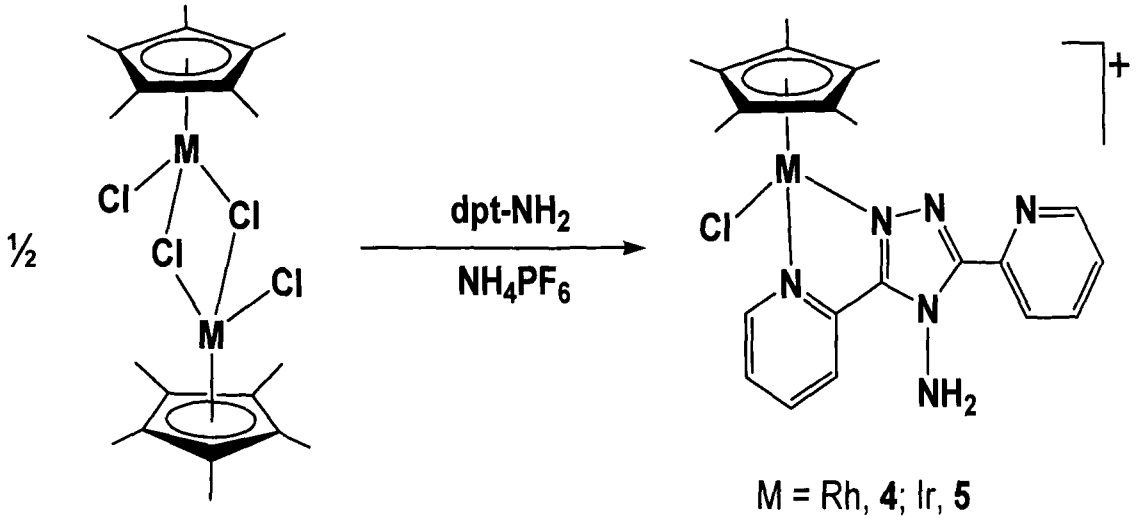
Scheme **5B.1**

The proton NMR spectra of all these complexes show downfield shift as compared to that of the free ligand. In the free ligand, five sets of signals *viz.* two doublets, singlet and two doublet of triplets in the aromatic region at around 7.34-8.66 ppm corresponding to the pyridyl and triazole protons are observed. Whereas in the complexes, it displays a total of nine sets of signals, namely four doublets, four triplets and a singlet as mentioned in the experimental section. Beside these signals complex **2** shows a singlet at 6.20 ppm corresponding to the benzene protons of the complex and complex **3** displays a singlet at 2.1 ppm which corresponds to the hexamethylbenzene protons. Complex **1** exhibits an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group display two doublets at *ca.* 1.24–1.19 ppm, instead of one doublet as

in the starting precursor. The aromatic protons of the *p*-cymene ligand for these complexes also display four doublets at *ca.* 5.98–5.67 ppm, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behaviour of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [34]. In other words we can say that the different signals are entirely due to the chiral nature of the metal [35, 36].

5B.4.2 Pentamethylcyclopentadienyl rhodium and iridium complexes 4 and 5

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with N,N'- bidentate nitrogen base (dpt-NH_2) ligand in methanol at room temperature leading to the formation of chloride displaced complexes **4** and **5**, respectively (Scheme **5B.2**).



Scheme **5B.2**

These complexes were also isolated as their hexafluorophosphate salts. Here also we are able to isolate only the mononuclear complexes. Change in concentration and longer reaction time do not change the reaction pathways. The orange-yellow complexes are air stable, soluble in polar solvents but insoluble in hexane, petroleum ether and diethylether. The infrared spectra of both the complexes exhibit a chelated N,N'-bidentate ligand as broad bands at 3446 cm^{-1}, 3434 cm^{-1}, 1632 cm^{-1}, 1630 cm^{-1} and 1457 cm^{-1} corresponding

to the stretching frequencies of N-H bond of NH_2 group of triazole ring, C=C and C=N bond of the pyridine ring of the ligand respectively. The infrared spectra of these complexes also exhibit a strong band at around 844 cm^{-1} due to the ν_{P-F} stretching frequency of the counter ion of these complexes. In proton NMR spectra of these complexes, the ligand peaks spread over a quite wide range as compared to that of the free ligand. The free ligand exhibits two doublets at around 8.37-8.66 ppm in proton NMR. However, after metallation, these doublets shifted to down field in the range of 9.31-9.65 ppm. Besides the ligand peaks as mentioned in the experimental section, the proton NMR spectra of these compounds also exhibit a singlet at 1.59 ppm for complex **4** and 2.29 ppm for complex **5** respectively, corresponding to the protons of the pentamethylcyclopentadienyl group. The molecular structure of complex **4** was solved by single crystal X-ray crystallography and the structure is presented in Figure **5B.1**.

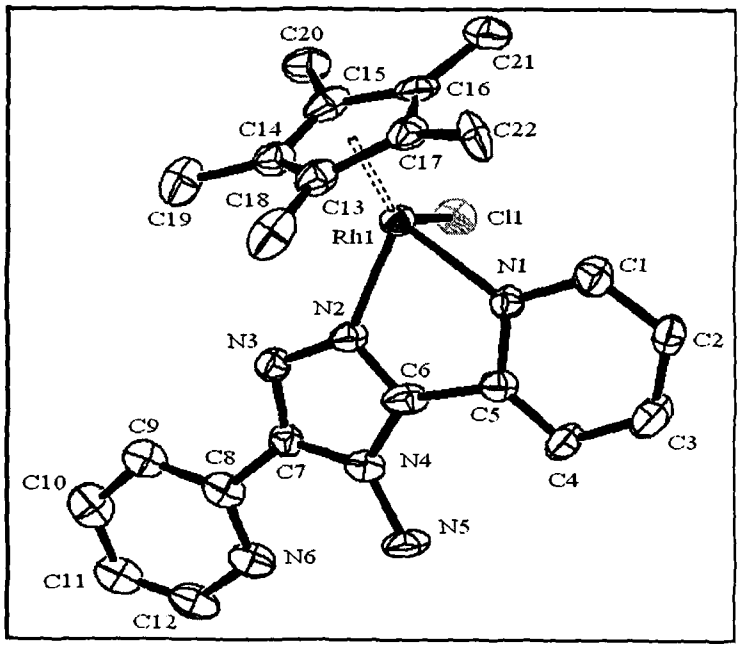


Figure **5B.1**: Molecular structure of a complex **4** with 35 % probability thermal ellipsoids. Hydrogen atoms and PF_6^- are omitted for clarity.

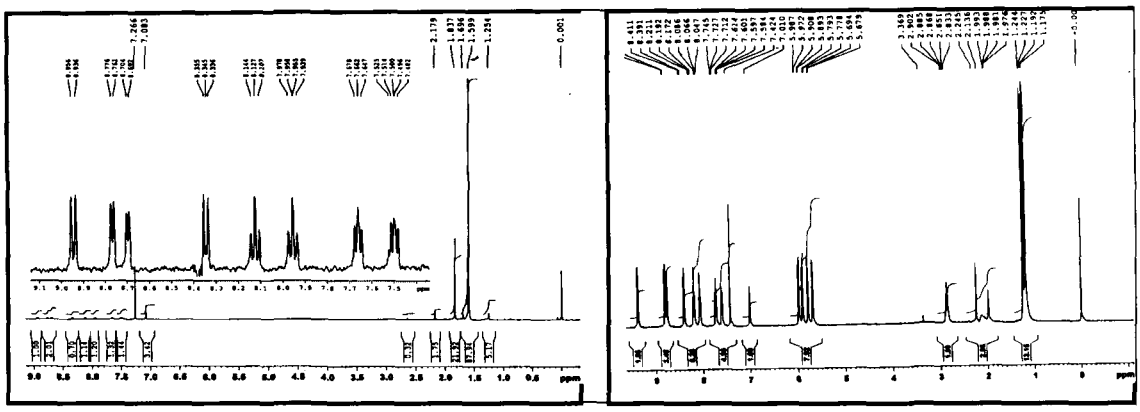


Figure **5B.2**: ^{1}H NMR spectra of complexes **1** and **4**

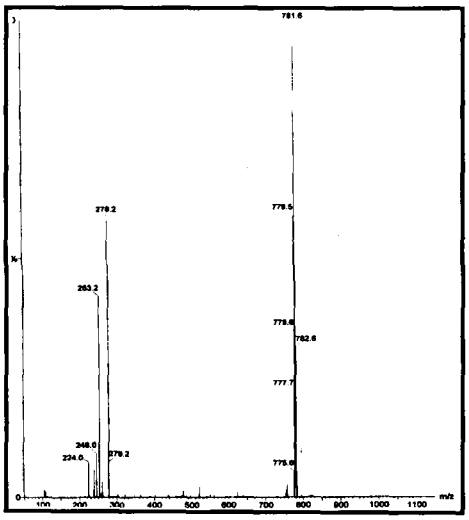


Figure **5B.3:** Mass spectrum of complex **7**

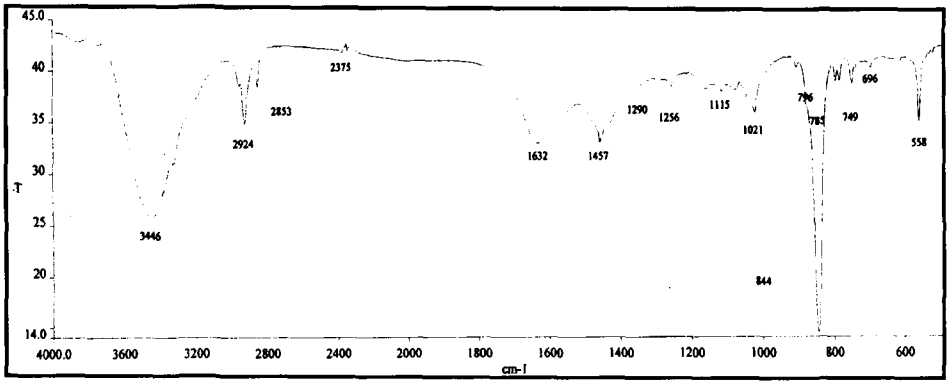
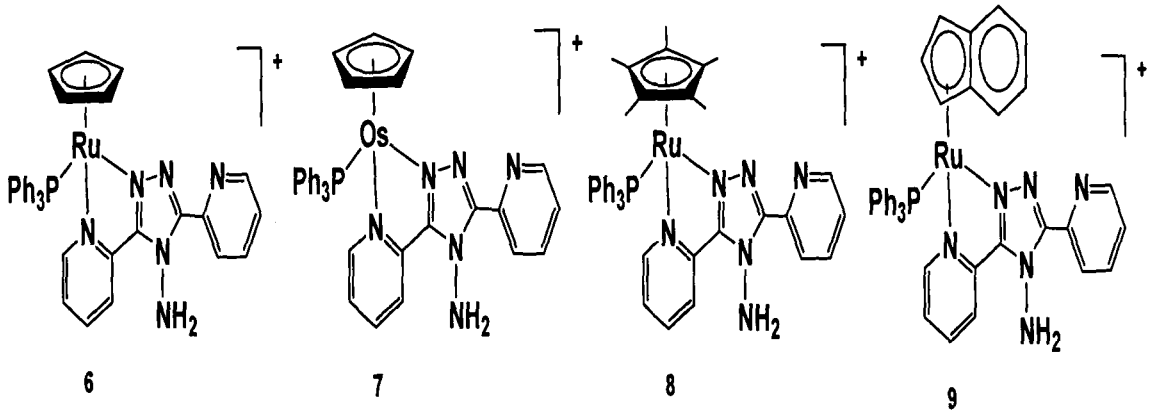


Figure **5B.4**: IR spectrum of complex **4**

5B.4.3 Cyclopentadienyl ruthenium and osmium complexes 6 - 9

The mononuclear cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ and pentamethylcyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ react with dpt-NH_2 in refluxing methanol to give the corresponding mononuclear complexes **6-9** (Chart **5B.1**). Compounds **6-9** are soluble in halogenated solvents and polar organic solvents such as tetrahydrofuran, methanol or dimethylsulfoxide but are insoluble in non-polar solvents. All these complexes are stable in solid state as well as in solution. All complexes were characterized by IR, ^{1}H NMR and mass spectrometry as well as by elemental analysis.



6 7 8 9

Chart 5B.1

The infra red spectra of these complexes exhibit a broad band between 3431 and 3446 cm^{-1} due to the stretching frequency of N-H bond NH_2 group of triazole ring and band between 1599 cm^{-1} and 1630 cm^{-1} and between 1437 and 1451 cm^{-1} corresponding to the stretching frequency of the C=C and C-N bond of the pyridine ring of the ligand. In addition to these all the complexes display a sharp peak at around 843 cm^{-1} due to the stretching frequency of the P-F bond of PF_6 for all the complexes. The protons of complexes **6-9** also show downfield shift with respect to the protons of the free ligand. Beside the aromatic protons of the ligand as mentioned in the experimental section, complexes **6** and **7** show a singlet at 4.91 and 4.59 ppm which correspond to the protons of the cyclopentadienyl ligand, while in the case of complex **8** it displays a singlet at 2.03 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ligand. These complexes also show a multiplet in the range of 6.80-7.38 ppm due to the protons of

the triphenylphosphine group of these complexes. Complex **9** exhibits a characteristic three sets of signals such as multiplet, triplet and doublet, for the protons of the indenyl group. The protons of the triphenylphosphine ligand exhibit a multiplet at 7.10-7.55 ppm. The ^{31}P $\{^{1}H\}$ NMR spectra of the complexes **6**, **7** and **9** exhibit a single sharp resonance for triphenylphosphine around 57.10-49.6 ppm respectively whereas in the starting precursors the signal appear in the up field region. In the case of complex **8** the ^{31}P $\{^{1}H\}$ NMR spectra displays a sharp singlet at -0.26 ppm as compared to the starting complex which shows at -6.29 ppm. The structure of a representative complex **6** was solved by single crystal X-ray diffraction study and is presented in Figure **5B.5**.

The *m/z* values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section, are in good agreement with the theoretically expected values. ESI mass spectra of the complexes also displayed prominent peaks corresponding to the molecular ion fragment. All the halogenated complexes displayed the prominent peak corresponding to the loss of chloride ion from the molecular ion peak, but the loss of arene or Cp or Cp* group is not observed indicating the stronger bond of metal to these groups and remains intact.

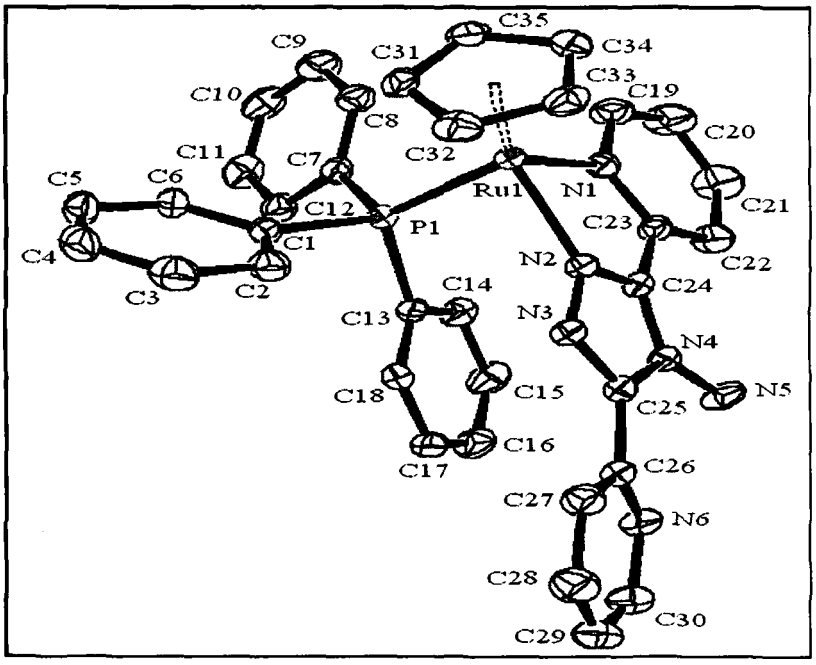


Figure **5B.5**: Molecular structure of complex **6** with 35 % probability thermal ellipsoids. Hydrogen atoms and PF_6^- are omitted for clarity.

5B.5 UV-Vis spectroscopy

UV-Vis spectra of some representative complexes were acquired in acetonitrile and spectral data are summarized in Table **5B.1**. Electronic spectra of these complexes are depicted in Figure **5B.6**. The spectra of these complexes are characterized by two main features, *viz.*, an intense ligand-localized or intra-ligand $\pi \rightarrow \pi^*$ transition in the ultraviolet region and metal to ligand charge transfer (MLCT) $d\pi(M) \rightarrow \pi^*$ (dpt-NH_2 ligand) bands in the visible region. Since the low spin d^6 configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru, Rh, Ir and Os centers, these can interact with low lying π^* orbitals of the ligands. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~ 429-422 and ~ 387-341 nm have been tentatively assigned on the basis of their intensity and position to $\pi \rightarrow \pi^*$ MLCT transitions. The bands on the higher energy side at ~302-220 nm have been assigned to ligand-centered $\pi \rightarrow \pi^*$/ n $\rightarrow \pi^*$ transitions [37, 38]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi \rightarrow \pi^*$ transition for pyrazolylpyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

Table **5B.1**: UV-Vis. absorption data of the representative complexes in acetonitrile at 298K.

Complex	λ_{max}/nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})		
1	235 (0.60)	288 (0.46)	387 (0.05)
2	220 (0.27)	291 (0.21)	352 (0.06)
4	250 (0.20)	302 (0.12)	420 (0.03)
5		294 (0.27)	429 (0.05)
7	244 (0.15)	298 (0.19)	341 (0.11)
8	229 (0.27)	294 (0.16)	
9	228 (0.30)	290 (0.20)	422 (0.09)

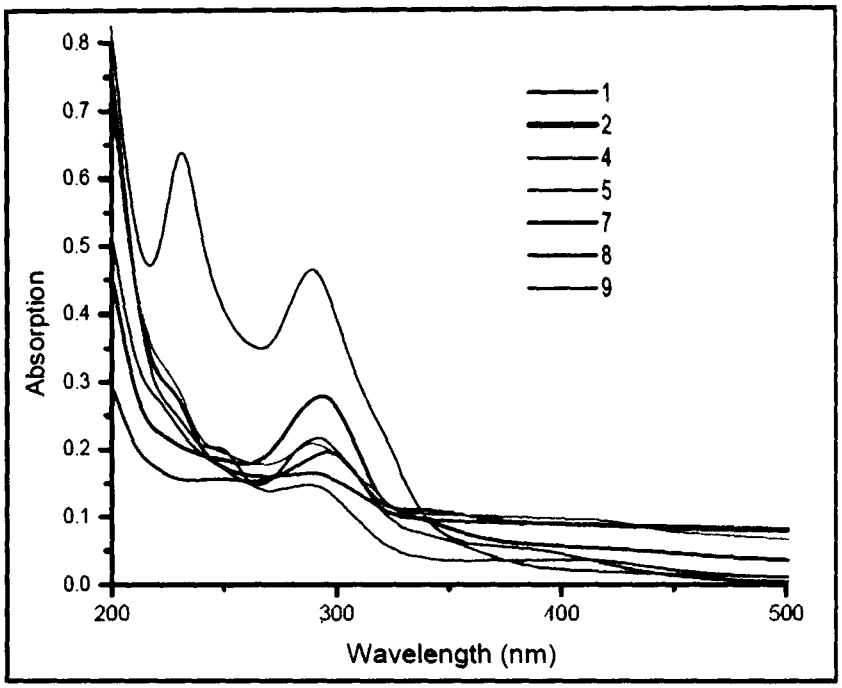


Figure **5B.6:** UV-vis. absorption spectra of mononuclear complexes **1**, **2**, **4**, **5**, **7**, **8** and **9** in acetonitrile at 298 K.

5B.6 Molecular structures

Molecular structures of **4** and **6** have been determined crystallographically. The complexes crystallize in $P\bar{1}$ and $P2_1/n$ space groups. Details about data collection, refinement and structure solution are recorded in Table **5B.2**, and selected bond lengths and angles are presented in Table **5B.3**. Crystal structures of **4** and **6** with atom-numbering schemes are shown in Figure **5B.1** and **5B.5**. In complex **4** the metal is bonded with the major coordinated sites N1 and N2 in a k^2 manner, one chloro group, and the pentamethylcyclopentadienyl (Cp*) ring in a η^5 manner. While in complex **6** the metal is also bonded to N1 and N2 in a k^2 manner, one phosphorus P1 of PPh_3, and the cyclopentadienyl (Cp) ring in a η^5 manner. Typical piano-stool geometry about the metal in complex **4** is maintained. The Cp* ring is planar with an average Rh-C distance of 2.149 Å and the Rh center is displaced by 1.769 Å from the centroid of the Cp* ring, which is comparable to the distances in other rhodium pentamethylcyclopentadienyl complexes. The Rh-N and Rh-Cl bond lengths are consistent with the values reported in the literature. The C-C bond lengths within the Cp* ring and C-Me distances are normal [39-41]. The bond lengths and bond angles observed in the structure **6** are typical of those found in other ruthenium polypyridyl complexes containing triazoles [42]. The Ru-N bond

lengths are in the range of 2.069(2) - 2.125(3) Å. The N-Ru-N angle in these complexes are in the range of 75.49(9)° and 133.52(17)°, which are comparatively less than other ruthenium polypyridyl-triazole complexes [43]. The distance between the ruthenium atom and the centroid of the Cp ring is 1.833 Å and is comparable to those in other reported complexes. The Ru-P distance is around 2.318 Å and N-M-P angle are normal and are in the range of 90.84(7)° - 88.41(6)°. The P-F lengths are consistant with the values reported previously [10].

Table **5B.2**: Crystallographic and structure refinement parameters for complexes **4** and **6**

Compound	**4**	**6**
Emperical formula	$C_{22}H_{25}ClF_6N_6PRh$	$C_{35}H_{30}F_6N_6P_2Ru$
Formula weight	656.81	811.66
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	P2(1)/n
Unit cell dimensions		
a (Å)	8.0012(15)	13.7582(5)
b (Å)	11.487(2)	14.2396(5)
c (Å)	14.975(3)	17.6420(6)
α(°)	73.695(12)	90
β(°)	88.467(14)	102.522(2)
γ(°)	87.830(14)	90
Volume (A^3)	1319.9(4)	3374.1(2)
Z, Calculated density (Mg/m^3)	2, 1.653	4, 1.598
Absorption coefficient (mm^{-1})	0.875	0.629
F(000)	660	1640
Crystal size(mm)	0.35 x 0.24 x 0.14	0.40 x 0.25 x 0.15
Θ range for data collection (deg)	1.42 to 28.17	1.71 to 28.33
Index ranges	-8<=h<=9, -12<=k<=15, 11<=l<=19	-18<=h<=18, -18<=k<=19, -23<=l<=23
Reflections collected / unique	7835/4827	35680/8395
R_{int}	0.1570	0.0261
Final R indices [I>2sigma(I)]	0.0616, wR2 = 0.1797	0.0418, wR2 = 0.1373
R indices (all data)	0.0965, wR2 = 0.2483	0.0546, wR2 = 0.1486
Largest diff. peak and hole ($e.Å^{-3}$)	0.913 and -0.721	0.875 and -0.626
Goodness-of-fit on F^2	0.994	1.088

Table **5B.3**: Selected bond lengths and angles for complexes **4** and **6**

	4	**6**
	Bond distances (Å)	
N(1)-M(1)	2.139(9)	2.125(3)
N(2)-M(1)	2.090(9)	2.069(2)
N(2)-N(3)	1.378(14)	1.373(3)
N(4)-N(5)	1.416(13)	1.402(3)
Cl(1)-M(1)	2.401(4)	
M(1)-CNT(1)	1.769	1.833
	Bond angles (°)	
N(1)-M(1)-N(2)	75.8(4)	75.49(9)
N(3)-N(2)-M(1)	134.0(7)	133.52(17)
N(1)-M(1)-Cl(1)	85.5(3)	
N(2)-M(1)-Cl(1)	88.7(3)	
N(1)-M(1)-P(1)		90.84(7)
N(2)-M(1)-P(1)		88.41(6)

5B.7 Conclusion

In summary, a series of new η^5-and η^6-cyclichydrocarbon platinum metal complexes bearing *dpt-NH_2* ligand, which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. Our attempts to synthesize a dimetallic derivative by addition of a second organometallic anion were unsuccessful. As a continuation of our studies, we have been able to condense the ligand *dpt-NH_2* with an aldehyde to form a corresponding hexadentate ligand and this work is still in progress.

Supplementary material

CCDC- **742500** (**4**) and **742501** (**6**) contain the supplementary crystallographic data for this chapter.

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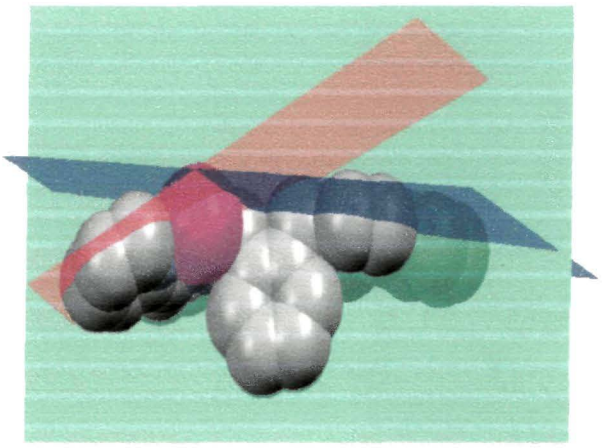
CHAPTER 6

Half sandwich platinum group metal complexes containing tetradentate N-donor ligand bearing two pyrazolyl-pyridine units linked by an aromatic spacer



Half sandwich platinum group metal complexes containing tetradentate *N*-donor ligand bearing two pyrazolyl-pyridine units linked by an aromatic spacer*.

6.1 Abstract

Reaction of the bis-bidentate ligand, 1,3-bis((3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene (*NN*∩*NN*), containing two chelating pyrazolyl-pyridine units connected by an aromatic spacer with platinum group metal complexes results in a series of cationic binuclear complexes, $[(\eta^6\text{-arene})_2Ru_2(NN\cap NN)Cl_2]^{2+}$ (arene = C_6H_6, **1**; *p*-^{i}PrC$_6$H$_4$Me, **2**; C_6Me_6, **3**), $[(\eta^5\text{-}C_5Me_5)_2M_2(NN\cap NN)Cl_2]^{2+}$ (M = Rh, **4**; Ir, **5**), $[(\eta^5\text{-}C_5H_5)_2M_2(NN\cap NN)\text{-}(PPh_3)_2]^{2+}$ (M = Ru, **6**; Os, **7**), $[(\eta^5\text{-}C_5Me_5)_2Ru_2(NN\cap NN)(PPh_3)_2]^{2+}$ (**8**) and $[(\eta^5\text{-}C_9H_7)_2Ru_2\text{-}(NN\cap NN)(PPh_3)_2]^{2+}$ (**9**). All these complexes have been isolated as their hexafluorophosphate salts and fully characterized by use of a combination of NMR spectroscopy, IR spectroscopy and mass spectrometry. The solid state structures of three complexes, [**2**][PF$_6$]$_2$, [**4**][PF$_6$]$_2$ and [**6**][PF$_6$]$_2$, has been determined by X-ray crystallographic studies.

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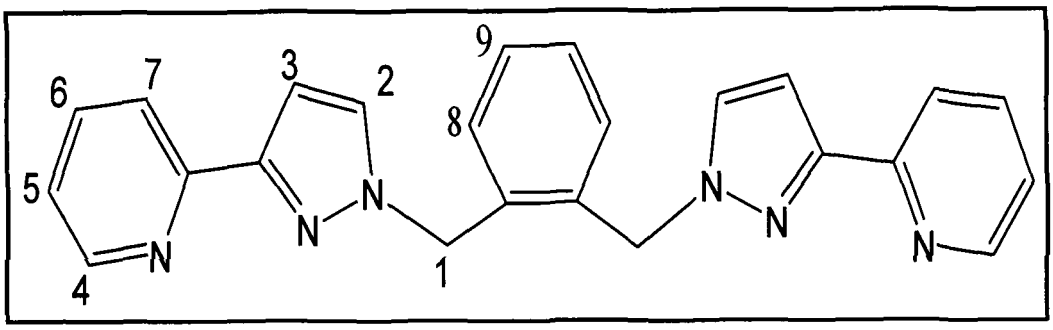
6.2 Introduction

The synthesis of metal complexes with multiple coordination domains is an area of significant current interest in organometallic chemistry. Such complexes have been prepared as part of studies in diverse areas such as inter-metallic communication [1], bioinorganic enzyme active site modeling [2], supramolecular approaches to chiral materials [3] and functional devices [4]. The organometallic chemistry of half-sandwich complexes have been broadly developed in the past few decades, due to their wide range of potential applications as catalyst precursors for hydrogen transfer [5, 6], ring opening metathesis polymerization [7, 8] and olefin oxidation [9]. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity [10, 11]. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic "piano stool" structure offers the possibility to vary the additional donors *via* substitution of halide(s) with a variety of σ-donors ranging from tertiary phosphines [12] to β-diketones [13] to aliphatic as well as aromatic amines [14-16].

We describe in this chapter the coordination chemistry of the tetradentate nitrogen donor ligand, 1,3-bis((3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene (*NN*∩*NN*), in which the two pyrazolyl-pyridine units are connected by an aromatic spacer. Although extensive studies have been carried out in the preparation of polyhedral cages of Cu, Ag, Ni and other metal complexes of pyrazolyl pyridine ligands by varying the spacer units, dinuclear complexes of platinum group metals with *NN*∩*NN* have not yet been investigated. This ligand has the ability to form both mono and dinuclear complexes with metals like Cu [17, 18] and Ag [18], but surprisingly in the case of arene ruthenium and Cp*rhodium and Cp*iridium systems, it only forms dinuclear complexes. Herein, we describe the syntheses of nine dinuclear η^5 and η^6-cyclic π-perimeter hydrocarbon platinum group metal complexes bearing the ligand *NN*∩*NN*. The complexes are characterized by a combination of NMR spectroscopy, IR spectroscopy, mass spectrometry and UV-visible spectroscopy. The solid state structures of three complexes are determined by single crystal X-ray crystallographic studies. The ligand used in this study is given below:



NN∩*NN* tetradentate ligand used in this study

6.3 Experimental

6.3.1 Physical measurements

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The NMR spectra were obtained using Bruker Advance II 400 spectrometer in CD_3CN, $CDCl_3$ and Acetone-d_6 respectively for complexes using TMS as an internal standard. Mass spectra were obtained from a Waters ZQ - 4000 mass spectrometer by the ESI method. All chemicals used were of reagent grade. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. All reactions were carried out in distilled and dried solvents. The ligand *NN*∩*NN* was prepared by following a literature procedure [17]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, *p*-$^iPrC_6H_4Me$ and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [19-23], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [24-28].

6.3.2 Single-crystal X-ray structures analyses

Crystals of **[2]**$(PF_6)_2 \cdot CH_2Cl_2$ were grown from dichloromethane/petroleum ether as small orange plates. Crystals of **[4]**$(PF_6)_2 \cdot H_2O$ and **[6]**$(PF_6)_2 \cdot 0.5\ Et_2O$ were grown by slow diffusion of petroleum ether into a wet acetone solution of the respective complexes as deep red blocks. The crystallizations were done at room temperature. Crystals of complexes **[2]**$(PF_6)_2$, **[4]**$(PF_6)_2$ and **[6]**$(PF_6)_2$ were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (α = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS–97 [29]. Refinement and all further calculations were carried out using SHELXL–97 [29]. 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 **[4]**$(PF_6)_2 \cdot H_2O$ and **[6]**$(PF_6)_2 \cdot 0.5\ Et_2O$ disordered solvent molecules were found and not refined anisotropically, while in **[2]**$(PF_6)_2 \cdot CH_2Cl_2$, the CH_2Cl_2 was well defined and refined anisotropically. Crystallographic details are summarized in Table **6.3**. Figures of the complexes were drawn with ORTEP–3 [30].

6.3.3 *Preparation of [(η^6-arene)$_2$M$_2$(NN∩NN)Cl$_2$](PF$_6$)$_2$ {M = Ru, arene = C$_6$H$_6$ [1](PF$_6$)$_2$, η^6-p-^{i}PrC$_6$H$_4$Me [2](PF$_6$)$_2$, C$_6$Me$_6$ [3](PF$_6$)$_2$, M = Rh, arene = C$_5$Me$_5$ [4](PF$_6$)$_2$ and M = Ir, arene = C$_5$Me$_5$ [5](PF$_6$)$_2$}*

A mixture of $[(\eta^6\text{-arene})M(\mu\text{-Cl})Cl]_2$ (M = Ru, Rh and Ir) (0.10 mmol), *NN∩NN* (40 mg, 0.10 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 hrs at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Compound [1](PF$_6$)$_2$: Yield: 102 mg, 81.7%. Elemental Anal (%) Calc. for $C_{36}H_{32}Cl_2F_{12}N_6P_2Ru_2$: C 38.93; H 2.92; N 7.57; found: C 39.21; H 3.08; N 7.32; IR (KBr pellets, cm^{-1}): 1616 (m), 1442 (s), 843 (s), 771 (s), 558 (s). IR (CsI pellets, cm^{-1}): 274 (s); ^{1}H NMR (400 MHz, CD_3CN): δ = 9.48 (d, 2H), 8.15 (d, J=7.4 Hz, 2H), 7.90 (d, J=8 Hz, 2H), 7.62 (q, 6H), 6.32 (s, 4H, $-CH_2$), 6.253 (s, 12H, C_6H_6), 5.98-5.82(m, 4H); ESI-MS (m/z): 821.5 $[M\text{-}(PF_6)_2]^+$, 863.3 $[M\text{-}(PF_6)_2\text{-}Cl_2]^+$.

Compound [2](PF$_6$)$_2$: Yield: 90 mg, 79.3%. Elemental Anal (%) Calc. for $C_{44}H_{48}Cl_2F_{12}N_6P_2Ru_2$: C 43.22; H 3.95; N 6.89; found: C 43.45; H 4.11; N 6.71. IR (KBr pellets, cm^{-1}): 1616 (m), 1439 (s), 843 (s), 773 (s), 558 (s). IR (CsI pellets, cm^{-1}): 279 (s); ^{1}H NMR (400 MHz, Acetone-d_6): δ = 9.51 (d, J=6 Hz, 2H), 8.57 (d, J=4.4 Hz, 2H), 8.30 (dt, J=4.4 Hz, 2H), 7.97 (d, J=6.4 Hz, 2H), 7.94-7.24 (m, 6H), 6.91 (s, 4H, $-CH_2$), 6.45 (d, J=6 Hz, 2H), 6.16(d, J=5.6 Hz, 2H, $Ar_{p\text{-}cy}$), 6.04 (d, J=6 Hz, 2H, $Ar_{p\text{-}cy}$), 5.89 (d, J=5.2 Hz, 2H, $Ar_{p\text{-}cy}$), 5.71 (d, J=6 Hz, 2H, $Ar_{p\text{-}cy}$), 2.71 (sep, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.05 (dd, J=7.2 Hz, 6H), 0.95 (d, J=7.2 Hz, 6H); ESI-MS (m/z): 933.8 $[M\text{-}(PF_6)_2]^+$, 750.7 $[M\text{-}(PF_6)_2\text{-}Cl_2]^+$.

Compound [3](PF$_6$)$_2$: Yield: 101 mg, 77.4%. Elemental Anal (%) Calc. for $C_{48}H_{56}Cl_2F_{12}N_6P_2Ru_2$: C 45.07; H 4.41; N 6.59; found: C 45.32; H 4.55; N 6.37. IR (KBr pellets, cm^{-1}): 1624 (m), 1384 (s), 847 (s), 775 (s), 561 (s). IR (CsI pellets, cm^{-1}): 288 (s);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (d, J=7.2 Hz, 2H), 8.96 (d, J=8 Hz, 2H), 8.73 (d, J=8 Hz, 2H), 8.42 (q, 6H), 6.11 (s, 4H, -CH_2), 5.78-5.61 (m, 4H), 2.17 (s, 36H, C_6Me_6); ESI-MS (m/z): 990.7 $[M-(PF_6)_2]^+$, 919.4 $[M-(PF_6)_2-Cl_2]^+$.

Compound [4](PF$_6$)$_2$: Yield: 103 mg, 82.1%. Elemental Anal (%) Calc. for $C_{44}H_{50}Cl_2F_{12}N_6P_2Rh_2$: C 43.01; H 4.12; N 6.86; found: C 43.23; H 4.33; N 6.71. IR (KBr pellets, cm^{-1}): 1615 (m), 1444 (s), 845 (s), 770 (s), 558 (s); ^{1}H NMR (400 MHz, Acetone-d_6): δ = 9.04 (d, J=5.6 Hz, 2H), 8.33 (dd, J=6.4 Hz, 4H), 7.96 (d, J=2.8 Hz, 2H), 7.848 (dt, J=4 Hz, 2H), 7.59-7.39 (m, 6H), 5.98 (d, J=14 Hz, 2H, -CH_2), 5.68 (d, J=14.4 Hz, 2H, -CH_2), 1.66 (s, 30H, C_5Me_5); ESI-MS (m/z): 940.3 $[M-(PF_6)_2]^+$, 869.2 $[M-(PF_6)_2-Cl_2]^+$.

Compound [5](PF$_6$)$_2$: Yield: 106 mg, 73.8%. Elemental Anal (%) Calc. for $C_{44}H_{50}Cl_2F_{12}N_6P_2Ir_2$: C 37.55; H 3.59; N 5.99; found: C 37.72; H 3.74; N 5.82. IR (KBr pellets, cm^{-1}): 1617 (m), 1446 (s), 842 (s), 770 (s), 558 (s); ^{1}H NMR (400 MHz, Acetone-d_6): δ = 8.73 (d, J=5.6 Hz, 2H), 8.12 (d, J=7.2 Hz, 4H), 7.66 (q, 4H), 7.520-7.381 (m, 6H), 5.57(s, 4H, -CH_2), 1.56 (s, 30H, C_5Me_5);
ESI-MS (m/z): 1117.7 $[M-(PF_6)_2]^+$, 1047.3 $[M-(PF_6)_2-Cl_2]^+$.

6.3.4 *Preparation of [(η^5-Cp)$_2$M$_2$(NN∩NN)(PPh$_3$)$_2$](PF$_6$)$_2$ {Cp = C$_5$H$_5$, M = Ru [6](PF$_6$)$_2$, Os [7](PF$_6$)$_2$, Cp = C$_5$Me$_5$, M = Ru [8](PF$_6$)$_2$ and Cp = C$_9$H$_7$, M = Ru [9](PF$_6$)$_2$}*

A mixture of [(η^5-Cp)M(PPh_3)$_2$X] {M = Ru, X = Cl and M = Os, X = Br} (0.20 mmol), *NN∩NN* (40 mg, 0.10 mmol) and two equivalents of NH_4PF_6 in dry methanol (30 ml) were refluxed for 12 hrs until the color of the solution changed from pale yellow to orange. The solvent was 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, upon addition of diethylether the orange-yellow complex was precipitated, which was separated and dried under vacuum.

Compound [6](PF$_6$)$_2$: Yield: 103 mg, 65.6%. Elemental Anal (%) Calc. for $C_{70}H_{60}F_{12}N_6P_4Ru_2$: C 54.64; H 3.93; N 5.45; found: C 54.79; H 4.17; N 5.33. IR (KBr pellets, cm^{-1}): 1624 (m), 1437 (s), 842 (s), 776 (s), 558 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ

= 9.00 (d, *J*=5.6 Hz, 2H), 8.62 (d, *J*=4.8 Hz, 2H), 8.56 (d, *J*=4.8 Hz, 2H), 7.96-7.01 (m, 36H, PPh_3 and pyridyl and phenyl), 6.95 (t, *J*=6.4 Hz, 2H), 6.63 (d, *J*=2.8 Hz, 2H), 5.49 (s, 4H, $-CH_2$), 4.66 (s, 10H, C_5H_5); ESI-MS (m/z): 1248.4 $[M-(PF_6)_2]^+$; ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 50.82 (s, PPh_3).

Compound [7](PF$_6$)$_2$: Yield: 109 mg, 62.2%. Elemental Anal (%) Calc. for $C_{70}H_{60}F_{12}N_6P_4Os_2$: C 48.97; H 3.53; N 4.89; found: C 49.18; H 3.75; N 4.71. IR (KBr pellets, cm^{-1}): 1615 (m), 1444 (s), 845 (s), 773 (s), 554 (s); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 9.31 (d, *J*=6.4 Hz, 2H), 8.69 (d, *J*=6.2 Hz, 2H), 8.55 (d, *J*=4.8 Hz, 2H), 7.83-7.11 (m, 36H, PPh_3 and pyridyl and phenyl), 7.10 (t, *J*=7.2 Hz, 2H), 6.72 (d, *J*=2.8 Hz, 2H), 5.55 (s, 4H, $-CH_2$), 4.59 (s, 10H, C_5H_5); ESI-MS (m/z): 1428.3 $[M-(PF_6)_2]^+$; ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): -0.26 (s, PPh_3).

Compound [8](PF$_6$)$_2$: Yield: 111 mg, 63.3%. Elemental Anal (%) Calc. for $C_{80}H_{80}F_{12}N_6P_4Ru_2$: C 57.24; H 4.80; N 5.01; found: C 57.45; H 4.98; N 4.79. IR (KBr pellets, cm^{-1}): 1617 (m), 1444 (s), 847 (s), 770 (s), 558 (s); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 8.65 (d, *J*=7.6 Hz, 2H), 8.34 (d, *J*=8 Hz, 2H), 8.27 (d, *J*=7.2 Hz, 2H), 7.21-7.09 (m, 36H, PPh_3 and pyridyl and phenyl), 7.84 (t, *J*=6.4 Hz, 2H), 6.64 (d, *J*=7.6 Hz, 2H), 5.75 (s, 4H, $-CH_2$), 2.03 (s, 30H, C_5Me_5). ESI-MS (m/z): 1390.6 $[M-(PF_6)_2]^+$.
^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 49.6 (s, PPh_3).

Compound [9](PF$_6$)$_2$: Yield: 107 mg, 64%. Elemental Anal (%) Calc. for $C_{78}H_{64}F_{12}N_6P_4Ru_2$: C 57.17; H 3.94; N 5.14; found: C 57.39; H 4.10; N 5.03. IR (KBr pellets, cm^{-1}): 1615 (m), 1442 (s), 842 (s), 773 (s), 558 (s); ^1H NMR (400 MHz, $CDCl_3$): *δ* = 9.22 (d, *J*=5.6 Hz, 2H), 8.75 (d, *J*=8 Hz, 2H), 8.67 (d, *J*=4.4 Hz, 2H), 8.23 (t, *J*=7.6 Hz, 2H), 7.55-7.10 (m, 48H), 6.82 (d, *J*=6.4 Hz, 2H), 5.53 (s, 4H, $-CH_2$), 4.97 (d, *J*=8 Hz, 2H), 4.85 (d, *J*=7.6 Hz, 2H), 4.43 (t, *J*=2.4 Hz, 2H). ESI-MS (m/z): 1349.7 $[M-(PF_6)_2]$.
^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 57.10 (s, PPh_3). ESI-MS (m/z): 719.1 $[M-PF_6]^+$.

6.4 Results and discussion

6.4.1 Dinuclear arene ruthenium, rhodium and iridium complexes 1–5

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ react with the *NN*∩*NN* tetradentate pyrazolyl-pyridine ligand in methanol to afford the cationic dinuclear

complexes $[(\eta^6\text{-arene})_2Ru_2(NN\cap NN)Cl_2]^{2+}$ (arene = C_6H_6, **1**; *p*-^{i}PrC_6H_4Me, **2**; C_6Me_6, **3**), isolated as their hexafluorophosphate salts (Scheme **6.1**). Compounds **[2]**$[PF_6]_2$ and **[3]**$[PF_6]_2$ are yellow in color, while **[1]**$[PF_6]_2$ is brown. These salts are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethylether and petroleum ether. All compounds are characterized by ^{1}H NMR spectroscopy, IR spectroscopy and mass spectrometry. In the mass spectra, they show the expected molecular ion peaks *m/z* at 821.5, 933.8 and 990.7, corresponding to compounds $[(\eta^6\text{-arene})_2Ru_2(NN\cap NN)Cl_2]^{2+}$ (arene = C_6H_6, **1**; *p*-^{i}PrC_6H_4Me, **2**; C_6Me_6, **3**). All these halogenated complexes also displayed prominent peaks corresponding to the loss of both chloride ions from the molecular ion peak $[M\text{-}(PF_6)_2]^+$, but the loss of arene group is not observed indicating the stronger bond of metal to arene group. The IR spectra of these complexes exhibit a sharp bands due to chelated *NN*∩*NN* tetradentate ligand in between 1616 and 1400 cm^{-1} corresponding to the different stretching frequencies of C=C and C=N bond of these complexes as mentioned in the experimental section. In the proton NMR spectra of **1–3**, the ligand peaks spread to the downfield region as compared to that of the free ligand. The free ligand exhibits two doublets at around δ 7.94-8.62 ppm for protons H4 and H7. However, after metallation, these doublets are shifted downfield in the range δ 8.15-9.51 ppm. In addition to the other ligand peaks as mentioned in the experimental section, the ^{1}H NMR spectrum of complex **2** exhibit four doublets in the range of δ 6.16-5.71 ppm corresponding to the aromatic *p*-cymene ring of the CH protons. It also exhibits a singlet at δ 2.26 ppm, a pair of doublets at δ 0.95 and δ 1.05 ppm and a septet at δ 2.71 ppm for the protons of the methyl and isopropyl groups of the *p*-cymene ligands. However in the case of **1**, the proton NMR spectrum displays a singlet at δ 6.25 ppm which corresponds to the protons of the benzene groups of the complex. The proton NMR spectrum of complex **3** exhibits a strong peak at δ 2.17 ppm for the hexamethylbenzene ligand, which is slightly shifted downfield in comparison to the starting complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$. The molecular structure of representative complex **2** is solved by single crystal X-ray diffraction study (Figure **6.2**).

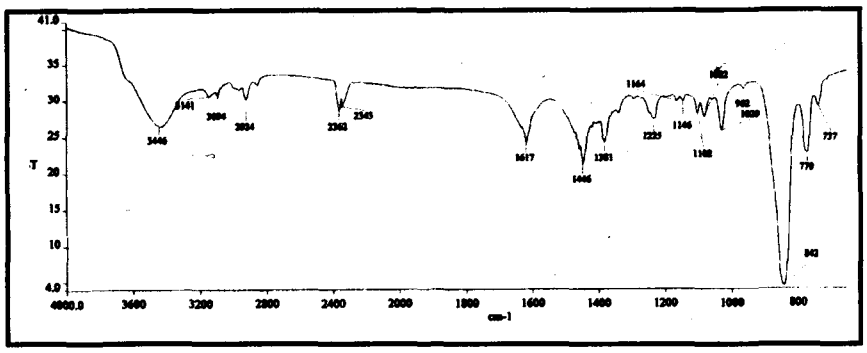


Figure **6.1**: IR spectrum of complex **5**

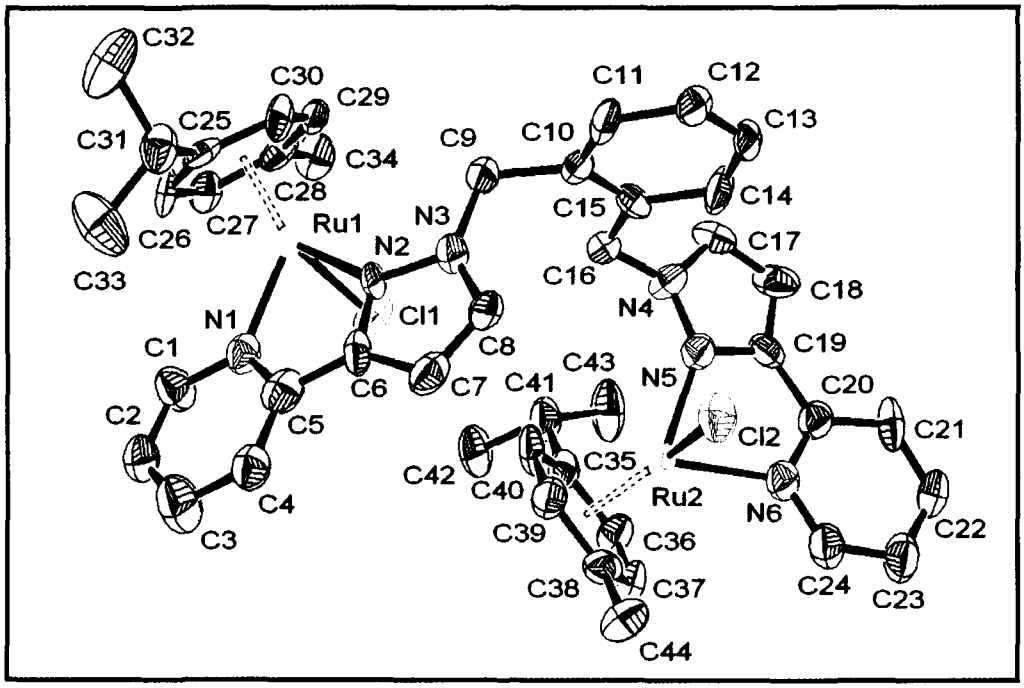
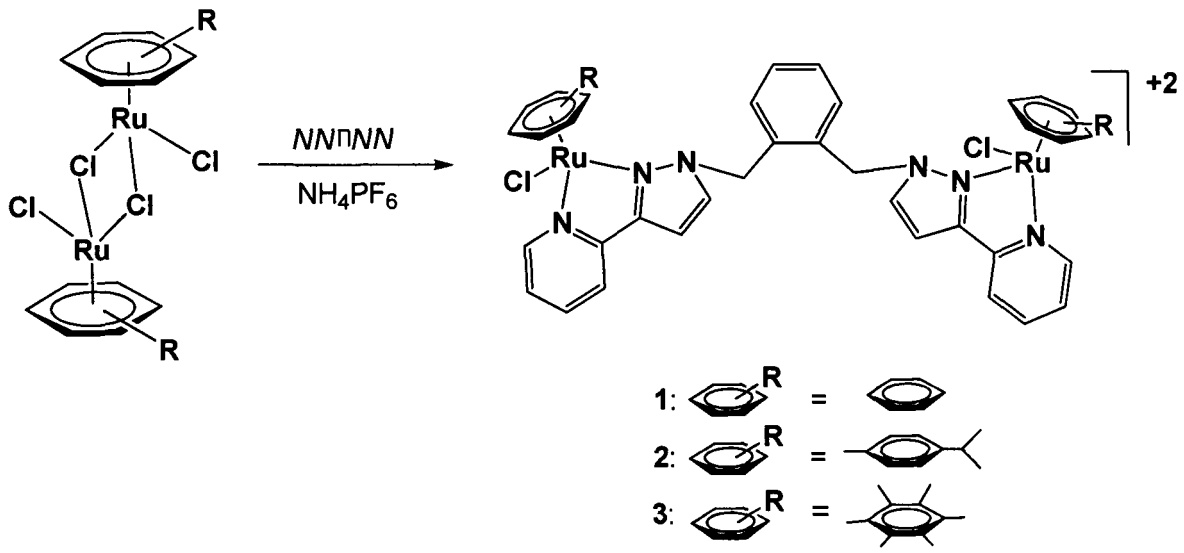


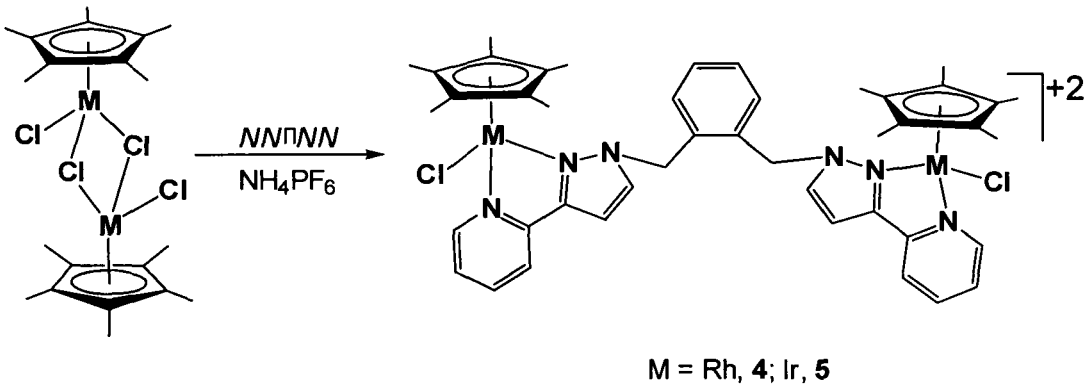
Figure **6.2:** Molecular structure of **[2]**(PF_6) · CH_2Cl_2 at 35% probability level. Hydrogen atoms, dichloromethane molecule and hexafluorophosphate anions have been omitted for clarity.



Scheme **6.1**

The reaction of the dimeric chloro complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) with one equivalent of tetradentate ligand *NN∩NN* in methanol results in the formation of the yellow colored, air stable dicationic dinuclear complexes $[(\eta^5\text{-}C_5Me_5)_2Rh_2(NN\cap NN)Cl_2]^{2+}$ (**4**) and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(NN\cap NN)Cl_2]^{2+}$ (**5**) which are isolated as their hexafluorophosphate salts (Scheme **6.2**). Complexes **4** and **5** are characterized by ^{1}H NMR spectroscopy, IR spectroscopy and mass spectroscopy. The infrared spectra of both the complexes exhibit a sharp bands due to bis-chelating *NN∩NN* ligand in between 1624 and 1400 cm^{-1} corresponding to the stretching frequencies of C=C and C=N bond of these complexes. The ^{1}H NMR spectra of these complexes show ligand peaks a downfield shift in the position of signals associated with protons of ligand *NN∩NN* compared to that of the uncoordinated ligand suggesting coordination of the nitrogen atoms to the metal center in a bidentate fashion. In the ^{1}H NMR spectra of complexes **1** to **3** and **5** to **9** exhibit a singlet in the range of δ 6.91 and δ 5.49 ppm corresponding to the CH_2 protons of the ligand, but surprisingly, in compound **4** (Figure **6.3**) these two CH_2 protons are diastereotopic and give rise to two doublets at approximately δ 5.9 ppm and δ 5.7 ppm for the four protons with a geminal coupling constant of 14 Hz. Besides this, the ^{1}H NMR spectra of these complexes display a singlet at around δ 1.66 and δ 1.56 ppm corresponding to the protons of the pentamethylcyclopentadienyl groups. The *m/z* values

of all these complexes and their stable ion peaks obtained from the ESI mass spectra, as listed in the experimental section, which are in good agreement with the theoretically expected values. ESI mass spectra of the complexes also displayed prominent peaks corresponding to the molecular ion fragment. These halogenated complexes displayed the prominent peak corresponding to the loss of chloride ion from the molecular ion peak, but the loss of Cp* group is not observed indicating the stronger bond of metal to this group and remains intact. The molecular structure of representative compound **4** is solved by single crystal X-ray diffraction study (Figure **6.4**).



M = Rh, **4**; Ir, **5**

Scheme **6.2**

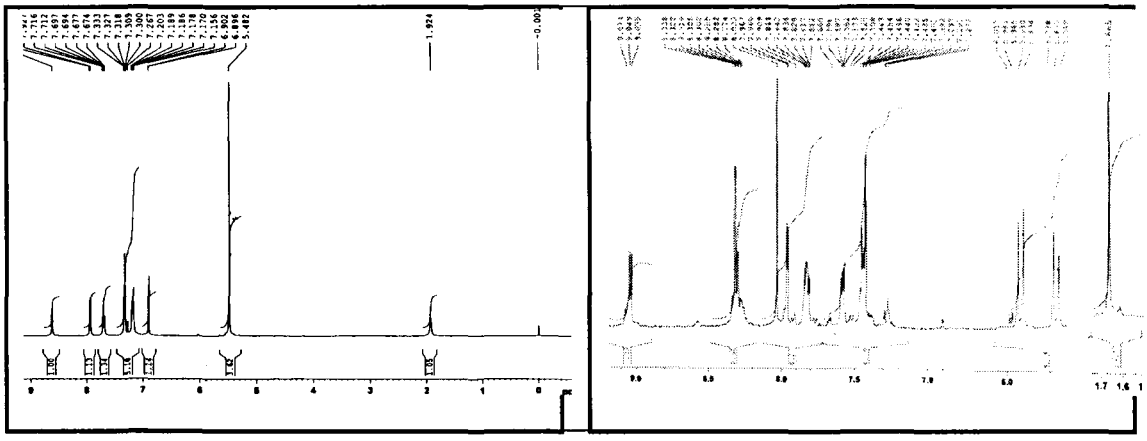


Figure **6.3**: ^{1}H NMR spectra of ligand *(NNNNN)* and complex **4**

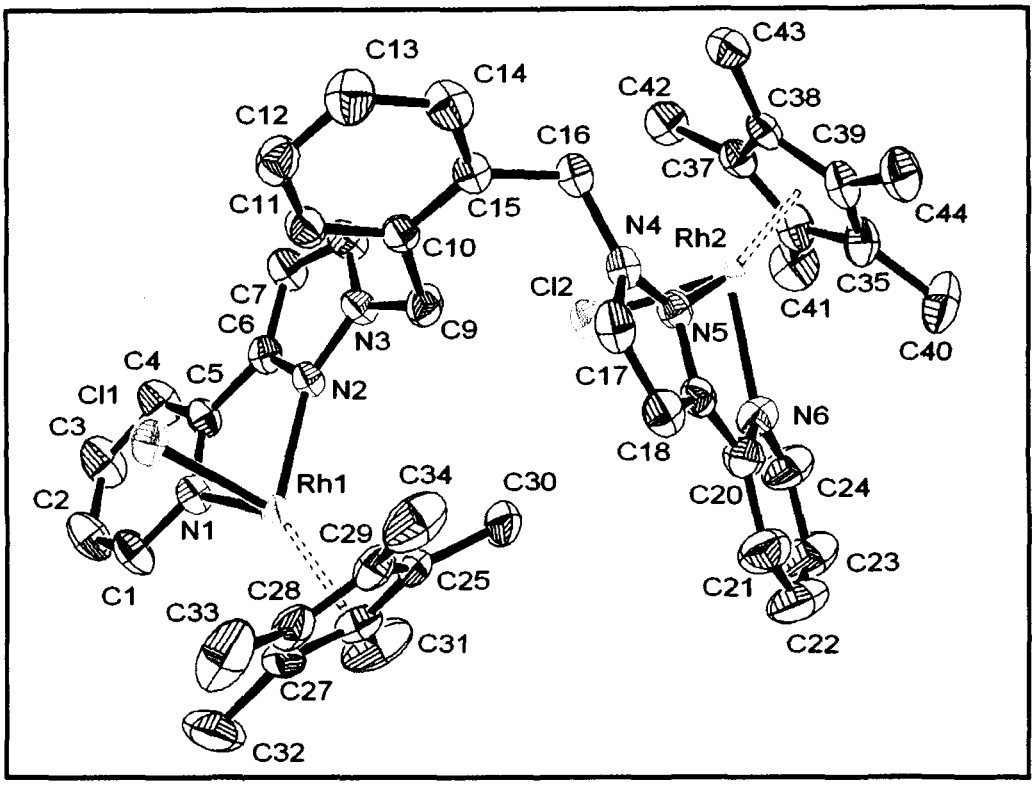
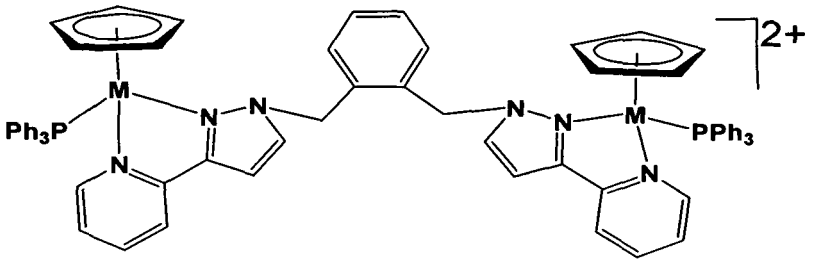


Figure **6.4:** Molecular structure of [**4**](PF_6) · 2 H_2O at 35% probability level. Hydrogen atoms, water molecules and hexafluorophosphate anions have been omitted for clarity.

6.4.2 Dinuclear cyclopentadienyl ruthenium and osmium complexes 6–9

Two equivalents of mononuclear cyclopentadienyl complexes [(Cp)M(PPh_3)$_2$Cl] (M = Ru, Os; Cp = η^5-C_5H_5, η^5-C_9H_7, η^5-C_5Me_5) react with tetradentate ligand *NN*∩*NN* in refluxing methanol to give the corresponding dinuclear complexes **6-9** which are isolated as their hexafluorophosphate salts (Chart **6.1**) The cationic complexes **6-9** are soluble in halogenated solvents and polar organic solvents such as tetrahydrofuran, methanol or dimethylsulfoxide but are insoluble in non-polar solvents. All these complexes are stable in solid state as well as in solution. All complexes were characterized by IR spectroscopy, ^{1}H NMR spectroscopy, ^{31}P {^{1}H} NMR spectroscopy and mass spectrometry. The analytical data of these compounds are consistent with the formulations. Besides the IR bands as mentioned in the experimental section, these complexes also display a strong band between δ 842 and δ 847 cm^{-1} due to the $\nu_{P\text{-}F}$ stretching frequency of the counter ion of these complexes. The ^{1}H and ^{31}P {^{1}H} NMR spectra of complexes were recorded in $CDCl_3$ and spectral data are summarized in the experimental section. Shift in the position

of signals associated with protons of ligand *NN∩NN*, suggested coordination of nitrogen atom to the metal centre ruthenium and osmium in bi-dentate fashion. The protons of the ligand in these complexes **6-9** show downfield shift with respect to the protons of the uncoordinated ligand. The ^{1}H NMR spectrum of the uncoordinated ligand displays two doublets at δ 8.62 and δ 7.94 ppm for protons H4 and H7, whereas in the case of the metal complexes this doublet shifts to the downfield region between δ 9.31 and δ 8.34 ppm. In addition to the aromatic protons mentioned in the experimental section, complexes **6** and **7** shows a singlet at δ 4.66 and δ 4.59 ppm which corresponds to the protons of the cyclopentadienyl ligand, while in the case of complex **8** it displays a singlet at δ 2.03 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ligand. These complexes also show multiplets in the range of δ 6.8-7.4 ppm due to the protons of the coordinated triphenylphosphine ligands. Complex **9** exhibits three sets of signals, triplet at around δ 4.43 ppm, doublets at δ 4.97 ppm and δ 4.85 ppm corresponding to the protons of the indenyl group. The protons of the triphenylphosphine ligands exhibit a large multiplet centered at δ 7.32 ppm. In the ^{31}P $\{^{1}H\}$ NMR spectra of the complexes **6**, **8** and **9**, the ^{31}P nuclei of the coordinated PPh_3 resonated as a sharp singlet in the range of δ 57.1-49.6 ppm respectively whereas in the starting precursors the signal appears in the upfield region. In the case of complex **7** the ^{31}P $\{^{1}H\}$ NMR spectrum displays a sharp singlet at δ -0.26 ppm as compared to the starting complex which is found at δ -6.29 ppm. The *m/z* values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section and are in good agreement with the theoretically expected values. ESI mass spectra of the complexes also displayed prominent peaks corresponding to the molecular ion fragment. The structure of representative compound **6** was solved by single crystal X-ray diffraction study and is presented in Figure **6.5**.



M = Ru, **6**; Os, **7**

8: = M = Ru

9: = M = Ru

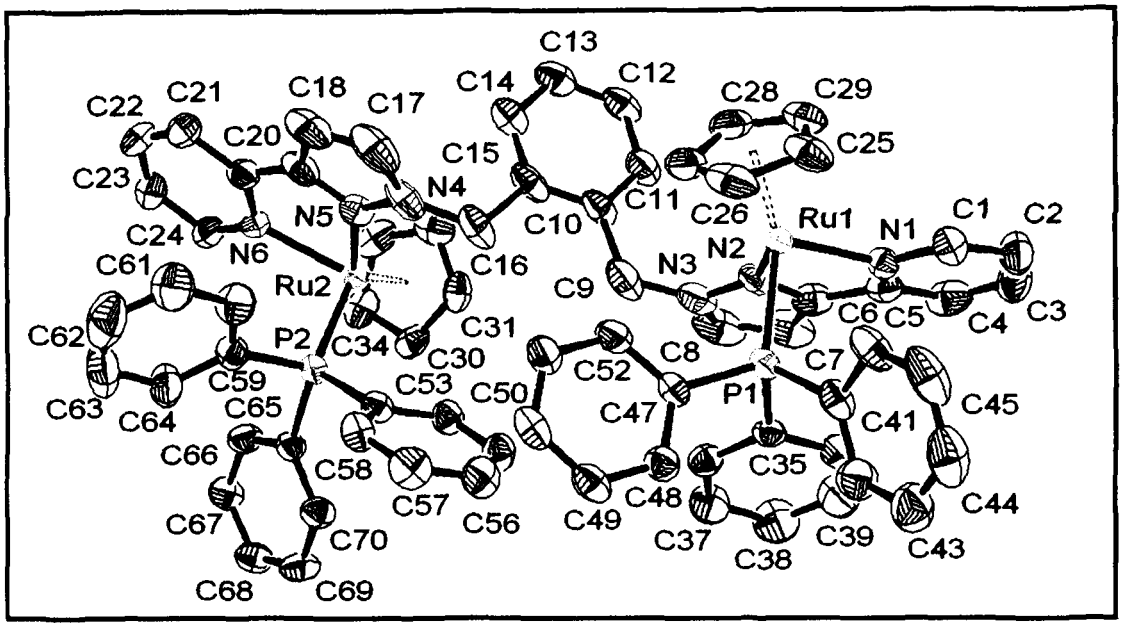


Figure **6.5:** Molecular structure of [**6**](PF_6) · 0.5 Et_2O at 35% probability level. Hydrogen atoms, diethyl ether molecule and hexafluorophosphate anions have been omitted for clarity.

6.5 Molecular structures

The molecular structures of compounds [**2**]$(PF_6)_2$, [**4**]$(PF_6)_2$ and [**6**]$(PF_6)_2$ are shown in Figures **6.2**, **6.4** and **6.5** respectively, and selected bond lengths and angles are presented in Table **6.1**. Complexes **2**, **4** and **6** contain two chiral Ru(II) or Rh(III) metal centers bonded to a η^6-*p*-^{i}PrC$_6$H$_4$Me or η^5-C_5H_5 and η^5-C_5Me_5 ligands, respectively, which are bridged by the *NN*∩*NN* ligand through four nitrogen atoms. Therefore, two five-membered metallacycles are formed upon coordination of *NN*∩*NN* to the half-sandwich platinum group metals, with a N-M-N bite angle ranging from 74.4(4) to 76.1(4)°. Despite the presence of two chiral centers in **2**, **4** and **6**, only racemic mixtures were obtained, and all compounds crystallize in centrosymmetric space groups.

In the dinuclear complexes **2** and **4**, the two metal centers are more than 7 Å apart, while in **6** the Ru-Ru separation is more than 9 Å. This difference is probably due to the presence of the sterically demanding triphenylphosphine ligands in **6** as compared to the small chlorido ligands in **2** and **4**. The angles observed between the two planes formed by

the coordinated pyridine-pyrazolyl units are 47.5(2)° in **2**, 74.7(1)° in **4** and 29.6(1)° in **6**, thus suggesting a great flexibility of the *NN*∩*NN* chelating ligand. Indeed, as emphasized in Figure **6.6**, the angles found between the least-square plane of the central -CH_2-Ph-CH_2- group and the pyridine-pyrazolyl planes are all comprised between 77.0(1)° and 89.5(1)°.

The presence of solvent molecules and of hexafluorophosphate anions in the crystal packing of **[2]**$(PF_6)_2 \cdot CH_2Cl_2$, **[4]**$(PF_6)_2 \cdot 2\ H_2O$ and **[6]**$(PF_6)_2 \cdot 0.5\ Et_2O$ gives rise to multiple hydrogen bonds and short contacts which are all showing of standard distances and angles.

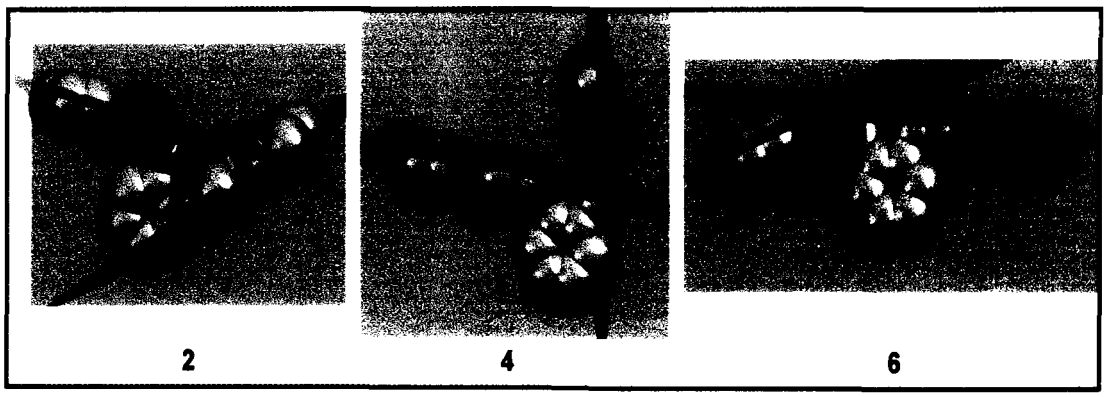


Figure **6.6:** Space filling views of the *NN*∩*NN*-M_2 moieties in **2**, **4** and **6**, and colored representations of the planes formed by the central phenyl (green) and the two pyridine-pyrazolyl units (red and blue) to emphasize the structural flexibility of the *NN*∩*NN* ligand.

Table 6.1: Selected bond lengths (Å) and angles (°) for **[2]**$(PF_6)_2 \cdot CH_2Cl_2$, **[4]**$(PF_6)_2 \cdot 2$ H_2O and **[6]**$(PF_6)_2 \cdot 0.5$ Et_2O

	[2]$(PF_6)_2$		**[4]**$(PF_6)_2$		**[6]**$(PF_6)_2$	
	Ru1	Ru2	Rh1	Rh2	Ru1	Ru2
Distances (Å)						
M-N_{pyr}	2.099(11)	2.152(9)	2.134(3)	2.124(4)	2.110(3)	2.099(3)
M-N_{prz}	2.120(9)	2.074(11)	2.124(3)	2.143(3)	2.094(3)	2.125(2)
M-Cl	2.386(3)	2.412(3)	2.384(1)	2.398(1)		
M-P					2.3413(9)	2.3172(9)
M-M	7.195(1)		7.4794(6)		9.0293(4)	
Angles (°)						
N_{pyr}-M-N_{prz}	74.4(4)	76.1(4)	75.78(13)	75.48(14)	75.29(11)	75.30(11)
N_{pyr}-M-Cl	86.7(3)	87.2(3)	86.93(10)	87.81(11)		
N_{prz}-M-Cl	83.6(3)	85.4(3)	87.39(10)	89.81(9)		
N_{pyr}-M-P					92.07(8)	92.98(8)
N_{prz}-M-P					88.61(8)	89.01(9)

6.6 UV-visible spectroscopy

UV-visible spectra of the complexes **1** to **6** and **8** were acquired in acetonitrile and spectral data are summarized in Table **6.2**. Electronic spectra of representative complexes are depicted in Figure **6.7**. The low spin d^6 configuration of these dinuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centers which can interact with the low lying π^* orbital of the ligands. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) $t_{2g} \rightarrow \pi^*$ transition in their electronic spectra [31-36]. The electronic spectra of these complexes display a medium intensity band in the UV-visible region. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~ 420–408 and ~ 395–345 nm have been tentatively assigned on the basis of their intensity and position to $t_{2g} \rightarrow \pi^*$ MLCT transitions. The bands on the high energy side at ~ 300–235 nm for the complexes **1** to **6** and **8**, have been assigned to ligand-centered $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions [37, 38]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi \rightarrow \pi^*$ transition for pyrazolyl pyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

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Table **6.2:** UV-vis absorption data in acetonitrile at 298 K

Complex	λ_{max}/nm ($\varepsilon/10^{-4}M^{-1}cm^{-1}$)		
1	250(0.97)	300(0.92)	420(0.11)
2	258(0.78)	285(0.63)	408(0.04)
3	255(0.83)	280(0.69)	410(0.05)
4	235(0.77)	291(0.33)	395(0.07)
5	253(0.52)	297(0.58)	345(0.12)
6	252(0.35)	283(0.28)	380 (0.07)
8	253 (0.58)	282(0.43)	382(0.08)

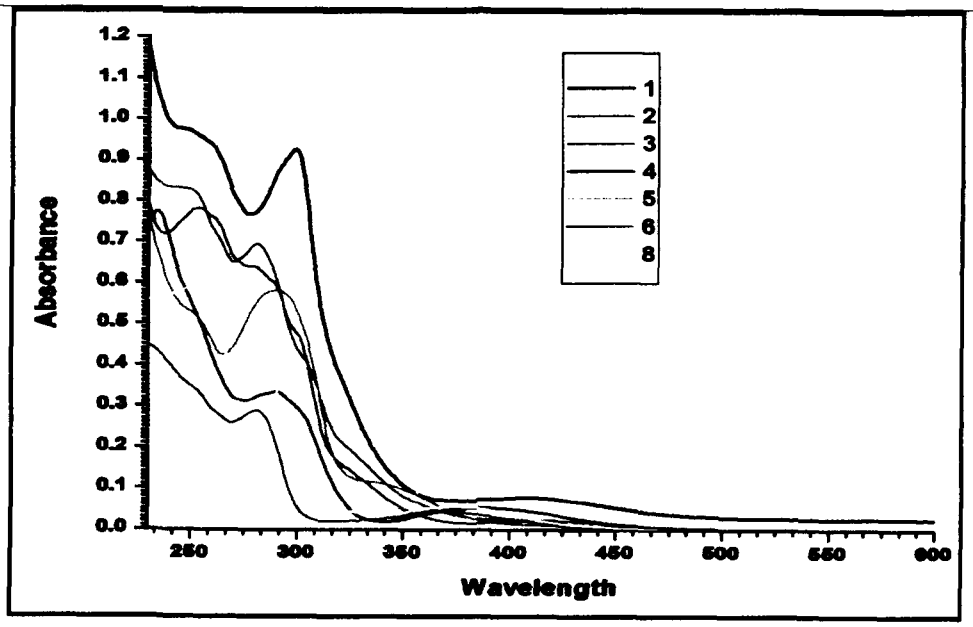

Figure **6.7:** UV-vis. absorption spectra of mononuclear complexes **1** to **6** and **8** in acetonitrile at 298 K.

Table **6.3:** Crystallographic and structure refinement parameters for complexes **[2]**$(PF_6)_2 \cdot CH_2Cl_2$, **[4]**$(PF_6)_2 \cdot 2\ H_2O$ and **[6]**$(PF_6)_2 \cdot 0.5\ Et_2O$

	[2]$(PF_6)_2$	**[4]**$(PF_6)_2$	**[6]**$(PF_6)_2$
Chemical formula	$C_{45}H_{50}Cl_4F_{12}N_6P_2Ru_2$	$C_{44}H_{54}Cl_2F_{12}N_6O_2P_2Rh_2$	$C_{71}H_{62.5}F_{12}N_6O_{0.5}P_4Ru_2$
Formula weight	1308.79	1265.59	1561.79
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P* $2_1/c$ (no. 14)	*P* $2_1/n$ (no. 14)	*P* $2_1/c$ (no. 14)
Crystal color and shape	orange block	red block	red block
Crystal size	0.24 x 0.18 x 0.16	0.28 x 0.23 x 0.18	0.33 x0.23x 0.20
a (Å)	23.4756(11)	14.0140(12)	14.0334(3)
b (Å)	12.2948(7)	13.1382(7)	17.2822(5)
c (Å)	18.9077(11)	29.572(2)	28.2555(6)
β (°)	110.810(6)	100.209(9)	96.182(2)
V ($Å^3$)	5101.3(5)	5358.6(7)	6812.9(3)
Z	4	4	4
T (K)	173(2)	173(2)	173(2)
D_c ($g.cm^{-3}$)	1.704	1.569	1.523
μ (mm^{-1})	0.948	0.858	0.618
Scan range (°)	$2.04 < \theta < 26.06$	$2.09 < \theta < 26.04$	$1.87 < \theta < 29.20$
Unique reflections	10043	10516	18392
Reflections used [$I>2\sigma(I)$]	2509	7081	9707
R_{int}	0.2202	0.0465	0.0865
Final R indices [$I>2\sigma(I)$]*	0.0563, wR_2 0.0860	0.0467, wR_2 0.1170	0.0415, wR_2 0.0829,
R indices (all data)	0.2315, wR_2 0.1268	0.0711, wR_2 0.1252	0.1037, wR_2 0.0957
Goodness-of-fit	0.617	0.897	0.805
Max, Min $\Delta\rho$/e ($Å^{-3}$)	0.559, -1.000	0.968, -0.739	1.251, -0.491

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

6.7 Conclusions

In summary, a series of new dinuclear η^5-and η^6-cyclic π-perimeter hydrocarbon metal complexes bearing ligand *NN∩NN*, which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. All these complexes have been fully characterized by a combination of NMR, IR, UV-vis spectroscopy and mass spectrometry. The ligand has ability to form both mononuclear and dinuclear complexes by variation of metal ligand ratio, however arene ruthenium and Cp*Rh and Cp*Ir reactions yielded dinuclear complexes only.

Supplementary material

CCDC- **753325** [**2**]$(PF_6)_2 \cdot CH_2Cl_2$, **753326** [**4**]$(PF_6)_2 \cdot 2\ H_2O$ and **753327** [**6**]$(PF_6)_2 \cdot 0.5\ Et_2O$ contain the supplementary crystallographic data for this chapter.

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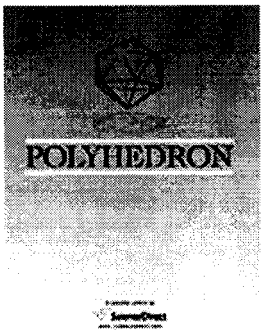
B.Sc	*Chemistry (Honours)*	*Don Bosco College, Tura, NEHU*	*2000 to 2003*	*First*



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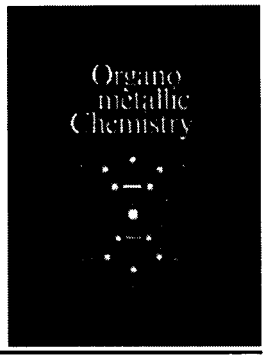

List of publications

1) Study of novel η^5-cyclopentadienyl and η^6 –arene platinum group metal complexes containing N_4-type ligand and their structural characterization.
Gajendra Gupta**, Glenn P. A. Yap, Bruno Therrien and Kollipara Mohan Rao* ***Polyhedron, 28 (2009) 844-850.

2) Ruthenium half-sandwich complexes with tautomerized pyrazolyl pyridazine ligands: Synthesis, spectroscopic and molecular structural studies.
Gajendra Gupta**, Kota Thirumala Prasad, Babulal Das, Glenn P. A. Yap and Kollipara Mohan Rao,* ***Journal of Organometallic Chemistry 694 (2009) 2618-2627.

3) New series of platinum group metal complexes bearing η^5- and η^6- cyclichydrocarbons and Schiff base derived from 2-acetylthiazole:Syntheses and structural studies.
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4) Novel mononuclear η^5-pentamethyl-cyclopentadienyl complexes of platinum group metals bearing pyrazolylpyridazine ligands: Syntheses and spectral studies
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5) Study of half–sandwich platinum group metal complexes bearing *dpt-NH_2* ligand.
Gajendra Gupta**, Kota Thirumala Prasad, Babulal Das and Kollipara Mohan Rao,* ***Polyhedron 29 (2010) 904-910.

6) Spectral, structural and DFT studies of platinum group metal 3,6-bis(2-pyridyl)-4-phenylpyridazine complexes and their ligand bonding modes.
Kota Thirumala Prasad, ***Gajendra Gupta****, A.K. Chandra, M. Phani Pavan, Kollipara Mohan Rao,* ***Journal of Organometallic Chemistry*** 695 (2010) 707–716.

7) Mononuclear complexes of platinum group metals containing η^6 and η^5 – cyclic Π-perimeter hydrocarbons and pyridylpyrazolyl derivatives: syntheses and structural studies.
Gajendra Gupta*, Chong Zheng, Peng Wang and Kollipara Mohan Rao,* ***Z. Anorg. Allg. Chem*** (in press, 2010).

8) Half sandwich platinum group metal complexes containing tetradentate *N*-donor ligand bearing two pyrazolyl-pyridine units linked by an aromatic spacer.
Gajendra Gupta *Bruno Therrien and Kollipara Mohan Rao,* ***Journal of Organometallic Chemistry*** 695 (2010) 753-759.

9) Neutral pentacoordinated diorganotin(IV) complexes derived from *ortho*-aminophenol Schiff bases: Synthesis, characterization and molecular Structures.
Smita Basu, ***Gajendra Gupta*** *Babulal Das, Kollipara Mohan Rao. (communicated to* ***Journal of Organometallic Chemistry****, 2010).*

10) Mononuclear complexes of platinum group metals bearing pyrazolyl pyridazine substituted ligands. Syntheses and molecular studies.
Gajendra Gupta*, Sairem Gloria, Babulal Das and Kollipara Mohan Rao (Manuscript under Preparation, 2010).*

11) Bridged and terminal chloro complexes of Ruthenium bearing tetradentate Schiff's base.
Gajendra Gupta*, Sairem Gloria, Bruno Therrien and Kollipara Mohan Rao (Manuscript under Preparation, 2010).*

12) Mono and dinuclear complexes of η^5 and η^6 – cyclic Π-perimeter hydrocarbons containing dipyridyl amine substituted ligand. Syntheses and characterization.
Gajendra Gupta*, Babulal Das and Kollipara Mohan Rao (Manuscript under Preparation, 2010).*

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Study of novel η^5-cyclopentadienyl and η^6-arene platinum group metal complexes containing a N_4-type ligand and their structural characterization

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ABSTRACT

The mononuclear η^5-cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ and pentamethylcyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ react in the presence of 1 eq. of the tetradentate *N,N'*-chelating ligand 3,5-bis(2-pyridyl)pyrazole (bpp-H) and 1 eq. of NH_4PF_6 in methanol to afford the mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ (**[1]**PF_6), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(bpp\text{-}H)]PF_6$ (**[2]**PF_6) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ (**[3]**PF_6), respectively. The dinuclear η^5-pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ as well as the dinuclear η^6-arene ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ react with 2 eq. of bpp-H in the presence of NH_4PF_6 or NH_4BF_4 to afford the corresponding mononuclear complexes $[(\eta^5\text{-}C_5Me_5)Rh(bpp\text{-}H)Cl]PF_6$ (**[4]**PF_6), $[(\eta^5\text{-}C_5Me_5)Ir(bpp\text{-}H)Cl]PF_6$ (**[5]**PF_6), $[(\eta^6\text{-}C_6H_6)Ru(bpp\text{-}H)Cl]BF_4$ (**[6]**BF_4) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(bpp\text{-}H)Cl]BF_4$ (**[7]**BF_4). However, in the presence of 1 eq. of bpp-H and NH_4BF_4 the reaction with the same η^6-arene ruthenium complexes affords the dinuclear salts $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]BF_4$ (**[8]**BF_4) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)_2Ru_2(bpp)Cl_2]BF_4$ (**[9]**BF_4), respectively. These compounds have been characterized by IR, NMR and mass spectrometry, as well as by elemental analysis. The molecular structures of **[1]**PF_6, **[5]**PF_6 and **[8]**BF_4 have been established by single crystal X-ray diffraction studies and some representative complexes have been studied by UV–vis spectroscopy.

1. Introduction

Within the large family of η^5- and η^6-cyclichydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. They have found applications in catalysis, supramolecular assemblies and molecular devices, and have shown antiviral, antibiotic and anticancer activities. These three-legged piano-stool complexes possess a pseudo-octahedral geometry at the metal center, the arene ligand occupying three coordinating sites (the seat) with three other ligands (the legs). Therefore, the octahedral geometry can be viewed as pseudo-tetrahedral, thus limiting the number of possible isomers.

Transition metal complexes containing polypyridyl ligands are associated with interesting photochemical and electrochemical properties [1–8], and they are used as catalysts [9,10], multi-electron storage systems [11–13], in the design of new materials [14–17] and as molecular devices [18–22]. Complexes with these ligands are also potential DNA intercalators with an ability to inhibit nucleic acid synthesis [23]. Recently, metal polypyridyl complexes have been widely used as building blocks [24–27]. The occurrence of isomers by the synthetic assembly of mononuclear building blocks is a major problem in the design of supramolecular systems.

Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses, and therefore, have attracted lot of attention [28–31]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [32]. Many studies of cyclopentadienyl and arene ruthenium(II) complexes with bidentate ligands have shown that substitution reactions occur predominantly with retention of the configuration at the metal center [33]. A few studies have been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with polypyridyl ligands [34]. The reactivity of ruthenium(II), osmium(II), rhodium(III) and iridium(III) with various polypyridyl ligands has been reported [35–37].

In this paper, we report a series of η^5-cyclopentadienyl ruthenium, osmium, η^5-pentamethylcyclopentadienyl ruthenium, rhodium and iridium and η^6-arene ruthenium complexes with a tetradentate *N,N'*-donor ligand, *viz.* 3,5-bis(2-pyridyl)pyrazole (bpp-H) (see below). The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ruthenium metal complexes are associated with being an extremely interesting water oxidation catalyst [38,39]. This ligand can act as

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Mononuclear Complexes of Platinum Group Metals Containing η^6 and η^5-Cyclic Π-Perimeter Hydrocarbon and Pyridylpyrazolyl Derivatives: Syntheses and Structural Studies

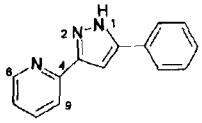
Gajendra Gupta,[a] Chong Zheng,[b] Peng Wang,[c] and Kollipara Mohan Rao*[a]

Keywords: Phenylpyrazolylpyridines; Ruthenium; Rhodium; Iridium; Osmium

Abstract. Piano-stool-shaped platinum group metal compounds, stable in the solid state and in solution, which are based on 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) with the formulas $[(\eta^6\text{-arene})Ru(L)Cl]PF_6$ {arene = C_6H_6 (**1**), *p*-cymene (**2**), and C_6Me_6, (**3**)}, $[(\eta^6\text{-}C_5Me_5)M(L)Cl]PF_6$ {*M* = Rh (**4**), Ir (**5**)}, and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(L)]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)]PF_6$ (**8**), and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(L)]PF_6$ (**9**) were prepared by a general method and characterized by NMR and IR spectroscopy and mass spectrometry. The molecular structures of compounds **4** and **5** were established by single-crystal X-ray diffraction. In each compound the metal is connected to N1 and N11 in a k^2 manner.

1. Introduction

Mononuclear compounds of platinum group metals containing nitrogen based ligands received considerable attention because of their photochemical properties [1–9], their catalytic activities [10–19], and their electrochemical behavior [20–26], as well as in the development of new biological active agents [27–33]. In particular, η^6-arene metal complexes emerged as versatile intermediates in organic synthesis; they contain three labile coordination sites, whereas another three coordination sites are occupied by a rigid arene ring [34, 35]. They have found application in catalysis, supramolecular assemblies, and in molecular devices. Additionally, η^6-arene metal complexes showed antiviral, antibiotic, and anticancer activities. Half-sandwich complexes attracted attention because they proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses [36–39]. The tetracoordinate, pseudo-tetrahedral arrangement makes them particularly suitable for investigation of the stereochemistry of reactions at the metal atom [40]. In recent years, we carried out reactions of η^5- and η^6- cyclic Π-perimeter hydrocarbon metal complexes with a variety of nitrogen-based ligands [41–48] including various polypyridyl ligands. Ruthenium compounds with these types of ligands have the capacity to function as catalysts for the oxidation of water to dioxygen [49, 50]. Although extensive studies were carried out on η^5- and η^6-transition metal complexes; compounds containing phenylpyrazolylpyridine ligands of the type shown below have not been investigated yet.



2-(5-phenyl-1H-pyrazol-3-yl)-pyridine (L)

Herein we describe the syntheses of nine mononuclear η^5- and η^6-cyclic Π-perimeter hydrocarbon platinum group metal compounds bearing the ligand phenylpyrazolylpyridine. Our main goal in choosing this phenyl-substituted ligand was to synthesize a series of mononuclear and dinuclear compounds by activating the carbon atom of the phenyl ring. But attempts to prepare a dimetallic derivative through the addition of a second organometallic anion by activation of the carbon atom were unsuccessful and we ended up with a series of mononuclear compounds only with metal bound to two nitrogen atoms (N1 and N11) of the ligand. All these compounds were fully characterized by IR and NMR spectroscopy, and mass spectrometry. Molecular structures of the two representative compounds are also presented in this paper.

2. Experimental Section

All solvents were dried and distilled prior to use. The ligand **L** was synthesized by following a literature method [51]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (*M* = Rh, Ir) [52–55], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$, and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [56–61]. NMR spectra were recorded with a Bruker AMX 400 MHz spectrometer.

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Ruthenium half-sandwich complexes with tautomerized pyrazolyl-pyridazine ligands: Synthesis, spectroscopic and molecular structural studies

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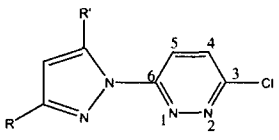
ABSTRACT

Condensation of 1,4-dichloropyridazine with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole yielded two types of pyrazolyl-pyridazine ligands, *viz.*, (i) products of substitution on one side of the pyridazine as 3-chloro-6-(pyrazolyl)pyridazine (Cl-L1), 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (Cl-L2) and 3-chloro-6-(3-methylpyrazolyl)pyridazine (Cl-L3), and (ii) products of substitution on both sides such as 3,6-bis(pyrazolyl)pyridazine (L1), 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (L2) and *tautomers* of 3,6-bis(3-methylpyrazolyl)pyridazine (L3). The reactions of η^6-areneruthenium complexes in methanol with the above mentioned pyrazolyl-pyridazine ligands form mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(Cl\text{-}L)(Cl)]^+$ and $[(\eta^6\text{-arene})Ru(L)(Cl)]^+$; (arene = benzene and *p*-cymene; Cl-L = Cl-L1, Cl-L2, Cl-L3; L = L1, L2, L3). All these complexes are characterized by IR, NMR, mass spectrometry and UV–vis spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

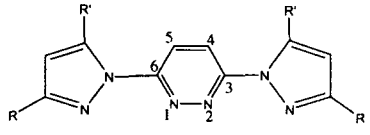
1. Introduction

Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 40 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. Coordination of a metal fragment to an arene ring dramatically facilitates electrophilic aromatic addition and substitution, arene deprotonation, and benzylic deprotonation. Arene metal complexes have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis and Diels–Alder cycloaddition [3–6]. In recent years, we have been carrying out reactions of arene ruthenium dimers with a variety of nitrogen-based ligands [7–12] including pyridyl-pyridazine and pyrazolyl-pyradazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [13,14]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing annular tautomerized pyrazolyl-pyradazine ligands have not yet been investigated.

Herein, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methylpyrazole moiety [15]; the existence of both tautomers in a single compound is reported here. The syntheses of 12 mononuclear arene ruthenium complexes incorporating these as well as some other pyrazolyl-pyridazine ligands are also reported. Given below are the structures of the ligands used in this study. All these complexes are characterized by IR, NMR, mass spectrometry and UV–vis spectroscopy. The molecular structures of the ligand (L3) and four representative complexes are also presented in this paper.



R=R'=H, Cl-L1 (3-chloro-6-(pyrazolyl)pyridazine)
R=R'=CH_3, Cl-L2 (3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, Cl-L3 (3-chloro-6-(3-methylpyrazolyl)pyridazine)



R=R'=H, L1 (3,6-Bis(pyrazolyl)pyridazine)
R=R'=CH_3, L2 (3,6-Bis(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, L3 (3,6-Bis(3-methylpyrazolyl)pyridazine)

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Half sandwich platinum group metal complexes containing tetradentate *N*-donor ligand bearing two pyrazolyl-pyridine units linked by an aromatic spacer

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ABSTRACT

Reaction of the bis-bidentate ligand, 1,3-bis((3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene (*NN*∩*NN*), containing two chelating pyrazolyl-pyridine units connected by an aromatic spacer with platinum group metal complexes results in a series of cationic binuclear complexes, $[(\eta^6\text{-arene})_2Ru_2(NN\cap NN)Cl_2]^{2+}$ (arene = C_6H_6, **1**; *p*-^{i}PrC$_6$H$_4$Me, **2**; C_6Me_6, **3**), $[(\eta^5\text{-}C_5Me_5)_2M_2(NN\cap NN)Cl_2]^{2+}$ (M = Rh, **4**; Ir, **5**), $[(\eta^5\text{-}C_5H_5)_2M_2(NN\cap NN)(PPh_3)_2]^{2+}$ (M = Ru, **6**; Os, **7**), $[(\eta^5\text{-}C_5Me_5)_2Ru_2(NN\cap NN)(PPh_3)_2]^{2+}$ (**8**) and $[(\eta^5\text{-}C_9H_7)_2Ru_2(NN\cap NN)(PPh_3)_2]^{2+}$ (**9**). All these complexes have been isolated as their hexafluorophosphate salts and fully characterized by use of a combination of NMR spectroscopy, IR spectroscopy and mass spectrometry. The solid state structures of three complexes, **[2]**$[PF_6]_2$, **[4]**$[PF_6]_2$ and **[6]**$[PF_6]_2$, has been determined by X-ray crystallographic studies.

1. Introduction

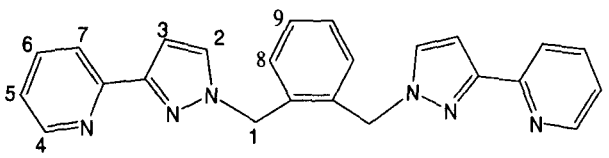
The synthesis of metal complexes with multiple coordination domains is an area of significant current interest in organometallic chemistry. Such complexes have been prepared as part of studies in diverse areas such as inter-metallic communication [1], bioinorganic enzyme active site modeling [2], supramolecular approaches to chiral materials [3] and functional devices [4]. The organometallic chemistry of half-sandwich complexes have been broadly developed in the past few decades, due to their wide range of potential applications as catalyst precursors for hydrogen transfer [5,6], ring opening metathesis polymerization [7,8] and olefin oxidation [9]. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity [10,11]. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic "piano stool" structure offers the possibility to vary the additional donors *via* substitution of halide(s) with a variety of σ-donors ranging from tertiary phosphines [12] to β-diketones [13] to aliphatic as well as aromatic amines [14–16].

We describe in this paper the coordination chemistry of the tetradentate nitrogen donor ligand, 1,3-bis((3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene (*NN*∩*NN*), in which the two pyrazolyl-pyridine units are connected by an aromatic spacer. Although extensive studies have been carried out in the preparation of polyhedral cages of Cu, Ag, Ni and other metal complexes of pyrazolyl-pyridine ligands by varying the spacer units, dinuclear complexes of platinum group metals with *NN*∩*NN* have not yet been investigated. This ligand has the ability to form both mono and dinuclear complexes with metals like Cu [17,18] and Ag [18], but surprisingly in the case of arene ruthenium and Cp*rhodium and Cp*iridium systems, it only forms dinuclear complexes. Herein, we describe the syntheses of nine dinuclear η^5 and η^6-cyclic π-perimeter hydrocarbon platinum group metal complexes bearing the ligand *NN*∩*NN*. The complexes are characterized by a combination of NMR spectroscopy, IR spectroscopy, mass spectrometry and UV–Vis spectroscopy. The solid state structures of three complexes are determined by single crystal X-ray crystallographic studies. The ligand used in this study is in Scheme 1.

2. Results and discussion

2.1. Dinuclear arene ruthenium, rhodium and iridium complexes 1–5

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ react with the *NN*∩*NN* tetradentate pyrazolyl-pyridine ligand in



Scheme 1. *NN*∩*NN* tetradentate ligand used in this study.

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Study of half-sandwich platinum group metal complexes bearing dpt-NH_2 ligand

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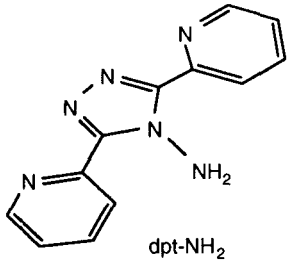
ABSTRACT

A quite general approach for the preparation of η^5-and η^6-cyclichydrocarbon platinum group metal complexes is reported. The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6) and η^5-pentamethylcyclopentadienyl rhodium and iridium complexes $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) react with 2 equiv. of 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) in presence of NH_4PF_6 to afford the corresponding mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(\text{dpt-}NH_2)Cl]PF_6$ {arene = $C_{10}H_{14}$ (**1**), C_6H_6 (**2**) and C_6Me_6 (**3**)} and $[(\eta^6\text{-}C_5Me_5)M(\text{dpt-}NH_2)Cl]PF_6$ {M = Rh (**4**), Ir (**5**)}. However, the mononuclear η^5-cyclopentadienyl analogues such as $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ complexes react in presence of 1 equiv. of dpt-NH_2 and 1 equiv. of NH_4PF_6 in methanol yielded mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**8**) and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**9**), respectively. These compounds have been totally characterized by IR, NMR and mass spectrometry. The molecular structures of **4** and **6** have been established by single crystal X-ray diffraction and some of the representative complexes have also been studied by UV–Vis spectroscopy.

1. Introduction

Within the large family of η^5- and η^6-cyclichydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 50 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer activities. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted more attention [3–6]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [7]. In recent years we have been carrying out reactions of η^5- and η^6-cyclichydrocarbon metal complexes with a variety of nitrogen-based ligands [8–15] including various poly-pyridyl ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [16,17]. Although comprehensive studies have been made on η^5- and η^6-transition metal complexes, complexes containing NH_2 substituted poly-pyridyl ligand of this type shown below have not yet been reported.



dpt-NH_2

Ligand used in this study

Herein we describe the syntheses of nine mononuclear η^5- and η^6-cyclichydrocarbon platinum group metal complexes bearing dpt-NH_2 ligand. Attempts to prepare dimetallic derivatives by addition of a second organometallic anion were unsuccessful. All these complexes have been fully characterized by IR, NMR, mass spectrometry and UV–Vis spectroscopy. Molecular structures of the two representative complexes are also presented in this paper.

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Spectral, structural and DFT studies of platinum group metal 3,6-bis(2-pyridyl)-4-phenylpyridazine complexes and their ligand bonding modes

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ABSTRACT

Reactions of 3,6-bis(2-pyridyl)-4-phenylpyridazine (L^{ph}) with $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$ and C_6Me_6), $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$, (M = Rh and Ir) and $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (Cp = C_5H_5, C_5Me_5 and C_9H_7) afford mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(L^{ph})Cl]PF_6$, $[(\eta^5\text{-}C_5Me_5)M(L^{ph})Cl]PF_6$ and $[(Cp)Ru(L^{ph})(PPh_3)]PF_6$ with different structural motifs depending on the π-acidity of the ligand, electronic properties of the central metal atom and nature of the co-ligands. Complexes $[(\eta^6\text{-}C_6H_6)Ru(L^{ph})Cl]PF_6$ **1**, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(L^{ph})Cl]PF_6$ **2**, $[(\eta^5\text{-}C_5Me_5)Ir(L^{ph})Cl]PF_6$ **5**, $[(\eta^5\text{-Cp})Ru(PPh_3)(L^{ph})]PF_6$, (Cp = C_5H_5, **6**; C_5Me_5, **7**; C_9H_7, **8**) show the *type-A* binding mode (see text), while complexes $[(\eta^6\text{-}C_6Me_6)Ru(L^{ph})Cl]PF_6$ **3** and $[(\eta^5\text{-}C_5Me_5)Rh(L^{ph})Cl]PF_6$ **4** show the *type-B* binding mode (see text). These differences reflect the more electron-rich character of the $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-Cl})Cl]_2$ and $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-Cl})Cl]_2$ complexes compared to the other starting precursor complexes. Binding modes of the ligand L^{ph} are determined by ^1H NMR spectroscopy, single-crystal X-ray analysis as well as evidence obtained from the solid-state structures and corroborated by density functional theory calculations. From the systems studied here, it is concluded that the electron density on the central metal atom of these complexes plays an important role in deciding the ligand binding sites.

1. Introduction

Polypyridyl complexes of platinum group metals are being continuously investigated because of their multiple applications in fields of science including photophysics and photochemistry [1–6], supramolecular chemistry [7], catalysis [8–13] and bioinorganic chemistry [14–19]. The organometallic complexes of η^6-arene ruthenium [20,21] and η^5-half-sandwich complexes of rhodium and iridium have attracted considerable current interest as potential anticancer agents (Dyson et al.) [14–19,22,23]. Another important aspect, especially from the catalytic prospective, is the design of Ru=O functional groups and analogues capable of reversibly accepting multiple electrons and protons within a relatively small potential range [24–26]. This capacity to modify the environment in order to induce electronic as well as steric effects gives scope for the design and fabrication of tailored catalysts for specific reactions.

The properties of metal complexes largely depend on how the nature of the bridging ligand mediates metal–metal interactions. This role of bridging ligands is strongly influenced by factors such as the acceptor and donor properties of coordination sites, the length and rigidity of the spacers, the presence or absence of conjugated bonds, the orientation of substituents and the scope for manipulating ligand charge. In this regard, bridging polypyridyl ligands (*viz.* 2,2′-bipyrimidine (bpym), 2,3-bis(2-pyridyl)pyrazine (bppz), 3,5-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), 3,6-bis(2-pyridyl)pyridazine (bppn), and 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligands) have received much attention [27–33]. The wider family of such ligands with 4- or 4,5-substituted pyridazine moieties (*viz.*, 3,6-bis(2-pyridyl)-4-phenylpyridazine (L^{ph}) (Fig. 1) has been relatively less studied. More recently, Constable and co-workers published a few reports on silver(I) complexes [34–37] incorporating such ligands.

Symmetrical 3,5-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) and to a lesser extent 3,6-bis(2-pyridyl)pyridazine (bppn) frequently bind *via* any two of the four nitrogen atoms present (N1 and N2 or N3 and N4) on the pyridine and tetrazine/pyridazine moieties, employing a bidentate κ^2 bonding mode to coordinate with d^6 metal centers [38,39]. A phenyl substituent introduces a element of asymmetry in the 3,6-bis(2-pyridyl)pyridazine (L) ligand moiety, as shown by the 3,6-bis(2-pyridyl)-4-phenylpyridazine (L^{ph}) ligand. This can bind to a metal *via* atoms N1 and N2 (*type-A*) or atoms N3 and N4 (*type-B*) (see Fig. 2) in a bidentate κ^2 bonding mode. The ligand is a four electron donor since the phenyl substituent creates differences in the electronic environment on the two available binding sites. Apart from the above two possibilities (*type-A* or *type-B*) (Fig. 2), a combination of the two types

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New series of platinum group metal complexes bearing η^5- and η^6-cyclichydrocarbons and Schiff base derived from 2-acetylthiazole: Syntheses and structural studies

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ABSTRACT

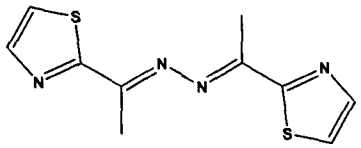
The mononuclear complexes $[(\eta^6\text{-arene})Ru(ata)Cl]PF_6$ (*ata* = 2-acetylthiazole azine; arene = C_6H_6 [(**1**)PF_6]; *p*-^{i}PrC_6H_4Me [(**2**)PF_6]; C_6Me_6 [(**3**)PF_6]), $[(\eta^5\text{-}C_5Me_5)M(ata)]PF_6$ (M = Rh [(**4**)PF_6]; Ir [(**5**)PF_6]) and $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (η^5-Cp = η^5-C_5H_5 [(**6**)PF_6]; η^5-C_5Me_5 (Cp*) [(**7**)PF_6]; η^5-C_9H_7 (indenyl); [(**8**)PF_6]) have been synthesised from the reaction of 2-acetylthiazole azine (*ata*) and the corresponding dimers $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$, $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$, and $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$, respectively. In addition to these complexes a hydrolysed product (**9**)PF_6, was isolated from complex (**4**)PF_6 in the process of crystallization. All these complexes are isolated as hexafluorophosphate salts and characterized by IR, NMR, mass spectrometry and UV–Vis spectroscopy. The molecular structures of [**2**]PF_6 and [**9**]PF_6 have been established by single-crystal X-ray structure analyses.

1. Introduction

Recent interest in half- sandwich platinum group metal complexes with symmetrical Schiff bases come from the fact they can serve as synthetic models related to biological systems [1–7], as homogeneous catalysts in systems like [8–17], and supported chemical processes [18,19], and very recently as non-linear optical (NLO) materials [20,21]. Their attractiveness does also come from their preparative accessibility, their structural variability in addition to many of these novel ruthenium complexes combine an appropriate balance between the electronic and steric environment around the metal core.

Moreover, some of the nitrogen-donor ligands impart to the catalyst for good tolerance towards various organic functionalities, air, and moisture, thus widening the scope and limit's of their application. Of the above mentioned ligands, Schiff bases are of a great interest for creating new active and selective ruthenium catalytic systems [22,23]. There are few reports of half-sandwich Ru(II), Rh(III) and Ir (III) complexes with *N,N*-donor polypyridyl azine Schiff base ligands [24,25], but there are no reports with thiazole azine ligand in the literature. Complexes imparting other than pyridyl azine ligands are yet to be explored, in view of the fact that ring size and the substituents in the heterocyclic ring system significantly modifies the acidity and regulate the physical and chemical properties of the complexes [26,27]. The arene and cyclopentadienyl platinum group metal complexes containing thiazole azine ligand is being reported for the first time.

In the present communication we focus on the synthetic methodology applied for the development of homogeneous and immobilized half- sandwich ruthenium, rhodium and iridium complexes bearing Schiff base (*ata*) as a specific *N,N*-bidentate bridging ligand has shown below.



2-acetylthiazole azine (*ata*)

2. Experimental

2.1. General remarks

All solvents were dried and distilled prior to use. Ruthenium trichloride trihydrate (Arora Matthey Ltd.), 2-acetylthiazole (Aldrich)

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