SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF ARENE AND CYCLOPENTADIENYL COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

ABSTRACT

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

By
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Abstract

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 (0) intermediates that have been used recently for carbon-hydrogen bond activation. Various methods of access to cyclopentadienyl, borane and carboranes 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. The η^6-arene ruthenium complexes are also the subject of intensive studies due to their interesting coordination chemistry and catalytic properties. Apart from these some of the arene ruthenium complexes are known to have antibacterial activity and have the potential for inhibiting enzymes involved in DNA biochemistry, for examples, $[(\eta^6\text{-arene})RuCl(YZ)]$ where YZ is a chelating diamine such as ethylenediamine are cytotoxic to cancer cells including cisplatin-resistant cell lines and $[(\eta^6\text{-p-cymene})RuCl_2(pta)]$ is also found to show interesting pH-dependent DNA-binding activity. Thus, keeping in mind the importance of these type of complexes, one part of this research work is based on the synthesis and characterization of new complexes arising from a very versatile starting material $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, hexamethylbenzene). Apart from these, another materials namely, $[CpM(PPh_3)_2X]$ (M = Ru, X = Cl; M = Os, X = Ru) are also chosen as a starting materials. The coordination chemistry of the cyclopentadienyl system forms one of the cornerstones of transition metal organometallic chemistry. The

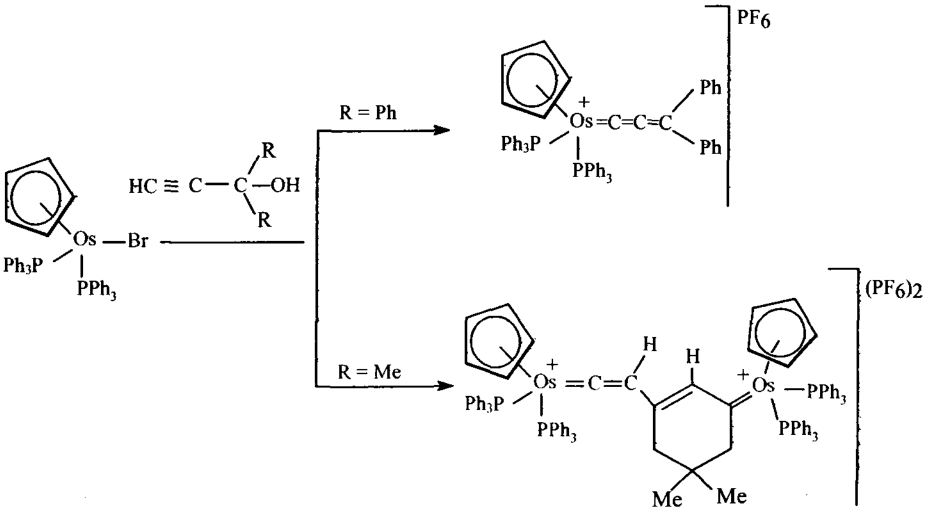
practical importance of these complexes especially, $[CpRu(PPh_3)_2Cl]$ is evident from its vast and continued appearance in literature. There are several papers that report the catalytic properties of this compound. But interestingly, there is noticeable lack of emphasis on the osmium analogue, $[CpOs(PPh_3)_2Br]$ as evident from the literature survey. There are reasons for this, such as the lower kinetic lability of osmium relative to ruthenium and possibly the greater cost of osmium. Numerous futile attempts made to redress this imbalance as far as the chemistry is concerned during this research work itself somehow prove why the chemistry of this system lag behind that of its ruthenium analogue.

Thus, this thesis consists of six chapters.

The first chapter 'Introduction' briefly highlight the status of relevant aspects of these complexes i.e. arene ruthenium(II) and cyclopentadienyl complexes of ruthenium(II) and osmium(II) and purpose of this 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.

Chapter two encompasses the results of the reaction of $[CpOs(PPh_3)_2Br]$ with monodentate anion or neutral ligands such as CH_3CN, CN, NCS, NO, which invariably led to the formation of new complexes resulting from the dissociation of the bromide ligand. The interesting observation is that the chelate ligand such as 2,2-bipyridine or 1,10-phenanthroline do not react cleanly with $[CpOs(PPh_3)_2Br]$ but with $[CpOs(PPh_3)_2(CH_3CN)]^+$ to give cationic complexes of the formula $[CpOs(PPh_3)(L_2)]^+$ resulting from the substitution of one of the PPh_3 as well as the acetonitrile ligand. The reaction of $[CpOs(PPh_3)_2Br]$ with diphenylpropargylic alcohol $HC{\equiv}CC(Ph)_2(OH)$

afforded cationic osmiumallenylidene complex $[CpOs(C{=}C{=}CPh_2)(PPh_3)_2]^+$, but with $HC{\equiv}CCMe_2(OH)$, unexpected dimerization product, a dicationic diosmium vinylidene-alkylidene complex of the formula $[(CpOs)_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4]^{2+}$ was obtained as shown in the figure below. The X-ray crystal structures of these complexes as well as that of $[CpOs(PPh_3)(phen)]BF_4$ are also presented in this chapter.



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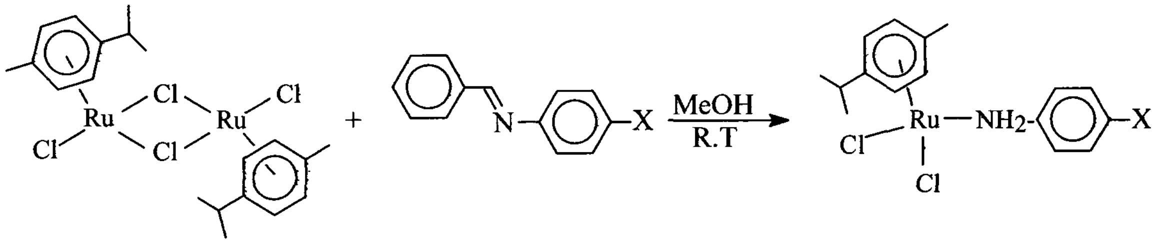

All repetition of the reactions led invariably to the same product as confirmed by spectroscopic data as well as X-ray crystallography, rather than the expected cyclometallated product, which of course could be due to the failure of complete exclusion of moisture in the laboratory working condition.

Chapter four 'A' described the facile preparation of $[(\text{x-phterpy})_2\text{Ru}]^{2+}$ under mild condition, starting from the reaction between $[(\eta^6\text{-arene})\text{RuCl}_2]$ and substituted phenylterpyridines (x-phterpy). This method provides a general route for the bis terpyridine complexes instead of starting from the usual ruthenium(III) precursors such as $[(\text{terpy})\text{RuCl}_3]$, which would essentially need more drastic conditions. This observation lead us to investigate and study the products resulting from the reaction between some sterically demanding N,N'-donor heterocycles and *p*-cymene dimer, however, *p*-cymene remain intact even at refluxing condition to afford chelate complexes of a general formula $[(\eta^6\text{-arene})\text{RuCl(N,N)}]^+$, confirmed by X-ray crystallographic studies on two of these compounds.

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'A' in such away that; (1) Cp ligands are not displaced at all by N,N',N"-donor ligands (2) no dinuclear ligand bridged complexes are formed (3) the products isolated are chelate complexes having the formula $[CpRu(PPh_3)(N,N')]^+$. Two compounds have been fully characterized with the help of X-ray crystallography.

In chapter five, the cyano-bridged homo- or hetero-bimetallic complexes essentially having the fragment $[M\ \text{-}C{\equiv}N\text{-}\ M]^{2+/\,+/\,0}$ that could be classified as dicationic, monocationic and neutral complexes have been described. The aid of X-ray crystallography apart from routine spectroscopic characterizations has been used to fully characterize a representative compound from each of these three classes.

The concluding chapter, the fifth chapter, describes various complexes arising from the reaction between EPh_3 (E = P, As, Sb), PPh_2Py, Sodium azide and β-diketonate (bzac, dbzm) ligands and *p*-cymene dimer. These could be very briefly summarized as,

(i) $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with excess of EPh_3 (ca. five fold excess in the case of PPh_3) afforded cationic $[(\eta^6\text{-}p\text{-cymene})RuCl(EPh_3)_2]^+$ confirmed by X-ray crystal structure in contrast to the reports available that claimed the displacement of arene ring (such as benzene) from the coordination sphere by some tertiary phosphines.

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(iii) The reinvestigated preparation of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ from $Na[N_3]$ and *p*-cymene dimer offer various complexes such as mono dentate phosphines azide complexes, dinuclear ligand bridged azide complexes, mononuclear cationic chelate azide complexes, dinuclear azide-bridged nitrato and trifluoroacetato complexes. Some representative compounds were fully characterized with X-ray crystallography.

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Declaration

I, R. Lalrempuia hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to anybody else to the best of my knowledge. I have not submitted the thesis for any research degree in any other University or Institution.

This is being submitted to the North Eastern Hill University, Shillong for the degree of Doctor of Philosophy in Chemistry.

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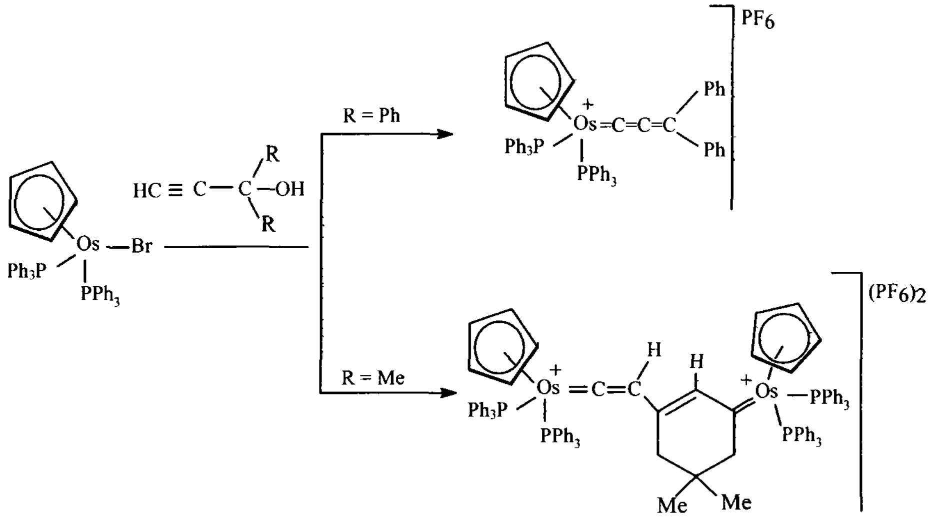

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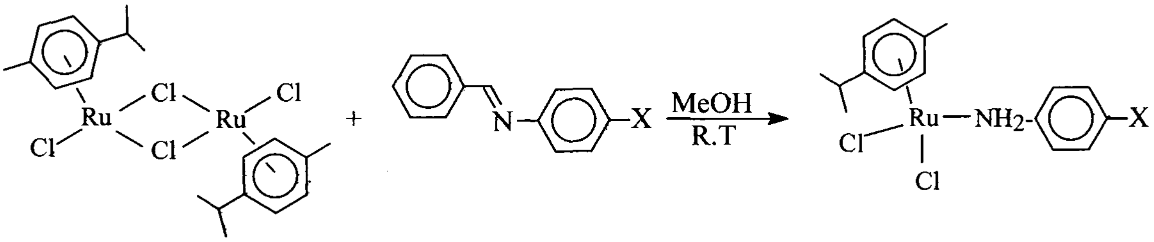

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Chapter I

Introduction

Research in 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 the one hand and that of coordination complexes on the other.

Studies on organoruthenium complexes containing arene and cyclopentadienyl system as coligands have been accompanied to a very large extent by an interest in the ligand substitution processes at plus two valent metal center. The areneruthenium(II) and cyclopentadienylruthenium(II) complexes play an increasingly important role in organometallic chemistry. They are good starting materials to access to reactive arene metal hydride or 16- electron metal (0) intermediate that has been used recently for carbon-hydrogen bond activation. Thus, the information obtained from the syntheses of new complexes based on the arene and cyclopentadienyl ligands, will focus not only in formulating the reaction pattern for various complexes but it may prove to be quite relevant for rationalization of their stability in terms of relative importance of π-donor or π-acceptor bonding shown by the bonded co-ligands and the change within the coordination sphere of the metal as indicated by various stereochemistry of the products.

Comprehensive review concerning the syntheses of complexes based on these systems, $[(\eta^6\text{-arene})RuCl_2]_2$ and $[CpM(PPh_3)_2X]$ (M = Ru, Os) would be too vast a subject to cover in one's thesis, the purpose of this 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 ruthenium(II) complexes

In recent years, π-arene metal complexes have generated considerable interest because of their potential roles as homogeneous catalysts. Much of the earlier work was concerned with complexes of zerovalent metals and it was found that although the hydrocarbons ligands retain their aromatic character, they are generally deactivated toward electrophilic attack and activated toward nucleophilic attack relative to free ligands.

The versatile starting materials $[(\eta^6\text{-arene})RuCl_2]_2$ are usually made by heating the appropriate cyclohexa-1,3-diene or cyclohexa-1,4-diene with $RuCl_3.xH_2O$ in ethanol, detailed procedures are available for the p-cymene (*p*-cymene, 1,4-$MeC_6H_4CHMe_2$) complex and for hexamethylbenzene analogue made from it by fusion with C_6Me_6 (hexamethylbenzene) [1]. The $[(\eta^6\text{-arene})RuCl_2]_2$ complexes of mesitylene, 1,2,3,4-tetramethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene [2] and tetramethylthiophene [3] have been made similarly from $[(\eta^6\text{-p-cymene})RuCl_2]_2$.

The arene-ruthenium(II) bond in $[(\eta^6\text{-arene})RuCl_2]_2$ is thermally stable but unstable under forcing conditions [4,5]. Two-electron electrochemical reduction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ or of the derived salt $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-}Cl)_3]PF_6$, gives a fairly long-lived p-cymene ruthenium(I) dimer, probably $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)]_2$ [6].

The halide ligands of $[(\eta^6\text{-arene})RuCl_2]_2$ can be replaced by a wide variety of neutral and anionic ligands. The degree of substitution with neutral ligands (L) (Scheme-1) depends strongly on the nature of L and on the solvent; solvents such as water and methanol that strongly solvate Cl^- tend to favor substitution of more than one chloride ligand.

$$[(\text{arene})RuCl_2]_2 \xrightarrow{L} [(\text{arene})RuCl_2(L)] \xrightarrow{L} [(\text{arene})RuCl(L)_2]^+ \xrightarrow{L} [(\text{arene})Ru)L)_3]^{2+}$$

Scheme 1.1

1.1.1 Derivatives with Nitrogen and Oxygen donors

The complex $[(\eta^6\text{-arene})Ru(H_2O)_3]^{2+}$ could be isolated as sulfate salt from dilute solution of $[(\eta^6\text{-arene})RuCl_2]_2$ in triflic acid [4], [7]. These compounds when irradiated in aqueous solution loss arene to form $[Ru(H_2O)_6]^{2+}$, the quantum yields decrease with increasing wavelength in the order: arene = *p*-cymene < C_6H_5Me< C_6H_6. Deprotonation of $[(\eta^6\text{-arene})Ru(H_2O)_3]^{2+}$ is complex, especially when the arene is C_6H_6. Treatment of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with aqueous Na_2CO_3 with excess of Na_2SO_4 afforded tetranuclear species $[\{Ru(\mu_3\text{-}OH)(\eta^6\text{-}C_6H_6)\}_4](SO_4)_2.12H_2O$ [8]. Addition of excess Na_2CO_3 or NaOH to $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ gives a mixture of $[(\eta^6\text{-} C_6H_6)(HO)Ru(\mu_2\text{-}OH)_2Ru(H_2O)(\eta^6\text{-}C_6H_6)]^+$ and the tetranuclear cations $[Ru_4(\mu_2\text{-}OH)_2(\mu_4\text{-}O)(\eta^6\text{-}C_6H_6)_4]^{2+}$ [9], [10]. The complex of the type $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}OR)_3]^+$ could be isolated by treating $[(\eta^6\text{-arene})RuCl_2]_2$ with NaOR/ROH [10], [11], [12] or TlOPh [13]. The hydroxo complexes $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}Cl)_2(\mu\text{-}OH)]^+$ have also been prepared recently [14]. The coordination properties of *p*-cymene ruthenium(II) complexes containing catechol and 5-hydroxyindole derivatives ligands have also been described [15]. The monomeric carboxylato [16] [17], nitrato, triflato [18] [19] and amidinates [20] complexes have been obtained from the dimer with the appropriate sodium, silver or ammonium salts. Monomeric and dimeric oxalato arene ruthenium(II) complexes have also been obtained [21]. The reaction of various aromatic amines [22-23], pyridine derivatives [24-26] and amino acid ligands [27-31] and $[(\eta^6\text{-arene})RuCl_2]_2$ have been reported. Recently *p*-cymene complex of enzyme 'lysozyme' has been reported [32]. The complex $[(\eta^6\text{-}C_6Me_6)RuCl_2(PMe_3)]$ reacts with aniline in the presence of $AgBF_4$ to afford $[(\eta^6\text{-}C_6Me_6)RuCl(NH_2Ph)(PMe_3)]BF_4$, this complex undergoes complex disproportionation and deprotonation reaction with $LiN(TMS)_2$ at 263 K to form the tri-μ-anilido complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}NH_2Ph)_3]BF_4$ [33]. Neutral and cationic $Ru(\eta^6\text{-}C_6H_6)$ complexes containing 4-vinylpyridine, pentachlorophenyl isonicotinate and pentachlorophenyl 3-(4-pyridyl)propionate have been made as precursors to potential protein-labelling agents [34]. The complexes of the type $[(\eta^6\text{-arene})Ru(NCMe)_3]^{2+}$ and $[(\eta^6\text{-arene})RuCl(NCMe)_2]^+$ can be easily obtained from treatment of $[(\eta^6\text{-arene})RuCl_2]_2$ with $AgBF_4$ or $AgPF_6$ in acetonitrile solvent in appropriate molar ratios. The coordinated acetonitrile ligands exchange rapidly with CD_3CN and are easily replaced by bidentate ligands [35-36].

Reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with bidentate N,N'- and N,O-Schiff base ligands have been studied [37] and optically active diastereomeric complexes have also been obtained from the reactions of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with bidentate chiral Schiff base analogues [38-39] as well as quinolin-8-olate ligand [40]. Optically active ortho-metalated complexes chiral at ruthenium center have been obtained from the reaction of (R_C)-(+)- or (S_C)-(-)- N,N- dimethyl-1-phenylethylamine with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ [41]. Reaction of flexible tridentate nitrogen-donor ligands such as [2-(2-pyridyl)ethyl](2-pyridylmethyl)methylamine, 2,6-bis(pyrazol-1-ylmethyl)pyridine, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine [42] and poly(pyrazolyl)borates or methanes [43], [44] with $[(\eta^6\text{-arene})RuCl_2]_2$ have been studied. Cycloruthenated complexes have been obtained from the reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with azobenzene [45] as well as from the reaction of $[(\eta^6\text{-arene})Ru(L)Cl_2]$ (L = PMe_3, PEt_3, CO) with phenylenediimine ligands [46-47]. In the latter case, careful exclusion of water is necessary to avoid hydrolysis of the imine ligands. The complex $[(\eta^6\text{-arene})RuCl(dad)]BF_4$ obtained from the reaction of $[(\eta^6\text{-arene})RuCl(NCMe)_2]BF_4$ with 1,4-diisopropyldiaza-1,3-diene (dad) are reduced to $[(\eta^6\text{-arene})Ru(dad)]$ and these complexes on treatment with RI afforded cationic salts $[(\eta^6\text{-arene})RuR(dad)]$ (R = Me, Et) [48]. Cationic Bis(oxazolines) complexes, $[(\eta^6\text{-arene})RuCl(N\text{-}N)]PF_6$ (arene = *p*-cymene, benzene, mesitylene, N-N = bis(2-oxazoline), 2,2-bis(2-oxazolinyl)propane, 1,2-bis(2-oxazolinyl)benzene) have been prepared and some of the dications obtained from treatment of these cation with $AgSbF_6$ are enantioselective catalyst for Diels-Alder reaction of methacrolein and cyclopentadiene [49].

Very stable arene ruthenium(II) complexes containing tripodal oxygen donor ligands have been prepared (Figure-1.1) [50-52].

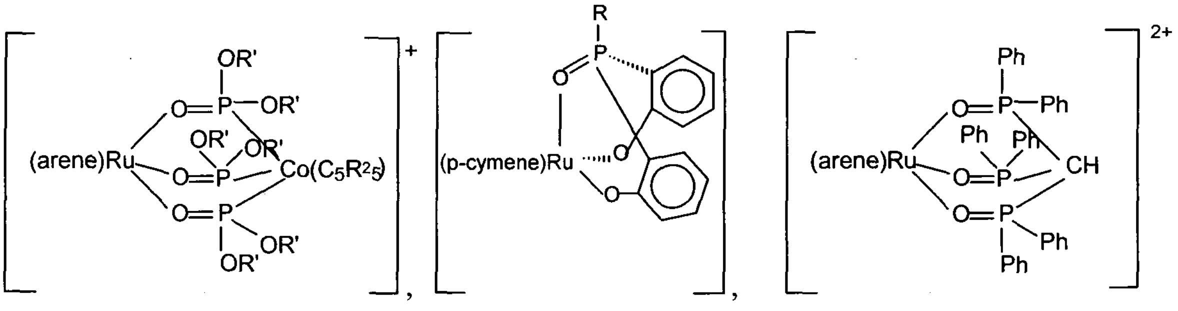


Figure-1.1

Self-assembled multinuclear metallamacrocycles have been prepared which showed strong affinity to bind Li and Na (Figure 1.2) [53].

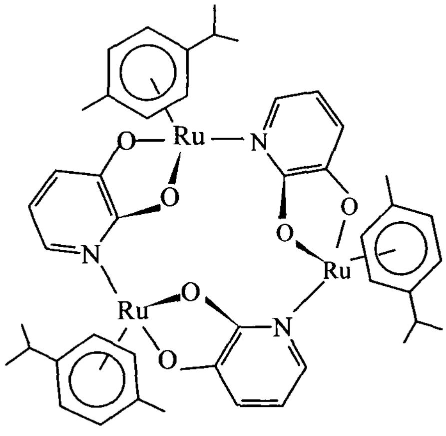


Figure 1.2

The reactions of $[(\eta^6\text{-arene})RuCl_2]_2]$ (arene = C_6H_5Me, *p*-cymene, C_6Me_6) with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ have been investigated and series of complexes with various nuclearities have been obtained [54].

1.1.2 Derivatives with CO, RNC, hydride, PR_3

The complexes, $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, C_6Me_6, mesitylene etc.,) react readily with CO at room temperature and pressure to give monomeric adducts $[(\eta^6\text{-arene})RuCl_2(CO)]$ [4], [55-59] where the stability is greater for more highly substituted arenes. Benzene complex has not been isolated because CO readily substitutes benzene. Apart from these, the complex $[(\eta^6\text{-}C_6Me_6)RuCl(CO)_2]^+$ [60] has also been isolated and the literature survey indicated that there is noticeable lack of emphasis on carbonyl adducts of arene ruthenium(II) system. Isocyanide complexes $[(\eta^6\text{-arene})RuCl_2(CNR)]$ [61-63] have been made similarly to their CO analogues.

The dinuclear hydrido complex $[(p\text{-}Me\text{-}C_6H_4\text{-}Pr^i)_2Ru_2Cl_2(\mu\text{-}Cl)(\mu\text{-}H)]$ has been prepared and its reactions with NaX and HX have been studied [64]. The trinuclear cations for examples, $[H_3Ru_3\{C_6H_5(CH_2)_2OC(O)C_6H_5\}(C_6Me_6)_2(O)]^+$, $[H_3Ru_3\{C_6H_5\text{-}(CH_2)_2OC(O)(CH_2)_3C_6H_5\}(C_6Me_6)_2(O)]^+$ and $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ are prepared recently [65].

A large number of monomeric complexes of the type $[(\eta^6\text{-arene})RuCl_2(L)]$ containing group 15 donors, mainly tertiary phosphines and phosphites have been made [3], [59], [66]. They have been widely used as precursors to hydrides, alkyls and zero valent metal complexes. There are also many reports on the reaction of $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ with simple ditertiary phosphines as well as chiral ditertiary phosphines. For example, chiral phosphine such as (S)-binap [(S)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] gives cations $[(\eta^6\text{-arene})\text{RuCl(binap)}]^+$, the arenes are easily liberated, either by heating in acetonitrile or under hydrogen, to provide an unsaturated species which catalyses the asymmetric hydrogenation of 2-benzamidomethyl-3-oxobutanoate with high stereoselectivity [67-69]. The reaction of the monoxidized binap (BINPO) with $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ have also been studied [70]. The compound $[(\eta^6\text{-}p\text{-cymene})\text{Ru(quinap)Cl}](\text{SbF}_6)$ [(quinap = 1-(2-diphenylphosphino-1-naphthyl) isoquinoline] has been prepared and the uncharacterized *insitu* prepared dicationic complexes from this cation with AgSbF_6 was found to be a good catalyst for enantio selective Diels-Alder reaction of cyclopentadiene and methacrolein [71]. Treatment of $[(\eta^6\text{-arene})\text{Ru(L)Cl}_2]$ with AgPF_6 in acetone gives labile solvento cations $[(\eta^6\text{-arene})\text{Ru(L)Cl(acetone)}]^+$ which decompose to dinuclear halo- bridged salts $[\{(\eta^6\text{-arene})\text{Ru(L)}\}_2(\mu\text{-Cl})_2]^{2+}$ (arene = C_6H_6, C_6Me_6, L = PMe_3, PMe_2Ph, PMePh_2, PPh_3, P(OPh)_3) [59]. Cationic bis(tertiary phosphine) or mixed-ligand complexes are easily made by the reaction as shown in Scheme-1.2 [60].

$$[(\text{arene})\text{RuX}_2]_2 + 4\,\text{L} \xrightarrow[\text{MeOH}]{\text{NH}_4\text{PF}_6} [(\text{arene})\text{RuX(L)}_2]\text{PF}_6$$

X = Cl, Br, I; L = PMe_3, PMe_2Ph, PPh_3, P(OPh)_3, P(OMe)_3

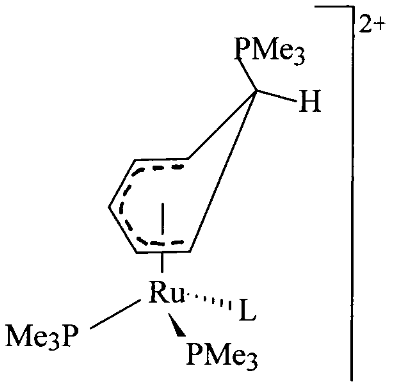
$$[(\text{arene})\text{Ru(L}^1)\text{X}_2] + \text{L}^2 \xrightarrow[\text{MeOH}]{\text{NH}_4\text{PF}_6} [(\text{arene})\text{RuX(L}^1)(\text{L}^2)]\text{PF}_6$$

X = Cl; L^1 = PMe_3, PMe_2Ph, PPh_3, P(OPh)_3, P(OMe)_3; L^2 = PMe_3, PMe_2Ph, PPh_3

$$[(\text{arene})\text{RuCl}_2(\text{CO})] + \text{PMe}_3 \xrightarrow[\text{MeOH}]{\text{NH}_4\text{PF}_6} [(\text{arene})\text{RuCl(CO)(PMe}_3)]\text{PF}_6$$

Scheme-1.2

Tris(tertiary phosphine) complexes of the type $[(\eta^6\text{-arene})\text{Ru(L)}_3]^{2+}$ are less easily prepared than their aqua, ammine or acetonitrile analogues, for example, treatment of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl(PMe}_3)_2]\text{PF}_6$ with PMe_3, even in the presence of AgPF_6 does not give an anticipated tris(PMe_3) complex. When this reaction is carried out in the presence of NH_4PF_6, the product is the η^5-cyclohexadienyl complex (L = PMe_3) as shown in Figure 1.3, formed by the nucleophilic addition of PMe_3 to the benzene ring. Similar complexes [L = PPh_3 and $P(NMe_2)_3$] are formed by reaction of PMe_3 with $[(\eta^6\text{-}C_6H_6)RuCl_2(PR_3)_2]$ and the complex (L = MeCN) is formed similarly from $[(\eta^6\text{-}C_6H_6)Ru(NCMe)_3](PF_6)_2$ [72-73].



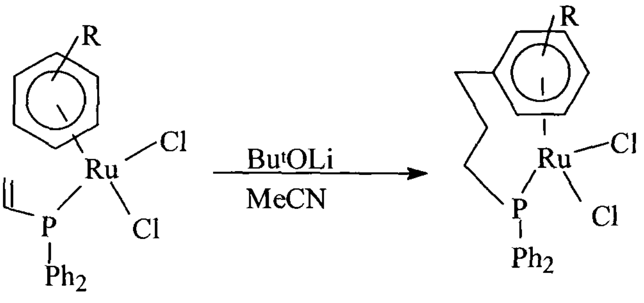
L = PMe_3, PPh_3, $P(NMe_2)_3$, MeCN

Figure 1.3

The exo-PMe_3 group in complexes of this type can be removed by an excess of TFA to give dicationic salts such as $[(\eta^6\text{-}C_6H_6)Ru(PMe_3)_3](PF_6)_2$, $[(\eta^6\text{-}C_6H_6)Ru(PMe_2Ph)(PMe_3)(PPh_3)](PF_6)_2$ and $[(\eta^6\text{-}C_6H_6)Ru(PMe_3)_2(NCMe)](PF_6)_2$. The coordinated benzene in $[(\eta^6\text{-}C_6H_6)Ru(PMe_3)_3](PF_6)_2$ undergoes nucleophilic attack by Et_3N to give $[(\eta^5\text{-}C_6H_6Nu)Ru(PMe_3)_3]^{n+}$ (Nu = Et_3N, n = 2; n =1); the reaction is reversed by acid [74]. The enthalpies of reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with a series of N-substituted tertiary phosphines ligand leading to the formation of $[(\eta^6\text{-arene})Ru(PR_3)Cl]$ have been measured by solution calorimetry, the relative stability is found to be in the order of, $P(NC_4H_4)_3 < P(NC_4H_4)_2(C_6H_5) < P(NC_4H_4)(C_6H_5)_2 < P(NC_4H_8)_3$ [75]. Iminophosphorane-phosphine and 2-diphenylphosphinobenzaldehyde complexes, $[(\eta^6\text{-arene})RuCl_2\{P\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}]$ [76] and $[Ru(\eta^6\text{-arene})Cl_2(P\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)]$ [77] (arene = C_6H_6 , p-cymene, mesitylene, 1,2,3,4-

$C_6H_2Me_4$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6) respectively have been prepared and subsequent reaction with $AgSbF_6$ yielded cationic species $[(\eta^6\text{-arene})RuCl\{P,N\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}]^+$ and $[Ru(\eta^6\text{-arene})Cl(P,O\text{-}2\text{-}Ph_2PC_6H_4CH=O)]^+$. The catalytic activity of some of these complexes in transfer hydrogenation of cyclohexanone and acetaphenone by propan-2-ol have been studied. The complex $[(\eta^6\text{-arene})RuCl\{P,N\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}]^+$ activates 1,1-diphenyl-2-propyn-1-ol to give new type of tethered-arene ruthenium complex via iminophosphorane-allenylidene coupling process [78].

The reaction of phenyllithium containing LiBr with $[(\eta^6\text{-}C_6H_6)RuCl(PMe_3)_2]PF_6$ gives $[(\eta^5\text{-}C_6H_6Ph)RuBr(PMe_3)_2]$ and this reacts further to give σ- phenyl compound $[(\eta^5\text{-}C_6H_6Ph)RuPh(PMe_3)_2]$; the corresponding reaction with methyllithium gives an inseparable mixture of compounds [79]. The complex $[(\eta^6\text{-}C_6Me_6)RuCl\{P(OMe_3)\}_2]PF_6$ undergo sequential Michaelis-Arbuzov on treatment with NaI in acetone to give $[(\eta^6\text{-}C_6Me_6)RuCl\{PO(OMe)_2\}\{P(OMe)_3\}]$ and $[(\eta^6\text{-}C_6Me_6)RuCl\{P(OMe)_2\}_2]^-$ [80-81]. The latter complexes are isolated as NaI adducts that can be converted to, for example, free acid, $[(\eta^6\text{-}C_6Me_6)RuCl\{P(OMe)_2\}_2H]$. The anion $[(\eta^6\text{-}C_6Me_6)RuCl\{P(OMe)_2\}_2]^-$ behaves as a tridentate (O, O, Cl) ligand and forms six coordinate $[ML_2]^{(n-2)+}$ complexes with many main-group and transition-metal ions M^{n+} [82]. The neutral diphenylvinylphosphine (DPVP) complex $[(\eta^6\text{-arene})RuCl_2(DPVP)]$ (arene = 1,3,5-C_6Me_3, *p*-cymene, C_6Me_6, *p*-MeC_6H_4Me, MeC_6H_5) undergo base promoted hydroalkylation reaction to give tethered complexes as shown in Scheme 1.3 and in the *p*-cymene case, the reaction proceeds regioselectively at methyl group to produce most stable product [83].



Scheme 1.3

Thermolysis of a 1:1.5:1 molar ratio of [(η^6-arene)Ru(DMPP)Cl_2] (arene = C_6Me_6, *p*-cymene), DMPP (1-phenyl-3,4-dimethylphosphole) and $NaPF_6$ in 1,2-dichloroethane at 84 ° C for 1 week produced mixture of unprecedented [4+4], [4+2] cycloaddition products a part from the product resulting from the [1,3]-hydrogen shift from a methyl group to the α-position of the phosphole ring [84]. Reaction of *P, O* chelate complexes, [(η^6-arene)RuCl(MDMPP-*P,O*)] and tridentate P,O,O' complexes, [(η^6-arene)RuCl(TDMPP-*P,O,O*)] ((MDMPP-*P,O* = P(2-O-6-$MeOC_6H_3$)Ph_2, TDMPP-*P,O,O* = P(2-O-6-$MeOC_6H_3$)$_2${2,6-$(MeO)_2C_6H_3$}), arene = p-cymene, C_6Me_6) with Lewis bases and alkynes have been reported [85]. The reactions of [(η^6-arene)$RuCl_2$]$_2$ with water-soluble phosphines tppts (*meta*-trisulfonated triphenylphosphine) and pta (1,3,5-triaza-7-phosphaadamantane) yielded depending on the reaction conditions neutral or cationic complexes [86], one these complexes [(η^6-*p*-cymene)Ru(pta)Cl_2] showed interesting pH-dependent DNA-binding activity [87].

The halide ligands in the tertiary phosphines complexes [(η^6-arene)RuX_2(L)] (X = Cl, Br; L = tertiary phosphines) can be replaced by hydride. Monohydrido complexes [(η^6-arene)RuH(X)(L)] are usually best prepared by reaction of the dihalo complexes with zinc dust in methanol at room temperature, [88-90] or by heating with anhydrous Na_2CO_3 in propan-2-ol [88], [91-93]. The dihydrido ruthenium(II) complexes such as [(η^6-C_6Me_6)RuH_2(L)] (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, PBu^tMe_2, $P(OR)_3$ and [(η^6-C_6H_6)RuH_2(PPr^i_3)] are obtained in moderate to good yield by the action of $NaBH_4$, LAH and Red-Al in propan-2-ol, and ether and THF respectively on the corresponding dichlorides or bis(trifluoroacetates) [91], [94-97]. The dihydrido complexes [(η^6-C_6Me_6)RuH_2(L)] are protonated by CF_3CO_2H/NH_4PF_6 or HBF_4/OEt_2 at 195 K to give cationic trihydrides [(η^6-arene)RuH_3(L)] (L = PMe_3, PPh_3) [98]. The complex [(η^6-C_6Me_6)RuH_2(PMe_3)] on treatment with NH_4PF_6 in acetone gives [(η^6-C_6Me_6)RuH(PMe_3)(NH_2Pr^i)], this isopropylamine complex is presumed to be the results of the reductive amination of the solvent by the dihydride [99].

Dimethyl complexes [(η^6-C_6Me_6)Ru(Me_2)(L)] (L = PMe_3, $PMePh_2$, PPh_3) have been obtained from treatment of the dihalides with methyllithium [94] and with 1,4-

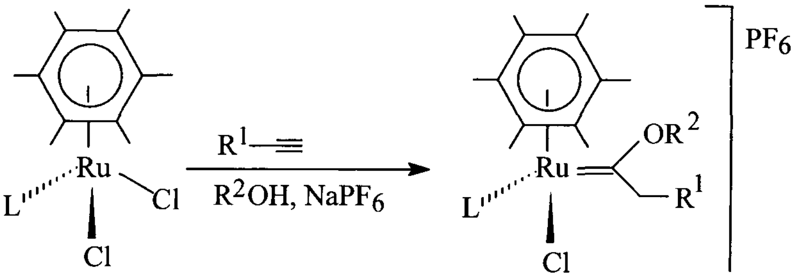
dilithiobutane, the dihalide gives $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(CH_2CH_2CH_2CH_2)(L)}]$ [100]. The methyl groups of the dimethyl complex $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(Me_2)(PPh_3)}]$ are cleaved stepwise by $\mathrm{CF_3CO_2H}$ to give $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(Me)(PPh_3)}(\eta^{1}\text{-}\mathrm{O_2CCF_3})]$ and $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(PPh_3)}(\eta^{1}\text{-}\mathrm{O_2CCF_3})_2]$; reaction with $\mathrm{HBF_4}$ in propionic anhydride gives $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(PPh_3)}(\eta^{2}\text{-}\mathrm{O_2CEt})]$ and protonation of dimethyl complex with $\mathrm{HBF_4}$ in the presence of CO or $\mathrm{C_2H_4}$ afforded $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(Me)(PPh_3)(CO)}]\mathrm{BF_4}$ and $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(Me)(L)(C_2H_4)}]\mathrm{BF_4}$ (L = $\mathrm{PMe_3}$, $\mathrm{PPh_3}$) where the latter complex (L = $\mathrm{PPh_3}$) in dichloromethane loses Me over 24 h to give a hydrido complex containing (2-vinylphenyl)diphenylphosphine, $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuH(CH_2{=}CHC_6H_4PPh_2)}]\mathrm{BF_4}$. This maybe formed by insertion of ethane into an unsaturated cation $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(C_6H_4PPh_2)}]^{+}$ which could arise by elimination of methane from the starting material [101]. With $[\mathrm{Ph_3C}]\mathrm{PF_6}$, the dimethyl complexes give $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuH(L)}(\eta\text{-}\mathrm{C_2H_4})]\mathrm{PF_6}$ (L = $\mathrm{PMe_3}$, $\mathrm{PMePh_2}$, $\mathrm{PPh_3}$) [102-103]. Although monomethyl complex $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuCl(Me)(PMe_3)}]$ maybe obtained in 46% from the reaction of the dichloro precursor with one equivalent of methyllithium, the better preparative route seems to be the action of mild methylating agents on the solution of $[(\eta^{6}\text{-arene})\mathrm{RuCl_2}]_2$ in donor solvents and subsequent addition of tertiary phosphines or phosphites [18]. An excess of $\mathrm{MgCl(CH_2TMS)}$ reacts with $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuCl(Me)(PMe_2Ph)}]$ to give monoalkyl $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuCl(CH_2TMS)(PMe_2Ph)}]$ and a dimeric $[\{(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(CH_2TMS)_2}(\mu\text{-P},\eta^{6}\text{-}\mathrm{PMe_2Ph})\}_2]$ [104].

Reaction of $[(\eta^{6}\text{-arene})\mathrm{RuCl_2}]_2$ with $\mathrm{SnMe_4}$ in acetonitrile afforded $[(\eta^{6}\text{-arene})\mathrm{RuCl(Me)(NCMe)}]$ [18]. Photolysis of $[(\eta^{6}\text{-arene})\mathrm{RuH_2(L)}]$ in benzene or toluene gives the corresponding hydrido(aryl)s, $[(\eta^{6}\text{-arene})\mathrm{RuH(Ar)(L)}]$ (L = $\mathrm{PPr^{i}_3}$, $\mathrm{PMe_3}$, $\mathrm{PHCy_3}$) arising from the oxidative addition of the 16-electron fragment $[(\eta^{6}\text{-arene})\mathrm{Ru(L)}]$ to the aromatic C-H bonds [90] [97] [105]. Treatment of $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{RuH(Cl)(L)}]$ (L = $\mathrm{PPh_3}$, $\mathrm{PPr^{i}_3}$ or $\mathrm{PBu^{t}Ph_2}$) with methyllithium generates the cyclometallated complexes $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru}(o\text{-}\mathrm{C_6H_4PPh_2})\mathrm{H})]$, $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(CH_2CHMePPr^{i}_2)H}]$ and $[(\eta^{6}\text{-}\mathrm{C_6Me_6})\mathrm{Ru(CH_2CMe_2PPh_2)H}]$ respectively [94], [106].

The complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = $C_6H_3Me_3$, C_6Me_6) react with functionalized phosphines, $Pr^i_2PCH_2X$ (X = CH_2OMe, CO_2Me) to give $[(\eta^6\text{-arene})RuCl_2(Pr^i_2PCH_2X)]$, which on treatment with $AgPF_6$ afforded chelate complexes $[(\eta^6\text{-arene})RuCl(P,O\text{-}Pr^i_2PCH_2X)]PF_6$, the reaction of these chelate complexes with monodentate ligands such as CO, $CNBu^t$ and bases, Na_2CO_3 and $KOBu^t$ have been studied [107]. The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, C_6Me_6, 1,2,3,4-$Me_4C_6H_4$, 1,2,3-$Me_3C_6H_3$) with trihapto ligands, tris-(2,6-dimethoxyphenyl)phosphines and Bis-(2,6-dimethoxyphenyl)phenylphosphine yielded complexes where the ligands bind metal as, *P,O*-chelate complexes or as tridentate *P,O,O* ligands depending on the reaction conditions [108]. The complexes $[(\eta^6\text{-arene})Ru(PPh_3)(N,O)]$ (arene = p-cymene, mesitylene, *N,O* = 2-acetamidocinnamic acid, 2-acetamidoacrylic acid) have been prepared from the reaction of $[(\eta^6\text{-arene})Ru(PPh_3)Cl_2]$ and the ligands in the presence of Ag_2O [109].

1.1.2.1 Vinyl, Acetylide, carbene (Alkylidene), Vinylidene, allenylidene, Cumulene and Azavinylidene Complexes

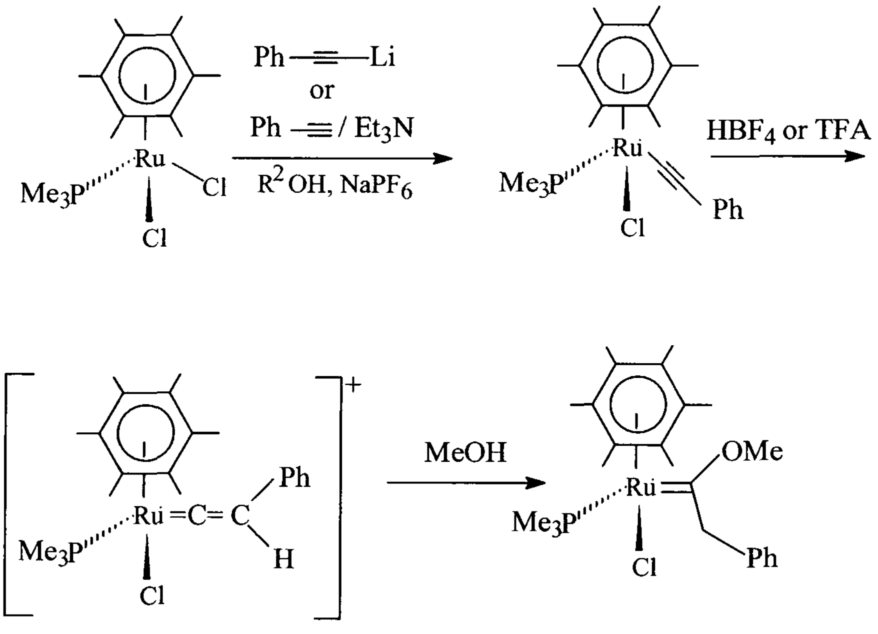
The ability of $[(\eta^6\text{-arene})RuCl_2(L)]$ (L = phosphines or phosphites) complexes to catalyze the addition of carboxylic acids and carbamic acids to terminal alkynes led to the discovery of the stoichiometric reaction of terminal alkynes with in alcohols in the presence of $NaPF_6$ to give cationic alkoxycarbene complexes (Scheme 1.4) [110]. Under the similar reaction condition trimethylsilylacetylene undergoes Si-C bond cleavage to give (methoxy)methylcarbene complex $[(\eta^6\text{-}C_6Me_6)RuCl\{C(OMe)Me\}(PMe_3)]PF_6$. Similar alkoxycarbene complexes are obtained from the reaction of phenylacetylene with $[(\eta^6\text{-arene})RuCl_2(PMe_3)]$, $[(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)RuCl_2(L)]$ (L = PPh_3, $P(OMe)_3$ [111] and $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)RuCl(SMe_2)_2]PF_6$ [112]. Mesitylene and p-cymene complexes (L = PMe_3) are too unstable to be isolated.



R^1 = Ph, R_2 = Me, Et, Pr^i; R^1 = Me, Bu^t, R^2 = Me, L = PMe_3, PMe_2Ph, PPh_3 .

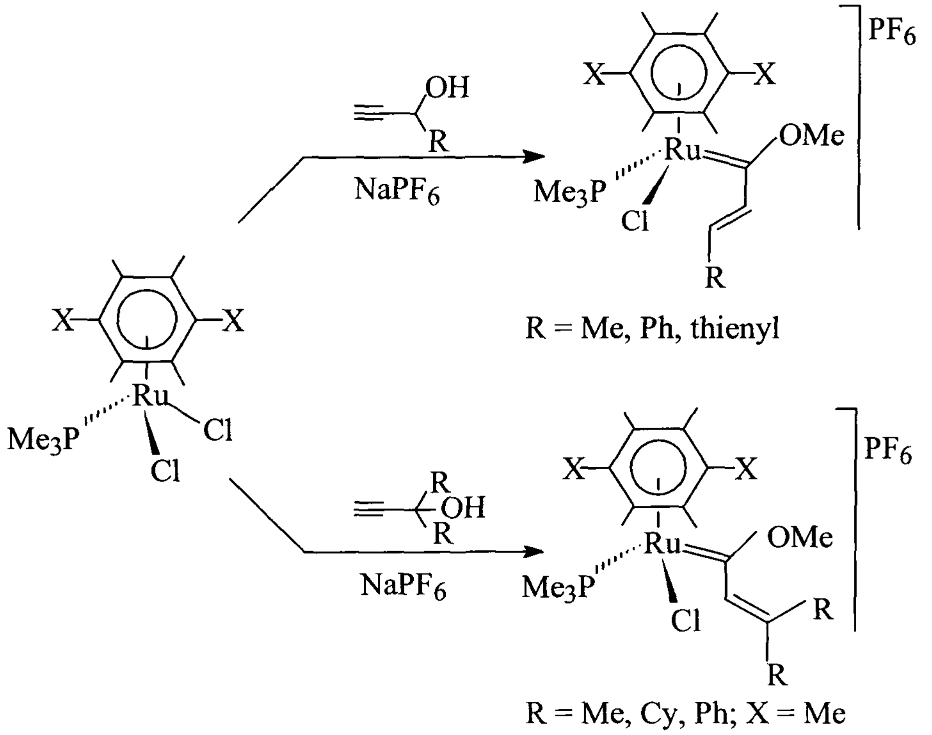
Scheme – 1.4

The phenylvinylidene cation $[(\eta^6\text{-}C_6Me_6)RuCl(C{=}CHPh)(PMe_3)]PF_6$ has been generated indirectly from the acetylide (Scheme 1.5) and it reacts rapidly with methanol to give methoxycarbene complex [113].



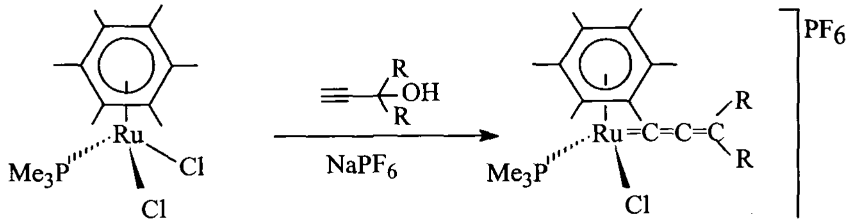
Scheme 1.5

Prop-3-yn-1-ol reacts with $[(\eta^6\text{-}C_6Me_6)RuCl_2(PMe_3)]$ in methanol/$NaPF_6$ to give cyclic oxycarbene salt $[(\eta^6\text{-}C_6Me_6)RuCl(PMe_3)\{C(OCH_2CH_2CH_2)\}]PF_6$ resulting from internal nucleophilic attack on the intermediate vinylidene whereas substituted prop-2-yn-1-ols give cationic methoxy(alkenyl)carbene complexes (Scheme 1.6) and these reactions probably proceed via allenylidene complexes (Scheme 1.7), which can be isolated in some cases. Propargyl alcohol under similar reaction conditions give, $[(\eta^6\text{-}C_6Me_6)RuCl(PMe_3)\{C(OMe)(CH_2CH_2OMe)\}]PF_6$ [114].


R = Me, Ph, thienyl

R = Me, Cy, Ph; X = Me

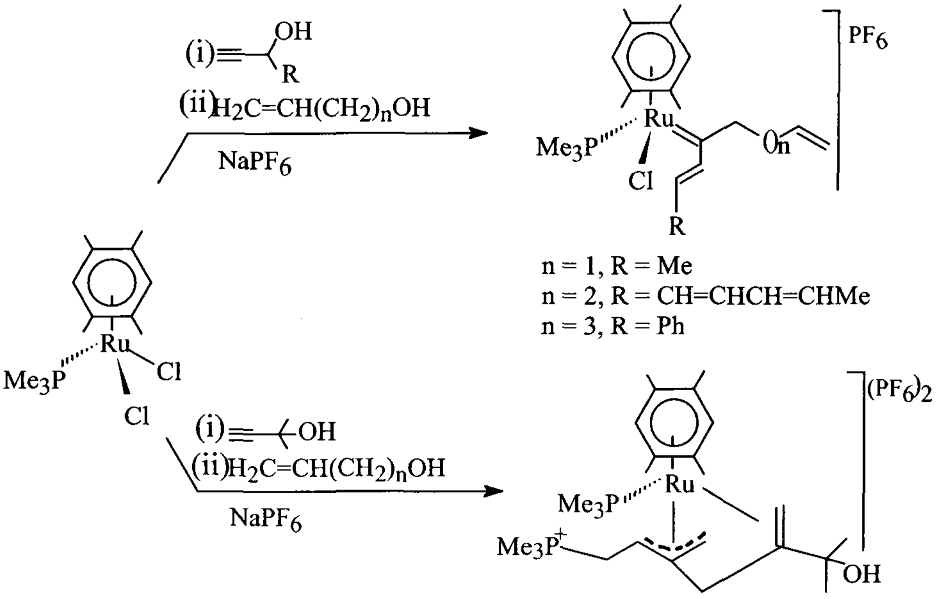
Scheme – 1.6


Scheme 1.7

Cationic alkoxy(alkenyl)carbene complexes are also formed by the reaction of vinylacetylenes(butenynes) with $[(\eta^6\text{-arene})RuCl_2(L)]$ / MeOH / $NaPF_6$ [115]. The cations $[(\eta^6\text{-arene})RuCl(PMe_3)\{C(OMe)(CH_2)_nR\}]PF_6$ (R = Ph; n = 4, 6) are generated by the reaction of ene- or diene-substituted propynols with $[(\eta^6\text{-arene})RuCl_2(PMe_3)]$ / MeOH / $NaPF_6$ [116].

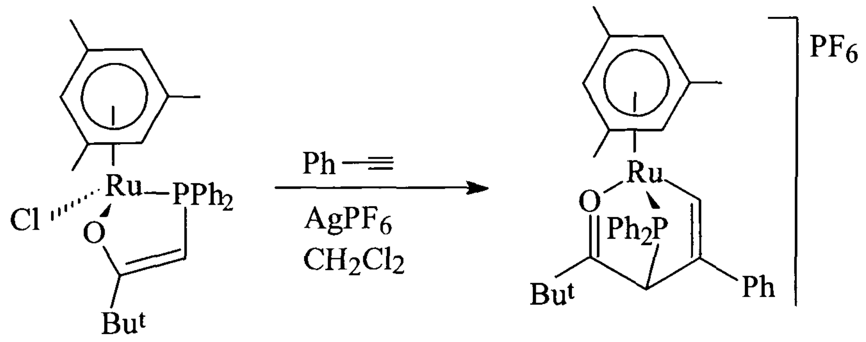
Treatment of $[(\eta^6\text{-}C_6Me_6)RuCl_2(L)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$) with 2,4-diyn-1-ol derivatives affords a variety ruthencumulene derivatives [117-118].

Reaction at room temperature of [(η^6-1,2,4,5-$C_6H_2Me_4$)$RuCl_2(PMe_3)$] with substituted prop-2-yn-1-ols in the presence of alkenic alcohol gives enyloxycarbene complexes and in contrast, 2-methylbut-3-yn-1-ol in the presence of allyl alcohol and $NaPF_6$ gives the dicationic chelate η^3-allyl-η-alkene complex (Scheme – 1.8) arising from coupling of two molecules of alkyne and hydrogen tranfer reactions [119].



Scheme 1.8

The diphenylphosphinoacetylene complexes [(η^6-arene)$RuCl_2(PPh_2C{\equiv}CH)$] (arene = *p*-cymene, $C_6H_3Me_3$) do not give well defined products with MeOH/$NaPF_6$ but the alkyne function of the *p*-cymene complex reacts with [(η^6-C_6Me_6)$RuCl_2(PMe_3)$]/NH_4PF_6 in methanol to give the binuclear alkoxy species [(η^6-p-cymene)$RuCl_2${μ-$Ph_2PCH_2C(OMe)$}$RuCl(PMe_3)$(η^6-C_6Me_6)]PF_6 [120]. Chelation of the phosphinoenolate complex disfavors the η^2-alkyne to η^1-vinylidene rearrangement and phenylacetylene attacks the nucleophilic carbon to give tridentate chelate η^1-vinyl complex as shown in Scheme 1.9 [121].



Scheme 1.9

The chelate complex $[(\eta^6\text{-}p\text{-cymene})RuCl(phen)]^+$ reacts with Na/Li acetylides to afford alkynyls $[(\eta^6\text{-}p\text{-cymene})Ru(CCR)(phen)]^+$ (R = H, Ph, $SiMe_3$), protonation of the complex (R = H) with HOTf gives acyl-complex $[(\eta^6\text{-}p\text{-cymene})Ru\{C(O)CH_3\}(phen)]^+$ [122].

1.1.4 Derivatives with Sulfur and Selenium Donors

The arene ruthenium complexes of disulfoxide ligands such as DMSO [123], 1,2-bis(ethylsulfinyl)ethane and 1,3-bis(ethylsulfinyl)propane [124] have been prepared and they showed in-vitro anti-cancer activity against a human mammary cancer cell line. Dimethyl sulfide, tetrahydrothiophene and trimethylene sulfide react with $[(\eta^6\text{-arene})RuCl_2]_2$ to give neutral complexes $[(\eta^6\text{-arene})RuCl_2(SR_2)]$ (arene = *p*-cymene, $C_6H_3Me_3$, C_6Me_6). Cationic complexes $[(\eta^6\text{-arene})RuCl(SR_2)_2]PF_6$ and $[(\eta^6\text{-arene})RuCl_2(SR)_2(PMe_3)]PF_6$ have also been made [112]. The tripodal sulfur donor 1,4,7-trithiacyclononane, $CH_2CH_2SCH_2SCH_2CH_2S$ (9S3), reacts with $[(\eta^6\text{-}C_6Me_6)Ru(acetone)_3]^{2+}$ to give $[(\eta^6\text{-}C_6Me_6)Ru(93S)]^{2+}$ which, on treatment with $KOBu^t$, undergoes two successive deprotonation and C-S bond cleavages to give the neutral complex (Figure 1.4)[125].

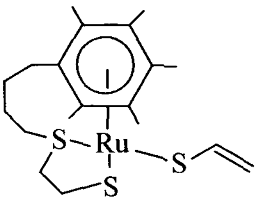


Figure 1.4

Reaction of 2,11-dithia[3^3](1,2)-cyclophane, $C_6H_4(CH_2SCH_2)_2C_6H_4$, with $[(\eta^6\text{-}C_6H_6)Ru(acetone)_3]^{2+}$ gives the BF_4 salt of cationic complex (Figure 1.5), formed from the deprotonation of one of the CH_2 groups and dihapto coordination of the resulting $-^{-}CH_2-$ fragment [126].

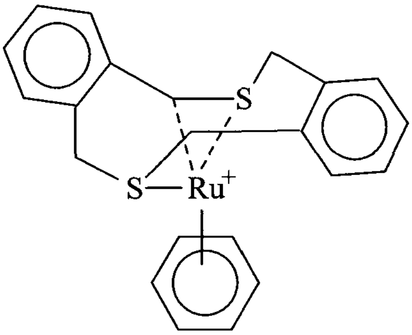


Figure 1.5

The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with dianion of bis(2-mercaptoethyl)sulfide, $(HSCH_2CH_2)_2S$ gives deep red complexes, $[(\eta^6\text{-arene})Ru(\eta^3\text{-}C_4H_8S_3]$ (arene = C_6Me_6, *p*-cymene) and $[(\eta^6\text{-arene})Ru(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C_4H_8S_3]^+$ (arene = C_6Me_6) depending on the reaction conditions [127]. Cationic dinuclear tri-μ-thiolato complexes are readily formed from and areneruthenium(II) halide precursors and sources of thiolate ions such as $Pb(SEt)_2$ [11], NaSPh [128], PhSH/MeLi or PhS(TMS) [129]. The cations have the usual confacial bioctahedral structure; the Ru-Ru separations (ca 0.335 nm) indicate that there is no direct metal-metal bond. Bulky arenethiolate anions react with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ to give deep-blue, monomeric, 16-electron complexes $[(\eta^6\text{-}p\text{-cymene})Ru(SR)_2]$ (R = 2,5-$C_6H_3Me_2$, 2,4,6-$C_6H_2Pr^i_3$), which have a two-legged piano-stool geometry with coplanar Ru-S-C units; this arrangement is attributed to empty d_π(Ru)-filled p_π(S) overlap [130]. A series of *p*-cymene Ru-S clusters complexes have been synthesized via photolysis of $[(\eta^6\text{-}p\text{-cymene})_3Ru_3S_2]^{2+}$ [131]

The complexes $[(\eta^6\text{-arene})RuCl_2]_2$ react with $(Ph_4P)_2[WS_4]$ to give $[\{(\eta^6\text{-arene})\}_2RuCl(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2WS_2)]$, whereas $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PPh_3)]$ gives monomeric $[(\eta^6\text{-}p\text{-cymene})Ru(\eta^2\text{-}S_2WS_2)(PPh_3)]$. The complexes $[(\eta^6\text{-}p\text{-cymene})Ru(\eta^2\text{-}S_2Re_2S_2)]$ and $Pt\{[RuCl(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2WS_2)](\eta^6\text{-}p\text{-cymene})\}_2$ have also been isolated from the halide precursor with $(Et_4N)[ReS_4]$ and $(NEt_4)_2[Pt(WS_4)_2$ respectively [132]. With $(TMS)_2S$, methanolic NaSH or aqueous Na_2S, the halide precursor forms $[(\eta^6$-*p*-cymene$)_3Ru_3(\mu_3$-$S)_2]^{2+}$ where the compound has a *closo*-trigonal bipyrimidal structure with the sulfur atoms at the apices. The compound $[(\eta^6$-*p*-cymene$)_3Ru_3(\mu^3$-$S)_2]^{2+}$ obtained from the dication by reversible two-electron electrochemical reduction or by reaction with cobaltocene, has a *nido* structure resulting from cleavage of one of the metal-metal bonds of the dication [133]. The dicationic selenium analogue $[(\eta^6$-arene$)_3Ru_3(\mu^3$-$Se)_2]^{2+}$ has been obtained by the ultrasound-promoted reaction of $[(\eta^6$-*p*-cymene$)RuCl_2]_2$ with zinc dust and selenium [134]. A new series of cationic dinuclear arene ruthenium thiolato complexes are also prepared recently [135].

1.1.5 Derivatives with Bridging and Bifunctional Ligands

Pyrazole (pzH) reacts with $[(C_6H_6)RuCl_2]_2$ in the appropriate molar ratio in water/methanol to give $[\{(\eta^6$-$C_6H_6)Ru\}_2(\mu$-Cl$)(\mu$-pz$)_2]$Cl and $[\{(\eta^6$-$C_6H_6)Ru\}_2(\mu$-Cl$)_2(\mu$-pz$)]$Cl. Similar complexes are formed by 4-methylpyrazole, but 3-methylpyrazole gives only $[\{(\eta^6$-$C_6H_6)RuCl_2(3$-Me-pzH$)]$ [136]. Mono- and di-μ-hydroxo complexes $[\{(\eta^6$-arene$)Ru\}_2(\mu$-OH$)(\mu$-pz$)_2]$Cl and $[\{(\eta^6$-arene$)Ru\}_2(\mu$-OH$)_2(\mu$-pz$)]$Cl are also obtained [137-138]. Heterobinuclear μ-pyrazolato complexes are obtained by treatment of $[(\eta^6$-p-cymene$)RuCl_2(pzH)]$ with suitable unsaturated metal fragments, for example, $[\{(\eta^6$-p-cymene$)Ru(\mu$-Cl$)_2(\mu$-pz$)Rh(tfb)]$ (tfb = tetrafluorobenzobarrelene) [139], $[\{(\eta^6$-p-cymene$)RuCl(\mu$-Cl$)(\mu$-pz$)Pd(\eta^3$-$C_8H_{11})]$ (C_8H_{11}= cyclooctenyl) [140] and $[\{(\eta^6$-p-cymene$)Ru(\mu$-Cl$)(\mu$-pz$)_2M(cod)]$ (M= Rh, Ir) from which cod can be displaced by ditertiary phosphines and CO [141-142].

The complexes $[\{(\eta^6$-p-cymene$)RuCl_2\}_2(\mu$-L-L$)]$ (L-L = pyrazine or 4,4'-bipyridine) undergo an electrochemical one-electron reduction to give a Ru^I-Ru^{II} species whose ESR spectrum is consistent with complete delocalization of the unpaired electron over the dinuclear unit [143]. In contrast, the corresponding complexes with L-L = dppm and dppf are electrochemically reduced to Ru^O species [144]. New series of mono and binuclear arene ruthenium complexes of immine/azine have been synthesized and the theoretical study on the effects of the arene ligands on coordination properties of the selected ligand, pyridine-2-carbaldehyde azine has been also described [145].

Reaction of secondary phosphines complexes such as $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PHPh_2)]$ with coordinatively unsaturated complexes gives heterodinuclear compounds, for example, $[(\eta^6\text{-}p\text{-cymene})Ru(OC)(\mu\text{-}PPh_2)Co(CO)_3]$ from $[Co_2(CO)_8]$ [146] and $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)M(diene)]$ (M = Rh, diene = cod, tfb; M = Ir, diene = cod) from $[\{M(OMe)(diene)\}_2]$ [147]. Terminal phosphido complexes of iridium(III) react with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ to give μ-phosphido heterodinuclear species, e.g., $[(\eta^6\text{-arene})RuCl_2(\mu\text{-}PH_2)IrHBr(CO)(PEt_3)_2]$ [148-149]. Heterobimetallic complexes such as $[(\eta^6\text{-arene})RuCl(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]$ are formed from $[(SPPh_2)_2Pt(S_2CNEt_2)]^-$ and *p*-cymene dimer. The tri- and penta-nuclear complexes such as $[(\eta^6\text{-}C_6H_6)_2\{(SPPh_2)_2Pt(S_2CNEt_2)\}_2Ru_2(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]^+$ can be obtained by addition of more $[(SPPh_2)_2Pt(S_2CNEt_2)]^-$ [150]. A cationic complex, $[(\eta^6\text{-}C_6Me_6)RuCl(\eta^2\text{-}S_2CPCy_3)]PF_6$ obtained from $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ and zwitterion $Cy_3P^+\text{-}CS_2^-$ reacts with $[(CO)_3M(NCMe)_3]$ (M = Mo, W) to form binuclear complexes (Figure 1.6). One of the CO groups is easily replaced by PEt_3 or $P(OMe)_3$ without disruption of the dinuclear framework [151].

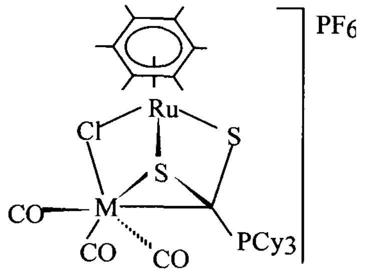


Figure 1.6

The bridging P, S or P, O – chelating ligands, 1,2-bis-S-[2'-(diphenylphosphino)-benzoyl]dithioethane (dppte) and 1,2-bis-N-[2'-(diphenylphosphino)benzoyl]diamino-naphthalene (dppan) react with $[(\eta^6\text{-p-cymene})RuCl_2]_2$ to give dicationic dinuclear complexes $[\{(\eta^6\text{-p-cymene})RuCl\}_2(L)]^{2+}$ (L = dppte, dppan) [152].

1.2 The Chemistry of cyclopentadienyl bistriphenylphosphine ruthenium(II) and osmium(II) complexes

The compound [$CpRu(PPh_3)_2Cl$], first prepared by Wilkinson (1969) and later developed by Bruce et al. [153] has shown that it is one of the most attractive molecule for synthetic manipulation. The primary motivation of our studies on this compound has been the synthetic reactions of [$CpRu(PPh_3)_2Cl$] with potentially bridging polypyridyl ligands to study the physical and chemical properties of the complexes formed and therefrom deriving, if possible any clue which might throw some light on the electronic or steric effects on their synthesis.

A closely related osmium analoque, [$CpOs(PPh_3)_2Br$] has been prepared [154-155]. However, literature survey reveal that there is noticeable lack of emphasis on this compound which could be due to the lower kinetic lability of osmium relative to ruthenium and more likely, the greater cost of osmium. The aim of our synthetic work on [$CpOs(PPh_3)_2Br$] is to study its reactivity towards mono-, di- or ter-dentate ligands keeping in mind to compare and contrast the structures and properties with that of the cyclopentadienyl ruthenium system.

Studies on ruthenium complexes containing cyclopentadienyl and triaryl or alkyl phosphine as coligands have been accompanied to a very large extent by an interest in the ligand substitution processes at plus two valent metal center. The literature survey reveals the excellent work of Bruce et al. where it has been shown that the complex [$CpRu(PPh_3)_2Cl$] is the one of the most attractive molecule for synthetic manipulation. Generally, two approaches have been applied to the synthesis of various complexes. One of them has centered around the reaction of the Ru-Cl bond resulting in the replacement of chlorine either by other anions or by neutral ligands to give cationic complexes of the type $[CpRu(PPh_3)_2(L)]^+$ which is possibly based on the fact that the following reaction equilibrium lies largely on the right in its methanolic solution [156].

$$CpRu(PPh_3)_2Cl \xrightleftharpoons{\text{MeOH}} [CpRu(PPh_3)2(MeOH)]^+Cl^-$$

The second approach is based on the ready loss of one the of PPh_3 molecules, a feature of the reactions of N,N'-donor bases. In addition, there is also a third possibility of the reactions, though very little studied, were C_5H_5 group could be activated towards substitution. The suggested factors for accounting these behaviors are: (a) the high electron density on ruthenium because of the presence of two PPh_3 ligands and (b) the steric interactions between the two bulky PPh_3 molecules [157]. At present it appears from the structural analysis that there exists a highly crowded environment around phenyl rings not only in the triphenylphosphine complexes, but also in the analogous complex $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2Cl]$ [158].

Although the continued appearance of scientific papers over the past 25 years concerning one or more aspects of the synthetic reaction of this molecule and its derivatives attests undoubtedly, the enduring importance of this molecule and its derivatives, examination of the literature however, indicates that in almost all these reactions emphasis has been given to the reactions with unsaturated organic compounds and their derivatives resulting in the formation of some unusual π and σ-bonded complexes. One cannot, however, overlook the fact that there are many hetero-cyclic bases having the delocalised π-electrons, capable of forming both σ and π type of complexes.

1.2.1 Complexes containing N-, P-, As, Sb- and O - donor

The compound $[CpRu(PPh_3)_2Cl]$ is an important precursor to other half sandwich ruthenium complexes. Detailed reviews of derivatives of this compound have been published [159-161]. The PPh_3 ligands are stepwise replaced by many monodentate and by bidentate ligands. Complexes of the general formula $[CpRu(L)_2Cl]$ are also readily prepared by displacement of cod from the complex [CpRu(cod)Cl] (Table 1.1) . The complexes $[CpM(PPh_3)_2Cl]$ (M = Ru, Os) have the expected pseudotetrahedral arrangement about the metal atom. The M-Cl bond length is ~ 0.0007 nm shorter for Ru then for Os as expected on the basis of atomic radii, whereas Ru-P is ~ 0.0015 nm longer than Os-P possibly reflecting severe steric interactions between the PPh_3 ligands [175]. The reaction of the complex $[CpM(PPh_3)_2Cl]$ with various phosphines or phosphites in benzene, according to the reactant concentrations, afforded mono or di-substituted product which results from the substitution of the triphenylphosphine(s). For example, with dppm in benzene, it gives either [CpRu(PPh_3)(dppm)Cl] or [CpRuCl(dppm)] but in acetonitrile the product is [CpRu(PPh_3)(dppm)]Cl which further dissociate PPh_3 with the second molecule of dppm to give $[CpRu(dppm)(dppm)]^+$. The uncoordinated P atom in [CpRu(PPh_3)(dppm)Cl] can be quarternized by methyl iodide to give [CpRuI(PPh_3)($Ph_2CH_2PMePh_2$)]I [176-177]. Unsymmetrical bidentate ditertiary phosphines such as (R)- $Ph_2PCH(RCH_2PPh_2$ (R = Me, Ph), (S)-$Ph_2PCH(Cy)CH_2PPh_2$, (2R,3R)-norbornene-2,3-diylbis(diphenylphosphine) (norphos) and (S)-N-diphenylphosphino-2-(diphenylphosphinoxymethane)pyrrolidine react with [CpRu(PPh_3)$_2$Cl] to give diastereomers [CpRuCl(P-P)] in nearly 1:1 ratio at 353 K, although in the first three cases one diastereomer is formed predominantly in the incomplete reaction at room temperature [178-180]. The carbonylation (1-3 bar) of [CpRu(PPh_3)$_2$Cl] in the presence sulfur removes one PPh_3 as Ph_3PS to give [CpRu(PPh_3)(CO)Cl] [181], this maybe prepared also by heating [CpRu(PPh_3)$_2$Cl] in ethylene glycol [182].

Table 1.1 [CpRu(L^1)(L^2)Cl] complexes

(L^1)(L^2)	*Method of preparation*[a]	*Reference*
$(PMe_3)_2$	A,B	162,163,164
$(PMe_2Ph)_2$	A	163
$(PMePh_2)_2$	A	163
$(PEt_2Ph)_2$	A	163
$\{P(OMe)_3\}_2$	A,B	163-116
$\{P(OEt)_3\}_2$	A	162
$\{PPh_2(OMe)\}_2$	A	162
$(AsPh_3)(PPh_3)$	A	167
$(ASPh_3)_2$	A	167, 168
$(SbPh_3)_2$	A[b]	167
$(PPh_2H)_2$	B	164
$\{P(OMe)_3\}(PPh_3)$	A	165
$\{P(OPh)_3\}(PPh_3)$	A	165
$(Bu^tNC)(PPh_3)$	A	168

$Ph_2PCH_2CH_2PPh_2$ (dppe)	A, B	163, 164
$Cy_2PCH_2PCy_2$ (dcpe)	C	169
$Cy_2PCH_2PCy_2$ (dcpm)	A	170
$Fe(C_5H_4PPh_2)_2$ (dppf)	A	171
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe)	A	172
(PPh_3)(py)	A	173
(PPh_3)(2- or 3-pic)	A	173
(EPh_3)(RCSNHCOOEt)	A	173
(EPh_3)(RCSNHCONHPh)[C]	A	174

[a] A, from $[CpRu(PPh_3)_2Cl]$; B, from [CpRu(cod)Cl]; from $RuCl_3$-EtOH, Cp and the ligand. [b] From $[CpRu(AsPh_3)_2Cl]$, [C] E = P, As; R = 2-pyrrole, 2- thiophene, 4- toluene.

The chloride ion is readily displaced from the $[CpRu(L)_2Cl]$ and [CpRu(L)(CO)Cl] complexes by a wide range of anionic and neutral ligands; the latter include both conventional π-acceptors, such as CO, RNC and PR_3, weaker π-acceptor N-donor ligands such as pyridine and nitrile, and saturated ligands such as NH_3. The reactions are generally carried out in polar solvents, such as alcohols, often in the presence of NH_4BF_4, NH_4PF_6 and similar salts, or by use of silver salts of weakly coordinating anions; in both cases, labile solvento-cations are likely intermediates. Some examples the many complexes isolated are given in Table 1.2.

Table 1.2 Cationic complexes derived from $[CpRuCl(L)_2]$

Complexes	*Reference*
$[CpRu(CO)(PPh_3)_2]^+$	183 -184
$[CpRu(CO)(PPh_3)(L)]^+$ [L= CO, PMe_3, $P(OPh)_3$, Bu^tNC]	181, 185
$[CpRu(CO)(PMe_3)(L)]^+$ [L = MeCN, CO, Bu^tNC, PMe_3)	162, 164
$[CpRu(CO)(dcpm)]^+$	170
$[CpRu(NCMe)(L)_2]^+$ (L = wide range of PR_3)	163
$[CpRu(DMSO)(L)_2]^+$ (L = PR_3; L_2 = dppm, dppe)	163
$[CpRu(L)\{P(OMe)_3\}_2]^+$ (L = MeCN, CO)	166, 186
$[CpRu(NCR)(L)_2]^+$ (L = PPh_3, PMe_3, $AsPh_3$, $SbPh_3$,, L_2 = dppm, dppe; R = alkyl and aryl substituents)	167,187-9
$[\{CpRu(PPh_3)_2\}_2(\mu\text{-}1,4\text{-}C_6H_4(CN)_2)]^{2+}$	189

$[CpRu(4\text{-}NCC_5H_4N)(L)_2]^+$, $[\{CpRu(L)_2\}_2(\mu\text{-}4\text{-}NCC_5H_4N)]^{2+}$ (L = PPh_3,$AsPh_3$, L_2 = dppm, dppe)	190
$[CpRu\{NC_5H_4CH{=}NNHPh)(PPh_3)]^+$, $[CpRu\{NC_5H_4CH{=}NNHPh)(py)]^+$	191
$[CpRu(N\text{-}N)(PPh_3)]^+$ (N-N= bipy, phen, pn, biimidazole, 2-(2'-pyridylbenzimidazole)	174, 192
$[CpRu(N_2C_6H_4OMe)(PPh_3)]^+$, $[CpRu(N_2C_6H_4OMe)(PPh_3)_2]^{2+}$	193

The complex $[CpRu(CO)(PPh_3)_2][Co(CO)_4]$ is one of the products formed from the reaction of $[CpRu(PPh_3)_2Cl]$ with $[Co(CO)_4]^-$ [183]. The Ru-Cl bond in [CpRu(dpfe)Cl] is significantly shorter as compared to that in $[CpRu(PPh_3)_2Cl]$ and so less labile and inert towards AgOTf, $TlBF_4$ and TMS-OTf but with $AgBF_4$-CH_2Cl_2 under CO, however give $[CpRu(CO)(dpefe)]BF_4$ [172]. The pseudo-first-order rates of solvolysis of Cl^- in $[CpRu(L)_2Cl]$ in DMSO-d_6 to give $[CpRu(DMSO)(L)_2]^+$ vary in the order $L_2 = 2PMe_3 > 2PMe_2Ph > 2PMePh_2 >$ dppe $> 2PPh_2(OMe) > 2PMe(OMe)_2$ and seem to be determined largely by the donor ability of L rather than by steric effects [194]. Treatment of $[CpRu(PPh_3)_2Cl]$ with appropriate Na or K salts gives $[CpRu(PPh_3)_2Y]$ (Y = NCS, NCO, NO_2, CN, NCS) [195-198]. The nitrogen atom in the cyano-complexes is attacked by many electrophiles [196, 199] and also bind to the second metal atom to form dinuclear cationic cyano-bridged complexes of the general formula $[Cp(L)_2Ru(\mu\text{-}CN)M(L)_2Cp]^+$ (M = Ru, $L_2 = 2PPh_3$, dppe; M =Fe, $(L)_2$ = dppe) [200]. μ-Cyano complexes of this type are also obtained by heating $[CpRu(L)_2Cl]$ complexes with 1,3,5-triazine [201]. Reactions between $[CpRu(PPh_3)_2Cl]$ and the appropriate cyano-substituted anion give $[CpRuR(PPh_3)_2]$ (R=$CH(CN)_2$, $C(CN)_3$, $N(CN)_3$, $C_3(CN)_5$ and $N\{C_2(CN)_3\}_2$) in which the anions are *N*-bonded to the metal atom [202-203].

The ammine complexes $[CpRu(NH_3)(PPh_3)_2]^+$ may be obtained by treatment of the chloro precursor with NH_4PF_6 in methanol or with AgOTf and NH_3 [204-205, 169] , the ammine cation $[CpRu(NH_3)(Cy_2PCH_2CH_2PCy_2)]$ is deprotonated by KH to give amide $[CpRu(NH_2)(Cy_2PCH_2CH_2PCy_2)]$ which is methylated to $[CpRu(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]$ by $[NMe_4]BF_4$. With CO, the amide forms carbomyl complex $[CpRu(CONH_2)(Cy_2PCH_2CH_2PCy_2)]$ and with CO_2 gives carbamate

$[CpRu(OCONH_2)(Cy_2PCH_2CH_2PCy_2)]$. The reaction of $[CpRu(PPh_3)_2Cl]$ with NH_4PF_6 in the presence of benzaldehyde gives benzaldimine complex [205] and with $AgBF_4$ in CH_2Cl_2 gives aqua salt $[CpRu(CO)(PPh_3)(H_2O)]BF_4$ [206]. Addition of alkyl or aryl Iodides to $[CpRu(L^1)(L^2)(Solv)]^+$ (solv = CH_2Cl_2, THF) gives cations $[CpRu(RI)(L^1)(L^2)]^+$ (L^1 = CO, Bu^tNC, $L^2 = PPh_3$; $L^1 = L^2 = PPh_3$; L^1,L^2 = dppe) [185], [207-208]. The complex $[CpRu(\eta^2\text{-}H_2)(CNBu^t)(PPh_3)]PF_6$ with MeI gives methyl iodide complex [185]. Phosphinoethers ligands cause complete or partial displacement of PPh_3 to give P-bound complexes $[CpRu(PPh_3)Cl(Ph_2CH_2CH_2OMe)]$ or $[CpRuCl(Ph_2CH_2CH_2OMe)]$ where the latter with $AgSbF_6$ give $[CpRu(Ph_2CH_2CH_2OMe)(Ph_2CH_2CH_2OMe)]SbF_6$ [209]. The tridenate ligands (P-P-P) with NH_4PF_6 give $[CpRu(P\text{-}P\text{-}P)]PF_6$ [210]. The diazabutadiene complex $[CpRuCl(RN{=}CHCH{=}NR)]$ are obtained by treating $[CpRu(PPh_3)_2Cl]$ with the ligands and with CF_3CN, it give $[CpRu\{NH{=}C(CF_3)N{=}C(CF_3)NH\}(PPh_3)]$ [211].

1.2.2 Hydrides Complexes

Monohydride complexes of the general formula $[CpRu(PPh_3)_2H]$ are best prepared by heating the chloro compound with sodium methoxide prepared in situ in methanol. The hydride are probably formed by the β-elimination from intermediate methoxides. Other reducing agents that have been used are secondary and tertiary alkyl Grignard reagents [212-213] and sodium formate [214]. [CpRu(L)H] (dppe, dcpe) are also obtained from the reaction of LAH on the appropriate chloro precursor [200, 169, 215]. Some monohydride complexes are listed in Table 1.3.

Table 1.3 Some monohydride complexes $[CpRuH(L^1)(L^2)]$

Cp M	L^1,L^2	Reference
Ru,Os	$(PPh_3)_2$	168, 195, 200, 216
Ru	$(AsPh_3)_2$	168
Ru	$(Bu^tNC)(PPh^3)$	168
Ru	$(PPh_3)\{P(OPh)_3\}$	168
Ru	dppm, dppe, dpae	168, 217
Ru	dppf	171

The halide complexes [CpMX(L)$_2$] are protonated, for example by HPF$_6$ at room temperature to give hydridometal(IV) salts [CpMHX(L)$_2$]$^+$ (M = Os, X = Cl, Br, I, L = PPh$_3$; M = Os, X = Br, L = PMePh$_2$; M = Ru, X = Cl, Br, L = PMe$_3$, PPh$_3$) which have trans structure (Figure 1.6) [218-219].

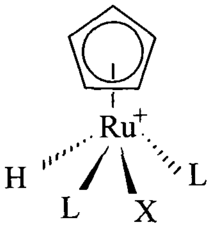


Figure 1.6

The complex [CpOsH(L)$_2$] are readily protonated, for example, by TfOH, TsOH or camphor-10-sulfonic acid, to give dihydridoosmium(IV) cations [CpOsH$_2$(L)$_2$]$^+$ (L = PPh$_3$, PMePh$_2$) [219-220]. Calometric studies of the protonations showed that the hydrides [CpOsH(L)$_2$] are 10^{14}- 10^{15} times more basic than the corresponding bromides. The basicities of [CpMX(L)$_2$] increase slightly in the order X = I < Br < Cl and correlate with the gas-phase proton affinities of the anions [219].

Extensive review on the σ-bonded carbon such as vinyl, acetylide, carbene (alkylidene), vinylidene, allenylidene, cumulene and azavinylidene complexes and cyclometallated complexes of cyclopentadienyl ruthenium and osmium complexes is available [221].

1.2.5 Complexes containing S-, Se-, Si- donor

The thiolato complexes [CpRu(PPh$_3$)$_2$(SR)] are obtained from the chloro compound with MSR (M = Na, Li) [222-226] and the SR ligands labilize PPh$_3$, for example, on treatment with CO (1 bar), it rapidly liberates [CpOs(PPh$_3$)(SR)(CO)] (R = H, Me) and on heating [CpRu(PPh$_3$)$_2$(SR)] loses PPh$_3$ to give [Cp$_4$Ru$_4$(μ_3-SR)$_4$] (R = Pr^n, Pr^i) [227-228]. Cationic complexes containing neutral thiols, [CpRu(RSH)(L^1)(L^2)]Y, are formed by treating the parent chloride with the thiol in the presence of NH$_4$PF$_6$ or AgBF$_4$ (R = Ph, Bu^t, PhCH$_2$, PhCH$_2$CH$_2$, L^1 = L^2 = P(OMe)Ph$_2$, P(OMe)$_2$Ph, P(OMe)$_3$; L^1 = PPh$_3$, L^2 = CO, P(OMe)$_3$, Bu^{t}NC; L^1, L^2 = dppm; Y = PF$_6$, BF$_4$ (not all combinations) [229-232].

Treatment of [$CpRu(PPh_3)_2(OTf)$] with ethane sulfide (thiirane) gives [$CpRu(PPh_3)_2(SCH_2CH_2)$]OTf [233] and with 2,5-dihydrothiophene (DHT) in the presence of $NaPF_6$ it gives [$CpRu(PPh_3)_2(DHT)$] where the ligand is S – bonded 234]. Similar complex containing S - bound thiophene is obtained from [$CpRu(PPh_3)_2Cl$], $AgBF_4$ and thiophene. The complex [$Ru(PPh_3)_2(\eta^5$-$C_5H_4CH_2C_4H_3S)$] is obtained from the reaction of $RuCl_3$, PPh_3 and cyclopentadienylthiophene ligand derived from $C_5H_5CH_2C_4H_3S$, in this compound, the ligand is not S - bound but on treatment with $AgBF_4$, it forms the chelate η^1-S-thiophene salt [$Ru(\eta^5$-$C_5H_4CH_2C_4H_3S)(PPh_3)_2$]$BF_4$ [235].

The selenolato-complexes [$CpRu(PPh_3)_2(SeH)$] is obtained by reaction of the chloro compound with NaSeH [236]. The dithiocarbamato and xanthates complexes of the type [$CpRu(PPh_3)(\eta^2$-$S_2CNR_2)$] and [$CpRu(PPh_3)_2(\eta^1$-$S_2COR_2)$] (R = Me, Et) respectively are obtained from the appropriate sodium salts and chloro compound in methanol [195, 237-239]. Complexes containing anionic sulfur donors are also obtained by insertion reactions into M - H, M - C, M - S bonds. Reaction of COS and CS_2 with [$CpRuH(PPh_3)_2$] form S-bonded thioformato complexes [$CpRu(PPh_3)_2(\eta^1$-SCHX)] (X = O, S) [215, 240]. Prolonged heating of [$CpRu(C_2Ph)(PPh_3)_2$] with CS_2 causes insertion into Ru - C_2Ph bond to give [$CpRu(\eta^2$-$S_2CC_2Ph)(PPh_3)_2$] [241]. The binuclear complexes [{$CpRu(PPh_3)$}$_2$(μ-η^2,η^2-MS_4)] (M = Mo, W) are also obtained from reaction of the chloro compound with [PPh_4][MS_4] [242-243].

Treatment of [$CpRu(PPh_3)_2Cl$] with SO_2 in the presence of NH_4PF_6 afforded S-bound SO_2 complex, [$CpRu(PPh_3)_2(\eta^1$-$SO_2)$], this compound is also obtained from treatment of [$CpRu(PPh_3)_2Cl$] with thiiran-1-oxide, CH_2CH_2SO by elimination of ethane [244-245]. S - bonded sulfinato complexes [$CpRu(\eta^1$-$SO_2R)(PPh_3)_2$] can be made by insertion of SO_2 into the Ru-C bonds of [$CpRuR(PPh_3)_2$] (R = Me, CH_2Ph) [246]. The SO_2 ligand adds to the S atom of thiolate ligands and substitute PPh_3 in [$CpRu(SR)(PPh_3)_2$] (R = Me, Pr^n, Pr^i, p-Tol), however, only the initial adduct [CpRu{η^1-$SR(SO_2)$}$(PPh_3)_2$] could be isolated and not the substitution products [247]. The thiolato complex [$CpRu(SH)(PPh_3)_2$] react with sulfinyl tranfer agent $RSONCOC_6H_4CO$ to give thiosulfinato complex [CpRu{S(SOR)}$(PPh_3)_2$] [248-249]. The reaction of alkyl complexes $[CpOs(CH_2SiMe_3)(PPh_3)_2]$ with excess $HSiR_2Cl$ afforded osmium(IV) complexes $[CpOs(H)(SiR_2Cl)_2(L)]$ (L = PPh_3; R = Ph, Me), in contrast, the complex $[CpOs(CH_2SiMe_3)(PMe_3)_2]$ afforded osmium(II) complex, $[CpOs(SiR_2Cl)(PMe_3)_2]$ (R = Ph not Me) [154].

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Chapter II

Synthesis, characterization and reactivity studies of cyclopentadienyl bis(triphenylphosphine) osmium(II) complexes [1,2]

2.1 Abstract

The reaction of [CpOs(PPh_3)$_2$Br] with monodentate anion or neutral ligands in dry methanol yielded complexes of the type [CpOs(PPh_3)$_2$X]$^{0/+}$ (X = CH_3CN, CN, NCS, NO). The reactions of the complex [CpOs(PPh_3)$_2$(CH_3CN)]$^+$ with chelating ligands L_2, where L_2 = 2, 2'- bipyridine (bipy), 1,10- phenanthroline (phen), yielded cationic complexes of the type [CpOs(L_2)(PPh_3)]$^+$. The cationic complexes were isolated as BF_4 salts. These compounds were characterized by ^{1}H NMR, ^{31}P{^{1}H}NMR and IR spectral data. The molecular structure of [CpOs(phen)(PPh_3)]BF_4 has been determined by single X-ray crystallographic method.

The reaction of [CpOs(PPh_3)$_2$Br] with diphenylpropargylic alcohol HC≡CPh$_2$(OH) in the presence of ammonium hexafluorophosphate leads to the formation of cationic osmiumallenylidene complex [CpOs(C=C=CPh$_2$)(PPh_3)$_2$][PF_6], but when the dimethylpropargylic alcohol HC≡CCMe$_2$(OH) was used as a substrate, unexpected dimerization product, a dicationic diosmium vinylidene-alkylidene complex of the formula [(CpOs)$_2$(μ-$C_{10}H_{12}$)(PPh_3)$_4$][PF_6]$_2$ was obtained.

2.2 Introduction

Cyclopentadienyl ruthenium half sandwich complexes are the most extensively studied class of cyclopentadienyl chemistry among the transition metal complexes. The spectrum of reactivity and chemical properties to date for this system is remarkable, especially considering the limited number of synthetic precursors, viz. [CpRu(PPh_3)$_2$Cl] and [CpRu(CO)$_2$Cl] [1]. Recently, more convenient routes have been developed by use of easily exchangeable ligands [2]. However, not much work has been carried out in the case [CpOs(PPh_3)$_2$Br], which could be due to lower kinetic lability of

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[1] R. Lalrempuia, Patrick J. Carroll, Mohan Rao Kollipara, *Polyhedron*, 22 (2003) 1391.

[2] R. Lalrempuia, Hemant Yennawar, Yurij Mozharivskyi, Mohan Rao Kollipara, *J. Organomet. Chem.*, 689 (2004) 539.

the phosphines compared to its ruthenium analogue. For instance, in the case of ruthenium, the substitution of two triphenylphosphines by chelating diphos ligands takes place readily in boiling benzene or toluene, whereas the same reaction requires boiling in decaline for several hours in case of its osmium analogue [3]. But it was observed that the dissociation of M-X bond takes place readily in polar solvents such as methanol for both the cases [4]. Our current interest in the cyclopentadienyl osmium complex bearing triphenylphosphines prompted us to investigate its reaction with some monodentate ligands as well as alkynols. The current interest in complexes containing unsaturated carbon chains arises mainly due to their potential to form molecular wires [5] and other nano-electric devices [6]. The use of transition metal allenylidene complexes in organic synthesis is also well documented [7]. Reliable methods of the preparation of the metal allenylidene complexes ($M=C=C=CR_2$) have been developed two decades ago [8,9]. The first example of a stable allenylidene complex $[CpRu(C=C=CPh_2)(PMe_3)_2]^+$, was obtained by the activation of dimethylpropargylic alcohol with $[CpRuCl(PMe_3)_2]$ [10] in methanol and this method has found widespread application for synthesis of allenylidene complexes of other elements. Recently, few reports are available on the allenylidene complexes containing $[CpOs(PiPr_3)_2]$ fragment [11], but the chemistry of more classical $[CpOs(PPh_3)_2Br]$ remains relatively unexplored [12].

One part of this chapter described the synthesis of some complexes arising from the substitution reactions at Os-Br and Os-P bonds. In methanol, bromide was replaced by other anions to give neutral complexes of the type $[CpOs(PPh_3)_2X]$ and cationic complex $[CpOs(PPh_3)_2(NCCH_3)]^+$ was isolated. Reaction of $[CpOs(PPh_3)_2(NCCH_3)]BF_4$ with chelating ligands L_2 by refluxing in toluene followed by methanol yielded cationic complexes $[CpOs(L_2)(PPh_3)]BF_4$ (L_2 = bipy, phen). In another part, we describe the synthesis and structure of new allenylideneosmium(II) complex $[CpOs(C=C=CPh_2)(PPh_3)_2][PF_6]$ and a diosmium vinylidene-alkyidene complex $[(CpOs)_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4][PF_6]_2$.

2.3 Experimental Section

All solvents were dried and distilled by standard methods. All chemicals were obtained from commercial source. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model-983 spectrophotometer. ^1H NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external tetramethylsilane. $^{31}P\{^1H\}$ NMR chemical shifts are recorded relative to H_3PO_4 (85%). Elemental analyses were performed by Regional Sophisticated Instrumentation Centre (RSIC), NEHU, Shillong. $[CpOs(PPh_3)_2Br]$ was prepared according to literature procedures [13].

2.3.1 Preparation of the complexes

Preparation of $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ ***(2.3a)***

A mixture of $[CpOs(PPh_3)_2Br]$ (100 mg, 0.116 mmol) and NH_4BF_4 (25 mg, 0.24 mmol) was refluxed in acetonitrile (20 ml) under nitrogen atmosphere. The insoluble starting material slowly dissolved and the color changed to very pale yellow solution after 1h. The solvent was then evaporated under reduced pressure. The residue was extracted with acetone, filtered and the volume of the filtrate was reduced to about 1 ml and addition of hexane yielded a cream colored product. The compound recrystallized from dichloromethane / diethylether giving grey needle shaped crystals. Yield: 86 mg, 82%.

Anal. Found: C, 56.88; H, 4.20; N, 1.56. Calc. for C43H38BF4NP2Os: C, 56.89; H, 4.21; N, 1.54

^1H NMR ($CDCl_3$, δ): 7.34-7.01 (m, 30 H, Ph), 4.66 (s, 5H, Cp), 2.41 (s, 3H, CH_3).

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

IR (KBr, cm^{-1}): 2282 m, $\nu_{(CN)}$, 1082 s, br, $\nu_{(BF)}$.

Preparation of $[CpOs(PPh_3)_2CN]$ ***(2.3b)***

A mixture of $[CpOs(PPh_3)_2Br]$ (200 mg, 0.233 mmol) and 600 mg of KCN was refluxed in methanol (20 ml) for 3 hours. A pale yellow solution was evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 and excess KCN was filtered off. Addition of excess hexane into CH_2Cl_2 solution yielded the product as a colorless crystalline solid.

Yield: 120 mg, 64 %.

Anal. Found: C, 62.55; H, 4.36; N, 1.69. Calc. for C42H35NP2Os: C, 62.59; H, 4.37; N, 1.73

^{1}H NMR ($CDCl_3$, δ): 7.33 (m, 30H, Ph), 4.46 (s, 5H, Cp).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 2.76 (s).

IR (KBr, cm^{-1}): 2063 s, $\nu_{(CN)}$

*Preparation of [CpOs(PPh$_3$)$_2$(NCS)] **(2.3c)***

This complex was prepared in similar manner to that of complex 3. Here KSCN was used instead of KCN. The compound is yellow in color.

Yield: 60 mg, 64 %.

Anal. Found: C, 59.99; H, 4.16; N, 1.59. Calc. for C42H35NP2SOs: C, 60.20; H, 4.21; N, 1.67

IR (KBr, cm^{-1}): 2108 s, $\nu_{(NCS)}$

*Preparation of [CpOs(PPh$_3$)$_2$(NO)](BF$_4$)$_2$ **(2.3d)***

The mixture of [CpOs(PPh_3)$_2$Br] (100 mg, 0.116 mmol) and HCl (1mL) were refluxed in EtOH (30 ml) for 1 hour. Then $NaNO_2$ (168 mg, 2.434 mmol) in water (1 ml) was added, the whole mixture turns homogeneous yellowish clear solution and was filtered while hot. NH_4BF_4 (aq) was added to the filtrate and was then left overnight resulting in the formation of a yellow precipitate that was collected by centrifuge.

Yield = 60 mg, 52.6%.

Anal. Found: C, 49.98; H, 3.00; N, 1.45. Calc. for C41H35B2F8NOP2Os: C, 50.07; H, 3.07; N, 1.42

^{1}H NMR ($CDCl_3$, δ): 7.51 – 7.05 (m, 30H, Ph), 6.23 (s, 5H, Cp).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): -2.06 (s).

IR (CsI, cm^{-1}): 1845 s, $\nu_{(NO)}$, 1062 s, br, $\nu_{(BF)}$.

*Preparation of [CpOs(PPh$_3$)(bipy)]BF$_4$ **(2.3e)***

A mixture of [CpOs(PPh_3)$_2$(CH_3CN)]BF_4 (100 mg, 0.110 mmol) and 2,2'-bipyridine (55 mg, 0.354 mmol) was refluxed in toluene (30 mL) for 12 hours and the solvent was removed in a rotary evaporator to dryness. Then methanol (30 mL) was added, the color of the solution turns deep red and was refluxed for 10 hours. Methanol was removed in rotary evaporator under reduced pressure. The residue was dissolved in dichloromethane and loaded onto silica gel column (hexane) where 20 ml of dichloromethane was first run to this column. The red band of the compound was eluted with a mixture of CH_2Cl_2 and methanol (3:1). The solution was evaporated to dryness, dissolved in acetone (1 ml) and addition of excess hexane precipitated the product as a dark red crystals.

Yield: 30 mg, 35.8%.

Anal. Found: C, 52.00; H, 3.56; N, 3.50. Calc. for C33H28BF4N2POs: C, 52.11; H, 3.71; N, 3.68

^{1}H NMR ($CDCl_3$, δ): 9.29 (d), 7.87 (d), 7.68 (t), 7.40-6.70 (m) and 4.90 (s, Cp).

^{31}P {^{1}H} NMR (CDC13, δ): 16.65 (s).

IR (KBr, cm^{-1}): 1089 s, br,$\nu_{(BF)}$. UV-Vis (λ max in CH_3CN) = 392 nm.

Preparation of $[CpOs(PPh_3)(phen)]BF_4$ ***(2.3f)***

This compound was prepared in similar manner to the preparation 6 except 1,10-phenanthroline was used instead of 2,2'-bipyridine.

Yield: 36 mg, 41.6 %.

Anal. Found: C, 53.55; H, 5.56; N, 3.50. Calc. for C35H28BF4N2POs: C, 53.57; H, 3.59; N, 3.57

^{1}H NMR (Acetone d_6, δ): 9.91 (d, 2H), 8.39 (d, 2H) 8.03 (s, 2H) 7.63 (d, 2H), 7.30-6.92 (m, 17H), 5.21 (s, 5H, Cp).

^{31}P {^{1}H} NMR (δ): 22.60 (s).

IR (KBr, cm^{-1}): 1089 s, br, $\nu_{(BF)}$.

UV-Vis (λ max, in CH_3CN) = 375 nm.

Preparation of $[CpOs\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ ***(2.3g)*** *and $[(CpOs)_2(PPh_3)_4(\mu\text{-}C_{10}H_{12})][PF_6]_2$* ***(2.3h)***

The mixture of $[CpOs(PPh_3)_2Br]$ (100 mg, 0.117 mmol), alkynols (0.312 mmol) and NH_4PF_6 (52 mg, 0.320 mmol) were refluxed in 45 mL methanol under dry nitrogen atmosphere for 6h. The whole solution was left at 0°C overnight whereby unreacted $[CpOs(PPh_3)_2Br]$ crystallized out which were removed by filtration. The solution was then rotary evaporated to dryness. The residue was extracted with dichloromethane and filtered through short silica gel to remove white precipitate of NH_4Cl. Subsequent concentration and addition of the excess hexane give **2.3g** as red brown solid and **2.3h** as red-purple solid.

(2.3g) Yield: 60 mg, 83 %

^{1}H NMR ($CDCl_3$, δ): 7.81 (t, 2H, J_{H-H} = 9Hz), 7.64 (d, 4H, J_{H-H} = 6Hz), 7.38-7.27 (m, 10H), 7.14-6.98 (m, 24H), 5.31 (s, 5H, Cp).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): - 0.66 (s), - 143 (sept).

IR (KBr pellet, cm^{-1}): 1924 $\nu_{(C=C=C)}$, 844 $\nu_{(PF6)}$.

UV-Vis (CH_2Cl_2): (λ_{max} = 474 nm, ε = 1.2 x 10^4)

Anal. Calcd. for C57 H45 Cl3 F6 Os1 P3: C, 55.50; H, 3.67. Found: C, 55.82; H, 3.46.

(2.3h) Yield: 80 mg, 68 %

^{1}H NMR ($CDCl_3$, δ): 7.70-6.90 (m, ph), 6.3 (s, 1H, vinyl), 5.44 (s, 5H, Cp), 4.95 (s, 5H, Cp), 2.34 (s, 6H, CH3), 1.07-1.00 (m, 4H, CH_2).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): - 0.74, - 6.27 (s), - 143 (sept).

IR (KBr pellet, cm^{-1}): 1573 $\nu_{(C=C)}$, 844 $\nu_{(PF6)}$.

UV-Vis (CH_2Cl_2): (λ_{max} = 498 nm, ε = 1.3 x 10^4)

Anal. Calcd. for C92H82F12O2Os2P6: C, 54.87; H, 4.10. Found: C, 54.91; H, 4.29.

2.4 Results and discussion

2.4.1 Cyanide and nitrogen donor complexes

The reaction of the complex [$CpOs(PPh_3)_2Br$] with anions take place by refluxing in methanol yielding complexes of the type [$CpOs(PPh_3)_2X$] via solvated compound [$CpOs(PPh_3)_2(MeOH)$]$^+$ as shown in Scheme 2.1. Complex **2.3a** was obtained by refluxing [$CpOs(PPh_3)_2Br$] in acetonitrile in the presence of NH_4BF_4.

$$CpOs(PPh_3)_2Br \xrightarrow{MeOH} [CpOs(PPh_3)_2(MeOH)]^+ \xrightarrow{NaX} [CpOs(PPh_3)_2X]$$

X = CN (**2.3b**), NCS (**2.3c**)

Scheme 2.1

The complexes **2.3a-2.3d** are colorless to pale yellow colored and soluble in most of the organic solvents. Complex **2.3a** displays $\nu_{(C\equiv N)}$ characteristic IR band at 2282 cm^{-1} due to the coordinated acetonitrile ligand. This compound has already been isolated as tetraphenylborate salt [3]. The ^{1}H NMR spectrum of the complex exhibited the resonance of the CH_3 protons of coordinated acetonitrile as a singlet at δ 2.41 [lit. 1.33 (t)]. The IR spectra of complexes **2.3b** and **2.3c** showed strong bands at 2063 cm^{-1} and 2108 cm^{-1} for $\nu_{(CN)}$ and $\nu_{(NCS)}$ respectively [4a].

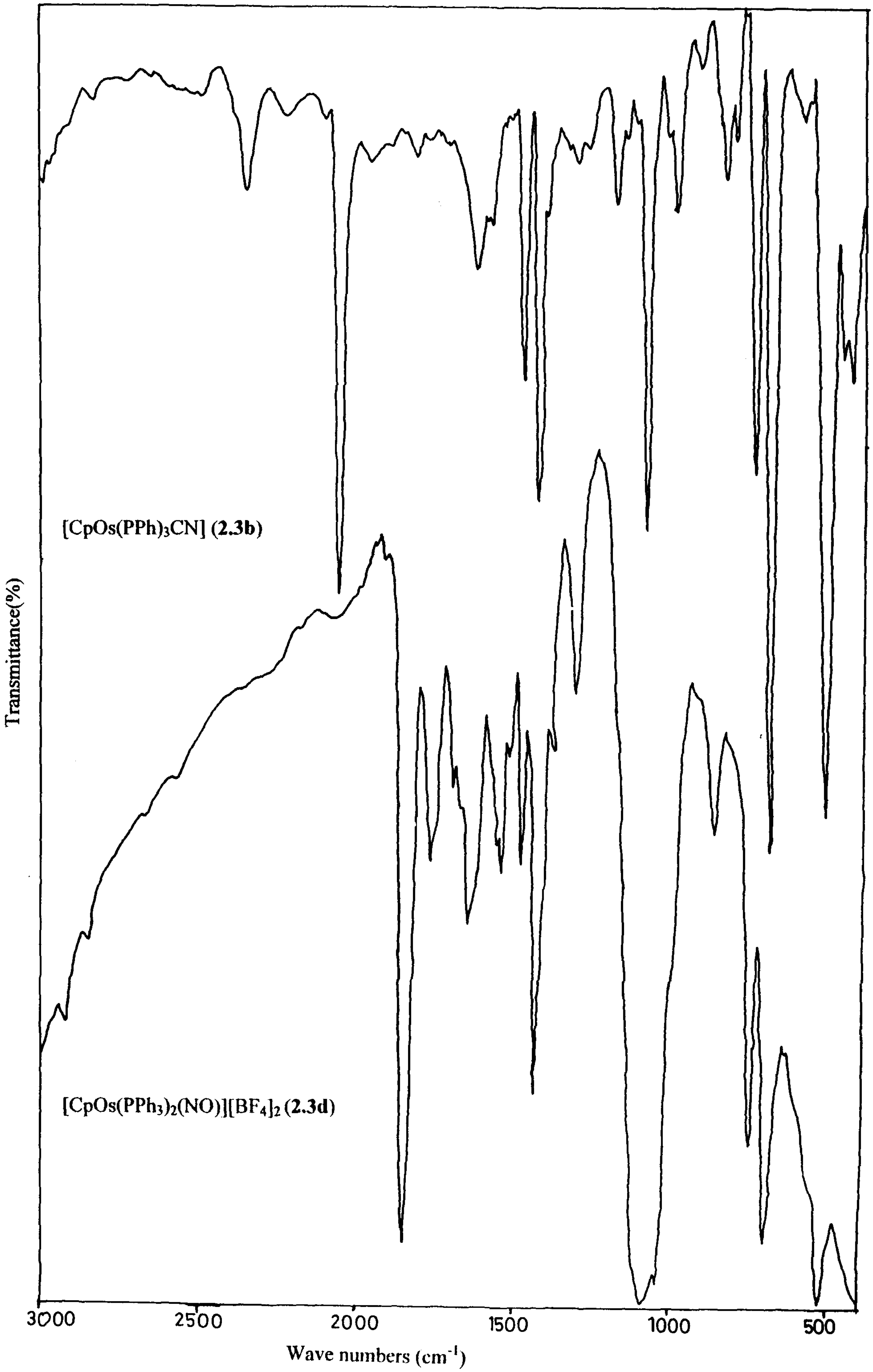
The reaction of $[CpOs(PPh_3)_2Br]$ with $NaNO_2$ and HCl (aq) in ethanol (Scheme yielded yellow compound which was characterized as $[CpOs(PPh_3)_2(NO)](BF_4)_2$ **(2.3d)**.

$$CpOs(PPh_3)_2Br \xrightarrow[H_2O\,/\,NH_4BF_4]{NaNO_2/\,HCl} [CpOs(PPh_3)_2(NO)](BF_4)$$

Scheme 2.2

The compound **2.3d** showed strong $\nu_{(NO)}$ band at 1848 cm^{-1} indicating a linear Os-NO bond [14]. ^{1}H NMR spectrum of this complex exhibited resonance for the deshielded cyclopentadienyl protons at δ 6.23, a very significant shift compared to the starting complex (δ 4.31) that indicate a good π-accepting ability of the nitrosyl ligand. However, the same reaction conditions in the case of ruthenium analogue resulted in the dissociation of one triphenylphosphine forming $[CpRu(PPh_3)(NO)Cl]BF_4$ [14]. The integration of the ^{1}H-NMR spectrum, the absence of band in the range of 200-300 cm^{-1} (Os-Br) in the far IR spectrum and the analytical data suggested the compound to be $[CpOs(PPh_3)_2(NO)](BF_4)_2$. Moreover, only a slight shift of phosphorus resonance in the ^{31}P NMR was observed in comparison to starting complex. We feel that there would be significant shift in the position of phosphorus peak in the ^{31}P-NMR if one triphenylphosphine had been replaced from the metal centre. The formation of dication $[CpOs(PPh_3)_2NO](BF_4)_2$ has been previously reported via different route [15]. IR spectra of **2.3b** and **2.3d** are shown in the next page.

Treatment of $[CpOs(PPh_3)_2Br]$ with excess of ligands L_2 such as 2,2'-bipyridine or 1,10- phenanthroline in methanol, toluene or benzene under refluxing condition even after 2 days does not give the expected compounds. However, the reaction of $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ **(2.3a)** with bipy and phen afforded cationic chelate complexes of the type $[CpOs(PPh_3)(L_2)]BF_4$, which were isolated as a dark red compounds.



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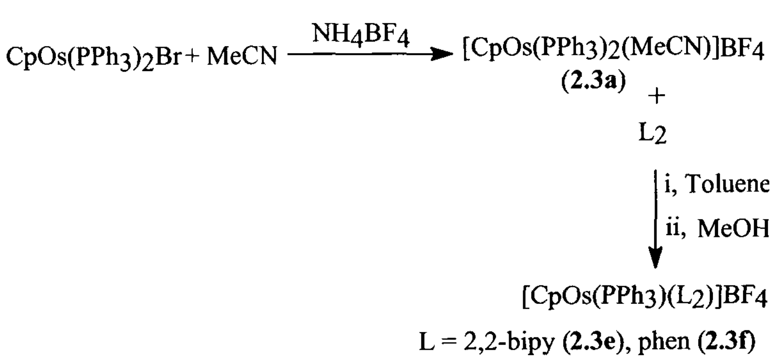
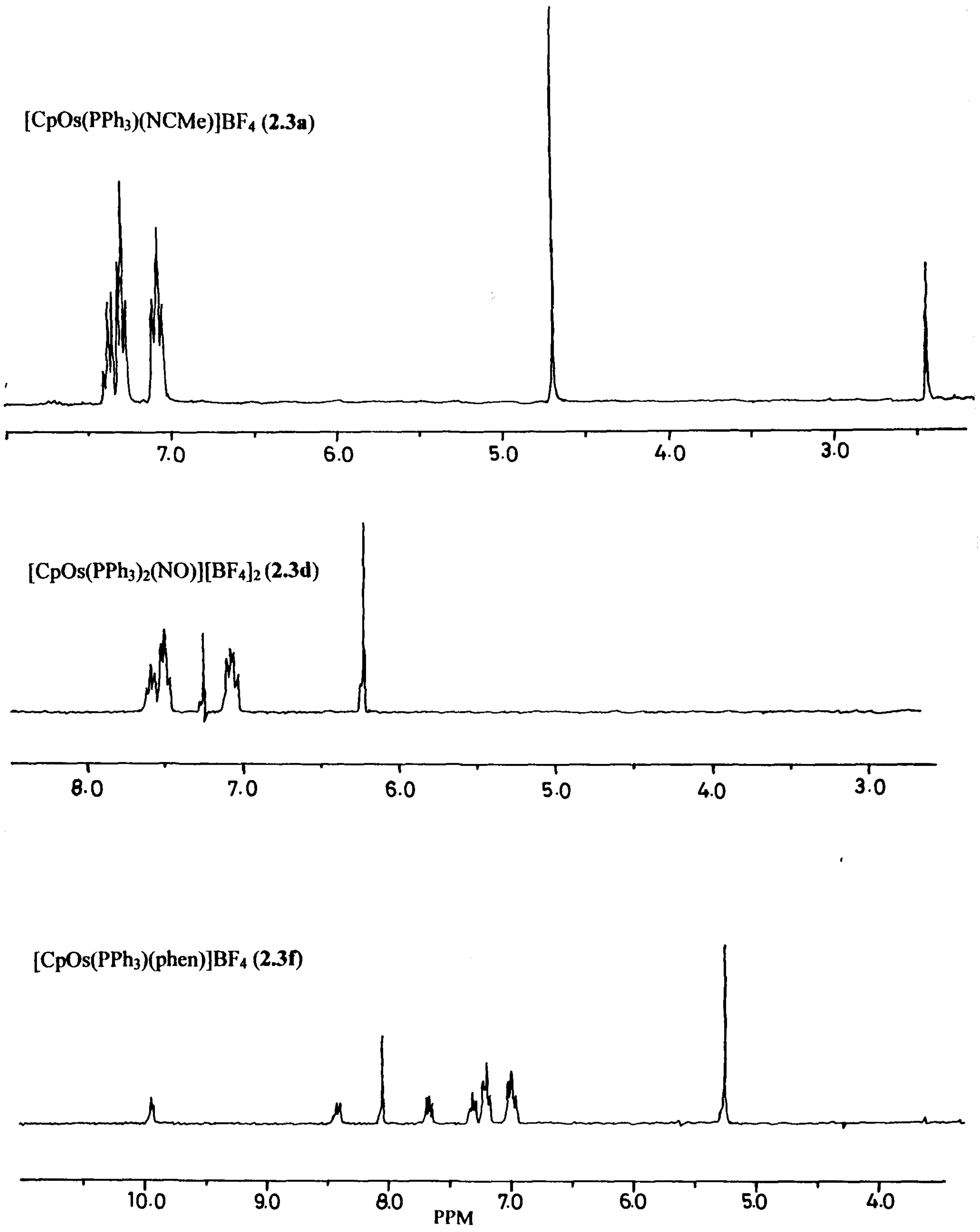


Scheme 2.3

The downfield shift of the cyclopentadienyl protons in comparison to the starting complex was observed in the ^{1}HNMR spectra. The parent complex [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (**2.3a**) showed the resonance for the cyclopentadienyl protons at 4.66 ppm while complexes **2.3e** and **2.3f** exhibited the resonance for the same at δ 4.91 and δ 5.21 respectively. This indicates that there is a significant deshielding after substituting CH$_3$CN and one PPh$_3$ with chelating N, N'-donor heterocyclic ligands. The ^{1}H NMR spectra of these complexes also showed multiplet in the range of δ 7.0-9.5 due to the phenyl protons of triphenylphosphine and of the heterocyclic N, N'-donor ligands. The ^{31}P NMR spectra of the **2.3e** and **2.3f** exhibited single sharp resonance at δ 16.65 and δ 22.60 ppm respectively while the starting complex [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ showed the same at δ 2.11. These distinct downfield shifts were observed because of the dissociation of one triphenylphosphine from the metal centre. The ^{1}H NMR spectra of spectra of **2.3a**, **2.3e** and **2.3f** are shown in the next page.

2.4.2 X-ray structure of [CpOs(PPh$_3$)(phen)]BF$_4$

The structure of [CpOs(PPh$_3$)(phen)]BF$_4$ (**2.3f**) is shown in Figure 2.1. The bond lengths and bond angles are listed in Table 2.1. The osmium atom is η^5-bonded to a cyclopentadienyl ligand and the other coordination sites are occupied by a chelating phenanthroline ligand and a triphenylphosphine. The cyclopentadienyl group is clearly bonded in pentahapto fashion to the metal. Two of the Os – C bond lengths, those involving the C(32) and C(33) are shorter (2.176 and 2.193 Å) than the other three C(31), C(34) and C(35) carbon atoms (2.210, 2.215 and 2.211 Å). The average Os - C bond



[CpOs(PPh$_3$)(NCMe)]BF$_4$ (**2.3a**)

[CpOs(PPh$_3$)$_2$(NO)][BF$_4$]$_2$ (**2.3d**)

[CpOs(PPh$_3$)(phen)]BF$_4$ (**2.3f**)

^{1}HNMR SPECTRA

distance being 2.201 Å slightly longer than the parent complex [CpOs(PPh_3)$_2$Br] (2.177 Å) [13(b)].

The Os – P bond length is 2.318 Å, which also is slightly longer than the average Os – P distance (2.293 Å) [13(b)]. The two Os – N bonds are almost equal 2.090 Å and 2.092 Å which also are little longer compared to Os – N bond lengths observed for osmium-phenanthroline complex [Os(phen)$_3$]$^{2+}$ which fall within a range of 2.066 – 2.1 Å [16]. The geometry of complex [CpOs(PPh_3)(phen)]BF_4 **(2.3f)** is octahedral about the metal center with the cyclopentadienyl ligand occupying the three coordination sites. This is evident by the near 90° angles between N(1)-Os-P (88.86°) and N(2)- Os -P (89.02 °).

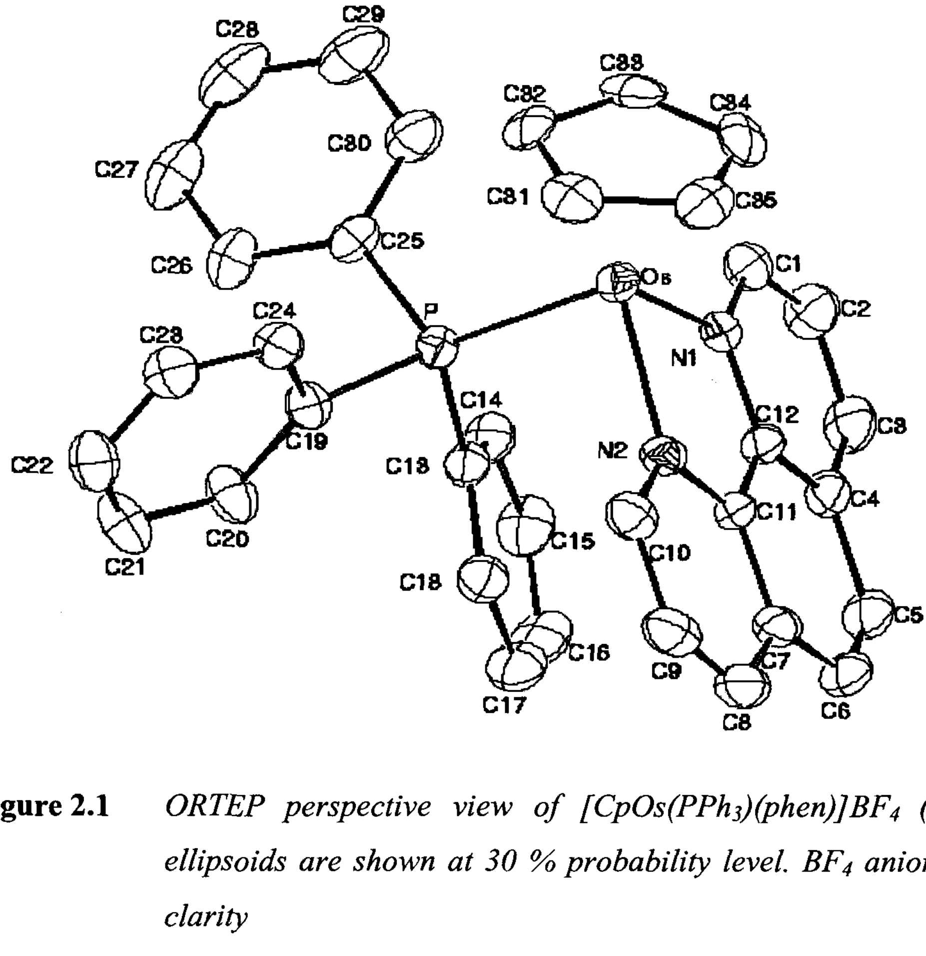


Figure 2.1 *ORTEP perspective view of* [CpOs(PPh_3)(phen)]BF_4 *(2.3f). Thermal ellipsoids are shown at 30 % probability level.* BF_4 *anion is omitted for clarity*

Table 2.4.1 *Selected Bond lengths (Å) and Bond angles (°) for the complex $[CpOs(PPh_3)(phen)]BF_4$ (**2.3f**) (estimated standard deviations in parentheses).*

Bond lengths

Os – N1	2.090(5)	Os – C35	2.211(6)
Os – N2	2.092(5)	Os – C34	2.215(6)
Os – P	1.844(7)	Os – C33	2.193(6)
Os – C31	2.210(6)	Os – C32	2.176(6)

Bond angles

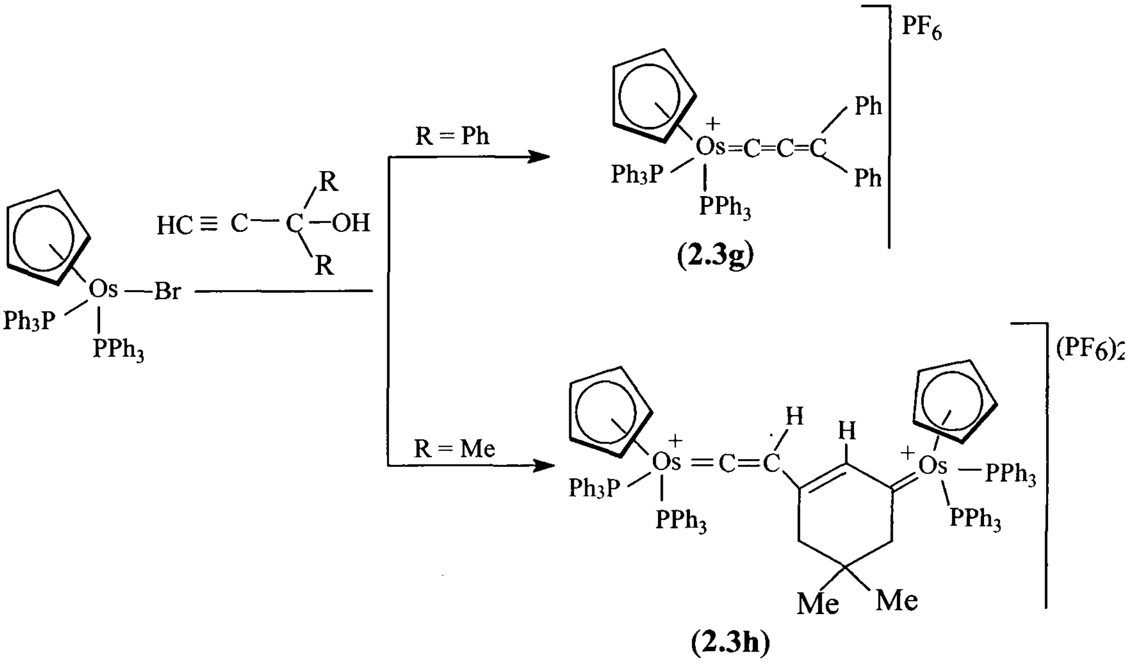
N1 – Os – N2	77.2(2)	N2 – Os – P	89.02(13)
N1 –Os - P	88.86(14)		

2.4.3 Allenylidene and Dinuclear Vinylidene complexes

Treatment of $[CpOs(PPh_3)_2Br]$ with excess $HC{\equiv}CC(OH)Ph_2$ in refluxing methanol in the presence of excess of NH_4PF_6 affords after 6h the cationic allenylideneosmium complex $[CpOs\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ (**2.3g**) in a fairly good yield (Scheme 2.4).We do not observe splitting of Os-P bonds when we reacted $[CpOs(PPh_3)_2Br]$ with $HC{\equiv}CC(OH)R_2$ in non polar solvents like pentane, toluene or benzene whereas Esteruelas and co-workers [17] have observed that the splitting of the Os-P bond by $HC{\equiv}CC(OH)Ph_2$ using pentane or toluene as a solvent to obtain a closely related but neutral complex $[CpOsCl\{C{=}C{=}C(Ph)_2\}(PiPr_3)_2]$.

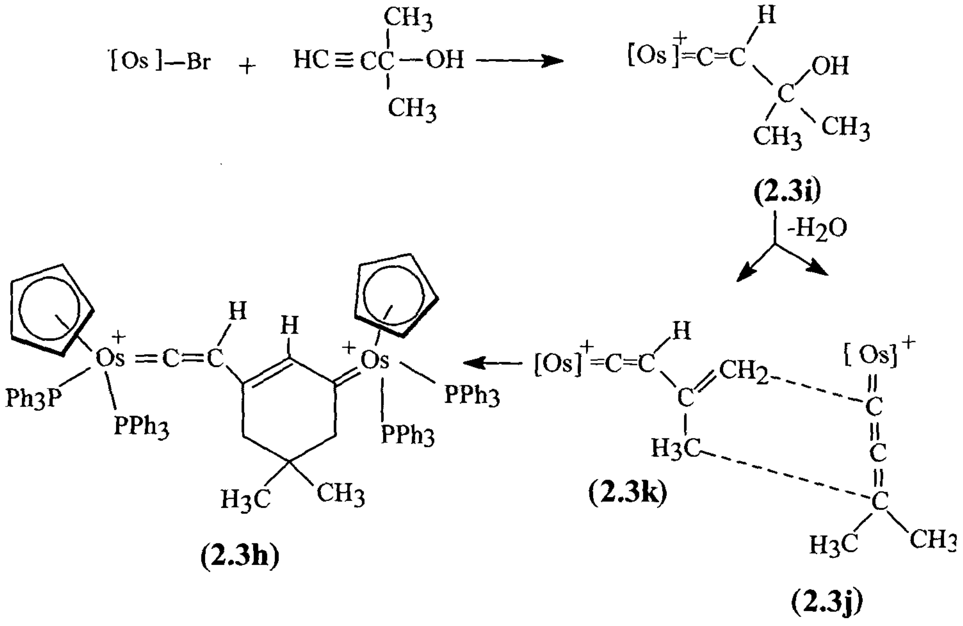
Complex **2.3g** is stable in air and is readily soluble in most of the polar solvents. The formation of the allenylidene chain is confirmed by the appearance of $\nu_{(C=C=C)}$ absorption (asymmetric stretching vibration) as a strong band at 1924 cm^{-1} in the IR spectrum. The ^1H-NMR spectrum of this complex showed as expected a single sharp signal for Cp ring at 5.31 ppm and the phenyl protons appeared in the aromatic region in the range of 7.81– 6.99 ppm. $^{31}P\{^1H\}$ NMR spectrum exhibited a single sharp peak at –0.66 ppm, which is consistent with the chemical equivalence of both phosphorus atoms and a septet at –143 ppm (septet) for PF_6^- ion, whereas the ^{31}P $\{^1H\}$ NMR spectrum of the starting $[CpOs(PPh_3)_2Br]$ showed a peak at – 3.85 ppm [18].

In contrast to the above reaction, [CpOs$(PPh_3)_2$Br] reacts with HC≡CC(OH)Me_2 in a different way and the product isolated was a diosmium vinylidene-alkylidene complex of the formulation $[(Cp)_2Os_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4][PF_6]_2$ **(2.3h)** apparently resulting from the dimerization of the dimethylallenylidene complexes [CpOs{C=C=C$(Me)_2$}$(PPh_3)_2$]PF_6 (Scheme 2.4).



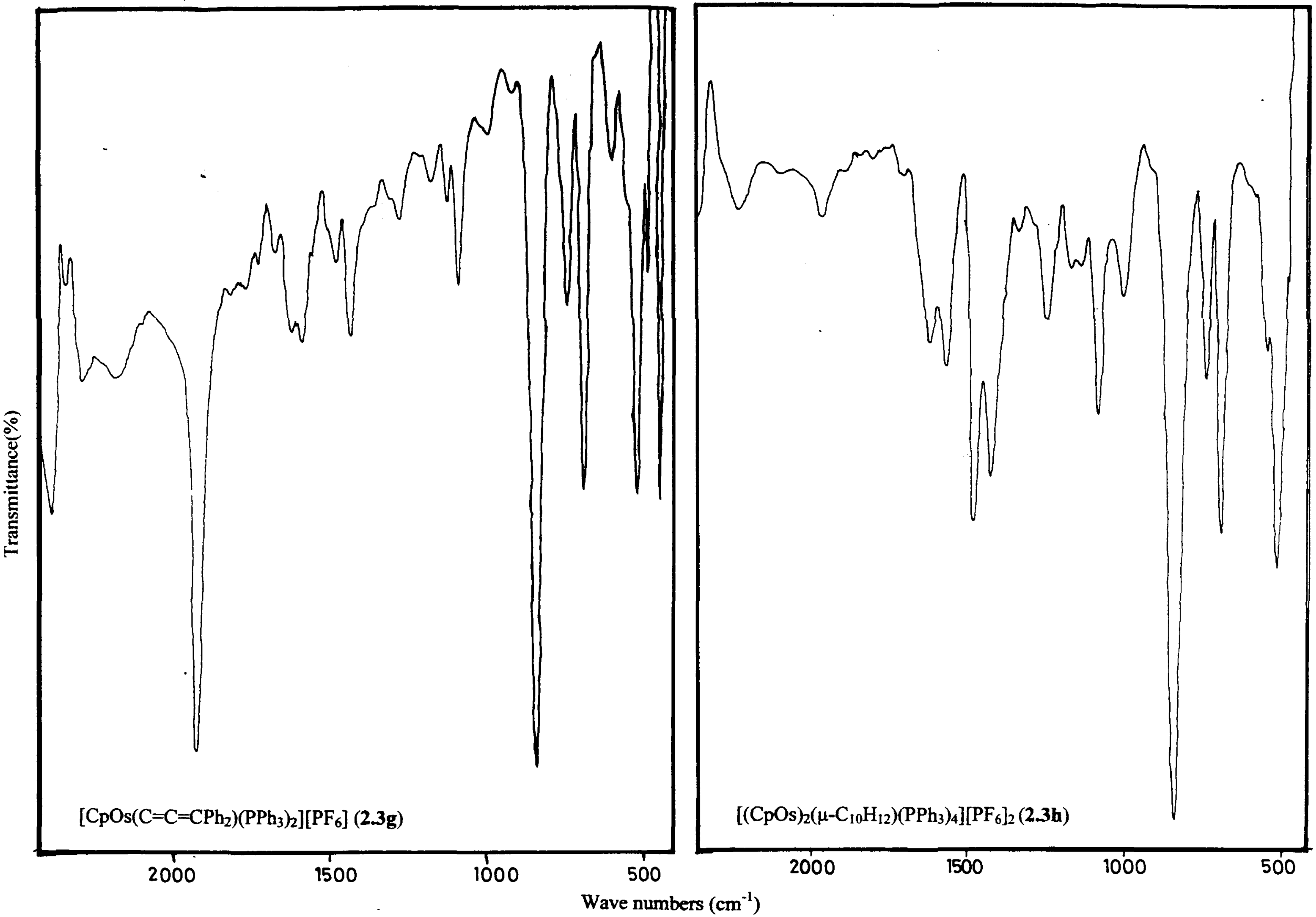
Scheme 2.4

The complex $[(Cp)_2Os_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4][PF_6]_2$ **(2.3h)** was obtained due to the formation of two carbon-carbon bonds between two C=C=CMe_2 ligands with concomitant proton shifts resulting in the cyclization and finally giving the $C_{10}H_{12}$ moiety. We believed that the mechanism of the formation of **(2.3h)** would apparently follow the mechanism proposed by Selegue [19] (Scheme 2.4) for ruthenium analogue where the alkynol reacts with the osmium bromide to give an intermediate hydroxyvinylidene complex **2.3i**, which undergoes dehydration to give dimethylallenylidene cation **2.3j** and isopropenylvinylidene **2.3k**. Bond formation between the two γ-carbons of **2.3k** and the α- and γ - carbons of **2.3j** occurs in stepwise manner.



Scheme 2.4

^{1}H NMR spectrum of the complex **2.3h** showed two distinct singlets for the two Cp's rings at 5.44 and 4.95 ppm respectively and the phenyl and vinyl protons appear in the aromatic region in the range of 7.81– 6.99 ppm. ^{31}P{^{1}H}NMR spectrum shows two signals, which is consistent with the non-equivalence of the phosphorus atoms coordinated to the two osmium centers. The appearance of medium intensity band at 1573 cm^{-1} in the IR spectrum confirm the $\nu_{(C=C)}$ [20] of the vinylidene moiety. The IR spectrum along with that of **2.3g** is shown on the next page. In ^{13}C {^{1}H} NMR spectra, we are unable to observe the corresponding signals of Cβ and Cγ carbons of the ligand in these complexes. The complexes, **2.3g**, **2.3h** show sharp unsymmetrical metal-to-ligand charge-transfer (MLCT) band at 474 and 498 nm respectively in the visible region of the spectrum. Upon addition of triethylamine to solution of **2.3h** in dichloromethane, the color of the solution immediately become deep blue violet and the MLCT band shifts to 584 nm suggesting the formation of new species that can be regarded as the resonance hybrid of alkynyl-alkylidene (**2.3l**) and allenylidene-vinyl (**2.3m**) complex (Scheme 2.5). This is further confirmed by the appearance of a new band at 1977 cm^{-1} in the IR spectrum.



[CpOs(C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$] (**2.3g**)

[(CpOs)$_2$(μ-C$_{10}$H$_{12}$)(PPh$_3$)$_4$][PF$_6$]$_2$ (**2.3h**)

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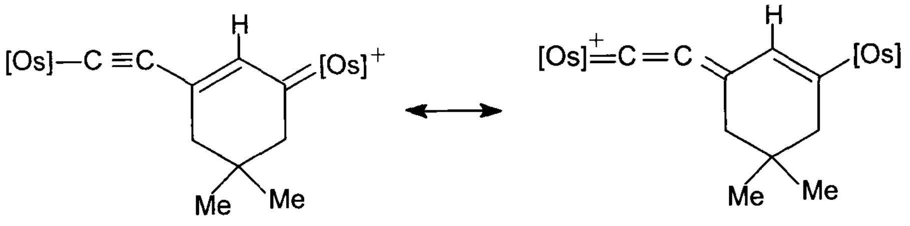

(2.3l) (2.3m)

Scheme 2.5

2.4.4 *X-ray structures of* $[CpOs\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ *(2.3g) and* $[(Cp)_2Os_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4][PF_6]_2$ *(2.3h)*

In order to confirm the structures suggested by the spectroscopic evidences, molecular structure of these complexes were determined using single crystal X-ray study. The summary of the single-crystals X-ray structure analyses are shown in Table 2.4.2 and the selected bond lengths and bond angles are presented in Table 2.3 and 2.4 respectively. The ORTEP drawing of the complex **2.3g** and **2.3h** are shown in Figure 2.2 and 2.3 respectively.

The geometry around the osmium center in the complex **2.3g** is close to octahedral; with cyclopentadienyl ligand occupying the three coordinate sites. The angles subtended by P1-Os-C1, P2-Os-C1 and P1-Os-P2 bonds showed a slight deviation from the ideal value of 90°. The average bond distance of osmium to the carbon atoms of the cyclopentadienyl ligand is 2.266 Å. A bond distance of 1.897 Å for Os-C1 is in consistent with the double bond character as evidence from the other allenylidene osmium complexes, for example $[CpOs\{C{=}C{=}C(Ph)_2\}(PiPr_3)_2]PF_6$ [1.875 Å] [17], $[(\eta^5\text{-}C_9H_7)Os\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ [1.895 Å], $[(\eta^6\text{-mes})Os(C{=}C{=}C(Ph)_2(PMe_3)Cl]PF_6$ [1.90 Å] [20]. The bond angles of Os-C1-C2 (170.2 Å) and C1-C2-C3 (172.4 Å) showed a deviation from the exact linear arrangement of the allenylidene chain. The C1-C2 bond length of 1.258 Å is nearly as short as carbon – carbon triple bond (1.20-1.21 Å) and the C2-C3 bond length is not typical of an allene C(sp)- C(sp^2) double bond [21] and the observe value is very similar to that observed for $[(\eta^5\text{-}C_9H_7)M\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ (M = Ru, Os) [22]. The observed carbon-carbon distances in the allenylidene chain are not of expected for carbon-carbon double bond lengths [23], indicating a substantial contribution of the canonical forms,

$$[\mathrm{Os}]\overset{+}{=}\mathrm{C}=\mathrm{C}=\mathrm{C(Ph)_2} \longleftrightarrow [\mathrm{Os}]-\mathrm{C}\equiv\mathrm{C}-\overset{+}{\mathrm{C}}\mathrm{(Ph)_2}$$

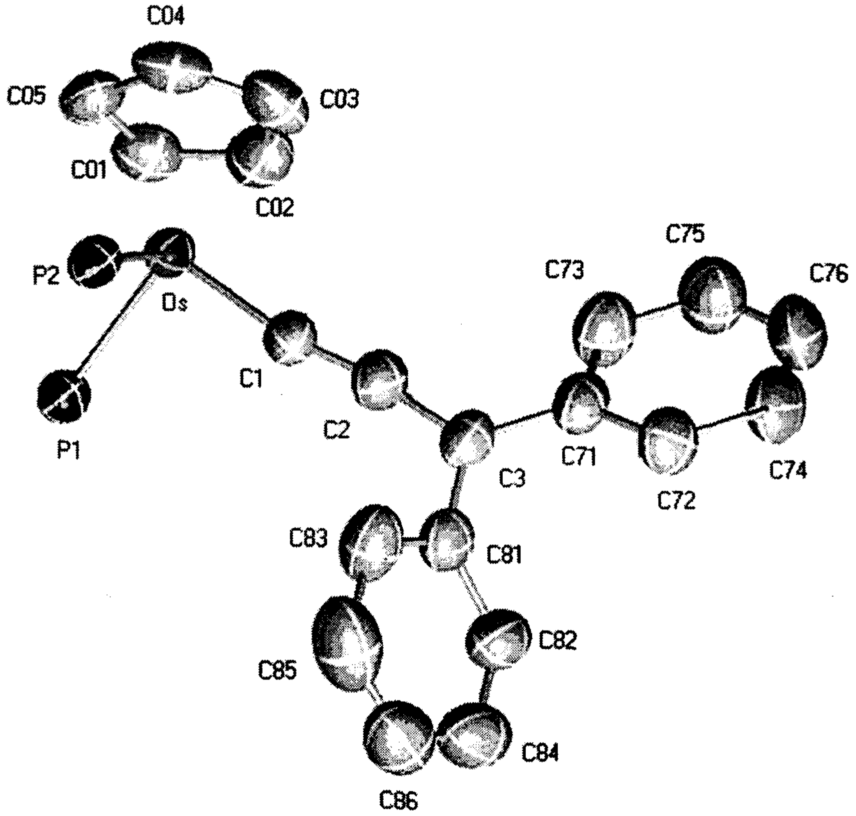

Figure 2.2 *Molecular structure of the complex* $[\mathrm{CpOs\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6}$ *(**2.3g**). All the hydrogens and the phenyl groups of phosphines are omitted for clarity.*

Table 2.4.2 *Selected Bond lengths (Å) and angles (°) for the complex $[CpOs\{C{=}C{=}C(Ph)_2\}(PPh_3)_2]PF_6$ (2.3g) (estimated standard deviations are shown in parentheses)*

Bond lengths		***Bond angles***	
Os-C01	2.280(5)	C1-Os-P1	97.76(13)
Os-C02	2.269(5)	C1-Os-P2	89.53(14)
Os-C03	2.249(5)	P1-Os-P2	96.02 (4)
Os-C04	2.254(5)	Os-C1-C2	170.2(4)
Os-C05	2.281(5)	C1-C2-C3	172.4(5)
Os-C1	1.897(4)	C2-C3-C7	1121.7(5)
Os-P1	2.3514(11)	C2-C3-C8	1118.0(5)
Os-P2	2.3271(11)		
C1-C2	1.258(6)		
C2-C3	1.350(6)		

In complex **2.3h**, two typical $[CpOs(PPh_3)_2]$ moieties are bonded to a bridging $C_{10}H_{12}$ ligand. The Os2-C31-C32-C33 group comprises a vinylidene linkage, as suggested by a short Os2-C31 bond of 1.825 Å and a nearly linear bond angle of Os2-C31-C32 [167.9(5) Å]. An akylidene bond with a length of 1.899 Å links the second Os1 and C37 of the cyclohexene ring. As in the case of complex **2.3g**, the geometry around the two-osmium atoms is slightly distorted octahedral. All the geometrical parameters are found to be in a close agreement with its ruthenium analogue [19]. The peculiar nature of the crystals of **2.3h** is that the residual electron density peaks, not within the bonding distance of any other atom, were refined as an oxygen molecule with a distance of 1.1 Å between the two oxygen atoms. Similar observation was observed in the case of ruthenium analogue [19] but only one of the oxygen atoms was found. It is presumably part of two water molecules although no associated protons were located.

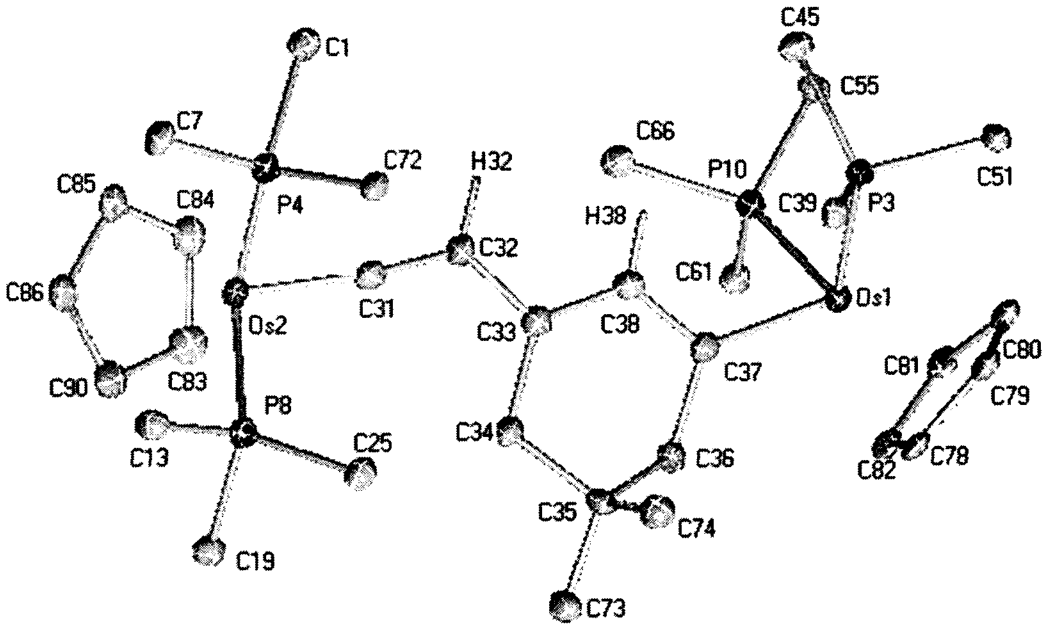

Figure 2.3 *Molecular structure of the complex* $[(CpOs)_2(PPh_3)_4(\mu\text{-}C_{10}H_{12})][PF_6]_2$ *(**2.3h**). All the hydrogens except H32 and the phenyl carbons (except ipso carbons) of phosphines are omitted for clarity.*

Table 2.4.3 **Selected Bond lengths (Å) and angles (°) for the complex** $[(CpOs)_2(PPh_3)_4(\mu\text{-}C_{10}H_{12})][PF_6]_2$ **(2) (estimated standard deviations are shown in parentheses)**

Bond lengths		Bond angles	
Os1-P10	2.3472(14)	P3-Os1-P10	100.62(5)
Os1-P3	2.3240(14)	C37-Os1-P3	95.13(17)
Os1-C37	1.988(6)	C37-Os1-P10	89.72(16)
Os1-Cena	1.9189	Os1-C37-C38	125.5(4)
Os2-P4	2.3591(14)	Os1-C37-C36	128.8(4)
Os2-P8	2.3758(14)	C31-Os2-P4	85.38(17)
Os2-C31	1.825(5)	C31-Os2-P8	101.47(17)
C31-C32	1.337(8)	Os2-C31-C32	167.9(5)
C32-C33	1.439(7)	C31-C32-C33	125.6(5)
Os2-Cenb	1.9609	C32-C33-C34	117.8(5)
		C32-C33-C38	112.7(5)

Table 2.3.4: Crystal Data summary and structure refinement for 2.3g, 2.3h and 2.3f

Empirical formula	C57H45Cl3F6Os1P3	C92H82F12O2Os2P6	OsC35BH28PN2F4
	(2.3g)	**(2.3h)**	**(2.3f)**
CCDC	**194247**	**219955**	**219956**
Formula weight	1233.38	2013.80	784.57
T (K)	293(2)	98(2)	293(2)
Wavelength Å	0.71073	0.71073	0.71069
Cryst. system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P1	$P2_1/_n$ (no. 14)
a (Å)	13.4083(6)	13.0396(11)	18.2243(2)
b (Å)	19.5700(9)	15.2420(13)	9.49800(10)
c (Å)	20.3806(9)	21.6406(19)	19.0352(2)
α (°)		72.5290(10)	
β (°)	100.3620(10)	75.1960(10)	113.8630(10)
γ (°)		85.6360(10)	
Volume ($Å^3$)	5260.7(4)	3966.5(6)	3013.22(6)
Z	4	2	4
Dcalc, (Mg/m^3)	557	1.686	1.729
F(000)	2452	2000	1536
θ range (°)	1.98 to 28.31	1.02 to 28.36	2.51 to 27.48
Index ranges	$-17 \leq h \leq 17$	$-17 \leq h \leq 17$	$-23 \leq h \leq 23$
	$-25 \leq k \leq 26$	$-20 \leq k \leq 20$	$-10 \leq k \leq 12$
	$-27 \leq l \leq 26$	$-27 \leq l \leq 28$	$-24 \leq l \leq 24$
Reflections collected	45511	36541	22223
Independent reflections	12418	18408	6737
	[R(int) = 0.0219]	[R(int)= 0.0267]	[R_{int} = 0.0395]
Refinement method		Full-matrix least-squares on F2	
Data / restr. / param.	12418 / 3 / 631	15206/0/1029	6737 / 0 / 398
GOF	1.032	1.043	1.134
R_1, wR_2 [$I>2\sigma(I)$]	0.0414, 0.1211	0.0267, 0.0444	0.0488, 0.1114
R indices (all data)	R1 = 0.0500,	R1=0.0338	0.0563
	wR2 = 0.1278	wR2=0.0896	0.1166
Largest diff.peak/hole(e.$Å^{-3}$)	1.031/ -1.757	2.810 / -1.196	1.170/-1.262

2.4 Conclusions

The reaction of [$CpOs(PPh_3)_2Br$] with monodentate anions and neutral ligand were described and they do not seems to differ much from their ruthenium analogues except in the formation of [$CpOs(PPh_3)_2NO]^{+2}$ apart from the general observation that the displacement reactions at Os–Br or Os–PPh_3 bonds are relatively difficult when compared to those of [$CpRu(PPh_3)_2Cl$]. It has been also observed that the acetonitrile complex, [$CpOs(PPh_3)_2(CH_3CN]^+$ is convenient precursor for the preparation of chelate complexes, [$CpOs(PPh_3)(L_2)]^+$.

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Chapter III

Syntheses and characterization of arene ruthenium(II) complexes containing N, N'-donor schiff base* and amine ligands.

3.1 Abstract

Reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with N, N'-donor Schiff bases *viz*, *para*-substituted N-(2-pyridinylmethylene)phenylamines and N-(2-pyridinylmethylene)cyclohexylamine (**2-PC**) yielded complexes of the formulation $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)Cl]^+$ [X = H (**3.1a**), CH_3 (**3.1b**), OCH_3 (**3.1c**), Cl (**3.1d**) and NO_2 (**3.1e**)] and $[(\eta^6\text{-arene})Ru(2\text{-}PC)Cl]^+$ [arene = hexamethylbenzene (**3.2a**), *p*-cymene (**3.2b**)] respectively. The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with imine ligands ($C_6H_5\text{-}HC{=}N\text{-}C_6H_4\text{-}p\text{-}X$) invariably leads to the hydrolysis of the imine ligands to afford the amine complexes of the formula $[(\eta^6\text{-}p\text{-cymene})RuCl_2(H_2N\text{-}C_6H_4\text{-}p\text{-}X]$ [X = H (**3.3a**), OMe (**3.3b**), $N(Me)_2$ (**3.3c**)]. All these complexes were isolated as PF_6 salts. These complexes were characterized by spectroscopic and analytical data. The molecular structure of $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)Cl]PF_6$ (**3.1e**), $[(\eta^6\text{-}p\text{-cymene})RuCl_2(H_2N\text{-}C_6H_4\text{-}p\text{-}H]$ (**3.3a**) have been determined by X-ray crystallography.

3.2 Introduction

Recent interest in half sandwich arene ruthenium complexes arises because of their use as catalysts [1] in organic syntheses and also recent studies have shown that some water soluble *p*-cymene ruthenium(II) complexes are capable of inhibiting cancer cell growth [2]. The photophysics, photochemistry and redox properties of α, α'-diimines ruthenium complexes have been prolific areas of research over the past two decades [3]. There are few reports of arene ruthenium complexes with α,α'-diimines [4] available in literature. This chapter describes the syntheses and characterization of arene ruthenium(II) complexes of N, N'-donor Schiff bases and the formation of amine complexes resulting from the reaction of some phenylimine ligands with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$.

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*R. Lalrempuia, Mohan Rao Kollipara, Patrick J. Carroll, *Polyhedron*, 22 (2003) 605.

3.3 Experimental

All reactions were carried out in distilled and dried solvents. Pyridine-2-carboxaldehyde (Fluka) was used as received. All liquid aromatic amines were reagent grade and were distilled prior to use and solid aromatic amines were used as such. ^1H NMR spectra were recorded in CD_3CN, $CDCl_3$ and $(CD_3)_2CO$ solvents with tetramethylsilane as an internal standard and recorded on a Bruker ACF-300 MHz spectrometer. Infrared spectra were taken on a Perkin-Elmer model 983 spectrophotometer using KBr pellets. Elemental analysis was performed in Perkin-Elmer-2400 CHNS/O analyzer. Conductivity measurement was performed in Wayne Kerr Automatic Precision Bridge B-905. The ligands $C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X$ (where X = H, CH_3, OCH_3, Cl, NO_2) and 2-PC were prepared according to the literature methods [5]. The precursor complexes $[(\eta^6\text{-arene})RuCl_2]_2$, (arene = C_6Me_6, *p*-cymene) are prepared by known methods [6]. The phenylimine ligands are prepared by condensation of the benzaldehyde with appropriate aromatic amines [7].

3.3.1 Preparation of the Schiff base complexes

Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)Cl]PF_6$ ***(3.1a-e)*** *(X = H,* CH_3, OCH_3, *Cl,* NO_2*).*

These complexes were prepared using a general procedure in which the mixture of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (0.15 mmol) and the ligand (0.30 mmol) in methanol (20 ml) were stirred at room temperature for 1h. The resulting solution was filtered and NH_4PF_6 (0.32 mmol) was added to the clear solution. Then stirred at 0 °C where by orange compound precipitated for complexes with X = CH_3, Cl, NO_2 which was collected and washed with water, methanol and finally with diethylether and dried in vacuum.

For the complexes with X = H and OMe, the dark brown solution was stirred for 2h and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane and filtered through short silica column. The resulting solution was reduced in volume to about 2 ml and hexane (15 ml) was added to give red brown compound, which was recrystallized from the mixture of acetone and hexane to give orange crystals. Yield ranges from 70-80 %.

*Preparation of [(η^6-arene)Ru(2-PC)Cl]PF_6; arene = C_6Me_6 (**3.2a**), p-cymene (**3.2b**):*

The complexes were prepared in similar manner to that of the preparation of **3.1a** and **3.2c** except that 2-PC was used and the oily product obtained was washed several times with hexane to gave dark brown solid in 65 % yield.

3.3.2 *Preparation of amine complexes*

Preparation of [(η^6-p-cymene)$RuCl_2(H_2N$-C_6H_4-p-X]; X = H (3.3 a), OMe (3.3 b), $N(Me)_2$ (3.3c)

A general procedure was used for the preparation of these three complexes. A suspension of [(η^6-*p*-cymene)$RuCl_2]_2$ (0.1g, 0.163 mmol), the ligand C_6H_5-HC=N-C_6H_4-*p*-X (0.326 mmol) in methanol (15 ml) was stirred at room temperature for 2h. The orange-red compound that separated this time were collected by centrifuge and dried in *vacuo* after washing with hexane.

3.3.3 *Crystallographic analysis of the complexes*

X-ray quality crystals of complex **3.1e** as PF_6 salt, were obtained by a diffusion of diethylether in to acetonitrile solution of the complex. An orange-red crystal was mounted on a glass fiber with epoxy cement. X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated MoK_α radiation (λ=0.71069 Å) at a temperature of 293 K. The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB [8]. The structure was solved by direct methods (SIR92) [9]. Refinement was by full-matrix least squares based on F^2 using SHELXL-93 [10]. While for orange block crystal of the complex **3.3a**, X-ray intensity data were collected on Bruker AXS APEX diffractometer equipped with a graphite monochromator and a MoK_α radiation (λ=0.71073 Å) at a temperature of 120 K. Data were corrected for absorption effects using the multiscan technique (SADABS) [11]. The structure was solved and refined using the Bruker SHELXTL-97 software package [12]. ORTEP [13] drawing of **3.1e** and **3.3a** are shown in Figure 3.1 and 3.2 respectively.

3.4 Results and Discussion

3.4.1 η^6-arene ruthenium(II) Schiff base complexes

The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with neutral N, N' - Schiff base ligands yielded complexes of the type **3.1** and 3.**2** in fairly good yield. The orange red colored complexes of **3.1** are air stable while the dark brown complexes of **3.2** are slightly air sensitive. These complexes are insoluble in water and non-polar solvents but soluble in polar solvents. These complexes exhibited 1:1 electrolyte system [14] in acetonitrile solution (~ 130 $ohm^{-1}cm^2mol^{-1}$).

$[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ + $2(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)$ $\longrightarrow$

$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)Cl]PF_6$

[X= H, CH_3, OCH_3, Cl, NO_2 (**3.1a-e**)]

$[(\eta^6\text{-arene})RuCl_2]_2 + 2(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_{11})$ $\longrightarrow$

$[(\eta^6\text{-arene})Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_{11})Cl]PF_6$

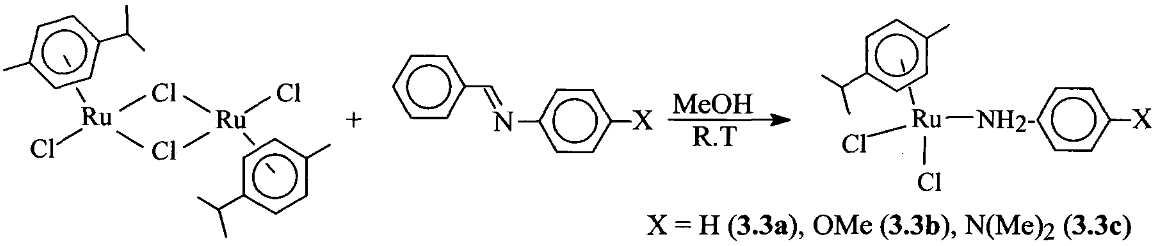
[arene = $\eta^6\text{-}C_6Me_6$ (**3.2a**); *p*-cymene (**3.2b**)]

Scheme 3.1

These complexes are characterized by elemental analyses, IR and ^1H NMR spectral data (table 3). All these complexes gave satisfactory analytical data. IR spectra of the complexes showed medium intensity bands in the range of 1600-1400 cm^{-1}, 770 and 557 cm^{-1} for the benzene ring. The complex $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)Cl]PF_6$ (**3.1e**) showed characteristic IR bands for ν_{NO2} at 1526 and 1488 cm^{-1} similar to the range observed for ν_{NO2} of other reported compounds. ^1H NMR data of complexes **3.1a-e** suggests the presence of the hexamethylbenzene and Schiff base ligands in 1:1 ratio. ^1H NMR spectra of the complexes **3.1a-e** and **3.2a** display sharp singlet for methyl protons of hexamethylbenzene at around δ 1.8 and δ 2.1 respectively and the peaks for the ligand moiety appeared in the range of δ 7-9. The methine proton appears in the range of δ 8.4 to δ 8.8. This proton resonated in the same range of corresponding *p*-cymene compounds [4b]. The α - proton of the pyridine ring of complex **3.2a** and **3.2b** showed an up field shift of about δ 0.3 in comparison to that of complex **3.1a-e** due to the cyclohexyl group. ^{1}H NMR spectrum of complex [(η^6-*p*-cymene)Ru(C_5H_4N-2-CH=N-C_6H_{11})Cl]PF_6 (**3.2b**) suggests the presence of η^6-*p*-cymene and 2-PC in 1:1 ratio. The protons of isopropyl group of the η^6-*p*-cymene ligand appear as two sets of doublets at around δ 1.16 due to the loss of planarity of the benzene ring because of steric nature of the ligand [15]. Septet at δ 2.70 was observed for single proton of isopropyl group. The benzene ring protons of p-cymene appeared as two doublets and a triplet in the range of δ 5.92 - 6.23 respectively due to long range coupling with isopropyl protons. The spectroscopic data are given in table 3.1. ^{1}H NMR spectra of complex **3.1b** and **3.2b** are shown the next two pages.

3.3.3 *η^6-p-cymene ruthenium(II) amine complexes (hydrolysis of phenylimines)*

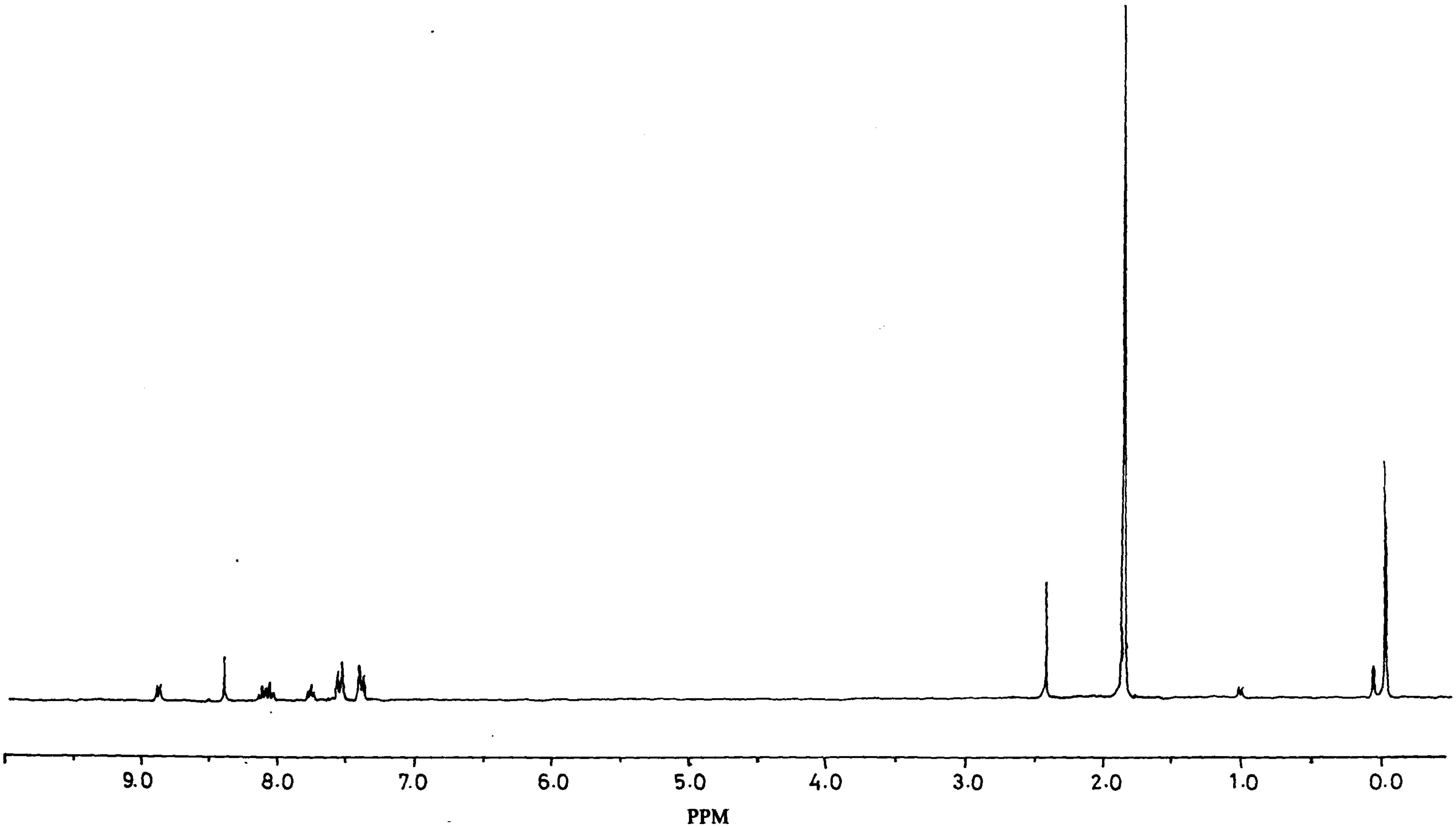
The chloro bridged dimer, [(η^6-*p*-cymene)RuCl_2]$_2$ react readily with 2 equivalent of imines C_6H_5-HC=N-C_6H_4-*p*-X, in methanol as shown in Scheme 3.2.



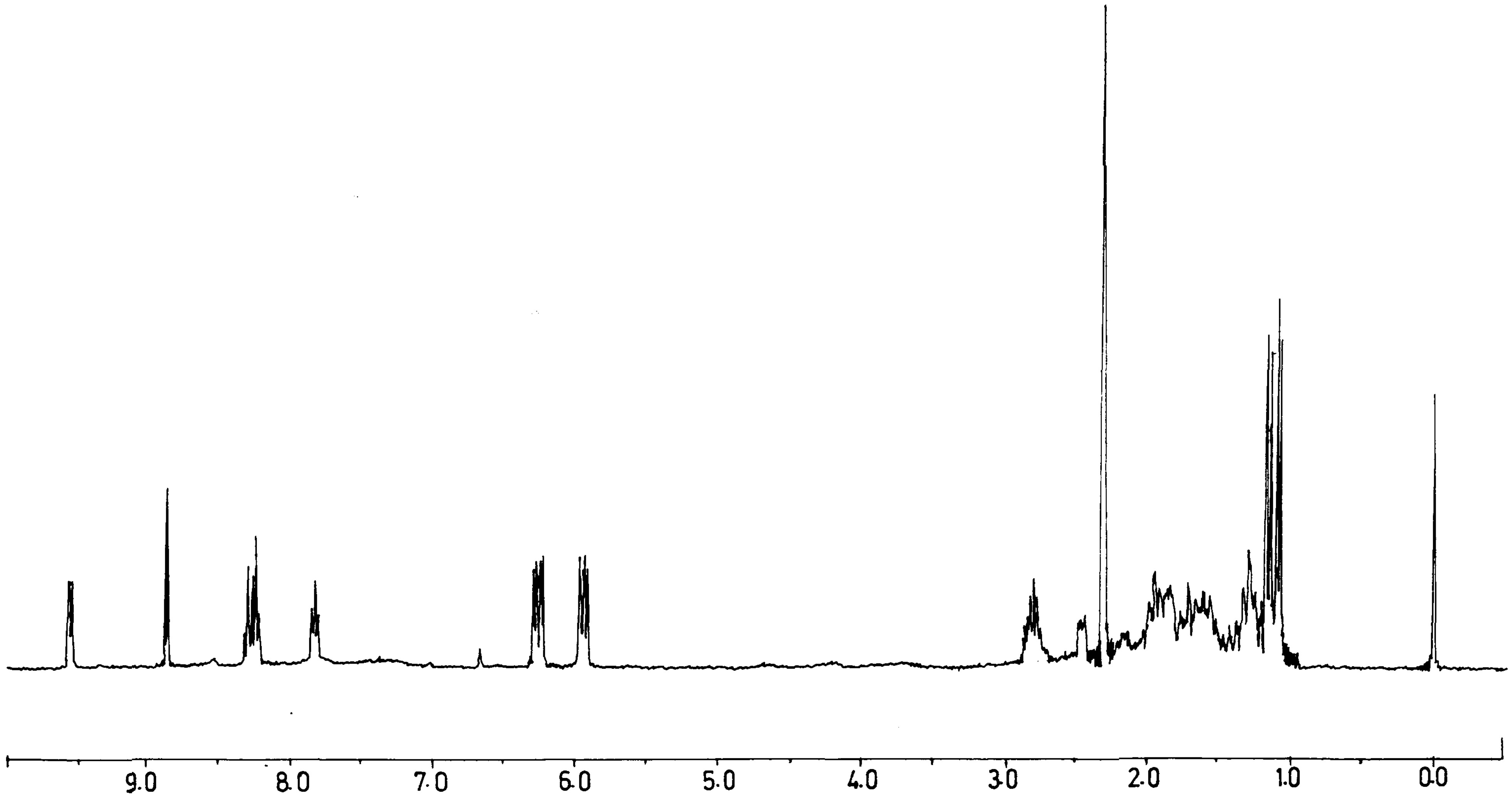
X = H (**3.3a**), OMe (**3.3b**), N(Me)$_2$ (**3.3c**)

Scheme 3.2

The complexes, **3.3a-c** are orange-red, air stable, crystalline solids, soluble in most of the common solvents except in hydrocarbons. They are partially soluble in diethylether and have been characterized by ^{1}H NMR and IR spectroscopy as well as by a single-crystal X-ray diffraction study on **3.3a**. These complexes are formed by hydrolysis of imine ligands in the reaction medium. We are aware of the fact that the reaction of a closely related material, [(η^6-arene)Ru(PMe_3)Cl_2] with the imine ligands (C_6H_5-HC=N-C_6H_4-*p*-X) in the presence of $AgBF_4$ leads to the formation of cationic *ortho*-metalated complexes, [(η^6-arene)Ru(R')N=C(R")C_6H_4(PMe_3)]$^+$ [16], but to our knowledge, no reactions of these imine ligands with the chloro bridge dimers have been reported. Nevertheless, our attempt to obtain analogous imine complexes leads invariably to the



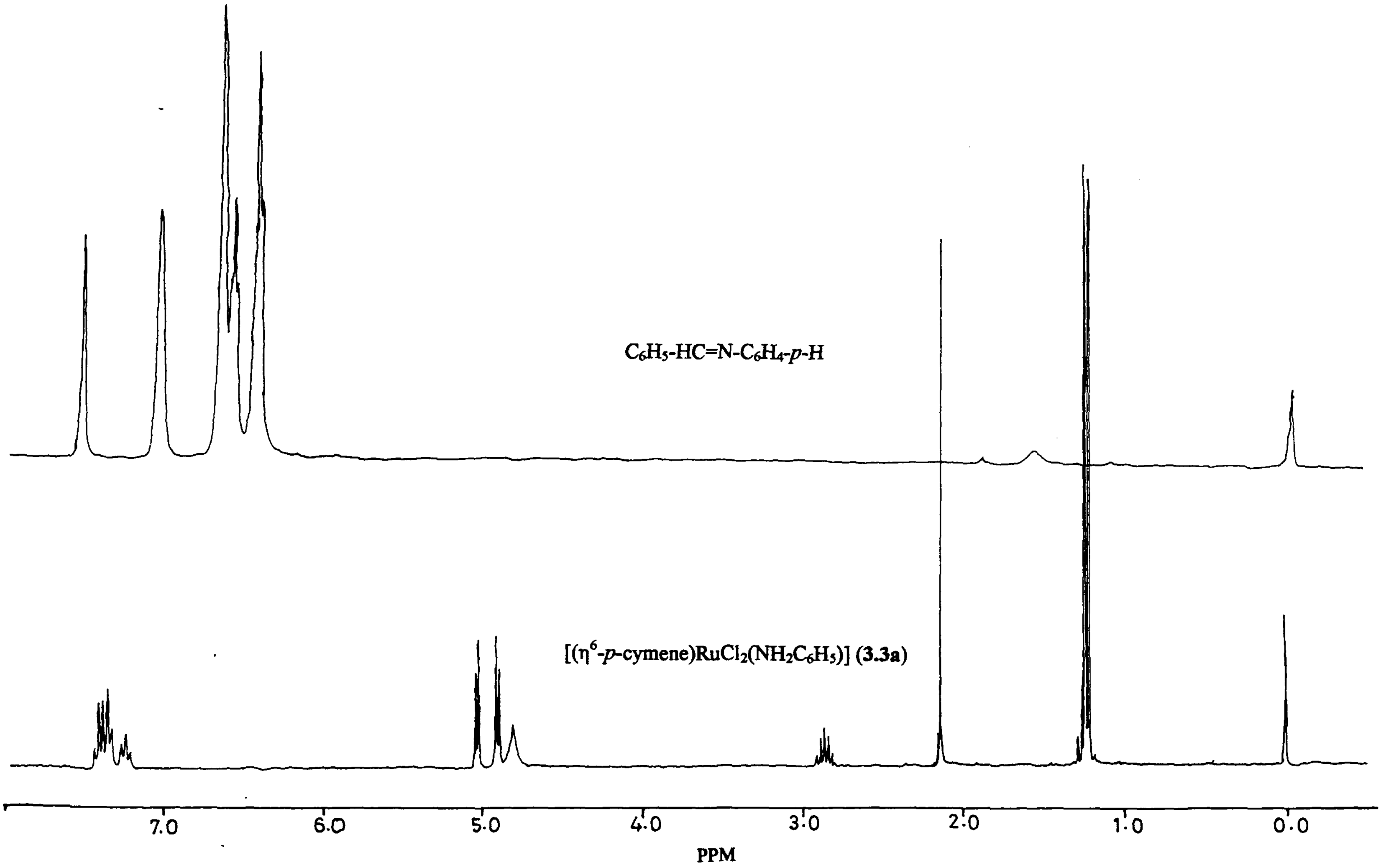
^{1}HNMR spectrum of $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}CH_3)Cl]PF_6$ **(3.1b)**



^{1}HNMR spectrum of [(η^6-*p*-cymene)Ru(C_5H_4N-2-CH=N-C_6H_{11})Cl]PF_6 **(3.2b)** amine complexes (Scheme 3.2); this observation seems to be the result of the hydrolysis of the imine ligands during the process of the reaction (facilitated by water present in the solvent which we fail to remove in our working condition). The ^{1}HNMR spectra of the crude complexes do not show any peaks that may be of the byproducts such as anticipated ortho-metalated complexes, benzaldehyde or its derivatives. The ^{1}H NMR spectra of these three complexes showed only the ring protons, NH_2 protons of amine ligands at around 7.4 ppm and 4.8 ppm respectively apart from the peaks corresponding to the *p-cymene* moiety (see table 3.1) and the ^{1}H NMR spectrum of the ligand C_6H_5-HC=N-C_6H_4-*p*-H as well as that of **3.3a** are shown together on the next page.

Table 3.1: Spectroscopic data

Complex	IR (KBr, cm^{-1})	^{1}H NMR (δ ppm) (Schiff base) {multiplicity, nH, J (Hz)}	^{1}H NMR (δ), (arene), {multiplicity, nH, J (Hz)}
3.1a	1590 ($\nu_{C=N}$) 844 (ν_{P-F})	9.16 (d, 1H, 3), 8.80 (s, 1H), 8.34 (m, 2H), 7.96 (m, 1H), 7.85 (d, 2H), 7.63 (m, 2H)	1.87 (s, 18 H)
3.1b	1586 ($\nu_{C=N}$) 844 (ν_{P-F})	8.90 (d, 1H, 3), 8.41 (s, 1H), 8.11 (m, 2H), 7.77 (t, 1H), 7.59 (d, 2H), 7.50 (d, 2H), 2.44 (s, 3H)	1.87 (s, 18 H)
3.1c	1589 ($\nu_{C=N}$) 839 (ν_{P-F})	8.89 (d, 1H, 3), 8.39(s, 1H), 8.10 (m, 2H), 7.75 (t, 1H), 7.62 (d, 1H), 7.13 (d, 1H), 3.98 (s, 3H)	1.88 (s, 18H)
3.1d	1589 ($\nu_{C=N}$) 843 (ν_{P-F})	8.92 (m, 1H, 3), 8.46 (s, 1H), 8.12 (m, 2H), 7.79 (t, 1H), 7.69-7.58 (m, 4H)	1.86 (s, 18H)



^{1}HNMR SPECTRA

3.1e	1584 ($\nu_{C=N}$) 836 (ν_{P-F})	8.96 (m, 1H), 8.53 (s, 1H), 8.45 (m, 2H), 8.17 (m, 2H), 7.92-7.83 (m, 4H)	1.93 (s, 18H)
3.2a[a]	1597 ($\nu_{C=N}$) 840 (ν_{P-F})	9.43 (d, 1H, 6), 8.74 (s, 1H), 8.42 (d, 1H),7.99 (m, 2H), 7.65 (m, 1H), 2.00-1.24 (m)	2.14 (s, 18H)
3.2b[a]	1589 ($\nu_{C=N}$) 840 (ν_{P-F})	9.54 (d, 1H, 6), 8.86(s, 1H), 8.29-8.24 (m, 2H), 7.81 (t, 1H, 6), 1.95-1.98 (m).	6.23 (dd, 2H, 6), 5.92 (t, 2H, 6), 2.70 (sp, 1H), 2.28 (s, 3H), 1.14 (dd, 6H, 6)
3.3 a[b]	3197, 3111, (ν_{N-H})	7.40-7.19 (m, 5H), 4.80 (br, s, 2H)	5.04 (d, 2H, 6), 4.91 (d, 2H, 6), 2.86 (sept, 1H), 2.13 (s, 3H), 1.24 (d, 6H, 6)
3.3b[b]	3211, 3119 (ν_{N-H})	7.43-7.23 (m, 4H), 4.83 (br, s, 2H), 3.87 (s, 3H)	5.23 (d, 2H, 6), 5.11 (d, 2H, 6), 2.86 (sept, 1H), 2.13 (s, 3H), 1.24 (d, 6H, 6)
3.3b[b]	3190, 3115 (ν_{N-H})	7.27 (d, 2H, 3), 7.23 (d, 2H, 3), 4.77 (br, s, 2H), 2.36 (s, 3H)	5.04 (d, 2H, 6), 4.92 (d, 2H, 6), 2.86 (sept, 1H), 2.13 (s, 3H), 1.24 (d, 6H, 6)

^{1}H NMR of these complexes have taken in CD_3CN, [a] in $(CD_3)_2CO$, [b] in $CDCl_3$; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad

Electronic spectra of the complexes **3.1a-e** and **3.2a** & **b** in acetonitrile exhibited bands in the range of 340-400 nm (table 3.2). These low-energy absorptions were assigned to Ru (dπ) to ligand (π*) metal to ligand charge transfer (MLCT) transition.

Table 3.2: ***MLCT absorption at room temperature.***

Sl. No.	Complex[a]	λ_{max}, nm
3.1a	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}H)Cl]PF_6$	374
3.1b	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}CH_3)Cl]PF_6$	366
3.1c	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}OCH_3)Cl]PF_6$	360
3.1d	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}Cl)Cl]PF_6$	374
3.1e	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)Cl]PF_6$	400
3.2a	$[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_{11})Cl]PF_6$	342
3.2b	$[(\eta^6\text{-}p\text{-}Cymene)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_{11})Cl]PF_6$	340

[a]acetonitrile solvent (1×10^{-3} M)

3.4.3 X-ray structure of $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]PF_6$ (3.1e)

The complex $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]PF_6$ (**3.1e**) has been structurally characterized by X-ray crystallography. An ORTEP view of the complex is shown in Figure 3.1. Selected bond lengths and angles are found in Table 3.3. The complex **3.1e** exist as half sandwich complex with the arene ring occupying three facial sites. The ruthenium atom is π- bonded to the hexamethylbenzene ligand with an average Ru-C distance 2.22 Å similar to that observed in related hexamethylbenzene ruthenium complexes [17]. The distance between ruthenium and the chloride ligand is 2.39 Å. In addition to being bonded to the arene and the chloride ligands, the ruthenium atom is also directly coordinated to two nitrogen atoms of the Schiff base ligand with an average distance of 2.10 Å. The bite angle of the chelating ligand is 75.90 (11) not very different from other related complexes [4b]. Notably, the phenyl and pyridyl ring of the Schiff base are not coplanar.

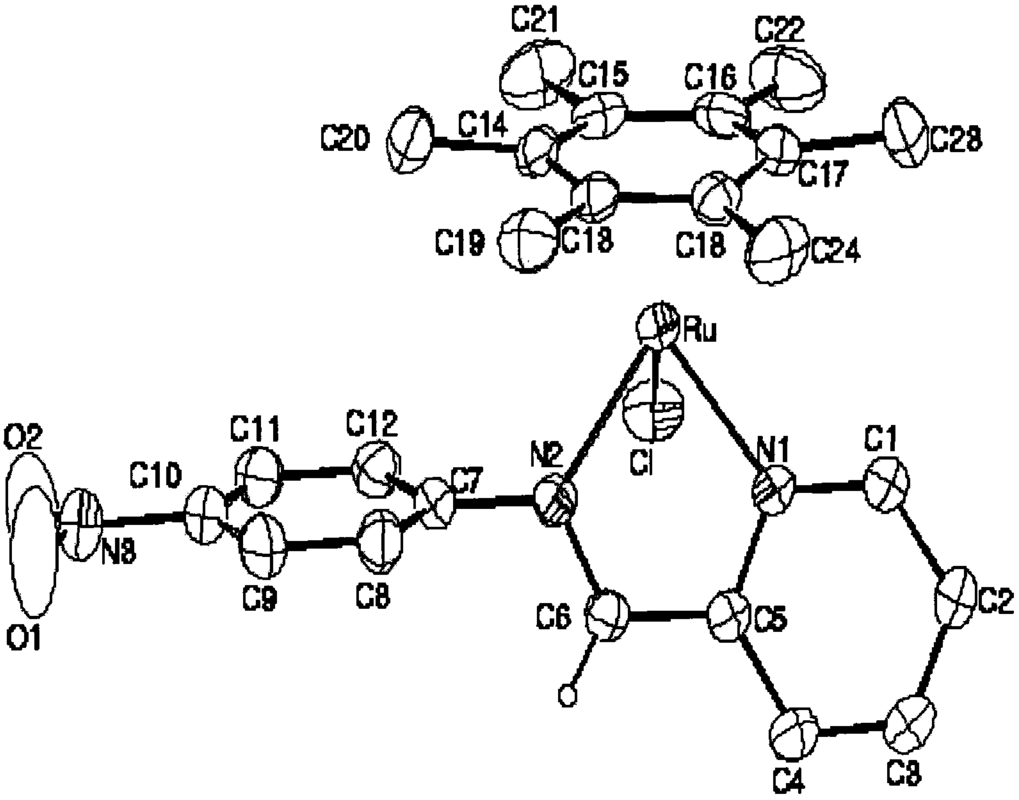


Figure 3.1: *Perspective view of the X-ray structure of $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]PF_6$ (3.1e) with atom labelling scheme. PF_6^- anion being omitted for clarity.*

The average C-C bond lengths in the hexamethylbenzene ring is 1.421 Å with alternate short and long bond lengths where C(13)-C(18), C(16)-C(17) and C(14)-C(15) bonds are shorter than the C(13)-C(14), C(15)-C(16) and C(17)-C(18) which could be due to the loss of planarity of the hexamethylbenzene ring. The alternate bond lengths are indicative of a contribution from the cyclohexatriene resonance structure to the overall resonance hybrid [18].

Table 3.3: *Selected Bond lengths (Å) and Bond angles (°) for the complex* $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]PF_6$ ***(3.1e)*** *(estimated standard deviations in parentheses)*

Bonds lengths

Ru – N1	2.099(3)	Ru – C13	2.404(3)
Ru – N2	2.106(3)	C13 – C14	1.435(5)
Ru – C14	2.250(3)	C14 – C15	1.395(6)
Ru – C15	2.227(3)	C15 – C16	1.448(6)
Ru – C16	2.225(4)	C16 – C17	1.410(6)
Ru – C17	2.251(4)	C17 – C18	1.422(6)
Ru – C18	2.190(3)	N2 – C6	1.288(4)
N3 – O1	1.184(8)	N2 – C7	1.431(4)
N3 – O2	1.207(8)	Ru – Cl	2.3093(10)

Bonds angles

N1 – Ru – N2	75.90(11)	N1 – Ru – C18	96.13(13)
N2 – Ru – C13	94.42(12)	C7 – N2 - Ru	126.5(2)
C6 – N2 – Ru	116.3(2)	C5 – N1 - Ru	116.2(2)
C15 – Ru – Cl	90.79(11)	C16 – Ru.- Cl	92.52(12)
N1 – Ru – Cl	83.92((9)	N2 – Ru –Cl	85.84(8)
O1 - N3 - O2	123.7(6)	O1 - N3 - C10	118.9(6)
O2 – N3 - C10	117.4(6)		

3.4.4 X-ray structure of $[(\eta^6\text{-p-cymene})RuCl_2(NH_2C_6H_5)]$ *(3.3a)*

Single crystals of the complex $[(\eta^6\text{-p-cymene})RuC12(NH_2C_6H_5)]$ (**3.3a**) suitable for X-ray analysis has been grown by addition of diethylether in to the NMR sample in $CDCl_3$. An ORTEP view of the complex is shown in Figure 3.2. Selected bond lengths and angles are found in table 3.4. The coordination of the metal atom to the p-cymene ring is not perfectly symmetric; the Ru – C11 and Ru – C7 bond distances are relatively shorter than the other metal ring distances. The Ru – Cl1 and Ru – Cl2 bond distances are almost the same and the angles subtended by Cl1-Ru - Cl2, N1- Ru - Cl1, N1-Ru-Cl2 bond angles confirm the three legged piano stool structure of the compound.

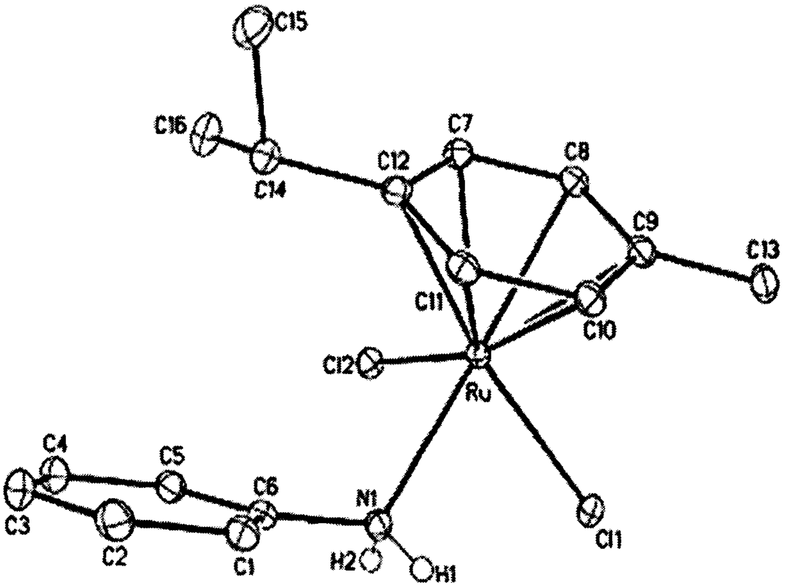


Figure 3.2 *Perspective view of the X-ray structure of [(η^6-p-cymene)RuCl$_2$(NH$_2$C$_6$H$_5$)] **(3.3a)** with atom labelling scheme.*

Table 3.4 *Selected Bond lengths (Å) and Bond angles (°) for the complex [(η^6-C$_6$Me$_6$)RuCl2(NH$_2$C$_6$H5)] (3.3a) (estimated standard deviations in parentheses)*

Bonds lengths

Ru – N1	2.1735(14)	Ru – C9	2.2218(16)
Ru – Cl1	2.4232(5)	Ru – C10	2.193(16)
Ru – Cl2	2.4071(5)	Ru – C11	2.1462(16)
Ru – C7	2.1521(16)	Ru – C12	2.1880(16)
Ru – C8	2.1930(16)		

Bonds angles

N1 – Ru – Cl1	80.27(4)	Cl1 – Ru – Cl2	87.641 (14)
N1 – Ru – Cl2	83.81(4)	Ru – N1 – C6	119.98(10)

Hydrogen bonds

D – H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
N(1)-H(1)...Cl(1)#1	0.80(2)	2.48(2)	3.2740(16)	170.7(19)
N(1)-H(2)...Cl(2)#2	0.85(2)	2.52(2)	3.3207(15)	160.3(18)

Table 3.5: ***Summary of Structure Determination of Compound 3.2e and 3.3a***

Formula	$RuC_{24}H_{27}N_3PO_2F_6Cl$ **3.2e**	C16H21Cl2NRu **3.3a**
CCDC	**193369**	-
Formula weight	670.98	399.31
T(K)	293(2)	120(2)
Crystal class	monoclinic	triclinic
Space group	$P2_1/n$ (#14)	P-1
Z	4	2
Cell constants:		
a(Å)	10.65120(10)	7.8494(13)
b(Å)	11.71340(10)	9.0039(15)
c(Å)	21.7134(3)	12.520(2)
α(°)		87.955(2)
β(°)	98.1180(10)	85.145(2)
γ(°)		69.541(2)
V(Å^3)	2681.86(5)	826.0(2)
crystal size(mm)	0.42 x 0.11 x 0.06	0.15 x 0.10 x 0.08
$D_{calc.}$(g/cm^3)	1.662	1.605
F(000)	1352	404
Radiation	Mo-K_α (λ=0.71069Å)	Mo-K_α (λ=0.71073Å)
θ range (°)	2.57 – 27.48	1.63 to 27.73
hkl collected	$-13 \leq h \leq 13$ $-14 \leq k \leq 15$ $-28 \leq l \leq 28$	$-10 \leq h \leq 10$ $-11 \leq k \leq 11$ $-15 \leq l \leq 16$
No. reflns. measd / unique	26725 / 5971 [R_{int}=0.0312]	8742 / 3490 [$R_{(int)}$ = 0.0150]

No. parameters	350	190
R indices (F>4σ)	R1 = 0.0534, wR2 = 0.1332	R1 = 0.0188 wR2 = 0.0479
R indices (all data)	R1 = 0.0592, wR2 = 0.1378	R1 = 0.0191 wR2 = 0.0482
GOF:	1.138	1.068
Final Difference Peaks,(e.Å^3)	0.659, -0.638	0.590 & -0.393

3.5 Conclusions

Reactions of [(η^6-arene)RuCl$_2$]$_2$ (arene = hexamethylbenzene, *p*-cymene) with Schiff bases *viz. para*-substituted N-(2-pyridinylmethylene)phenylamines and N-(2-pyridinylmethylene)cyclohexylamine yielded mononuclear cationic complexes resulting from the cleavage of the chloro- bridges while phenylimines ligands undergo hydrolysis when reacted with [(η^6-*p*-cymene)RuCl$_2$]$_2$ to afford amine complexes.

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Chapter IV

A. Reactivity studies of η^6-arene ruthenium(II) dimers with polypyridyl ligands: Isolation of mono, binuclear *p*-cymene ruthenium(II) complexes and bis-terpyridine ruthenium(II) complexes.*

4.1 Abstract

The complexes $[(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$ where L_2 = 2, 2'- biquinoline (biqui) (**4.1**), 2, 9-dimethyl 4, 7-diphenyl-1, 10-phenanthroline (ddp) (**4.2**), 2,3-bis (α-pyridyl) quinoxaline (bpq) (**4.3**) were obtained by halide bridge cleavage of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]$ with the corresponding ligands. The ligand bridged binuclear compound $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(bpq)]^{2+}$(**4.4**) was also obtained by treating $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with stoichiometric amount of bpq in methanol. The reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, hexamethylbenzene) with substituted phenylterpyridines (x-phterpy, x = H, CH_3, OCH_3) yielded bis terpyridine complexes of the type $[(x\text{-phterpy})_2Ru]^{2+}$ by the facile displacement of η^6-arene ring as well as chloride ligands. These complexes were characterized by FT-NMR, FT-IR spectroscopy and analytical data. The molecular structures of $[(\eta^6\text{-}p\text{-cymene})RuCl(biqui)]PF_6$ (**4.1**) and $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]PF_6$ (**4.3**) have been determined by single crystal X-ray diffraction study.

4.2 Introduction

It has been previously reported the reactivity of terdentate polypyridyl ligands toward cyclopentadienyl, indenyl and pentamethylcyclopentadienyl ruthenium systems where η^5-bonded moieties remain intact and thus forming $[(\eta^5\text{-L})Ru(terpy)(PPh_3)]^+$, (L = C_5H_5, C_9H_7, C_5Me_5) [1] or $[(\eta^5\text{-}C_5Me_5)MCl(phterpy)]^+$ (M= Rh, Ir) [2], however, the reaction of these ligands with the isoelectronic halide bridged arene ruthenium complexes of the type $[(\eta^6\text{-arene})RuCl_2]_2$, (arene = *p*-cymene, hexamethylbenzene), do not form the expected $[(\eta^6\text{-arene})RuCl(phterpy)]^+$ but instead irrespective of the solvents used gave

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* R. Lalrempuia and Mohan Rao Kollipara, *Polyhedron*, 23 (2003) 3155.

only known bis terpyridine ruthenium complexes [3]. This observation prompted us to investigate the reactivity of $[(\eta^6\text{-arene})RuCl_2]_2$, with more steric and bulkier chelating N,N'-heterocycles. Initial studies of these complexes with 2,2'-bipyridine and 1,10-phenanthroline have been reported [4].

This chapter described the formation of $[(\eta^6\text{-arene})RuCl(L_2)]^+$ complexes and also the facile displacement of η^6-bonded arene as well as the chloride ligands by phenylterpyridines from $[\{(\eta^6\text{-arene})RuCl_2]_2$ forming known complexes of the type $[(phterpy)_2Ru]^{2+}$. In order to confirm the nature of bonding, the structures of $[(\eta^6\text{-}p\text{-cymene})RuCl(biqui)]PF_6$ and $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]PF_6$ have been solved by x-ray crystallography.

4.3 Experimental Section

All chemicals used were of reagent grade. All reactions were carried out in purified and dried solvents. ^{1}H NMR and IR were recorded as chapter II. Elemental analysis was performed in Perkin-Elmer-2400 CHN analyzer. $[\{(\eta^6\text{-arene})RuCl_2]_2$ [5], 2,3-Bis(α-pyridyl) quinoxaline [6], 4'-phenyl-2,2':6',2''-terpyridine (phterpy) [7], 4'-p-methylphenyl-2,2':6',2''-terpyridine (Me-phterpy) and 4'-p-methoxyphenyl-2,2':6',2''-terpyridine (OMe-phterpy) [8] were prepared according to the procedure described in the literature.

4.3.1 Preparation of the complexes

Preparation of $[(\eta^6\text{-cymene})Ru(biqui)Cl]PF_6$ *(4.1)*

The mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.05 g, 0.081 mmol), 2,2'-biquinoline (0.055 g, 0.214 mmol) and NH_4PF_6 (0.080 g, 0.488 mmol) was stirred in a mixture of methanol (10 ml) and CH_2Cl_2 (10 ml) at room temperature for 1.5 h and the solvents were removed under reduced pressure. The residue was redissolved in acetone and filtered to remove any insoluble materials. The volume was reduced to about 2 ml and addition of excess hexane gave yellow compound. Single crystals were grown by slow evaporation of acetonitrile solution.

Yield: 0.155 g, 70.76 %

Anal. Calc. for C28H26ClN2F6PRu: C, 50.04; H, 3.90; N, 4.16. Found C, 50.10; H, 3.94; N, 4.19 %

^{1}H NMR (δ, CD_3CN): 8.94 (d, J = 8.7 Hz), 8.59 (d, J = 8.4 Hz), 8.40 (d, J = 8.4 Hz), 8.11 (m), 7.91 (t, J = 7.5 Hz), 5.72 (d, J = 6 Hz), 5.57 (d, J = 6 Hz), 2.31 (s), 0.79 (d, J = 6.9 Hz).

IR (CsI, cm^{-1}): 844 (s,ν_{P-F}), 557 (s), 310 (m, ν_{Ru-Cl}).

Preparation of [(η^6-p-cymene)Ru(ddp)Cl)]PF$_6$ (4.2)

The mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.074 g, 0.122 mmol), 2,9-dimethyl, 4,7-diphenyl-1,10-phenanthroline (ddp) (0.088 g, 0.244 mmol) and NH_4PF_6 (0.080 g, 0.488 mmol) in methanol (20 ml) was stirred at room temperature for two hours. Then the solvent was removed under reduced pressure, the residue was redissolved in acetone and then filtered to remove any insoluble materials. The volume was reduced to about 2 ml and addition of excess hexane gave a yellow product. Yield: 0.150 g, 59.19 %.

Anal. Calc. for C36H34N2ClF6PRu: C, 61.90; H, 3.89; N, 3.60. Found C, 62.04; H, 3.90; N, 3.69 %

^{1}H NMR (δ, CD_3CN + $CDCl_3$): 8.06 (s), 7.86 (s), 7.62 (m), 5.83-5.50(m), 3.09 (s), 2.86 (sept), 2.24 (s), 1.32 (dd, J = 3.6 Hz).

IR (CsI, cm^{-1}): 844 (s,ν_{P-F}), 558 (s), 306 (m, ν_{Ru-Cl})

Preparation of [(η^6-p-cymene)RuCl(bpq)]PF$_6$ (4.3)

The mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.1 g, 0.163 mmol), 2,3-bis(α-pyridyl)quinoxaline (0.098 g, 0.347 mmol) and NH_4PF_6 (0.061 g, 0.376 mmol) in 10 ml of methanol was refluxed under dry nitrogen atmosphere for 1 hour. The resulting solution was filtered to remove insoluble brown product. The filtrate was then evaporated under vacuum on a rotary evaporator, the residue was redissolved in CH_2Cl_2 and filtered, the volume was reduced to about 2 ml, then excess hexane was added which give an oily material. It was washed several times with hexane to give orange-red microcrystalline solid. Suitable crystals for x-ray structure determination were grown by slow diffusion of hexane into acetone solution. Yield: 0.152 g, 66.6 %.

UV-vis (CH_3CN, 1 x 10^{-3}M): λ_{max} 392 nm.

Anal. Calc. for C28H26ClF6N4PRu: C, 48.04; H, 3.74; N, 7.99. Found C, 48.14; H, 3.90; N, 8.04 %

^{1}HNMR {δ, $(CD_3)_2CO$}: 9.55 (d, J = 1.5 Hz), 8.99 (d, J = 2.4 Hz), 8.67 (t, J = 1.5 Hz) 8.42-8.15 (m), 8.02 (t, J = 6 Hz), 7.80-7.70 (m), 7.3 (d, J = 1.8 Hz), 6.44 (d, J = 6.6 Hz), 6.28 (d, J = 6.6 Hz), 6.12 (d, J = 5.1 Hz), 2.60 (sept), 2.42 (s), 1.15 (d, J = 7.2 Hz), 1.07 (d, J = 6.9 Hz).

IR (CsI, cm^{-1}): 844 (s,ν_{P-F}), 557 (s), 304 (br, m, ν_{Ru-Cl}).

Preparation of $[\{(\eta^6$-p-cymene)RuCl$\}_2$(bpq)$](PF_6)_2$ (4.4)

Method (i): The brown insoluble product from the preparation of complex **4.3** was dissolved in acetone to give a violet color solution, filtered and the volume was reduced to a few ml and addition of diethylether gave the complex **4.4**.

Method (ii): The mixture of $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (0.1 g, 0.163 mmol) and 2,3-bis (pyridyl)quinoxaline (0.046 g, 0.163 mmol) and NH_4PF_6 (0.06 g, 0.373 mmol) was refluxed in methanol (10 ml). Violet color precipitate appears after 15 minutes and the whole reaction mixture was refluxed for 1 hour. The reaction mixture was cooled to room temperature and filtered; the precipitate was washed several times with water and then with methanol and then finally with diethylether to give the compound as dark violet shiny crystalline solid. It was air-dried. Yield: 0.160 g, 87.91 %

Anal. Calc. for C38H40Cl2N4P2F12Ru2: C, 40.91; H, 3.58; N, 5.02. Found C, 41.12; H, 3.60; N, 5.13 %

UV-vis (CH_3CN, 1 x 10^{-3} M): $\lambda_{max:}$ 463 nm.

^{1}HNMR {δ, $(CD_3)_2CO$}: 9.44 (d, J=6 Hz), 8.88 (m), 8.48 (d, J = 8.1 Hz), 8.41 (m), 8.15 (t, J = 8.1 Hz), 7.90 (t, J = 6.6 Hz), 6.19 (d, J = 6.3 Hz), 6.10 (d, J = 6.3 Hz), 5.87 (t, J = 5.7 Hz), 2.75 (sept), 2.23 (s), 1.20 (d, J = 6.9 Hz), 1.09 (d, J = 6.9 Hz).

IR (CsI, cm^{-1}): 844 (s, ν_{P-F}), 557 (s), 306 (m, ν_{Ru-Cl}).

4.3.2 Preparation of $[\{(\eta^6-C_6Me_6)RuCl_2]_2$

The mixture of $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (0.13 g, 0.21 mmol) and hexamethylbenzene (1.3 g, 0.21 mmol) was refluxed in diglyme (18 ml) with stirring under dry nitrogen atmosphere for around 9 h. The solution was cooled to room temperature and the red brown product was filtered off. Washed with hexane (5 × 10 ml) to remove excess hexamethylbenzene and *p*-cymene dimer and finally with diethylether. The compound was recrystallized from chloroform/diethylether.

Yield: 0.026g, 18.5 %.

^{1}HNMR($CDCl_3$): δ 2.02 (s) [lit. [7(b)]: 2.03]. ^{13}C-NMR ($CDCl_3$): δ 89.61 (s), δ 15.92 (s). IR (CsI, cm^{-1}): 297 (s), 259 (s) {lit. [7(b)]: 299, 258}.

4.3.3 η^6-arene displacement reactions

The mixture of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, hexamethylbenzene) (0.163 mmol), phenylterpyridine ligands (0.407 mmol) and NH_4BF_4 (0.489 mmol) was stirred in dry methanol (15 ml) at room temperature, the color of the solution immediately changed to purple, stirred for 2 hours whereby red brown compound precipitated out. The solvent was slowly removed in rotary evaporator. The residue was redissolved in acetone and filtered to remove any insoluble materials. Acetone solution was reduced to about 2 ml and addition of excess hexane precipitated out red brown compound.

$[(phterpy)_2Ru](BF_4)_2$ (4.3.6a)

Yield: 0.120 g, 41.09 % (from **1**), UV-vis(1x10^{-3} M, CH_3CN): λ_{max} 489 nm. Anal. Calc. for C42H30BF4N6Ru: C, 56.48; H, 3.35; N, 9.45. Found C, 56.52; H, 3.40; N, 9.49.

^{1}HNMR {δ, $(CD_3)_2CO$}: 9.46 (2H, s), 9.11 (2H, d, J = 8.1 Hz), 8.36 (2H, dd, J =1.2 Hz), 8.14 (3H, dt, J = 1.2 Hz), 7.85-7.69 (4H, m), 7.38 (2H, dt, 1.2 Hz).

$[(Me\text{-}phterpy)_2Ru](BF_4)_2$ (4.3.6b)

Yield: 0.125 g, 41.66 % (from **1**), UV-vis(1x10^{-3} M, CH_3CN): λ_{max} 480 nm. Anal. Calc. for C44H34BF4N6Ru: C, 57.35; H, 3.68; N, 9.16. Found C, 57.39; H, 3.72; N, 9.2.

^{1}HNMR {δ, $(CD_3)_2CO$}: 9.43 (2H, s), 9.08 (2H, d, J = 8.1 Hz), 8.29 (2H, d, J = 8.7 Hz), 8.11 (2H, dt, J =1.2 Hz), 7.82 (2H, dd, J = 1.2 Hz), 7.58- 7.36 (4H, m), 2.52 (3H, s).

$[(OMe\text{-}phterpy)_2Ru](BF_4)_2$ (4.3.6c)

Yield: 0.127 g, 40.83 % (from **1**), UV-vis(1x10^{-3} M, CH_3CN): λ_{max} 482 nm.

Anal. Calc. for C40H34BF4N6O2Ru: C, 55.42; H, 3.56; N, 8.85. Found C, 55.48; H, 3.60; N, 8.91.

^{1}HNMR {δ, $(CD_3)_2CO$ }: 9.40 (2H, s), 9.07 (2H, d, J = 8.1 Hz), 8.36 (2H, d, J = 8.7 Hz), 8.08 (2H, dt, 1.2 Hz), 7.82 (2H, dd, J = 0.9 Hz), 7.36- 7.28 (4H, m), 3.99 (3H, s).

4.3.4 *Crystal structure determination of 4.1 and 4.3*

A suitable size crystal were mounted on the end of the glass fiber and mounted on a Nonius MACH3 diffractometer with graphite monochromatized MoKα (λ= 0.70930 Å) radiation at a temperature of 293 K for the cell determination and intensity data collection. All crystallographic calculations were performed with using the Maxus software. The structure was solved by direct methods (SHELXS 1997). Refinement was by full-matrix least squares based on F^2 using SHELXL-93. Lorentz and polarization corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. The crystallographic details are summarized in Table 4.3.

4.4 Results and Discussion

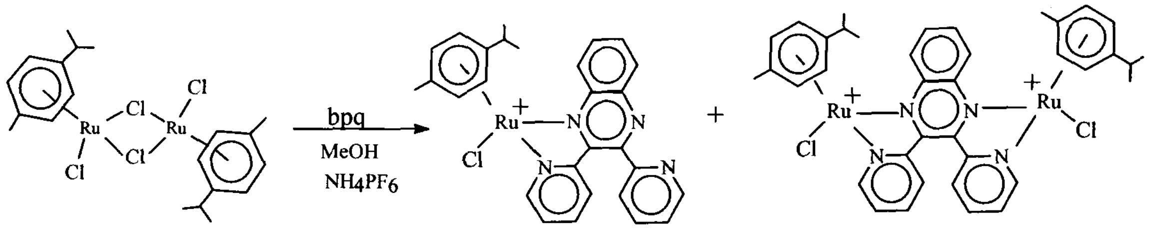
The cationic mono nuclear complexes with the general formulation $[(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$ (L_2 = biqui, ddp and bpq) were prepared by the reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with excess of L_2 in methanol however, addition of dichloromethane as a co-solvent is necessary to prepare complex **4.1**. These complexes are soluble in acetone, acetonitrile and DMSO.

$$[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2 \xrightarrow{\qquad} [(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$$

L_2 = 2,2'-biquinoline (2,2'-biqui.) (**4.1**), 2,9-Dimethyl 4,7-diphenyl-phenanthroline (ddp) (**4.2**), 2,3-bis (α-pyridyl)quinoxaline (bpq) (**4.3**)

Scheme 4.1

The reaction of *p*-cymene dimer with two and half fold excess of bpq in methanol in refluxing condition yielded two compounds, the ^{1}HNMR spectrum of the main product showed unsymmetrical splitting pattern of the bpq ligand in aromatic region which suggests the compound to be a mononuclear complex $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]^+$ (**4.3**). The byproduct, which could also be isolated from the reaction between p-cymene dimer and bpq in 1:1 molar ratio, showed six distinct peaks in the aromatic region apart from the characteristic signals arising from the *p*-cymene moiety. The integration of the spectrum suggests the compound to be binuclear ligand bridged compound of the formula $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(bpq)](PF_6)_2$ **(4.4)** as shown below (Scheme 4.2), ^{1}H NMR spectrum of the mononuclear complex **(4.3)** and its dinuclear counterpart **(4.4)** is shown in the next page.



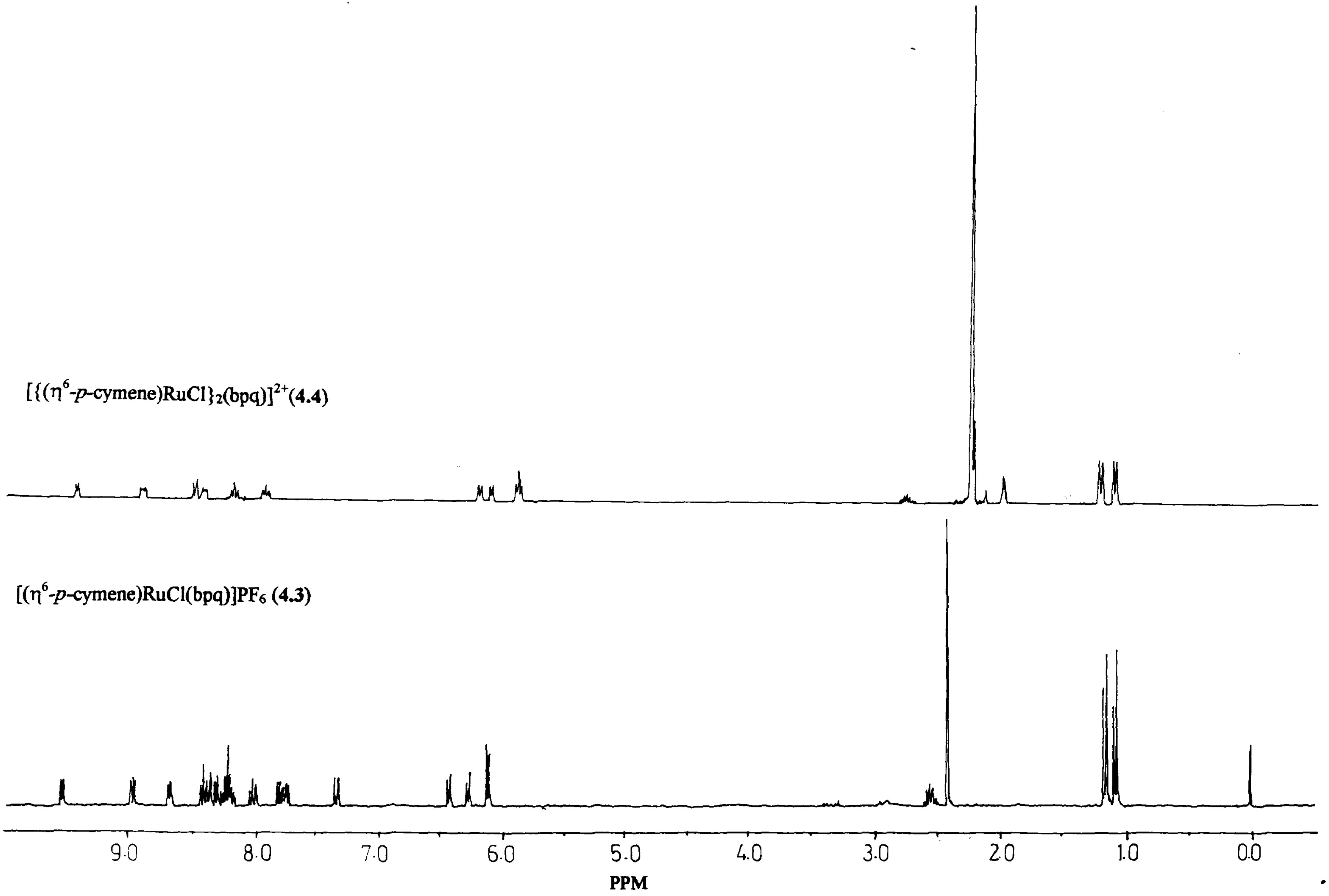
(4.3) **(4.4)**

Scheme 4.2

The ^{1}HNMR spectra of the complexes **4.2** and **4.3** exhibited the resonance of the methyl protons of isopropyl group as two doublets at ca.1.32 ppm and 1.13 ppm respectively and more than two sets of doublets for the *p*-cymene ring protons at around 6 ppm which could be due to loss of planarity of the *p*-cymene ring because of steric nature of the ligands. This splitting pattern is solely due to the nature of the incoming ligands. Complex **4.1** exhibited the resonance of methyl protons of the isopropyl group as a doublet at 0.79 ppm and *p*-cymene ring protons appeared as two sets of doublet at 5.72 and 5.57 ppm respectively. The far infrared spectra of these complexes showed bands at around 304-310 cm^{-1}, which were assigned to terminal ν(Ru-Cl) stretching vibrations, these values are slightly higher compared to the values observed for the closely related complexes [4].

It was observed the MLCT band of complex **4.4** shows considerable red shift compared to the mononuclear complex **4.3**. The red shift in the position of Ru → bpq CT transition towards lower energy may result from the stabilization of bpq π* orbital upon coordination to the second ruthenium center [9].

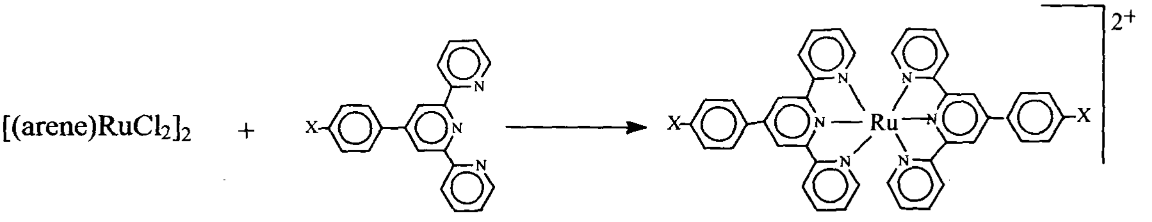
The complex $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ was also prepared by the arene displacement reaction starting from p-cymene dimer with hexamethylbenzene in refluxing diethylene glycol dimethyl ether (diglyme). The literature method sometimes resulted in the



^{1}HNMR SPECTRA

decomposed product. The desired compound was successfully isolated but in unrepeatable low yield.

Terpyridines in principle can bind metals in bidentate fashion leaving one pyridyl ring uncoordinated [2] and also as monodentate or tridentate or as bridging ligand. The reaction of the complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with stoichiometric or excess amount of para substituted phenylterpyridines in different solvents such as acetonitrile, chloroform, ethanol and methanol at room temperature or refluxing condition resulted only in the facile displacement of the *p*-cymene ring as well as the chloride ligands. The ^{1}HNMR data, far IR spectra suggested absence of *p*-cymene ring and halide ligand in these complexes and analytical data indicated the products as a well known dicationic complexes of the type $[(x\text{- phterpy})_2Ru]^{2+}$. The reaction between these ligands and $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ also resulted the similar products. ^{1}H NMR spectrum of a representative compound $[(OMe\text{-phterpy})_2Ru]^{2+}$ is shown after this page.

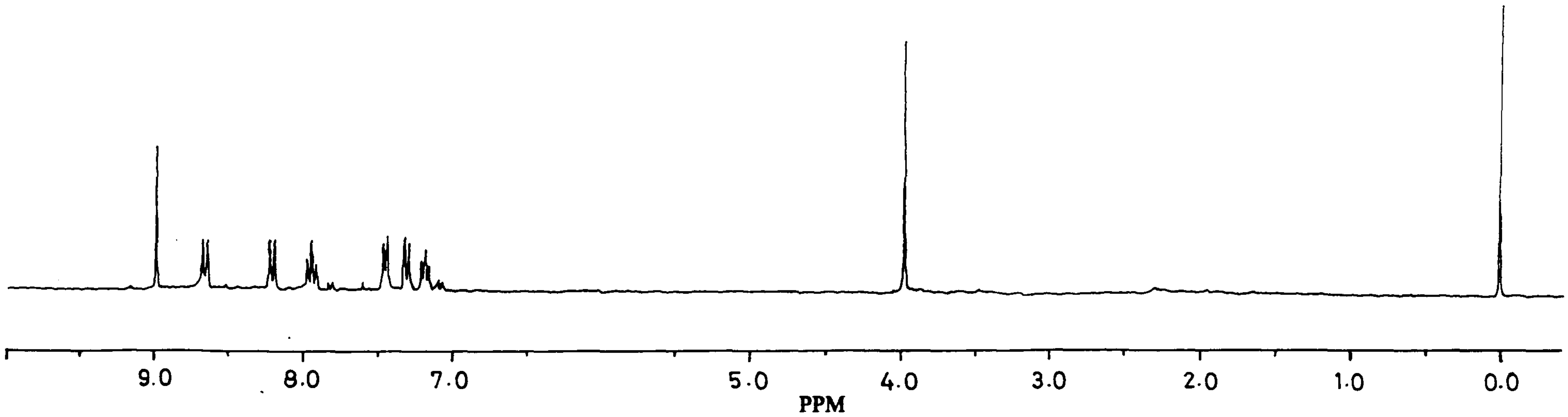


X = H, CH$_3$, OCH$_3$

Scheme 4.3

4.4.1 Crystal structure of 4.1 and 4.3

Single crystal X-ray structure determinations were carried out for complexes **4.1** and **4.3** (Figures 4.2 and 4.3) for confirmation of the formulation. However, the low accuracy of the result from **4.1** would render meaningless a discussion of the metrical parameters. Selected bond lengths and bond angles are listed in Table 4.1 and Table 4.2 and the data collection parameters are listed in Table 4.3. The ruthenium atom is bonded to the two nitrogen atoms of the ligand, one chloride ligand and to a p-cymene group through the six carbon atoms. The geometry about the metal atom can be regarded as distorted octahedral if the η^6-*p*-cymene group is assumed to occupy three facial coordinated positions. In complex **4.3**, the average Ru-C bond length is 2.195 Å with Ru-



^{1}HNMR spectrum of $[(OMe\text{-}phterpy)_2Ru](BF_4)_2$ **(4.3.6c)**

C(20) and Ru-C(25) bond distances slightly longer than the rest. The average C-C distance is 1.399 Å with alternate short and long bond length.

The Ru–Cl(1) bond length is 2.3804 Å, which falls within the usual range of Ru-Cl bond distance [10]. The bite angle of the chelating ligand is 76.12 °(17). The two Ru–N bond lengths are slightly different (2.059 Å and 2.089 Å). The bond angles of N(1)-Ru-Cl(1) and N(2)-Ru-Cl(1) are 84.61(3)° and 87.67(3)° respectively indicating the three legged piano stool type structure of the compound.

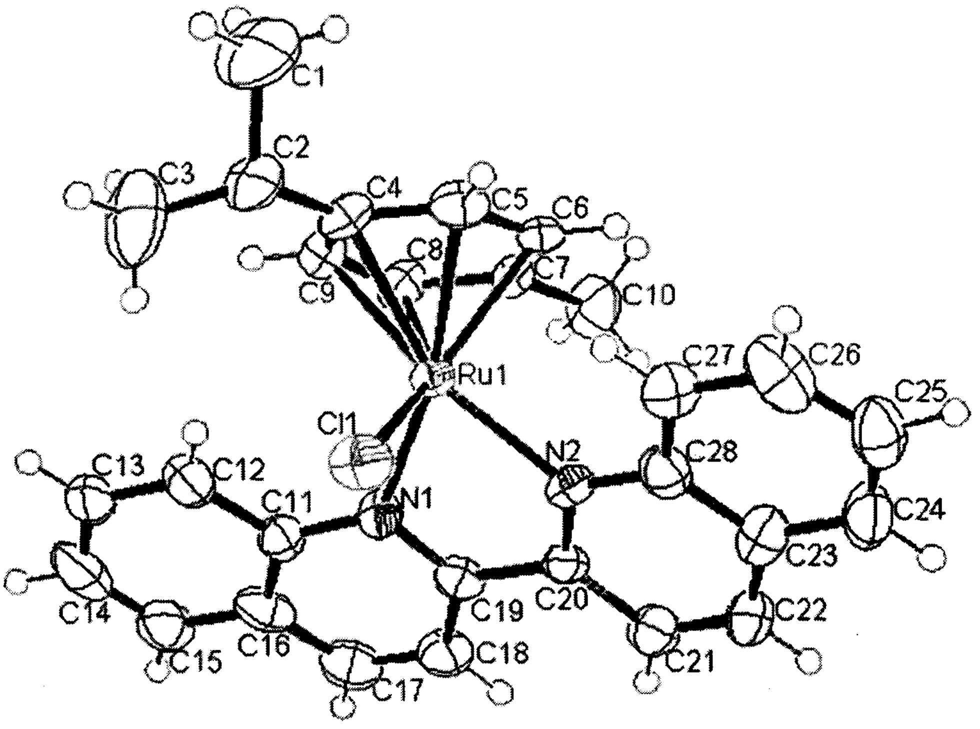


Figure 4.1: *Perspective view of [(η⁶-p-cymene)Ru(biqui)Cl]PF₆ (4.1) with atom numbering scheme, PF₄⁻ anion being omitted for clarity. Thermal ellipsoids are shown at the 50 % probability level.*

Table 4.1: *Selected Bond lengths (Å) and Bond angles (°) for the complex [(η^6-p-cymene)RuCl(biqui)]PF_6 (4.1) (estimated standard deviations in parentheses).*

Bond lengths

Ru(1)-N(1)	2.101(12)	Ru(1)-N(2)	2.126(10)
Ru(1)-C(8)	2.157(15)	Ru(1)-C(6)	2.174(13)
Ru(1)-C(7)	2.193(14)	Ru(1)-C(5)	2.196(14)
Ru(1)-C(9)	2.210(14)	Ru(1)-C(4)	2.243(14)
Ru(1)-Cl(1)	2.388(8)	C(4)-C(9)	1.371(19)
C(4)-C(5)	1.392(18)	C(5)-C(6)	1.395(18)
C(6)-C(7)	1.395(19)	C(7)-C(8)	1.432(17)
C(8)-C(9)	1.412(17)		

Bond angles

N(1)-Ru(1)-N(2)	76.6(4)	N(2)-Ru(1)-Cl(1)	86.4(3)
N(1)-Ru(1)-Cl(1)	87.8(3)		

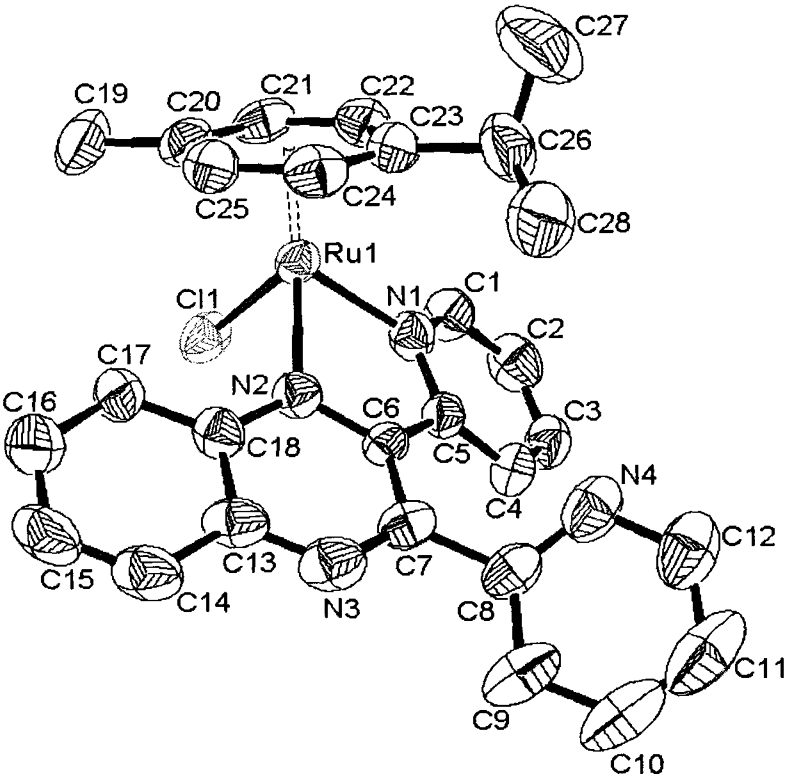


Figure 4.2: *Perspective view of [(η^6-p-cymene)Ru(bpq)Cl]PF_6 (4.3) with atom numbering scheme, BF_4^- anion being omitted for clarity.*

Table 4.2: *Selected Bond lengths (Å) and Bond angles (°) for the complex [(η^6-p-cymene)Ru(bpq)Cl]PF_6 (4.3) (estimated standard deviations in parentheses)*

Bond lengths

Ru(1)-N(1)	2.059(4)	Ru(1)-C(25)	2.208(6)
Ru(1)-Cl(1)	2.3804(15)	Ru(1)-N(2)	2.089(4)
C(20)-C(21)	1.423(9)	Ru(1)-C(20)	2.239(6)
C(20)-C(25)	1.376(9)	Ru(1)-C(21)	2.183(6)
C(21)-C(22)	1.395(9)	Ru(1)-C(21)	2.183(6)
C(22)-C(23)	1.428(9)	Ru(1)-C(22)	2.184(6)
C(23)-C(24)	1.391(9)	Ru(1)-C(23)	2.194(6)
C(24)-C(25)	1.409(9)	Ru(1)-C(24)	2.165(6)

Bond Angles

N(1)-Ru(1)-N(2)	76.17(17)	N(1)-Ru(1)-Cl(1)	84.61(13)
N(2)-Ru(1)-Cl(1)	87.67(13)		

Table 4.3: ***Summary of structure determinations of compounds 4.1 and 4.3***

	4.1	**4.3**
CCDC	**196366**	**209301**
Empirical formula	C28H26ClF6N2PRu	C28H26ClF6N4PRu
Formula weight	671.998	700.02
Temperature	293 (2) K	293 (2) K
Wavelength	0.70930 Å	0.70930 Å
Crystal system, space group	Monoclinic, P 21/n	Monoclinic P 21/n
Unit cell dimensions		
a (Å)	12.47 (5)	9.9920 (11)
b (Å)	15.22 (5)	16.3600 (15)
c (Å)	13.96 (5)	17.6190 (12)
β (°)	94.3 (2)	95.406 (7)
Volume (Å^3)	2641 (17)	2867.4 (5)
Z, D_{calc} (Mg/m^3)	4, 1.687	4, 1.622
Absorption coefficient (mm^{-1})	0.820	0.761
F (000)	1348	1408
Crystal size	0.4 x 0.35 x 0.35 mm	0.35 x 0.20 x 0.15 mm
θ range for data collection	1.98 to 24.92 °.	1.70 to 24.93°
Index ranges	$0 \leq h \leq 14$, $0 \leq k \leq 18$, $-16 \leq l \leq 16$	$0 \leq h \leq 11$, $0 \leq k \leq 19$, $-20 \leq l \leq 20$
Reflections collected / unique	4041 / 4041 [R (int) = 0.0000]	4272 / 4272 [R (int) = 0.0000]
Completeness to 2θ =	24.92 83.8 %	24.93 81.7 %
Absorption correction	Psi-scan	Psi-scan
Max. and min. transmission	1.000 and 0.797	1.000 and 0.904
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4041 / 0 / 352	4272 / 0 / 450
Goodness-of-fit on F^2	1.653	1.059
Final R indices [I>2σ(I)]	R1 = 0.1313, wR2 = 0.3402	R1 = 0.0457, wR2 = 0.1088
R indices (all data)	R1 = 0.1444, wR2 = 0.3600	R1 = 0.0618 wR2 = 0.1203
Largest diff. peak and hole(e Å^{-3})	4.278 and -2.858	0.659 and -0.558

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B. Reactivity studies of cyclopentadienyl bis(triphenylphosphine) ruthenium(II) complex towards some polypyridyl ligands*.

4b.1 Abstract

The reaction of [CpRu(PPh_3)$_2$Cl] with excess of some potentially bridging ligands *viz.* 2,3-bis(α-pyridyl)pyrazine (bpp), 2,3-bis(α-pyridyl)quinoxaline (bpq), 1,3,5-tris(pyridyl)-2,4,6-triazine (tptz) and 2,3,5,6-tetrakis(pyridyl)pyrazine (tppz) yielded cationic mononuclear complexes of the type [CpRu(PPh_3)(bpp)]PF_6 (**4b.1**), [CpRu(PPh_3)(bpq)]PF_6 (**4b.2**), [CpRu(PPh_3)(tptz)]PF_6 (**4b.3**) and [CpRu(PPh_3)(tppz)]PF_6 (**4b.4**) respectively. These complexes were characterized by FT-IR, ^{1}H-NMR and ^{31}P{^{1}H}NMR spectroscopy.

4b.2 Introduction

The current interest in complexes of polypyridyl ligands such as 2,2'-bipyridine, 1,10-phenanthroline, 2,2':6',2"-terpyridine etc., is associated with the extremely interesting electrochemical, photophysical, and photoelectrochemical properties that they exhibit [1-4]. Complexes with these ligands are also DNA intercalators, showing an ability to inhibit nucleic acid synthesis in vivo [5]. The previous Chapter IV A described the syntheses of some arene ruthenium(II) polypyridyl complexes, the displacement of arene moiety from the coordination sphere by some substituted terpyridines and also ligand bridged dinuclear complex. This part of the fourth chapter describe some complexes resulting from the reaction between [CpRu(PPh_3)Cl] and the ligands shown in chart 4b.1.

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* R. Lalrempuia, P. Govindaswamy, Yurij A. Mozharivskyj, Mohan Rao Kollipara, *Polyhedron*, 23 (2004) 1069.

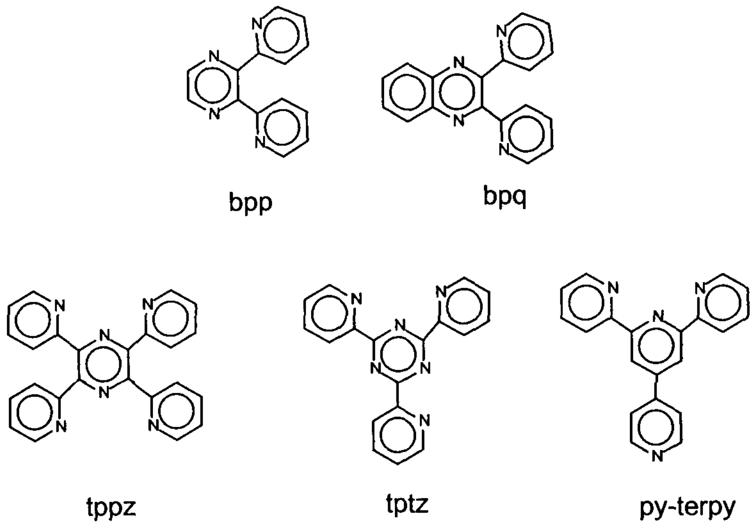


Chart 4b.1

Ligands used in this work

4b.3 Experimental Section

The solvents were purified and dried by standard methods and all reactions were carried out under dry nitrogen atmosphere. The ligands 2,3-bis(α-pyridyl)pyrazine (bpp), 2,3-bis(α-pyridyl)quinoxaline (bpq), 2,3,5,6-tetrakis(pyridyl)pyrazine (tppz) [6] and 4’-(4-pyridyl)-2,2’:6’,2”-terpyridine (py-terpy) [7] and [CpRu(PPh$_3$)$_2$Cl] [8] were synthesized according to the literature methods. 1,3,5-tris(pyridyl)-2,4,6-triazine (tptz) was purchased from Loba Chemie Private Limited and used as such.

4b.3.1 Preparation of the complexes (4b.1 – 4)

The following general procedure was used for the preparation of these mononuclear complexes.

The mixture of the complex [CpRu(PPh$_3$)$_2$Cl] (0.1 g, 0.110 mmol), the ligand (0.220 mmol) and NH$_4$PF$_6$ (0.220 mmol) were refluxed in methanol (40 ml) whereby the orange color suspension gradually changes to intense dark red color. It was refluxed for 5 h, then the solvent was rotary evaporated. The residue was extracted with CHCl$_3$ and filtered through short silica gel column to remove insoluble material, the filtrate was again concentrated to about 2 ml and addition of excess diethylether precipitated the product as red-brown solid.

[CpRu(PPh$_3$)(bpp)]PF$_6$ ***(4b.1)***

^{1}H NMR (δ, CDCl$_3$): 9.53 (s, 1H), 9.32 (d, 1H, J = 4.8 Hz), 8.63 (d, 1H, J = 4.7), 8.32 (s, 1H), 8.02 (t, 1H, J= 6.8 Hz), 7.65 (d, 1H, J = 7.6 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.33-6.98 (m, 17H), 6.56 (d, 1H, J = 8.2 Hz), 4.84 (s, 5H).

^{31}P {^{1}H} NMR (δ, CDCl$_3$): 48.81 (s), -143 (sept).

Anal. Calc. For C37H20N4Ru1P2F6: C, 55.02; H, 3.74; N, 6.96. Found: C, 55.20; H, 3.78; N, 7.00.

UV-Vis (CH$_2$Cl$_2$, 10^{-3}M): λ_{max} = 489 nm

[CpRu(PPh$_3$)(bpq)]PF$_6$ ***(4b.2)***

^{1}H NMR (δ, CD$_3$CN): 9.23 (d, 1H, J = 5.4 Hz), 8.74 (d, 1H, J = 8.9 Hz), 8.58 (d, 1H, J = 4.3 Hz), 8.10 (t, 1H, J = 8.1 Hz), 8.01-7.86 (m, 3H), 7.79 (t, 1H, J = 6.8 Hz), 7.60 (t, 1H, J = 6.9 Hz), 6.39-7.71 (m, 9H), 7.09 (t, 1H, J = 9.9 Hz), 6.90 (m, 7H), 6.76 (d, 1H, 8.4), 5.04 (s, 5H).

^{31}P {^{1}H} NMR (δ, CDCl$_3$): 52.66 (s), -143(sept).

Anal. Calc. For C41H32N4Ru1P2F6: C, 57.41; H, 3.73; N, 6.52. Found: C, 57.56; H, 3.82; N, 6.44.

UV-Vis (CH$_2$Cl$_2$, 10^{-3}M): λ_{max} = 486 nm

[CpRu(PPh$_3$)(tptz)]PF$_6$ ***(4b.3)***

^{1}H NMR (δ, CD$_3$CN): 9.30 (d, 1H, J = 5.2 Hz), 8.91 (d, 1H, J = 4.2 Hz), 8.68 (d, 1H, J= 7.9 Hz), 8.64 (d, 1H, J=8 Hz), 8.39 (d, 1H, J = 4.8 Hz), 8.03-7.84 (m, 3H), 7.56-7.46 (m, 4H), 8.36- 6.96 (m, 17H), 4.53 (s, 5H, Cp).

^{31}P {^{1}H} NMR (δ, CDCl$_3$): 48.98 (s), -143 (sept).

Anal. Calc. For C41H32N6Ru1P2F6: C, 55.60; H, 3.64; N, 9.49. Found: C, 55.83; H, 3.72; N, 9.63.

UV-Vis (CH$_2$Cl$_2$, 10^{-3}M): λ_{max} = 477 nm

[CpRu(PPh$_3$)(tppz)]PF$_6$ ***(4b.4)***

^{1}H NMR (δ, CDCl$_3$): 8.95 (m, 1H), 8.63 (d, 1H, J = 6 Hz), 8.19 (m, 1H), 8.03 (t, 1H, J = 6.6), 7.92 (m, 1H), 7.62-6.75(m, 26H), 4.95 (s, 5H, Cp).

^{31}P {^{1}H} NMR (δ, CDCl$_3$): 46.21 (m), -143 (sept).

Anal. Calc. For C47H36N6Ru1P2F6: C, 58.69; H, 3.74; N, 8.73. Found: C, 58.75; H, 3.67; N, 8.81.

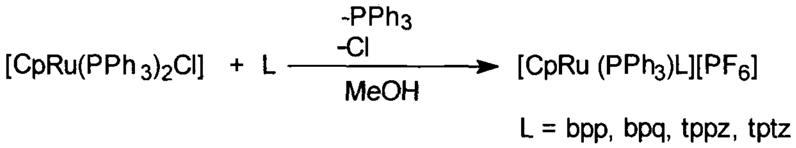
UV-Vis (CH_2Cl_2, 10^{-3}M): λ_{max}= 461 nm

4b.3.2 Crystal structure determination of 4b.2 and 4b.4

Suitable single crystals of **4b.2** were grown by slow diffusion of hexane into acetone solution and of **4b.4** were grown from hexane into chloroform solution. A suitable size crystal of complex **4b.2** was mounted on the end of the glass fiber and mounted on a Nonius MACH3 diffractometer where as complex **4b.4** was mounted on Bruker Smart Apex CCD system equipped with graphite monochromatized MoKα (λ= 0.70930 Å) radiation at a temperature of 293 K for the cell determination and intensity data collection. The structure was solved by direct methods (SHELXS 1997). Refinement was by full-matrix least squares based on F^2 using SHELXL-93. Crystal data collection parameters are summarized in Table 4b.3.

4b.4 Results and discussion

The reaction of the complex $[CpRu(PPh_3)_2Cl]$ with excess of the ligands (scheme 4.1) in methanol under refluxing condition resulted in the dissociation of one of the triphenylphosphines and chloride ligand to yield the monomeric chelate complexes **4b.1-4b.4** (scheme-2). We are unable to isolate the anticipated dimeric complexes by changing the molar ratio of the starting complex to the corresponding ligand. These complexes are soluble in most of the polar solvents.



$$[CpRu(PPh_3)_2Cl] + L \xrightarrow[MeOH]{-PPh_3,\ -Cl} [CpRu(PPh_3)L][PF_6]$$

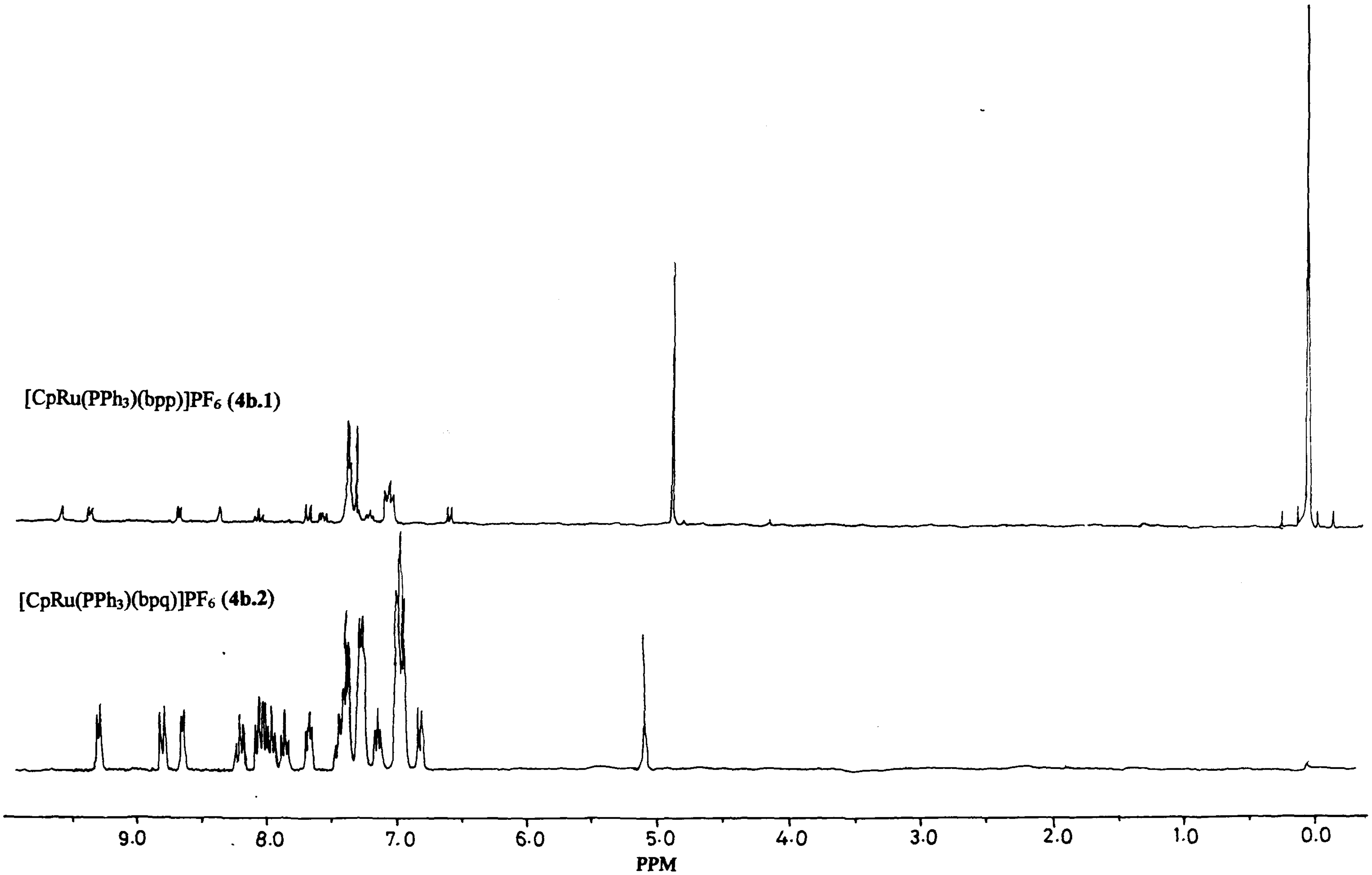
Scheme 4b.1

All these complexes showed a sharp singlet in the region of 4.53-5.04 ppm in ^1H NMR spectra, which can be assigned unambiguously to the resonance of cyclopentadienyl ligand. The analytical data, integration of the spectrum and a rather complicated peaks originating from the potentially bridging ligands in the ^1H NMR spectrum suggest the unsymmetrical coordinating nature of this ligand to the metal center i.e. two nitrogens chelate the ruthenium center leaving other pyridyl groups uncoordinated. The peaks corresponding to the protons of the triphenylphosphine and the chelate ligands appear in the aromatic region in the range of 7 – 9 ppm. The $^{31}P\ \{^{1}H\}$ NMR spectrum of these complexes showed single peak at around 48 ppm and septet at – 143 ppm for triphenylphosphine and PF_6^- ion respectively. In the case of complex **4b.4** a multiplet was observed at 46 ppm for triphenylphosphine, which may be due to the interaction between the phosphorus and the protons of the highly strained tppz ligand. In the next page, ^{1}H NMR spectra of **4b.1** and **4b.2** are shown together after this page.

In contrast to the above reactions, the product isolated from the reaction between complex $[CpRu(PPh_3)_2Cl]$ and py-terpy contains a mixture of products. The ^{1}H NMR spectrum shows three equally intense cyclopentadienyl peaks at 4.4 ppm, 4.38 ppm and 4.36 ppm suggesting the presence of three different environments for the cyclopentadienyl ligand. $^{31}P\ \{^{1}H\}$ NMR spectrum is also complicated and shows peaks at 49.7 ppm (singlet), 45.9 ppm (singlet) and 42.8 ppm (multiplets). The UV-Vis spectrum also shows two very broad bands at 450 nm and 520 nm. An attempt to separate the mixture by crystallization and column chromatography was unsuccessful.

4b.4.1 Crystal structures

The ORTEP drawing of the complexes **4b.2** and **4b.4** are shown in Figures 4b.1 and 4b.2 respectively. Selected bond lengths and angles are given in Table 4b.1 and 4b.2. The complex $[CpRu(PPh_3)(bpq)]PF_6$ **(4b.2)** crystallizes with one acetone per molecule but only two protons of the acetone were located. The geometry about the metal atom can be regarded as distorted octahedral with the bpq ligand chelating the ruthenium atom with two nitrogen atoms and the other coordination sites occupied by triphenylphosphine and a pentahapto bound cyclopentadienyl ligand. The average Ru-C (Cp) bond length is 2.202 Å where the individual bond length falls within the range of 2.172 – 2.230 Å. The two nitrogens chelate the ruthenium (N1-Ru-N2) with an angle of 76.11° and the bond lengths are almost the same with 2.090 Å and 2.070 Å for Ru-N1 and Ru-N2 respectively. The angle subtended by N1-Ru-P2 and N2-Ru-P2 is 94° and 95.01°



^{1}HNMR SPECTRA

respectively. The distance between the ruthenium atom and phosphorus atom of the triphenylphosphine ligand is 2.322 Å. Even with the rather low accuracy of the results from the x-ray determination, all the metrical parameters are in a close agreement with those of complex **4b.4** and other related works [9].

The complex [CpRu(PPh$_3$)(tppz)]PF$_6$ (**4b.4**) crystallized with three molecules of chloroform per molecule. The crystal diffracts weakly and the maximum angle at which I > 2σ(I) is 15°. Due to the small ratio of data to parameter, only the PF$_6$ and chloroform units were refined anisotropicaly and the rest was refined isotropicaly. The average Ru- C (Cp) bond length is 2.211 Å. The nitrogen atoms N12 and N21 chelate the ruthenium atom with an angle of 75.9°. The bond distance between the ruthenium and N12, N21 and P of PPh$_3$ is 2.093 Å, 2.113 Å and 2.336 Å respectively. The angle subtended by N12-Ru-P1 and N21-Ru P1 is 93.7° and 92.4° respectively. The bond angles and bond lengths are comparable in both these structures as well as with those of related complexes.

Table 4b.2 *Selected bond lengths (Å) and bond angles (°) for [CpRu(PPh$_3$)(bpq)]PF$_6$ .C$_3$H$_3$O (**4b.2**)*

Bond lengths

Ru(1)-N(1)	2.090	Ru(1)-N(2)	2.070	Ru(1)-P(2)	2.322
Ru(1)-C(5)	2.172	Ru(1)-C(1)	2.188	Ru(1)-C(2)	2.230
Ru(1)-C(3)	2.217	Ru(1)-C(4)	2.203	P(2)-C(24)	1.805
P(2)-C(30)	1.818	P(2)-C(36)	1.833	N(1)-C(9)	1.391
N(1)-C(6)	1.375	N(2)-C(23)	1.343	N(2)-C(19)	1.343

Bond angles

N(2)-Ru(1)-N(1)	76.11	N(2)-Ru-P(2)	95.01
N(1)-Ru(1)-P(2)	94.00		

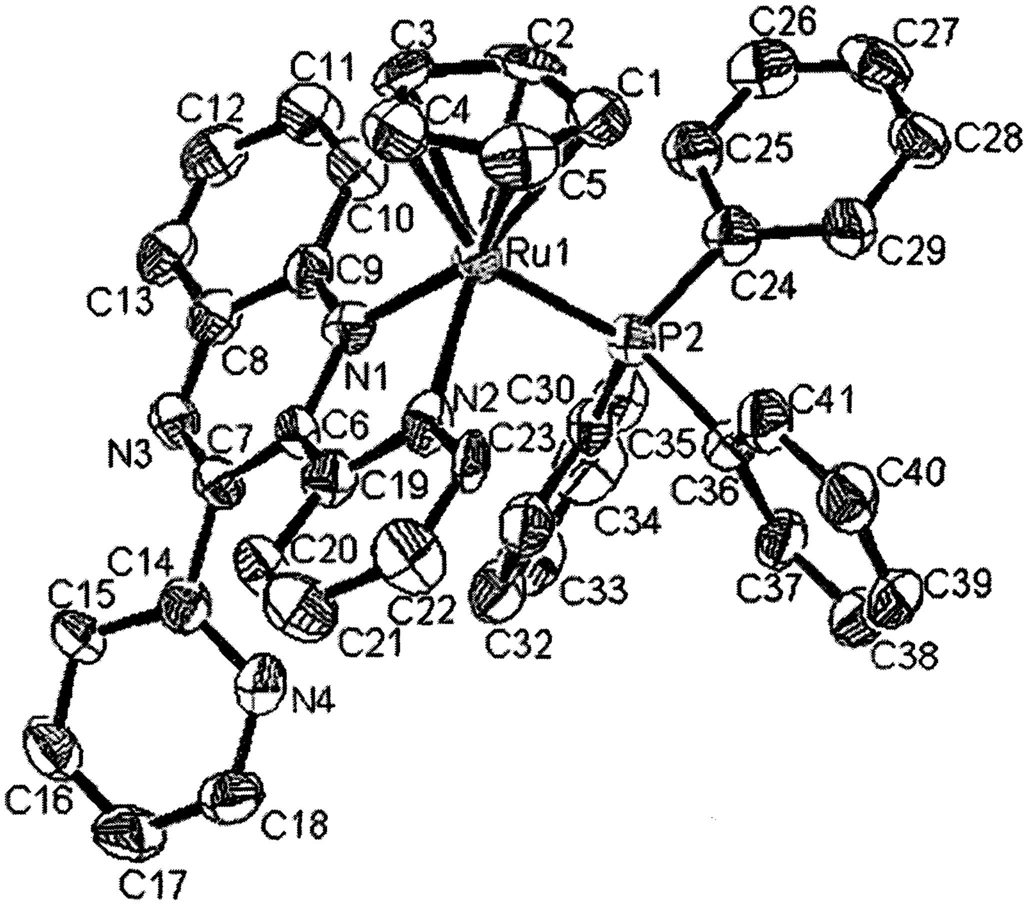


Figure 4b.1: *Molecular structure of [CpRu(PPh_3)(bpq)]PF_6.C_3H_3O (**4b.2**). The entire hydrogen atoms, hydrogens, PF_6 and part of acetone molecules are removed for clarity.*

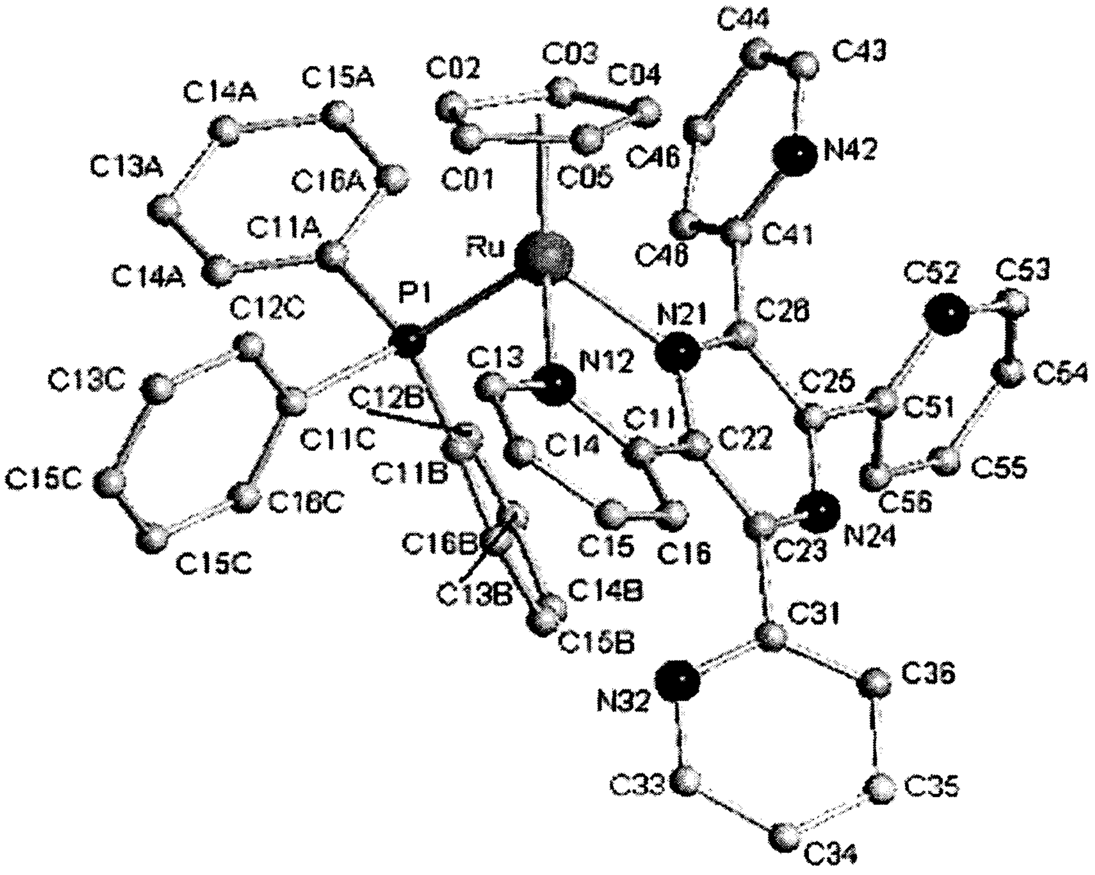


Figure 4b.2: *Molecular structure of [CpRu(PPh$_3$)(tppz)]PF$_6$.3CHCl$_3$ (**4b.4**) with atom numbering scheme. The entire hydrogen atoms, PF$_6$ and chloroform molecules are removed for clarity.*

Table 4b.2 *Selected bond lengths (Å) and bond angles (°) for [CpRu(PPh$_3$)(tppz)]PF$_6$.3CHCl$_3$ (**4b.4**) (estimated standard deviations are shown in parentheses)*

Bond lengths

Ru(1)-N(12)	2.093(12)	Ru(1)-N(21)	2.113(12)	Ru(1)-P(1)	2.336(5)
Ru(1)-C(01)	2.207(11)	Ru(1)-C(02)	2.193(11)	Ru(1)-C(03)	2.197(10)
Ru(1)-C(04)	2.214(11)	Ru(1)-C(05)	2.220(11)	P(1)-C(11A)	1.849(10)
P(1)-C(11B)	1.837(9)	P(1)-C(11C)	1.834(9)		

Bond angles

N(12)-Ru-N(21)	75.9(5)	N(12)-Ru-P(1)	93.7(3)
N(21)-Ru-P(1)	92.4(3)		

Table 4b.3: ***Crystal data and structure refinement for 4b.4.$CHCl_3$ and 4b.2.C_3H_2O***

Empirical formula	C50 H39 Cl9 F6 N6 P2 Ru	C44 H34 F6 N4 P2 O Ru
	4b.4	**4b.2**
CCDC	**222043**	**222042**
Formula weight	1319.93	911.79
Temperature (K)	293 (2)	293 (2)
Wavelength	0.71073 Å	1.5418 Å
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	P21/n
Unit cell dimensions		
a (Å)	15.2504(12)	14.2780(10)
b(Å)	19.1960(15)	9.9760(10)
c(Å)	37.199(3) Å	28.9110(10)
β (°)		103.48 Å
Volume ($Å^3$)	10889.8(15)	4004.6(5)
Z	8	4
Density (calc)(Mg/m^3)	1.610	1.512
Crystal size (mm^3)	0.6 x 0.5 x 0.3	0.6 x 0.6 x 0.2
θ range for data collection(°)	1.73 to 15.07.	0 to 70
Index ranges	$-11 \leq h \leq 11, -14 \leq k \leq 13$	$0 \leq h \leq 17, 0 \leq k \leq 12$
	$-27 \leq l \leq 27$	$-35 \leq l \leq 34$
Reflections collected	22053	7411
Independent reflections	2214 [R(int) = 0.0583]	5586
Absorption coeff.(mm^{-1})	0.851	4.517
F (000)	5296	1848
Absorption correction	Empirical (SADABS)	Empirical
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2214 / 9 / 352	5586/0/524
Goodness-of-fit on F^2	1.002	1.162
Final R indices [I>2sigma(I)]	R1 = 0.0665, wR2 = 0.1598	R1 = 0.0819, wR2 = 0.2046
R indices (all data)	R1 = 0.0789, wR2 = 0.1717	R1 = 0.1134, wR2 = 0.2418

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Chapter V

Synthesis and characterization of cyano-bridged home and heterobimetallic complexes containing η^5 and η^6-cyclic hydrocarbons

5.1 Abstract

Reaction of [(ind)Ru(PPh$_3$)$_2$CN] (ind = η^5-C$_9$H$_7$) (**5.1**) and [CpRu(PPh$_3$)$_2$CN] (**5.2**) with [(η^6-*p*-cymene)Ru(bipy)Cl]Cl (**5.3**) in the presence of AgNO$_3$ / NH$_4$BF$_4$ in methanol yielded dicationic cyano bridge complex [(ind)(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-*p*-cymene)](BF$_4$)$_2$ (**5.4**) and [Cp(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-*p*-cymene)](BF$_4$)$_2$ (**5.5**) respectively, whereas reaction of [CpRu(PPh$_3$)$_2$CN] (**5.2**), [CpOs(PPh$_3$)$_2$CN] (**5.6**) and [CpRu(dppe)CN] (**5.7**) with the corresponding halo complexes as well as [(η^6-*p*-cymene)RuCl$_2$]$_2$ form cyano-bridge cationic complexes [Cp(PPh$_3$)$_2$Ru(μ-CN)Os(PPh$_3$)$_2$Cp](BF$_4$) (**5.8**), [Cp(PPh$_3$)$_2$Os(μ-CN)Ru(PPh$_3$)$_2$Cp](BF$_4$) (**5.9**), [Cp(dppe)Ru(μ-CN)Os(PPh$_3$)$_2$Cp](BF$_4$) (**5.10**) and neutral complexes [Cp(PPh$_3$)$_2$Ru(μ-CN)Ru(η^6-*p*-cymene)Cl$_2$] (**5.11**), [Cp(PPh$_3$)$_2$Os(μ-CN)Ru(η^6-*p*-cymene)Cl$_2$] (**5.12**), [Cp(dppe)Ru(μ-CN)Ru(η^6-*p*-cymene)Cl$_2$] (**5.13**) respectively. These complexes were characterized by FT IR, ^{1}H NMR, ^{31}P {^{1}H} NMR spectroscopy and the molecular structures of complexes **5.4**, **5.8** and **5.11** have been solved by X-ray crystallography.

5.2 Introduction

Cyanide has been frequently used as a bridging ligand and evoked continuous interest because of their interesting magnetic properties [1] and of recently, cyanide-bridge, dinuclear transition metal compounds have seen application in the areas of electron delocalization and charge tranfer [2]. G. J. Baird *et al.* have successfully demonstrated the nucleophilic character of the terminal cyano-ligand in M-CN to afford to cationic M-CN-M$^+$ or isonitrile cations M$^+$-CNR by reacting with metal or alkyl halides (RX) [3]. This synthetic strategy has been often utilized to provide a general route to cationic dinuclear cyano-bridged complexes.

This chapter described the synthesis of cyano-bridged cationic, dicationic and neutral complexes arising from the reaction between the appropriate [M]-CN and [M]-X fragments.

5.3 Experimental Section

All chemicals were obtained from commercial source. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model-983 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external TMS. ^{31}P{^{1}H}NMR chemical shifts are recorded relative to H_3PO_4 (85%). The starting cyanide donating 'ligands', [CpOs(PPh_3)$_2$CN] [4], [(ind)Ru(PPh_3)$_2$CN] [5], [CpRu(PPh_3)$_2$CN] [6], [CpRu(dppe)CN] [7] were prepared according to the literature procedures.

5.3.1 Preparation of the complexes

[(η^6-p-cymene)Ru(bipy)Cl]Cl (5.3)

A suspension of [(η^6-*p*-cymene)RuCl_2]$_2$ (0.1g, 0.163 mmol) and 2,2'-bipyridine (0.063 g, 0.407 mmol) was stirred at room temperature for 1h. Methanol was removed and the residue was extracted with acetone, subsequent concentration and addition of excess hexane afforded orange-red microcrystalline compound.

^{1}H NMR (Acetone- D_6, δ): 9.46 (d, 2H, 6), 8.46 (d, 2H, 6), 8.167 (t, 2H, 6.5), 7.66 (t, 2H, 6.5), 6.10 (d, 2H, 6), 5.84 (d, 2H, 6), 2.63 (sept, 1H, 6.9), 2.16 (s, 3H), 0.94 (s, 6H, 6).

[(L)(PPh_3)$_2$Ru(μ-CN)Ru(bipy)(η^6-p-cymene)](BF_4)$_2$ [L = ind (5.4), L = Cp (5.5)]

A suspension of [(L)Ru(PPh_3)$_2$CN] (1.22 mol), [(η^6-*p*-cymene)Ru(bipy)Cl]Cl (1.22 mmol), $AgNO_3$ (2.44 mmol) and NH_4BF_4 (3.66 mmol) in distilled acetone (25 ml) was refluxed for 2h. Filtration, concentration and addition of excess hexane gave yellow microcrystalline compound.

[(ind)(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-p-cymene)](BF$_4$)$_2$ ***(5.4)***

IR (KBr, cm^{-1}): 2085

^{1}H NMR (CDCl$_3$, δ): 9.84 (d, 1H, 6), 8.63 (d, 1H, 9), 8.14 (t, 1H, 6), 7.82 (t, 1H, 6), 7.45-6.59 (m, 34H), 6.28 (d, 1H, 6), 5.96 (d, 1H, 6), 5.75 (m, 2H), 4.67 (t, 1H, 2), 4.07 (d, 2H, 2), 2.21 (sept, 1H), 0.83 (d, 6H, 9).

^{31}P{^{1}H} NMR (CDCl$_3$, δ): 49.39 (s)

[Cp(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-p-cymene)](BF$_4$)$_2$ ***(5.5)***

IR (KBr, cm^{-1}): 2075

^{1}H NMR (CDCl$_3$, δ): 9.45 (d, 2H, 6), 8.44 (t, 2H, 6), 8.20 (t, 2H, 6), 8.05 (d, 2H, 6), 7.88-6.79 (m, 30H), 6.20 (d, 1H, 6), 6.09 (d, 1H, 9), 6.02 (d, 1H, 6), 5.81 (d, 1H, 9), 4.38 (s, 5H), 2.4 (sept, 1H), 2.1 (s, 3H), 1.08 (d, 6H, 9).

^{31}P{^{1}H} NMR(CDCl$_3$, δ): 50.42 (s)

Preparation of [Cp(PPh$_3$)$_2$Ru(μ-CN)Os(PPh$_3$)$_2$Cp]BF$_4$ ***(5.8)****, [Cp(PPh$_3$)$_2$Os(μ-CN)Ru(PPh$_3$)$_2$Cp]BF$_4$* ***(5.9)*** *and [Cp(dppe)Ru(μ-CN)Os(PPh$_3$)$_2$Cp]BF$_4$* ***(5.10)***

A suspension of equimolar amount of the cyanide complex and halo complex in the presence of slight excess of NH$_4$BF$_4$ in distilled methanol (20 ml) was refluxed for 3h (1h for **5.8**). The color changed to greenish yellow. Methanol was removed by rotary evaporator, the residue was extracted with dichloromethane and the insoluble white material was filtered off, concentration of the filtrate and addition of excess hexane to the concentrated solution afforded the compounds **5.8** and **5.9** as very pale green and **5.10** as pale yellow crystals.

[Cp(PPh$_3$)$_2$Ru(μ-CN)Os(PPh$_3$)$_2$Cp]BF$_4$ ***(5.8)***

IR (KBr, cm^{-1}): 2077

^{1}H NMR (CDCl$_3$, δ): 7.25-7.00 (m, 60H), 4.25 (s, 5H), 4.23 (s, 5H)

^{31}P{^{1}H} NMR (CDCl$_3$, δ): 48.56 (s), 0.50 (s)

[Cp(PPh$_3$)$_2$Os(μ-CN)Ru(PPh$_3$)$_2$Cp]BF$_4$ ***(5.9)***

IR (KBr, cm^{-1}): 2069

^{1}H NMR (CDCl$_3$, δ): 7.25-7.00 (m, 60H), 4.32 (s, 5H), 4.10 (s, 5H).

^{31}P{^{1}H} NMR (CDCl$_3$, δ): 42.94 (s), 2.00 (s)

[Cp(dppe)Ru(μ-CN)Os(PPh$_3$)$_2$Cp]BF$_4$ ***(5.10)***

IR (KBr, cm^{-1}): 2080

^{1}H NMR (CDCl$_3$, δ): 7.77-6.85 (m, 40H), 4.7 (s, 5H), 3.79 (s, 5H), 2.93-2.71 (m, 4H)

^{31}P{^{1}H}NMR(CDCl$_3$, δ): 82.63 (s), 0.50 (s)

Preparation of [Cp(L)$_2$M(μ-CN)RuCl$_2$(η^6-p-cymene)] (M = Ru, L = PPh$_3$ ***(5.11)****, M = Os, L = PPh$_3$* ***(5.12)****; M = Ru* ***(5.13)****, L$_2$ = dppe)*

The above procedure is adapted to the preparation of these complexes, except NH$_4$BF$_4$ is not included in the reaction. Work up afforded orange red crystalline compounds.

[Cp(PPh$_3$)$_2$Ru(μ-CN)RuCl$_2$(η^6-p-cymene)] ***(5.11)***

IR (KBr, cm^{-1}): 2110

^{1}H NMR (CDCl$_3$, δ): 7.35-7.17 (m, 30H), 5.49 (d, 1H, 6), 5.35 (d, 1H, 3), 5.24 (d, 1H, 6), 5.04 (d, 1H, 6), 4.40 (s, 5H), 2.90(sept, 1H), 2.18 (s, 3H), 1.23 (d, 6H, 9).

^{31}P{^{1}H} NMR (CDCl$_3$, δ): 49.32

[Cp(PPh$_3$)$_2$Os(μ-CN)RuCl$_2$(η^6-p-cymene)] ***(5.12)***

IR (KBr, cm^{-1}): 2105

^{1}H NMR (CDCl$_3$, δ): 7.35-7.17 (m, 30H), 5.42 (d, 1H, 6), 5.33 (d, 1H, 3), 5.16 (d, 1H, 6), 5.12 (d, 1H, 6), 4.52 (s, 5H), 2.82(sept, 1H), 2.00 (s, 3H), 0.98 (d, 6H, 9).

^{31}P{^{1}H} NMR (CDCl$_3$, δ): 1.32

[Cp(dppe)Ru(μ-CN)RuCl$_2$(η^6-p-cymene)] ***(5.13)***

IR (KBr, cm^{-1}): 21o3

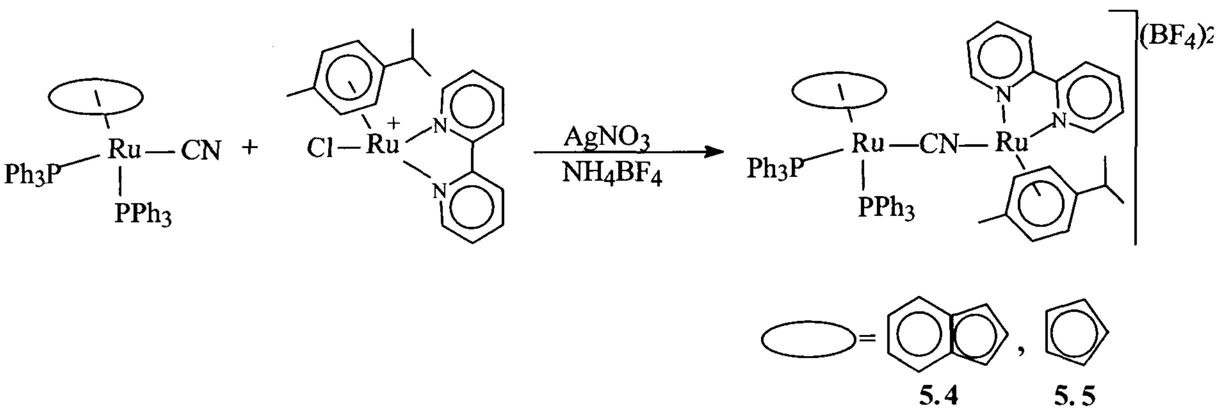
^{1}H NMR (CDCl$_3$, δ): 7.41-7.11 (m, 20H), 4.65 (s, 5H), 2.89-2.71 (m, 4H), 6.12 (d, 2H, 6), 6.07 (d, 2H, 6), 4.23 (s, 5H), 2.93-2.71 (m, 4H), 2.4 (sept, 1H), 2.21 (s, 3H), 1.02 (d, 6H, 9).

^{31}P{^{1}H}NMR (CDCl$_3$, δ): 83.4 (s)

5.4 Results and Discussion

5.4.1 *Dicationic Complexes*

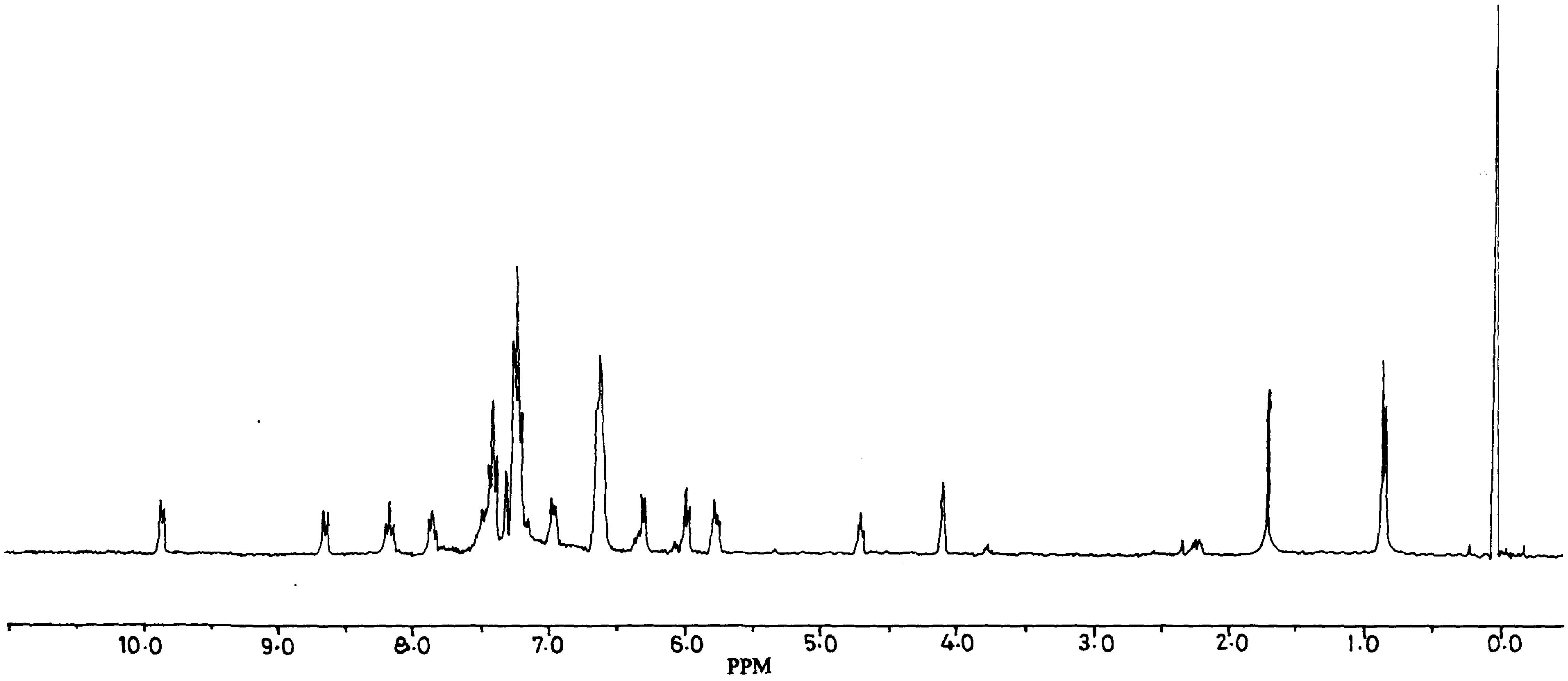
Treatment of cyano-complexes with halo complexes at refluxing condition in the presence of $AgNO_3$ (as a halide scavenger) after work up afforded the dicationic complexes, $[(ind)(PPh_3)_2Ru(\mu\text{-}CN)Ru(bipy)(\eta^6\text{-}p\text{-cymene})]^{2+}$ **(5.4)** (ind = η^5-C_9H_7) and $[Cp(PPh_3)_2Ru(\mu\text{-}CN)Ru(bipy)(\eta^6\text{-}p\text{-cymene})]^{2+}$ **(5.5)** (Cp = η^5-C_5H_5) which are isolated as tetrafluorobarate salt (Scheme 5.4.1).



Scheme 5.4.1

These two new dimetallic cations **5.4** and **5.5** exhibit medium intensity IR band assignable to $\nu_{(C\equiv N)}$ at 2085 cm^{-1} and 2075 cm^{-1} respectively and these stretching frequency of the cyanide ligand shifted towards higher energy as compared to the parent mononuclear cyano-complexes **(5.2)** [$\nu_{(C\equiv N)}$ 2065 cm^{-1}] and **(5.1)** [$\nu_{(C\equiv N)}$ 2070 cm^{-1}]. Very strong broad band assignable to $\nu_{(BF)}$ of BF_4 is also observed at 1080 cm^{-1} for both the complexes beside other triphenylphosphines characteristic absorption bands. They are also characterized by ^1H and ^{31}P $\{^1H\}$ NMR spectroscopy. In the ^{31}P NMR spectrum of these complexes exhibit only one singlet suggesting that the both the P atoms of triphenylphosphines are in similar chemical environment in both these complexes. ^1H NMR spectrum of $[(ind)(PPh_3)_2Ru(\mu\text{-}CN)Ru(bipy)(\eta^6\text{-}p\text{-cymene})]^{2+}$ **(5.4)** is shown in the next page.

It is worth mentioning that in a compounds such as $[(\eta^6\text{-arene})Ru(N,N')Cl]^+$ the arene ligand tends to be very labile on attempts to substitute the chloride ligand and often



^{1}HNMR spectrum of [(ind)(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-*p*-cymene)](BF$_4$)$_2$ (5.4) resulted in the displacement of the arene from the coordination sphere. Even though arene ruthenium(II) complexes containing tripodal nitrogen donor ligands are available, but to our knowledge, complexes **5.4** and **5.5** offer an example of complexes having [(η^6-arene)Ru] fragment, where the other available coordination sites are occupied by a chelate and a nitrogen donor ligand. Our attempts to prepare [(η^6-*p*-cymene)Ru(bipy)(CN)]$^+$ are so far unsuccessful and orange-red compound isolated from the reaction between [(η^6-*p*-cymene)Ru(bipy)Cl]$^+$ and MCN (M = Na, K) the un-characterizable because of its low solubility.

5.4.1.1 *X-ray structure of [(ind)(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-p-cymene)](BF$_4$)$_2$* ***(5.4)***

Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of hexane into a concentrated acetone solution of the compound. ORTEP representation of perspective view is shown in Figure 5.4.1a and 5.4.1b (full diagram) and the selected bond lengths and angles are shown in Table 5.4.1 and the summary of X-ray structure determination is shown in Table 5.4.4. Because of the rather poor quality of the data obtained from the complex [(ind)(PPh$_3$)$_2$Ru(μ-CN)Ru(bipy)(η^6-*p*-cymene)](BF$_4$)$_2$ (**5.4**), discussion of the metrical parameters will be just for the sake of comparisons and nevertheless the data obtained display no exceptional bonds lengths or angles. The disposition of the bridging cyano-ligand is such that the four atoms Ru(1), N(1), C(10), and Ru(2) are almost collinear with an angle of 170.3° at nitrogen and 168° at carbon. The Ru(1) – N(1) bond length of 2.055(12) Å is similar to that of [Cp(dppe)Ru(μ-CN)Ru(PPh$_3$)$_2$Cp]$^+$ (2.05 Å) [3] but slightly shorter than that of a typical ruthenium N-donor systems, for example, [(η^4-C$_8$H$_{12}$)RuCl$_2$(CO)(NCM$_2$)], 2.165 Å [8], this supports the charge distribution Ru$^+$-N≡C-Ru with the positive charge being localized on the metal bearing nitrogen. The CN bond length, 1.111(17) Å is also slightly shorter than that of in [Cp(dppe)Ru(μ-CN)Ru(PPh$_3$)$_2$Cp]$^+$, 1.14(2) Å. The Ru(2)–C(10) bond length of 1.957(13) Å is also shorter than that of Ru-C bond length, 2.03 Å of the compound [Cp(dppe)Ru(μ-CN)Ru(PPh$_3$)$_2$Cp]$^+$ [3] and is closer to those found in ruthenium-isonitrile complexes, for example [RuCl$_2$(CO)(PPh$_3$)$_2$(CNC$_6$H$_4$Me-*p*].EtOH, 1.94 Å [9] and [RuI$_2$(CO)(PPh$_3$)-{CH(NMe)C$_6$H$_4$Me-*p*}(CNBu^t)], 1.998 Å [10].

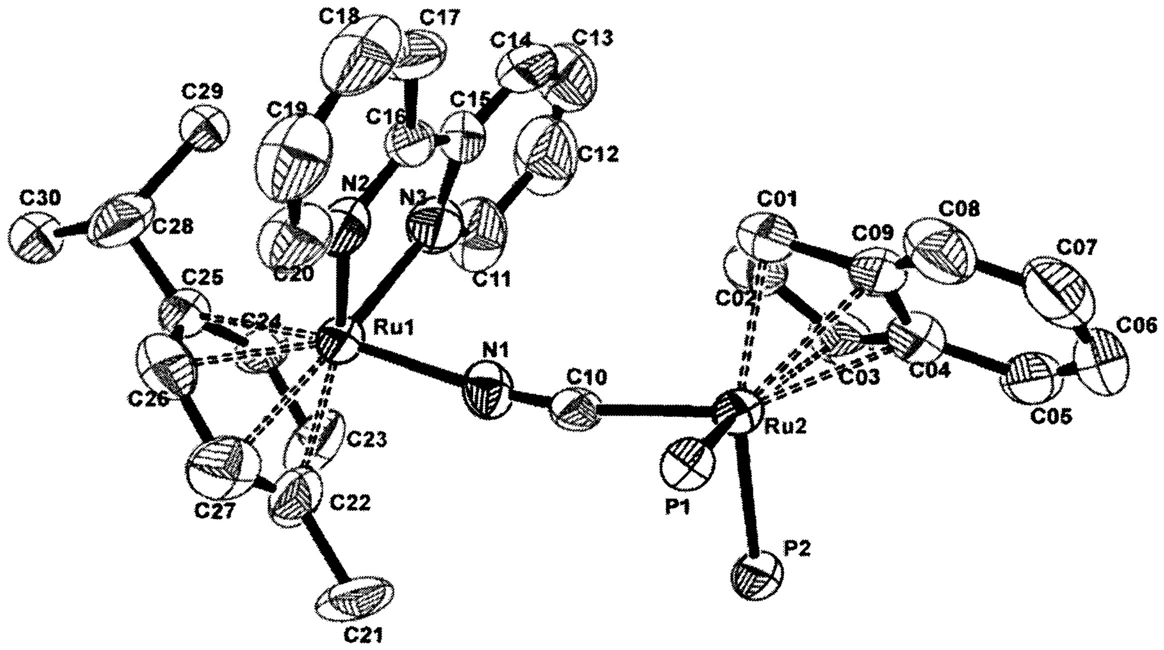


Figure 5.4.1a *Thermal ellipsoid (drawn at the 30 % probability level) plot of* $[(ind)(PPh_3)_2Ru(\mu\text{-}CN)Ru(bipy)(\eta^6\text{-}p\text{-}cymene)]^{+2}$*(5.4) with hydrogens,* BF_4 *groups and phenyl groups of* PPh_3 *are omitted for clarity.*

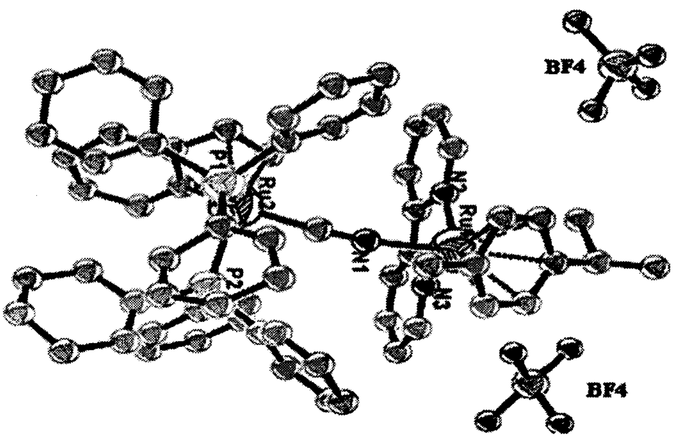


Figure 5.4.1b. ORTEP representation of **5.4** (full diagram)

Table 5.4.1 *Selected bond lengths (Å) and bond angles (°) for the complex* $[(ind)(PPh_3)_2Ru(\mu\text{-}CN)Ru(bipy)(\eta^6\text{-}p\text{-}cymene)](BF_4)_2$ *(**5.4**) (estimated standard deviations in parentheses)*

Bond lengths

Ru(1) – N(1)	2.055(12)	Ru(1) – N(2)	2.165(16)
Ru(1) – N(3)	2.071(13)	Ru(1) –C(22)	2.17(2)
Ru(1) – C(23)	2.21(2)	Ru(1) – C(24)	2.130(17)
Ru(1) – C(25)	2.177(13)	Ru(1) – C(26)	2.143(17)
Ru(1) – C(27)	2.21(2)	Ru(2) – C(10)	1.957(13)
Ru(2) – P(1)	2.341(4)	Ru(2) – P(2)	2.362(3)
Ru(2) – C(01)	2.201(15)	Ru(2) – C(02)	2.170(15)
Ru(2) – C(03)	2.218(16)	Ru(2) – C(04)	2.367(15)
Ru(2) – C(09)	2.441(15)	C(10) – N(1)	1.111(17)

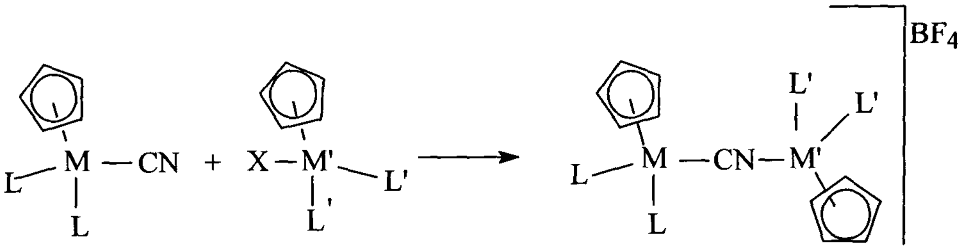
Bond angles

N(1) – Ru(1) – N(3)	83.5(5)	N(1) – Ru(1) – N(2)	83.5(5)
N(3) – Ru(1) – N(2)	79.0(6)	Ru(1) – N(1) – C(10)	170.3(12)
N(1) – C(10) – Ru(2)	168.0(11)	C(10) – Ru(2)- P(1)	85.7(4)

5.4.2 *Mono cationic complexes*

Reactions of cyanide complexes, **5.2, 5.6** and **5.7** with the corresponding halo-complexes are also investigated and the cyano-bridged complexes thus formed offer an example of the heterobimetallic cyano-bridged species (Scheme 5.4.2). The stretching frequencies of the cyano-group observed from these complexes **5.8** - **5.10** differs very little from those of the parent cyano-complexes, **5.6** (2063 cm^{-1}), **5.7** (2075 cm^{-1}) (shifted to higher wave number by only ca. 5 cm^{-1}). Here, the CN stretching frequency may not be the ideal gauge to determine whether coordination had taken place since, the absorption of the bridging cyano-group is generally much higher than these observations [11]. ^1H

NMR spectrum clearly indicates the presence of two cyclopentadienyl ligand in all the complexes but in the case of complex **5.8**, the two Cp peaks are closely spaced and appear almost like doublet and unambiguous assignment could not be made. ^{31}P spectrum of these complexes showed two singlets, one at the high field region maybe assigned to the resonance of the P atoms attached to the osmium atom. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of these complexes are shown in the next three pages.



5.8 - 5.10

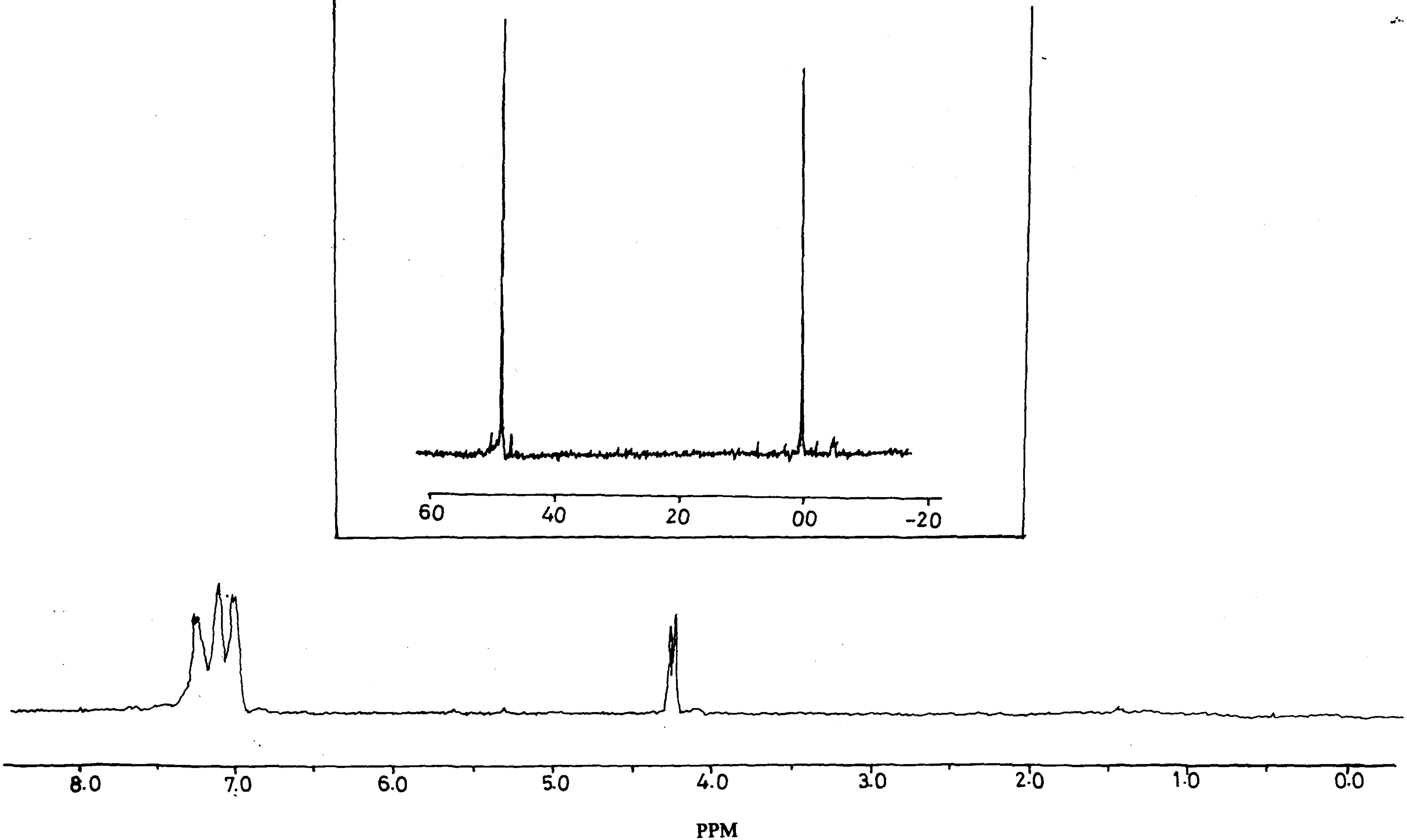
	L_2	M	M'	X
(**5.2**)	$(PPh_3)_2$	Ru	Os	Br
(**5.6**)	$(PPh_3)_2$	Os	Ru	Cl
(**5.7**)	dppe	Ru	Os	Br

	L_2	M	M'
(**5.8**)	$(PPh_3)_2$	Ru	Os
(**5.9**)	$(PPh_3)_2$	Os	Ru
(**5.10**)	dppe	Ru	Os

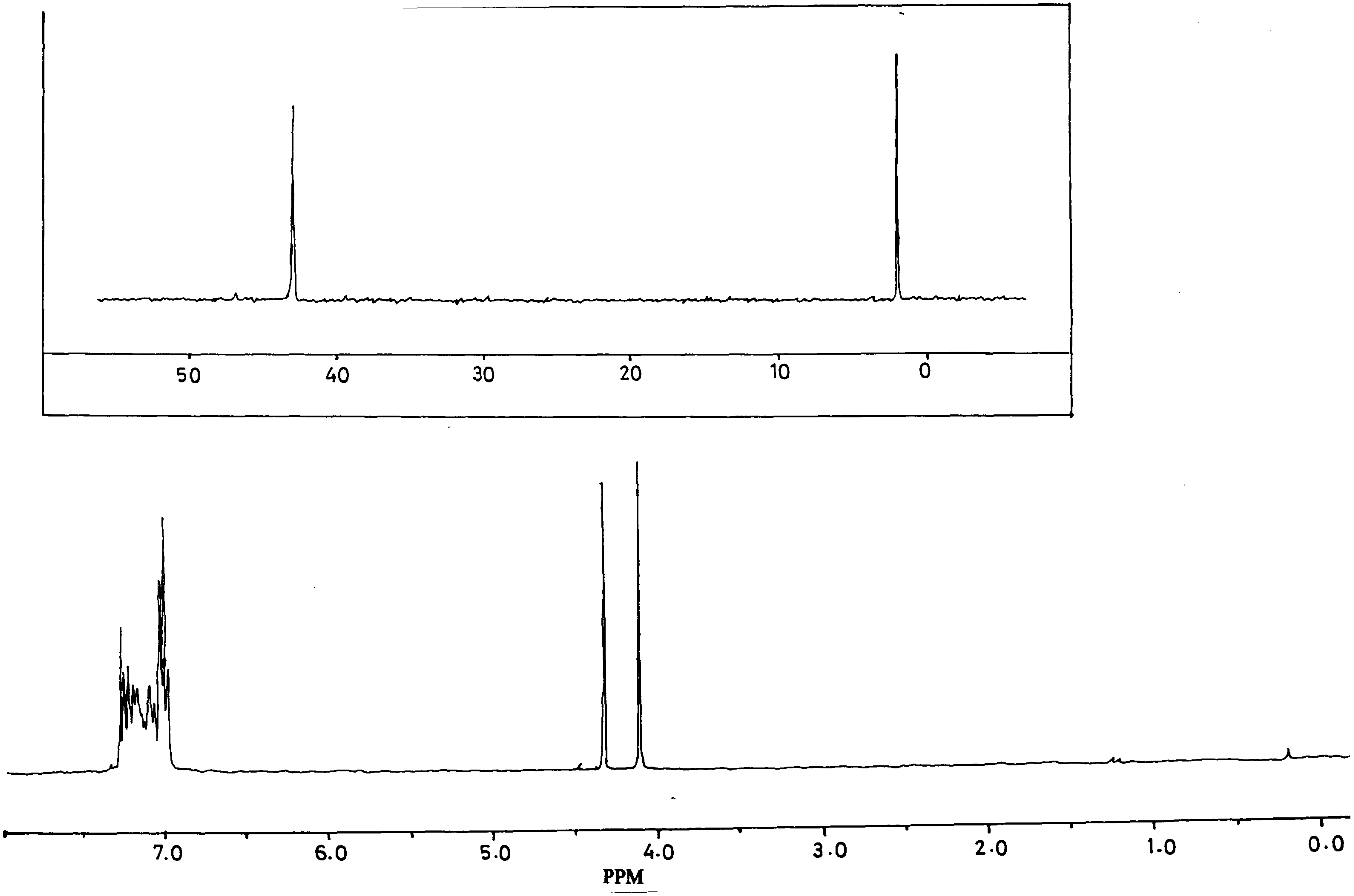
Scheme 5.4.2

5.4.2.1 *X-ray structure of* $[Cp(PPh_3)_2Ru(\mu\text{-}CN)Os(PPh_3)_2Cp]BF_4$ *(5.8)*

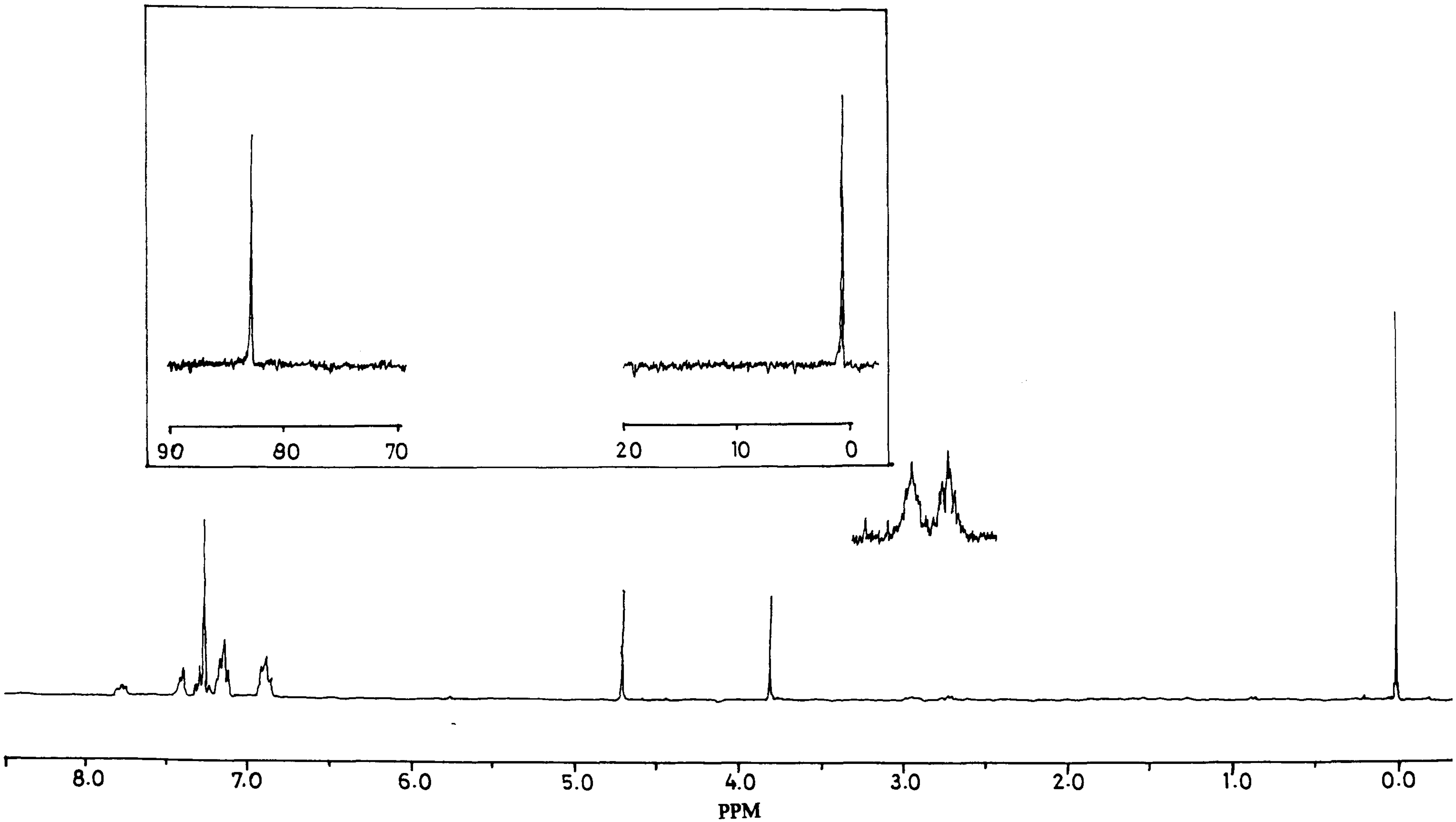
Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of hexane into a concentrated dichloromethane solution of the compound. ORTEP representation of perspective view is shown in Figure 5.4.2 and Summary of X-ray structure determination is found in Table 5.4.4. The selected bond lengths and angles are shown in Table 5.4.2. The molecule lies on a crystallographic center of symmetry (the midpoint of the C1-N1 bond is on the center at 1/4, 1/4, 1/2); this serves to disorder completely the Os and Ru atoms and the C1 and N1 atoms. Thus, it is not possible to differentiate the Ru atom from the Os atom or N1 atom from the C1 atom. In addition, the BF_4 ion is disordered over at least three areas and could not be reliably modeled. Thus, the only reliable metrical parameter as far as the cyano-bridge is concerned seems to be the bond length of C1(N1)- C1(N1)*, 1.139(6) Å which is close to that observed in



^1H and $^{31}P\{^1H\}$(inset) NMR spectra of [Cp(PPh$_3$)$_2$Ru(μ-CN)Os(PPh$_3$)$_2$Cp](BF$_4$) **(5.8)**



^{1}H and ^{31}P{^{1}H}(inset) NMR spectra of [Cp(PPh)Os(μ-CN)Ru(PPh)Cp](BF) (5.9)



^{1}H and $^{31}P\{^{1}H\}$(inset) NMR spectra of [Cp(dppe)Ru(μ-CN)Os(PPh)Cp](PF) (5.10)

$[Cp(dppe)Ru(\mu\text{-}CN)Ru(PPh_3)_2Cp]^+$, 1.14(2) Å and longer than that of the bond length observed from the complex **5.5.**

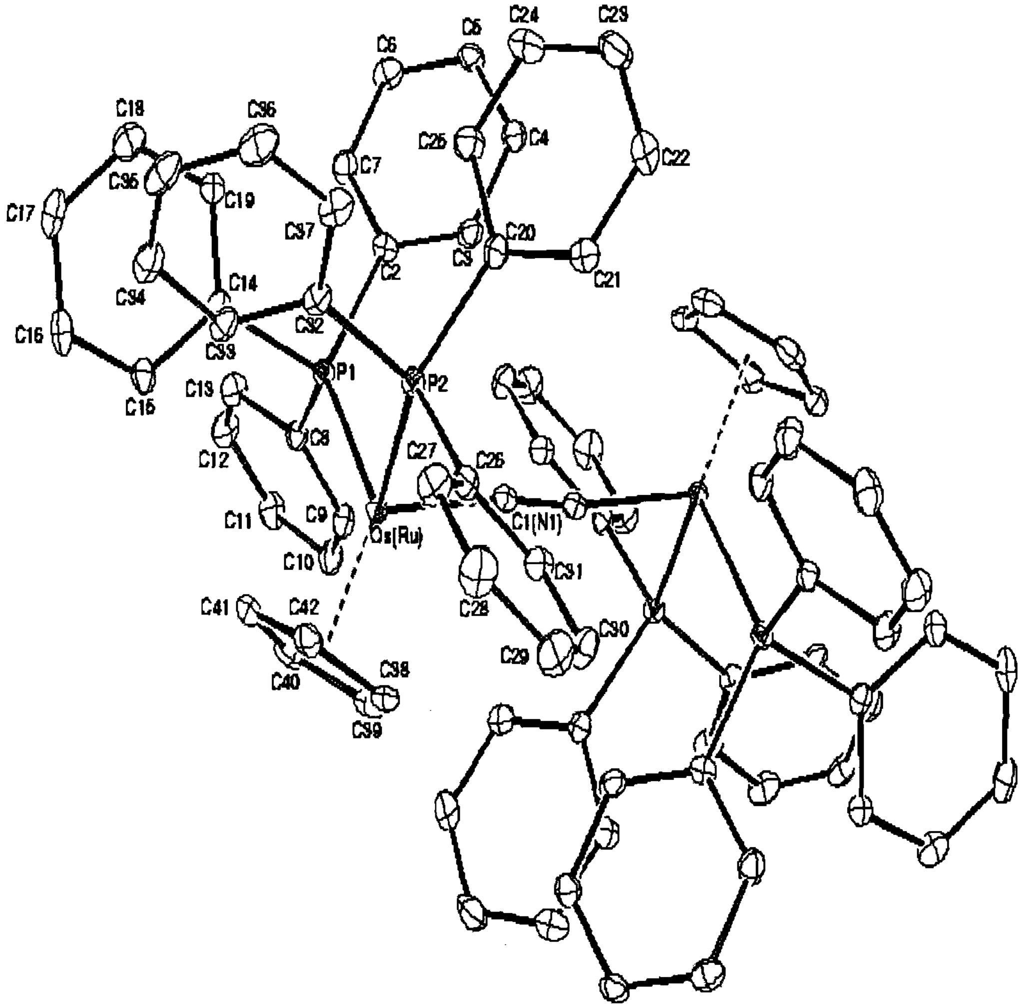


Figure 5.4.2. *ORTEP drawing of the*$[Cp(PPh_3)_2Ru(\mu\text{-}CN)Os(PPh_3)_2Cp]BF_4$ ***(5.8)*** *with 30% probability thermal ellipsoids.* BF_4^- *anion omitted for clarity.*

Table 5.4.2 *Selected Bond lengths (Å) and Bond angles (°) for the complex* $[Cp(PPh_3)_2Ru(\mu\text{-}CN)Os(PPh_3)_2Cp]BF_4$ *(5.8) (estimated standard deviations in parentheses).*

Bond lengths

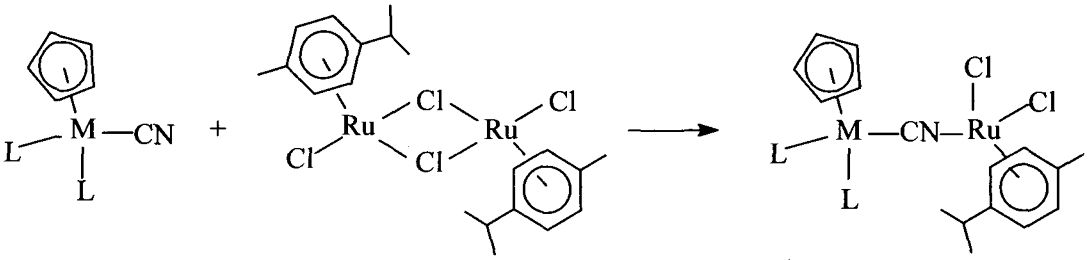
Os(Ru)-C1(N1)	2.058(3)	Os(Ru)-P2	2.3328(9)
Os(Ru)-P1	2.3327(9)	C1(N1)-C1(N1)*	1.139(6)

Bond angles

C1 - Os(Ru)- P2	89.73(9)	C1(N1)*-C1(N1)-Os(Ru)	172.1(4)
C1-Os(Ru) - P1	95.70(8)		

5.4.3 Neutral Complexes

It is very well known that the complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ is versatile starting material for synthetic manipulations. The chloride bridges may be easily broken to give diverse range of complexes. Thus, the reaction of cyano-complexes **5.2, 5.6 and 5.7** with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ afforded neutral bimetallic cyano-bridged complexes as shown in the reaction scheme 5.4.3 even though the possibilities of formation of compound(s) with higher nuclearities can not be ruled out.



5.11 - 5.13

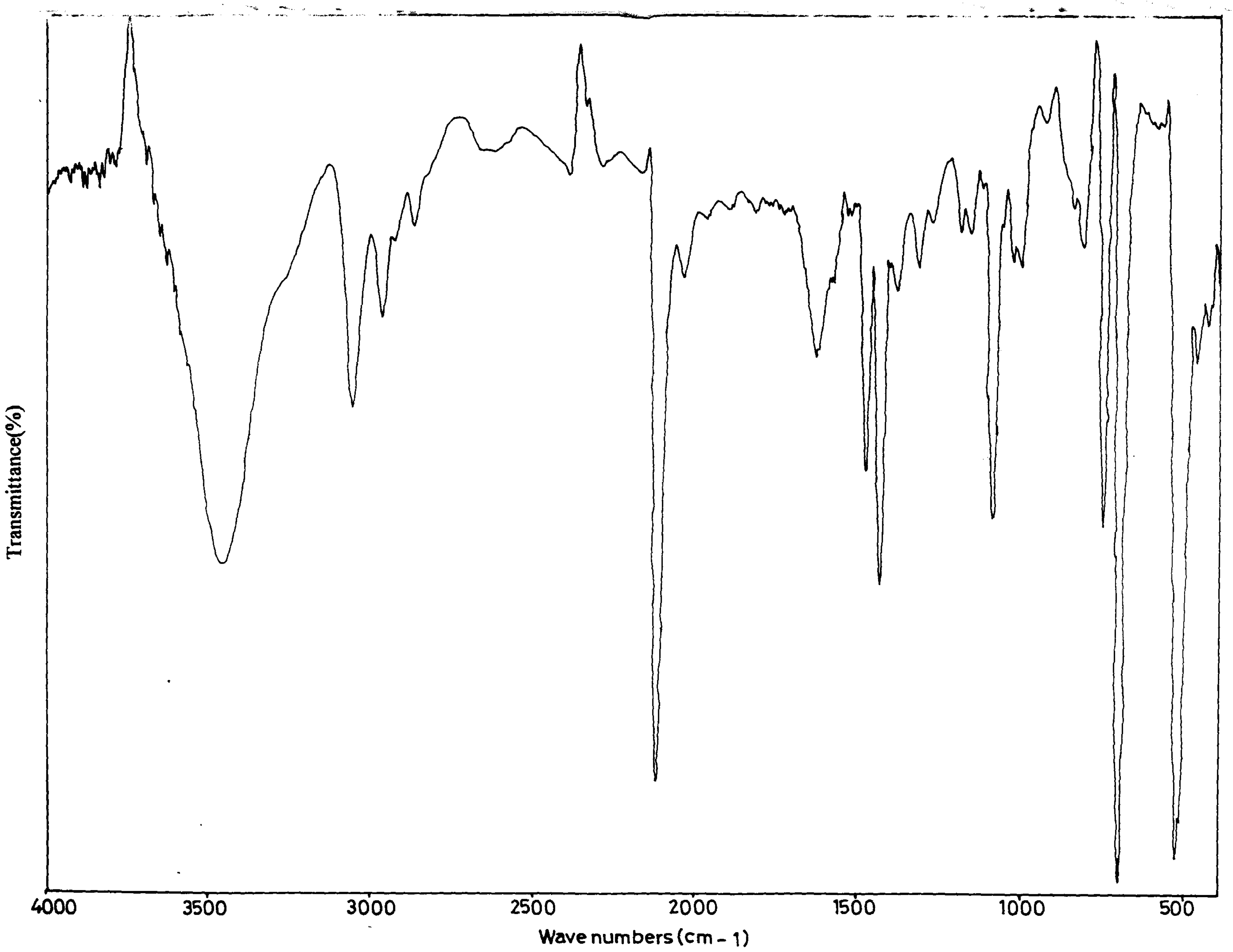
	L_2	M
(5.11)	$(PPh_3)_2$	Ru
(5.12)	$(PPh_3)_2$	Os
(5.13)	dppe	Ru

Scheme 5.4.3

Here, the infrared spectroscopy seems to be the ideal gauge to determine whether the coordination has taken place or not. The infrared spectrum of the complexes **5.11, 5.12** and **5.13** exhibited band assignable to $\nu_{(C\equiv N)}$ at 2110, 2105 and 2103 cm^{-1} respectively. The stretching frequency of the cyanide band shifted by about 30 cm^{-1}, quite a significant shift when compared with that observed from the previous cationic complexes. These complexes are also characterized by ^{1}H NMR and $^{31}P\{^{1}H\}$NMR spectroscopy as well as single crystal X-ray crystallography. The infrared spectrum of the complex $[Cp(PPh_3)_2Ru(\mu\text{-}CN)RuCl_2(\eta^6\text{-}p\text{-cymene})]BF_4$ **(5.11)** is shown in the next page.

5.4.3.1 *X-ray structure of* $[Cp(PPh_3)_2Ru(\mu\text{-}CN)RuCl_2(\eta^6\text{-}p\text{-cymene})]BF_4$ *(5.11)*

Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of diethylether into a concentrated solution of the compound in methanol. ORTEP representation of the compound is shown in Figure 5.4.3 and the selected bond lengths and angles are shown in Table 5.4.3 and Summary of X-ray structure determination is shown in Table 5.4.4. The disposition of the bridging cyano-ligand is such that the four atoms Ru(1), C(42), N(1) and Ru(2) are almost collinear with an angle of 169.7° at carbon and 168.7° at nitrogen and these data are quite similar to those of the complex **5.5**. The Ru(2)–Cl(1) and Ru(2)–Cl(2) bond distances of 2.4230(9) Å and 2.4235(9) Å respectively are essentially similar and quite comparable with those of other neutral *p*-cymene ruthenium complex, for example $[(\eta^6\text{-}p\text{-cymene})RuCl_2(NC_5H_4NH_2)]$ [12] and $[(\eta^6\text{-}p\text{-cymene})RuCl_2(NH_2C_6H_5)]$ **(3.3a)** and Ru(1)–P(1) and Ru(1)–P(2) bond lengths of 2.2976(8) Å and 2.2973(8) Å respectively are more or less similar but slightly shorter than those found in $[CpRu(PPh_3)_2Cl]$ [13].



IR spectrum of $[Cp(PPh_3)_2Ru(\mu\text{-}CN)Ru(\eta^6\text{-}p\text{-cymene})Cl_2]$ (5.11)

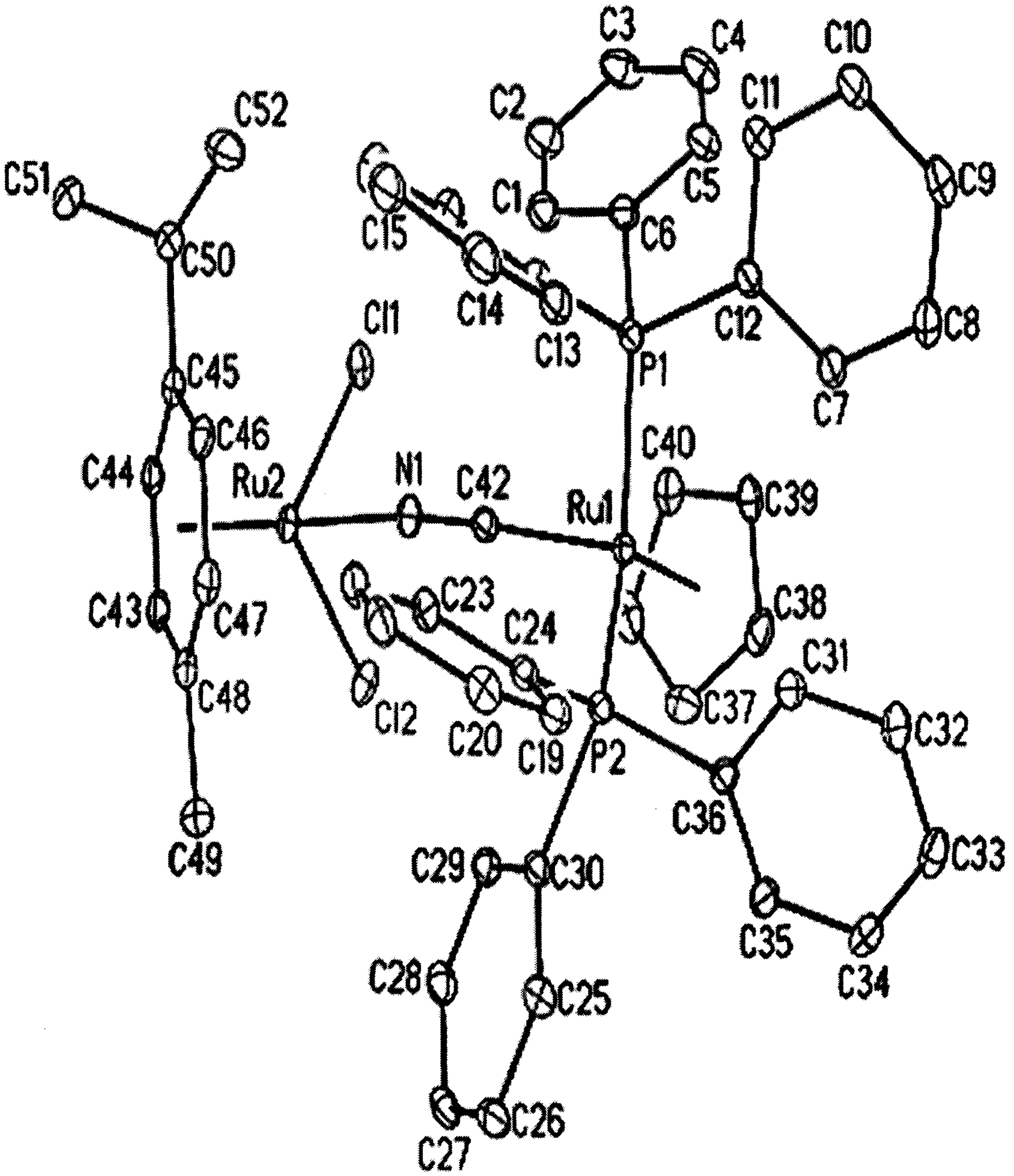


Figure 5.4.3 *Thermal ellipsoid (drawn at the 30 % probability level) plot of* $[Cp(PPh_3)_2Ru(\mu\text{-}CN)RuCl_2(\eta^6\text{-}p\text{-}cymene)]BF_4$ *(5.11) with labelling scheme, hydrogen atoms are omitted for clarity.*

Table 5.4.3 *Selected Bond lengths (Å) and Bond angles (°) for the complex [Cp(PPh$_3$)$_2$Ru(μ-CN)RuCl$_2$(η^6-p-cymene)]BF$_4$ (5.11) (estimated standard deviation in parentheses)*

Bond lengths

Ru(1) – C(42)	1.975(3)	Ru(1) – P(1)	2.2976(8)
Ru(1) – P(2)	2.2973(8)	C(42) – N(1)	1.153(4)
Ru(2) – N(1)	2.048(3)	Ru(2) – Cl(1)	2.4230(9)
Ru(2) – Cl(2)	2.4235(9)		

Bond angles

Ru(1) – C(42) – N(1)	169.7(3)	P(1) – Ru(1) – P(2)	102.55(3)
P(1) – Ru(1) – C(42)	88.77(9)	P(2) – Ru(1) –C(42)	91.52(9)
Ru(2) – N(1) – C(42)	168.7(3)	N(1) – Ru(2) – Cl(1)	84.68(8)
N(1) – Ru(2) – Cl(2)	85.02(8)	Cl(1) – Ru(2) – Cl(2)	88.03(3)

Table 5.4.4: Summary of structure determination of compounds 5.4, 5.8 and 5.11.

Empirical formula	C52 H49Cl2NP2Ru2	C83BH70NP4F4OsRu	C66H59B2F8N3P2Ru2
	5.11	**5.8**	**5.4**
CCDC	**257429**	**257428**	**257427**
Formula weight	1024.50	1583.36	1331.86
Temperature	120(2) K	143(2)	293(2)
Wavelength (Å)	0.71073	0.71069	1.54178
Crystal system	monoclinic	monoclinic	monoclinic
space group	C2/c	C2/$_c$	P21/c

Unit cell dimensions			
a (Å)	25.485(5)	25.510(4)	13.9100(10)
b (Å)	20.779(4)	13.863(2)	23.0670(10)
c (Å)	20.931(4)	20.050(3)	19.7260(10)
β (°)	124.913(2)	93.430(3)	108.46
Volume (Å^3)	9089(3)	7078(2)	6003.6(6)
Z, D_{calc} (Mg/m^3)	4, 1.495	4, 1.486	4, 1.474
F (000)	4160	3184	2704
Crystal size	0.40 x 0.29 x 0.18	0.46 x 0.20 x 0.10	0.1 x 0.2 x 0.4
θ range for data collection (°)	1.38 to 28.29	5.02 to 54.96	3.04 to 70.83
Limiting indices	$-33 \leq h \leq 33$,	$-31 \leq h \leq 30$,	$0 \leq h \leq 16$,
	$-26 \leq k \leq 26$	$-12 \leq k \leq 17$	$0 \leq k \leq 28$
	$-27 \leq l \leq 26$,	$-25 \leq l \leq 18$,	$-23 \leq l \leq 22$
Reflections collected / unique	50186 / 10540	22729 / 7619	10787 / 10787
	[R(int) = 0.0238]	[R(int) = 0.0315]	[R(int) =0. 0000]
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	10540 / 0 / 532	7619 / 0 / 406	10787 / 9/ 732
Goodness-of-fit on F^2	1.073	1.089	0.757
Final R indices [$I>2\sigma(I)$]	R1 = 0.0363,	R1 = 0.0384	R1 = 0.0935
	wR2 = 0.1145	wR2 = 0. 0948	wR2 = 0.2553
R indices (all data)	R1 = 0.0399,	R1 = 0.0505	R1 = 0.1038
	wR2 = 0.1188	wR2 = 0.0987	wR2 = 0.2693
Largest diff. peak and hole	3.670 and -0.453	2.183 and – 0.591	1.475 and – 2.809

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Chapter VI

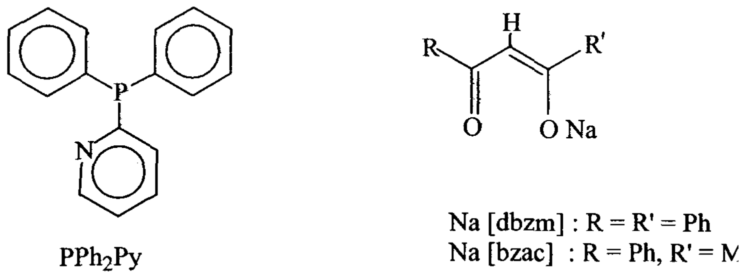
Reactivity studies of *p*-cymene dimer towards EPh_3[1], PPh_2Py[2], azide and β-diketonate ligands.

6.1 Abstract

The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with EPh_3 (E = P, As, Sb), PPh_2Py, NaN_3 and β-diketonate ligands (dbzm, bzac) invariably leads to the cleavage of the chloride bridges of the starting dimer and the subsequent reactivity of the products so formed are described in this chapter.

6.2 Introduction

The possibility of cleaving the chloride bridges in $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ by diverse range of ligands offers a vast range of complexes. This concluding chapter reports such a reactions where the chloro-bridges are broken by P-, N- and O-donor ligands. Some of the ligands are shown in Chart 6.1.



PPh_2Py

Na [dbzm] : R = R' = Ph
Na [bzac] : R = Ph, R' = M

Chart 6.1

Synthesis of arene ruthenium(II) complexes containing phosphine ligands have received considerable attention owing to their catalytic properties [1]. Recently, the neutral complexes of the type $[(\eta^6\text{-}p\text{-cymene})RuCl_2(ER_2R')]$ (E = P, As, Sb; R, R'= H, Alkyl, arylalkyl) were synthesized and used as catalyst for ring opening metathesis polymerization (ROMP) [2].

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Pyridylphosphines in general, continue to induce much interest as excellent ligands due to their ability to stabilize unusual transition-metal co-ordination and organometallic complexes [3]. Particularly, diphenyl-2-pyridylphosphine (PPh_2Py) displays numerous ligating modes ranging from P coordination [4], P, N-chelation [5] and more commonly, P, N-bridging between two metal centers [6].

It is widely accepted that optically active organometallic complexes are powerful tools for asymmetric organic syntheses as effective catalytic or stoichiometric mediators [7]. Synthesis of such a compound would be of great importance from this standpoint. Having in mind that developing a versatile precursor for chiral complexes would be very important for synthetic manipulation, we reinvestigated the preparation of azide-bridged complex, $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ [8] and this chapter described its reaction towards some nitrogen, oxygen and phosphorus based ligands. Arene ruthenium complexes containing β-diketonato ligand are somehow rare and the only available reports are concerned with acetylacetonate (acac) [9]. Thus, this chapter also reports the new complexes prepared from the *p*-cymene dimer with sodium salt of dibenzoylmethane (dbzm) and 1-benzoylacetone (bzac).

6.3 Experimental Section

All solvents are dried and purified by standard procedure. Reactions are performed without attempt to exclude air and all the work up are done in air. Sodium azide, $AsPh_3$, PPh_3, PMe_2Ph, $P(OPh)_3$, dppm, dppe, dppp, pyrazine, 4,4'-bipy, $AgNO_3$ and AgO_2CCF_3 are obtained from commercial sources and used without further purification.

6.3.1 Preparation of EPh₃ complexes

*Preparation of $[(\eta^6\text{-}p\text{-cymene})Ru(EPh_3)_2Cl]BF_4$ [(E =P (**6.1**), As (**6.2**), Sb (**6.3**)]*

The mixture of $[(\eta^6\text{-p-cymene})RuCl_2]_2$ (100 mg, 0.163 mmol), PPh_3 (256 mg, 0.978 mmol); $AsPh_3$ (mg, 0.407 mmol); $SbPh_3$ (mg, 0.407 mmol) and NH_4BF_4 (85 mg, 0.815 mmol) was refluxed in dry methanol (25 ml) for 4h under nitrogen atmosphere. Solvent was rotary evaporated and the residue was redissolved in chloroform (15 ml) and then filtered through short silica gel column to remove white precipitate. For complex **6.1**, keeping overnight this solution resulted in the formation of red crystals. For complex

6.2 and **6.3**, the solvent was concentrated to about 2 ml and addition of excess of diethylether resulted in the precipitation of orange-red solid.

[(η^6-p-cymene)Ru(PPh$_3$)$_2$Cl]BF$_4$ ***(6.1)***

Anal. Calcd. for RuC46BH44P2F4Cl (**1**) (%): C, 62.6; H, 5.0. Found: 62.4; H, 5.0.

^{1}H-NMR (CDCl$_3$, δ): 7.43-7.22 (m, 30H, Ph), 5.67 (broad s, 2H, cymene ring), 5.07 (d, 2H, cymene ring), 2.70 (sept, 1H, HC(Me)$_2$), 1.23 (d, 6H, HC(Me)$_2$, 1.12 (s, 3H, Me).

^{31}P {^{1}H} NMR (CDCl$_3$, δ): 21.18

IR (KBr, cm^{-1}): 1082 (ν_{B-F})

[(η^6-p-cymene)Ru(AsPh$_3$)$_2$Cl]BF$_4$ ***(6.2)***

Anal. Calcd. for RuC46BH44As2F4Cl (**2**) (%): C, 59.7; H, 4.8. Found: 59.4; H, 4.5.

^{1}H-NMR (CDCl$_3$, δ): 7.78-7.33 (m, 30H, Ph), 5.77 (d, 2H, cymene ring), 5.57 (d, 2H, cymene ring), 2.75 (sept, 1H, HC(Me)$_2$), 1.92 (s, 3H, Me).1.07 {d, 6H, HC (Me)$_2$}.

IR (KBr, cm^{-1}): 1080 (ν_{B-F})

[(η^6-p-cymene)Ru(SbPh$_3$)$_2$Cl]BF$_4$ ***(6.3)***

Anal. Calcd. for RuC46BH44Sb2F4Cl (**3**) (%): C, 56.8; H, 4.6. Found: 56.5; H, 4.4.

^{1}H NMR (CDCl$_3$, δ): 7.93-7.37 (m, 30H, Ph), 5.83 (d, 2H, cymene ring), 5.66 (d, 2H, cymene ring), 2.82 (sept, 1H, HC(Me)$_2$), 1.96 (s, 3H, Me).1.02 {d, 6H, HC(Me)$_2$}.

IR (KBr, cm^{-1}): 1080 (ν_{B-F})

6.3.2 Preparation of PPh$_2$Py complexes

[(η^6-p-cymene)RuCl$_2$(PPh$_2$Py)] ***(6.4)***

Diphenyl-2-pyridylphosphine (0.043 g, 0.163 mmol) was added to a dichloromethane solution (10 ml) of the complex [{(η^6-*p*-cymene)RuCl$_2$]$_2$ (0.100g, 0.163 mmol) and the resulting solution was stirred at room temperature for 1 hour. The solvent was reduced to about 2 ml and addition of excess diethylether with vigorous stirring gave the product as a microcrystalline red solid.

Yield: 0.148 g, 79.58 %.

Anal. Calc. for C27H28NPRuCl2: C, 56.98; H, 4.92; N, 2.46. Found C, 56.14; H, 5.10; N, 2.49 %

^{1}H-NMR ($CDCl_3$, ppm): 8.85 (d, J_{HH} = 4.5 Hz), 8.03-7.96 (m), 7.56-7.11(m), 5.45(d, J_{HH} = 6.3 Hz), 5.32 (d, J_{HH} = 6.3 Hz), 2.59 (sept), 1.68 (s), 0.93 (d, J_{HH} = 6.6 Hz).

^{31}P {^{1}H} NMR ($CDCl_3$, ppm): 21.41 (s)

IR (CsI pellet, cm^{-1}): 288 ($\nu_{\text{Ru-Cl}}$).

Preparation of $[(\eta^6\text{-}p\text{-cymene})RuCl(PPh_2Py)]BF_4$ ***(6.5)***, $[RuCl_2(PPh_2Py)_2]$ ***(6.6)***

The mixture of $[\{(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.100 g, 0.163 mmol), diphenyl-2-pyridylphosphine (0.214 g, 0.815 mmol) and NH_4BF_4 (0.085 g, 0.78 mmol) were refluxed in methanol (25 ml). The color of the solution immediately changed to orange leaving some red solid material at the bottom of the flask, which completely dissolved after refluxing for 3 hours to give yellow solution. Then the solution was rotary evaporated, extracted with acetone and filtered through short silica gel column to remove any insoluble material. Recrystallization of the crude product from the mixture of acetone and hexane yielded complex **6.5** as a orange-red and complex **6.6** as yellow crystals. These were easily separated by careful selection form the color.

$[(\eta^6\text{-}p\text{-cymene})RuCl(PPh_2Py)]BF_4$ ***(6.5)***

Anal. Calc. for C27H28BClF4NPRu: C, 52.25; H, 4.57; N, 2.26. Found: C, 52.34; H, 4.78; N, 2.32 %.

^{1}H-NMR ($CDCl_3$, ppm): 9.10 (d, J_{HH} = 5.4 Hz), 8.24-8.18 (m), 8.01-7.85(m), 7.61-7.44(m), 6.12 (t, J_{HH} = 6.3 Hz), 5.90 (d, J_{HH} = 6.0 Hz), 5.58 (d, J_{HH} = 6.0 Hz), 2.57 (sept), 1.97 (s), 1.16 (d, J_{HH} = 6.9 Hz), 1.05 (d, J_{HH} = 7.2 Hz).

^{31}P {^{1}H} NMR: -11.72 (s)

IR (CsI pellet, cm^{-1}): 283 ($\nu_{\text{Ru-Cl}}$).

*[$RuCl_2(PPh_2Py)_2$] (**6.6**)*

Anal. Calc. for C34H28Cl2Ru: C, 58.46; H, 4.04; N, 4.00; Found: C, 58.50; H, 4.25; N, 4.16 %.

^{1}H-NMR ($CDCl_3$, ppm): 8.55 (d, J_{HH} = 0.3 Hz), 8.32 (t, J_{HH} = 7.5 Hz), 8.02 (d, J_{HH}= 7.8 Hz), 7.86 (t, J_{HH}= 6.0 Hz), 7.68 (t, J_{HH}= 7.5 Hz), 7.52-7.37 (m), 7.17 (t, J_{HH}= 7.2 Hz), and 6.79 (m).

^{31}P {^{1}H} NMR: 1.50 (s)

IR (CsI, cm^{-1}): 280 ($\nu_{Ru\text{-}Cl}$).

*Method 2: Synthesis of [(η^6-p-cymene)RuCl(PPh_2Py)]BF_4 (**6.5**)*

The mixture of the complex [(η^6-*p*-cymene)$RuCl_2$(PPh_2Py)] (**1**) (0.100g, 0.161 mmol) and NH_4BF_4 (0.042g, 0.40 mmol) in methanol (15 ml) were stirred at room temperature for 5 hours. The clear orange colored solution was then rotary evaporated. The residue was extracted with acetone and filtered to remove any insoluble material. The filtrate was then reduced to about 1 ml and addition of excess hexane gave orange-red solid. Yield: 0.085 g, 84 %.

6.3.3 Preparation of azido complexes

*[(η^6-p-cymene)RuCl(N_3)]$_2$ (**6.7**)*

The mixture of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (**1**) (0.1g, 0.163 mmol) and sodium azide (0.026 g, 0.407 mmol) was suspended in absolute alcohol (10 ml) and stirred at room temperature whereby orange precipitates appear after few minutes and the whole suspension was stirred for two hours to ensure that the completion of the reaction. The orange-red precipitates were collected by centrifuge and washed with diethyl ether (2 x 20 mL) and vacuum dried. Additional product may be obtained by evaporating the filtrate under reduced pressure and extracting with CH_2Cl_2 and filter. Crystals maybe obtained by slow evaporation of this solution.

Yield: 85 %

IR (KBr, cm^{-1}): 2057 (s, bridging ν_{N3})

^{1}H NMR($CDCl_3$, δ): 5.32 (d, 2H), 5.24(d, 2H), 2.95 (sept, 1H), 2.27 (s, 3H), 1.29 (d, 6H)

*Preparation of [(η^6-p-cymene)RuCl(N_3)(L)]; (L= PPh_3 **(6.8)**, $P(OPh)_3$ **(6.9)**, PMe_2Ph **(6.10)**, PPh_2Py **(6.11)**, dppm **(6.12)***

The mixture of [(η^6-p-cymene)RuCl(N_3)]$_2$ (0.1g, 0.159 mmol) and L (0.318 mmol, PPh_3 (0.084 g), $P(OPh)_3$ (0.098 g), PMe_2Ph (0.044g), PPh_2Py (0.084g), dppm (0.122 g) in acetone (15 ml) was stirred at room temperature for ~ 3h. Filter the clear solution, concentrate to about 2 ml and addition of excess diethylether or hexane precipitate the compound as orange-red to red brown solid.

*[(η^6-p-cymene)RuCl(N_3)(PPh_3)] **(6.8)***

Yield: 68 %

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 7.80 – 7.36 (m, Ph, 15H), 5.45 – 4.86 (m, cym, 4H), 2.85 (sept, cym, 1H), 1.86-1.82 (m, cym, 3H), 1.31- 1.08 (m, cym, 6H).

*[(η^6-p-cymene)RuCl(N_3)$P(OPh)_3$] **(6.9)***

Yield: 65 %

IR(KBr, cm^{-1}): 2044 (vs, ν_{N3})

^{1}H-NMR ($CDCl_3$, δ): 7.29 (m, Ph, 15H), 5.42, 5.35 (d, cym, 2H), 5.15, 5.01 (d, cym, 2H), 2.61 (sept, cym, 1H), 1.83 (s, cym, 3H), 1.19 (dd, cym, 6H).

^{31}P{H}-NMR ($CDCl_3$, δ): 108. 43 (s).

*[(η^6-p-cymene)RuCl(N_3)(PMe_2Ph)] **(6.10)***

Yield: 75 %

IR (KBr, cm^{-1}): (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 7.7-7.50 (m, Ph, 5H), 5.21(m, cym, 4H), 2.55 (sept, cym, 1H), 1.84-1.71 (m, cym + Me, 9H), 1.17- 1.10 (m, cym, 6H)

^{31}P{H}NMR ($CDCl_3$, δ): 12.054

*[(η^6-p-cymene)RuCl(N_3)(κ-P-PPh_2Py)] **(6.11)**:*

Yield: 78 %,

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 8.87 (d, 1H), 8.03-7.06(m, 13H), 5.56 (t), 5.43 (s), 5.33 (t), 5.24(d), 2.55 (sept, 1H), 1.75 (s, 3H), 1.14 (d, 1H), 1.04(t, 4H), 0.93(d, 1H).

^{31}P {^{1}H}NMR ($CDCl_3$, δ): 20.84 (s)

[(η^6-p-cymene)RuCl(N_3)(κ-P-dppm)] ***(6.12)****:*

Yield: 60 %

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 9.93-9.03(m, 20H), 5.31-5.07(m, 4H), 3.48-3.40 (m, 2H), 1.87, 1.78 (s, 3H), 1.0, 0.78 (d, 6H).

^{31} P {^{1}H}NMR ($CDCl_3$, δ): 25.9 (d, P-Ru of dppm), -28.27 (dd, pendent P of dppm).

Preparation of [{(η^6-p-cymene)RuCl(N_3)}$_2$(L)]: (L = 4,4'-bipy, pyrazine, dppe).

The mixture of [(η^6-*p*-cymene)RuCl(N_3)]$_2$ (0.1g, 0.159 mmol) and L [0.159 mmol, 4,4'-bipy (0.25 g), pyrazine (0.013 g), dppe (0.063 g)] in acetone (15 ml) was stirred at room temperature for 2h. Filter the clear solution; concentrate to about 2 ml and addition of excess diethylether or hexane precipitate the compound as orange-red solid.

[{(η^6-p-cymene)RuCl(N_3)}$_2$(μ-4,4-bipy)] ***(6.13)***

Yield: 62 %

IR (KBr, cm^{-1}): 2039 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 8.84 (dd, bpy, 2H), 7.61 (d, 2H), 5.45 (t, cym, 2H), 5.25, 5.21 (d, cym, 1H), 2.87 (sept, cym, 1H), 2.08 (d, cym, 3H), 1.32 (d, cym, 6H).

[{(η^6-p-cymene)RuCl(N_3)}$_2$(μ-pyrazine)] ***(6.14)***

Yield: 70 %

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 8.60 (s, 4H), 5.34- 5.25 (m, 8H), 2.92 (sept, 2H), 2.26(s, 6H), 1.33- 1.28 (m, 12H).

[{(η^6-p-cymene)RuCl(N_3)}$_2$(μ-dppe)] ***(6.15)***

Yield: 57 %

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR ($CDCl_3$, δ): 7.48–7.36 (m, 20H), 5.17(m, 8H), 2.45-2.31(m, 6H), 1.75(s, 6H), 1.06- 0.84(m, 12H).

^{31} P{H}NMR ($CDCl_3$, δ): 26.7(d).

Preparation of $[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(L\text{-}L)]^+$*; L-L = dppm (**6.16**), dppe (**6.17**), PPh*$_2$*Py (**6.18**), 2,2'- bipy (**6.19**).*

The mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)]_2$ (0.1g, 0.159 mmol), L-L [0.318 mmol, dppm (0.122 g), dppe (0.127 g), PPh_2Py (0.084 g), 2,2'-bipy (0.05 g)] and NH_4BF_4 (0.042 g, 0.400 mmol) was stirred in methanol (15 mL) at room temperature for 3h. Solvent was removed under reduced pressure and extracted with CH_2Cl_2 and filtered to remove white insoluble material. Concentration of the filtrate and subsequent addition of excess hexane afforded red to yellow compound.

$[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(dppm)]BF_4$ *(**6.16**)*

Yield: 50 %, red

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^1H NMR ($CDCl_3$, δ): 9.93-9.03(m, 20H), 5.29(t, 2H), 5.09 (t, 2H), 3.03-2.95 (m, 2H), 2.49 (sept, 1H), 0.89 (d, 6H).

$^{31}P\{H\}$NMR ($CDCl_3$, δ): 27.9(d).

$[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(dppe)]BF_4$ *(**6.17**):*

Yield: 55 %, red

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^1H NMR ($CDCl_3$, δ): 7.48–7.36 (m, 20H), 5.17(m, 8H), 2.45-2.31(m, 6H), 1.75(s, 6H), 1.06- 0.84(m, 12H).

$^{31}P\{H\}$NMR ($CDCl_3$, δ): 68.07(s).

$[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(\kappa\text{-}P,N\text{-}PPh_2Py)]BF_4$ *(**6.18**)*

Yield: 75 %, Yellow

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^1H NMR ($CDCl_3$, δ): 9.24 (d, 1H), 9.18 (d,1H), 8.44 – 8.30 (m, 12H), 6.21 (m, 2H), 6.09, 5.86 (d, 1H), 2.59 (sept, 1H), 2.12 (s, 3H), 1.19 (dd, 6H).

$^{31}P\{^1H\}$NMR ($CDCl_3$, δ): -10.41(s)

$[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(2,2'\text{-}bipy)]BF_4$ *(**6.19**)*

Yield: 75 %, yellow

IR (KBr, cm^{-1}): 2037 (vs, ν_{N3})

^{1}H NMR (Acetone-d_6, δ): 9.56 (d, 2H, 6), 8.52 (d, 2H, 6), 8.23 (t, 2H, 6), 6.78 (t, 2H, 6), 6.17 (d, 2H, 6), 5.66 (d, 2H, 6), 2.16 (s, 3H), 2.12 (sept, 1H), 1.03 (dd, 6H).

Preparation of $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)\}_2L_2]$ *(L =* NO_3, O_2CCF_3*)*

Method 1: To the filtrate from the preparation of **6.7**, silver or sodium salt of the corresponding L was added and the reaction mixture was stirred at room temperature for 4h. Filter to remove any insoluble materials and crystalline compound were obtained by slow evaporation of this solution.

Method 2: A suspension of $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)]_2$ (**6.7**) (0.1g, 0.159 mmol) and silver nitrate (0.067 g, 0.397 mmol) or silver trifluoroacetate (0.087 g, 0.397 mmol) was stirred at room temperature in ethanol (20 ml) for 4h. Filter and crystalline compound were obtained as method 1.

$[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)_2(ONO_2)]_2$ ***(6.20)***

Yield: 78 %, orange-red

IR (KBr, cm^{-1}): 2077 (vs, ν_{N3}), 1467(s), 1387(s),1275(s), 1003(s)

$[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)(OCOCF_3)]_2$ ***(6.21)***

Yield: 80 %, orange-red

IR (KBr, cm^{-1}): 2070 (vs, ν_{N3}), 1868 (vs), 1195(s), 1135(m).

6.3.4 Preparation of β-diketonato complexes.

$[(\eta^6\text{-}p\text{-cymene})Ru(LL)Cl]$*; LL = dbzm* ***(6.22)****, bzac* ***(6.23)***

A suspension of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.285g, 0.465 mmol) and sodium salt of dbzm / bzac (1.163 mmol) in methanol (50 ml) was stirred at room temperature for 2 hours. Solvent was stripped off and the residue was extracted with chloroform and filtered to remove any insoluble materials. Addition of excess hexane resulted in precipitation of the desired compounds as orange red microcrystalline solid.

$[(\eta^6\text{-}p\text{-cymene})Ru(dbzm)Cl]$ ***(6.22)***

Yield: 85 %,

IR (KBr): 1592m, 1543s, 1520s ($\nu_{C=O} + \nu_{C=C}$)

^{1}H NMR ($CDCl_3$, δ): 7.90 (m, 4H), 7.38 (m, 6H), 6.44 (s, 1H), 5.58 (d, 2H, 6), 5.32 (2H, 6), 3.02 (sept, 1H, 6), 2.34 (s, 3H), 1.42 (d, 6H, 6).

[(η^6-p-cymene)Ru(bzac)Cl] ***(6.23)***

Yield: 85 %

IR (KBr): 1589m, 1556s, 1518s ($\nu_{C=O}+\nu'_{C=C}$)

^{1}H NMR (CDCl$_3$, δ): 7.81 (d, 2H, 7.2), 7.42-7.31 (m, 3H), 5.78 (s, 1H), 5.35 (d, 1H, 5.5), 5.51(d, 1H, 5.5), 5.24 (t, 2H, 5), 2.94 (sept, 1H, 8), 2.28 (s, 3H), 2.11 (s, 3H), 1.36 (d, 6H, 7).

[{(η^6-p-cymene)Ru(dbzm)}$_2$(4,4-Bipy)](BF$_4$)$_2$ ***(6.24)***

A suspension of the complex **6.23** (0.08 g, 0.162 mmol), 4,4-bipyridine (0.026 g, 0.162 mmol) and NH_4BF_4 (0.032g, 0.324 mmol) was refluxed in methanol (10 ml) for 2h whereby the initial red color changed to deep red. Solvent was stripped off in rotary evaporator. The residue was extracted with chloroform; filtered and subsequent concentration and addition of excess diethylether afforded the compound as red brown solid.

Yield: 65 %

IR (KBr): 1589m, 1522 vs ($\nu_{C=O}+\nu_{C=C}$), 1057 ($\nu_{B\text{-}F}$)

^{1}H NMR (CDCl$_3$, δ): 8.61 (d, 2H, 6), 7.88 (d, 4H, 6), 7.65 (d, 2H, 6), 7.54-7.40 (m, 10H), 6.33 (s, 1H), 5.74 (d, 2H, 6), 5.62 (d, 2H, 6), 2.89 (sept, 1H, 7), 2.17 (s, 3H), 1.34 (d, 6H, 6).

[{(η^6-p-cymene)Ru(dbzm)}$_2$(pyr)](BF$_4$)$_2$ ***(6.25)*** (pyr = pyrazine)

The procedure was essentially similar to the preparation of **6.25** except pyrazine (0.013 g) was used instead of 4,4'-bipyridine.

Yield: 68 %

IR (KBr): 1587m, 1514s($\nu_{C=O}+\nu_{C=C}$), 1059 ($\nu_{B\text{-}F}$)

^{1}H NMR (CDCl$_3$, δ): 8.81 (d, 2H, 6), 7.92–7.33 (m, 10H), 6.07 (s, 1H), 5.87-5.73 (m, 4H), 2.95 (sept, 1H), 2.28 (s, 3H), 1.37 (dd, 6H, 6), 2.89 (sept, 1H, 6.9).

[{(η^6-p-cymene)Ru(dbzm)(N$_3$)] ***(6.26)***

A suspension of [(η^6-*p*-cymene)Ru(dbzm)Cl] (0.1 g, 0.202 mmol) and NaN_3 (0.013 g, 0.2 mmol) in ethanol (15 ml) was stirred at room temperature for 1h. Solvent was pumped off to dryness and extracted with diethylether, filtered and on slow evaporation; the compound was obtained as red crystals. The remaining ether insoluble red-brown residue was extracted with acetone, filtered and concentrated and on addition of excess hexane orange-red solid precipitated out. It was ambiguously characterized to be $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)]_2$ **(6.7)**

Yield: 70 %

IR (KBr): 2030 (s, ν_{N3} terminal), 1593m, 1533s ($\nu_{C=O} + \nu_{C=C}$).

^{1}H NMR ($CDCl_3$, δ): 7.87 (m, 4H), 7.42 (m, 6H), 6.41 (s, 1H), 5.58 (d, 2H, 6), 5.32 (2H, 6), 3.0 (sept, 1H, 6), 2.32 (s, 3H), 1.32 (d, 6H, 6).

$[\{(\eta^6\text{-}p\text{-cymene})Ru(dbzm)(PPh_3)]BF_4$ ***(6.27)***

A suspension of $[(\eta^6\text{-}p\text{-cymene})Ru(dbzm)Cl]$ (0.04 g, 0.081 mmol), PPh_3 (0.02 g, 0.081 mmol) and NH_4BF_4 (0.017g, 0.162 mmol) in methanol (10 ml) was refluxed for 2h. Solvent was pumped off to dryness and extracted with chloroform, filtered and addition of excess hexane to the concentrated solution afforded compound as yellow solid.

Yield: 68 %

IR (KBr): 1590m, 1526 s($\nu_{C=O} + \nu_{C=C}$), 1080m ($\nu_{B\text{-}F}$)

^{1}H NMR ($CDCl_3$, δ): 7.90-6.95 (m, 25H), 6.41 (s, 1H), 5.40 (d, 2H, 6), 5.35 (2H, 6), 2.72 (sept, 1H, 6), 2.23 (s, 3H), 1.12 (d, 6H, 6).

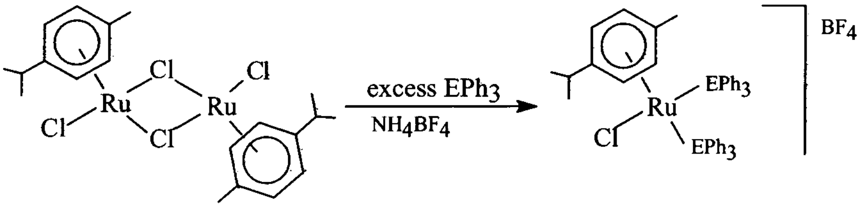
6.3.5 X-ray structure analysis

X-ray intensity data of the compounds **6.1** and **6.4** were collected on a Rigaku R-AXIS IIc area detector (Rigaku Mercury CCD for **6.5**) employing graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). The crystal of **6.5** was found to be twinned by a rotation of 180° about normal to $30\bar{1}$ (twin indexing and processing of twinned data was performed by TwinSolve [10] module of CrystalClear). The structures were solved by direct methods (SIR92). Refinement was by full-matrix least squares based on F^2 using SHELX-93. The X-ray intensity data for the compounds **6.9**, **6.15**, **6.20** and **6.21** were measured on Bruker SMART APEX CCD area detector system equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were corrected for absorption effects using the multiscan technique (SADAPS). The structures were solved and refined using Bruker SHELXTL (Version 6.1) Software Package. For the complexes **6.23** and **6.27**, Nonius MACH3 diffractometer with graphite monochromatized MoKα (λ= 0.70930 Å) radiation at a temperature of 293 K was used for the cell determination and intensity data collection. All crystallographic calculations were performed with the use of the Maxus software. The structures were solved by direct methods (SHELXS 1997). Refinement was by full-matrix least squares based on F^2 using SHELXL-93.

6.4 Results and discussion

6.4.1 EPh_3 Complexes

The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with excess of EPh_3 in the presence of NH_4BF_4 under refluxing condition in methanol resulted the formation of disubstituted products which are soluble in most of the polar solvents.



E = P (**6.1**), As (**6.2**), Sb (**6.3**)

Scheme 6.1

The reaction carried out in methanol at room temperature even with prolonged reaction time does not yield the anticipated product but only known neutral monosubstituted product of the composition $[(\eta^6\text{-}p\text{-cymene})RuCl_2(EPh_3)]$ [11]. For the preparation of complexes **6.2** and **6.3**, only two and half equivalent of the ligand *viz.* $AsPh_3/SbPh_3$ was used (see experimental section) since displacement of *p*-cymene occurs under similar reaction conditions for the preparation of complex **6.1**. Preliminary reactions carried out in the presence or absence of halide scavengers on these complexes with some monodentate ligand so far leads only to uncharacterizable products.

The most unusual observation from ^1H NMR spectrum of the complex **6.1** is that unlike **6.2** and **6.3**, the isopropyl group of the *p*-cymene ligand appear at a lower field than that for the methyl peak, whereas $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PPh_3)\}$ showed the same at 1.9 ppm [11] and $[(\eta^6\text{-}p\text{-cymene})RuH(PPh_3)_2]PF_6$ at 2.33 ppm [12]. The molecular structure does not reveal any useful information regarding this unusual chemical shift.

^{31}P{^{1}H}NMR spectrum of **6.1** exhibits a singlet at 21.18 ppm indicating the equivalence of the two phosphorus atoms. ^{1}HNMR and ^{31}P{^{1}H}NMR spectra are shown in the next page.

6.4.1.1 X-ray structure of [(η^6-p-cymene)Ru(PPh$_3$)$_2$Cl]BF$_4$ (6.1)

Complex **6.1** adopts a three-legged piano stool structure with Cl and two phosphorus atoms as the legs. The π-bonded *p*-cymene moiety occupies the three facial coordination sites.

Ru-Cl bond length is 2.3911(2) Å and is not very different from other related half-sandwich *p*-cymene ruthenium complexes. Ru-P1 and Ru-P2 bond lengths are almost same, 2.3649(6) Å and 2.4042(6) Å respectively. The bond angles P1-Ru-Cl (87.61°), P2-Ru-Cl (90.13°), P1-Ru-P2 (97.97°) confirm the piano stool structure of the complex. The ORTEP view of the compound is shown in Figure 6.1 and the selected bond length and angles are shown in Table 6.1

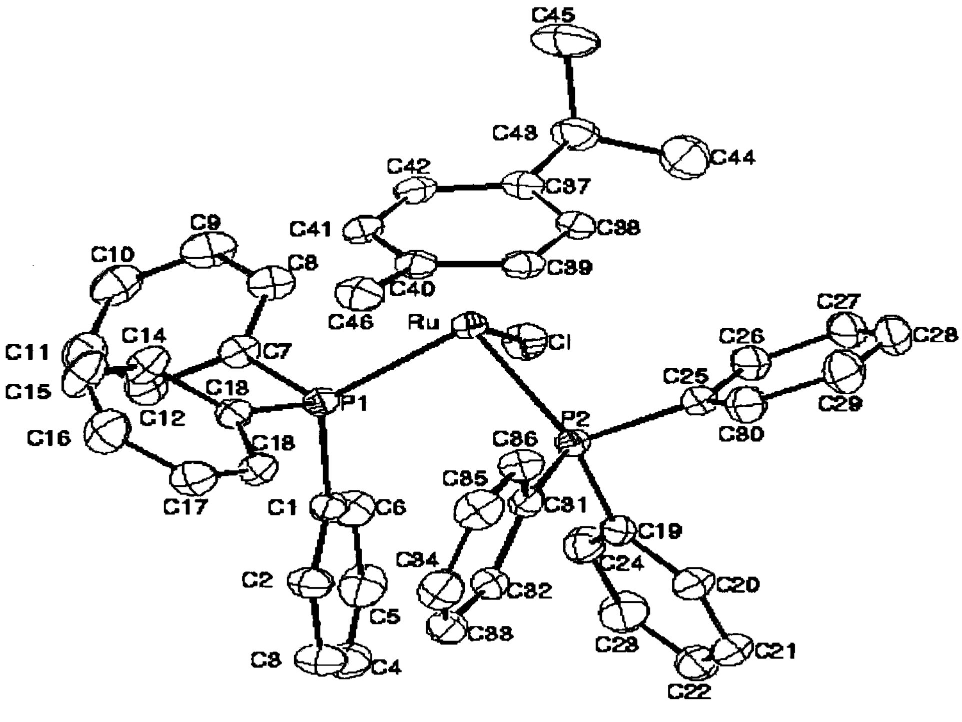
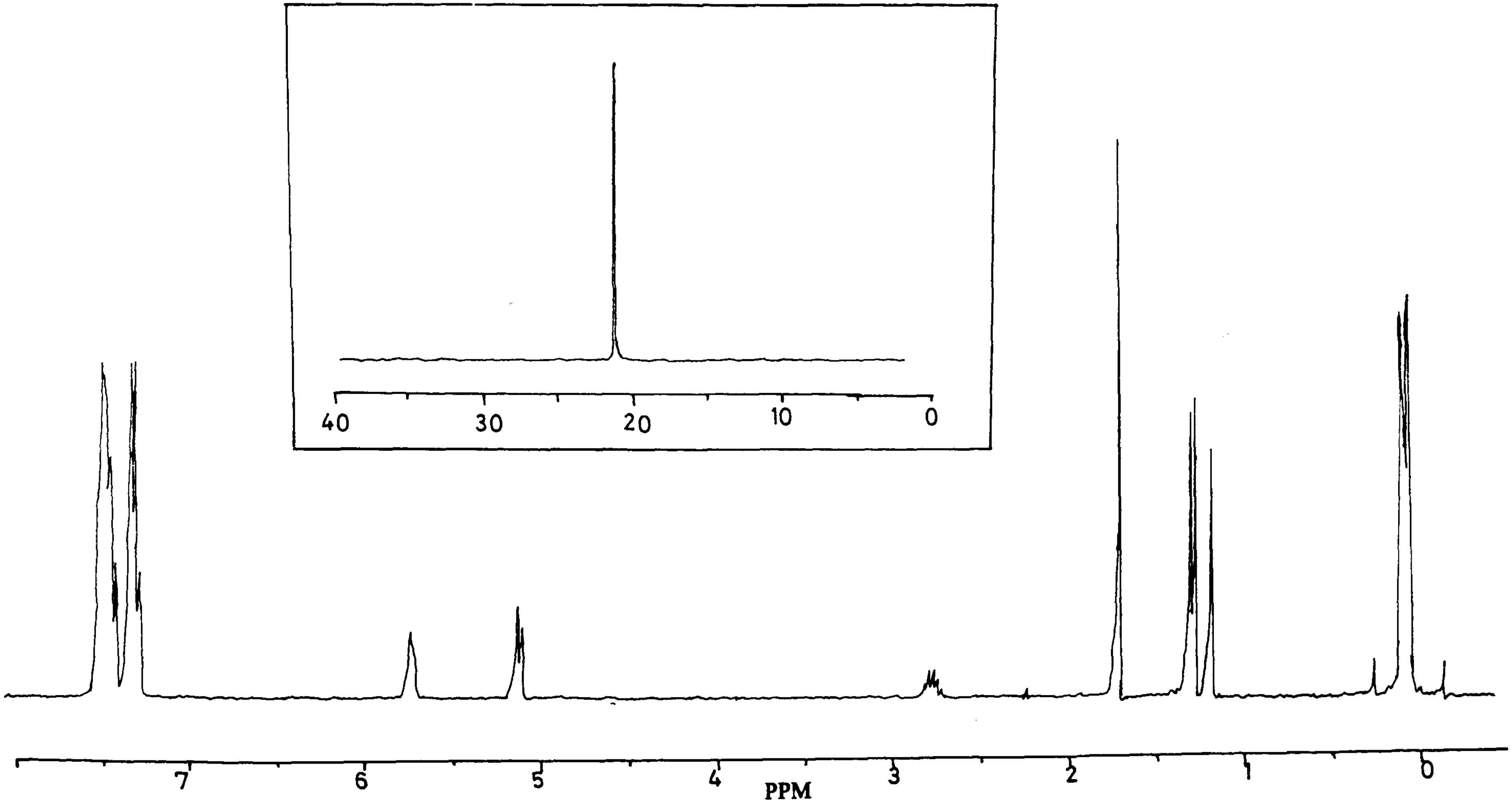


Figure 6.1 *ORTEP representation of [(η^6-p-cymene)Ru(PPh$_3$)$_2$Cl]BF$_4$ (6.1) drawn at 30% probability thermal ellipsoids displayed with numbering scheme, BF$_4$ anion omitted for clarity.*



^{1}H and $^{31}P\{^{1}H\}$(inset) NMR spectra of $[(\eta^{6}\text{-}p\text{-cymene})Ru(PPh_3)_2Cl]BF_4$ **(6.1)**

Table 6.1: *Selected Bond distances (Å) and Bond angles $(^0)$ for $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)_2Cl]BF_4$ (6.1) (estimated standard deviations are shown in parenthesis).*

Bond distances

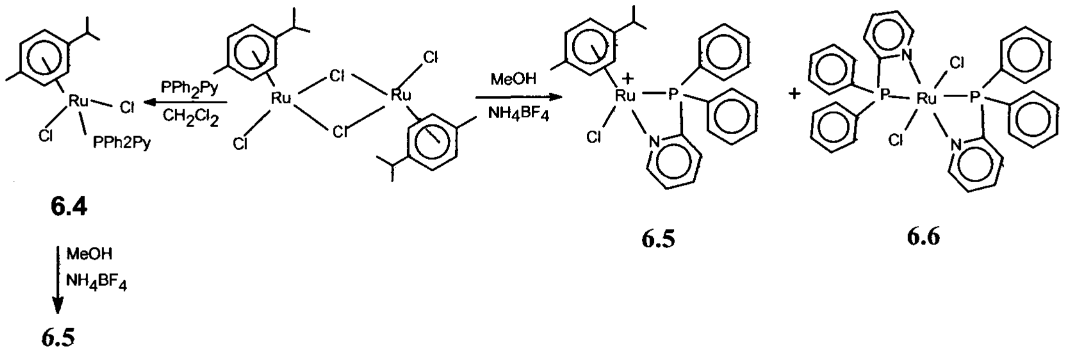
Ru-C39	2.235(2)	Ru-C41	2.241(2)	Ru-C42	2.271(2)
Ru-C38	2.279(2)	Ru-C40	2.299(2)	Ru-C37	2.344(2)
Ru-P1	2.3649(6)	Ru-Cl	2.3911(7)	Ru-P2	2.4042(6)
C37-C38	1.393(4)	C37-C42	1.414(4)	C38-C39	1.414(4)
C39-C40	1.407(4)	C40-C41	1.415(4)	C41-C42	1.400(4)

Bond angles

P1-Ru-Cl	87.61(2)	P1-Ru-P2	97.97(2)
P2-Ru-Cl	90.13(2)		

6.4.2 PPh_2Py complexes

The dinuclear complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ also undergoes bridge cleavage reaction with diphenyl-2-pyridylphosphine yielding neutral P bonded $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa\text{-P-}PPh_2Py)]$ (**6.4**), cationic P, N chelate $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa\text{-P,N-}PPh_2Py)]$ (**6.5**) and neutral P, N chelate $[RuCl_2(PPh_2Py)_2]$ complexes as shown in Scheme 6.2.



Scheme 6.2

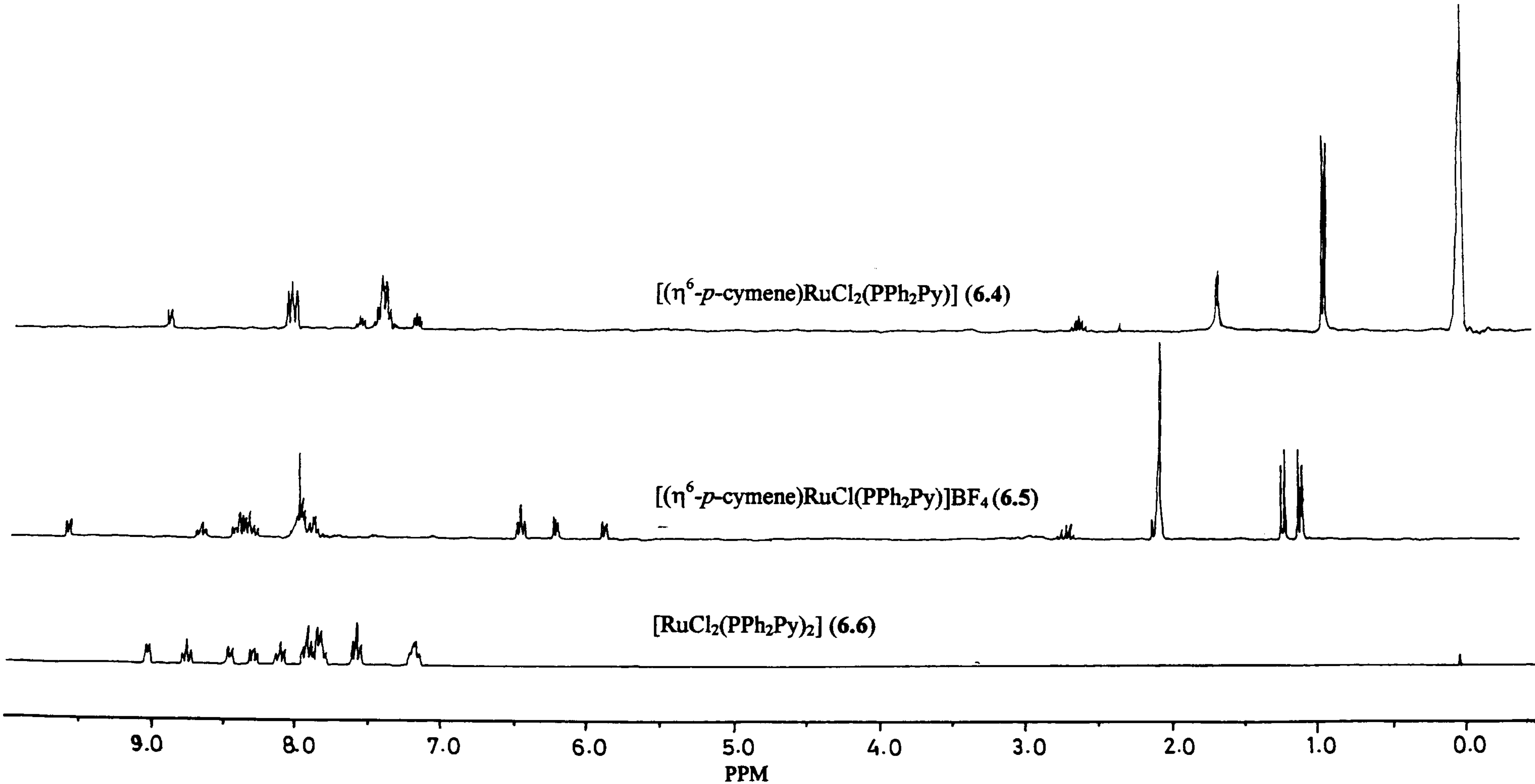
The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with one equivalent of the PPh_2Py in dichloromethane yielded stable neutral complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PPh_2Py)]$ (**6.4**) which is soluble in most of the polar solvents. The spectroscopic data clearly suggest the coordination of the ligand to the metal as evidence from the shift of the phosphorous and protons resonance as compared to the starting materials, but of course without any certain assignment through which atom is bonded to the metal. ^{1}HNMR spectrum of the complex **6.4** showed resonance for the phosphine ligand in the aromatic region in the range of 8.85-7.11 ppm. The *p*-cymene signals are well-resolved and exhibited only H-H coupling. The arene ring protons appear as two sets of doublets at 5.45 and 5.52 ppm while a septet is observed for $\underline{H}C(Me)_2$, as found in other *p*-cymene ruthenium complexes. The water peak from the deutero chloroform solvent obscured CH_3 signal (~1.6 ppm). The protons of isopropyl group ($HC(\underline{Me})_2$) signals appeared as a doublet at 0.93 ppm. The ^{31}P NMR showed one signal at 21.41 ppm due to phosphine ligand, a significant down field shifted after coordination to the metal as compared to free ligand (–3.43 ppm). The far IR spectrum showed a medium intensity band for terminal stretching vibration of $\nu_{Ru\text{-}Cl}$ at 288 cm^{-1}.

The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with two equivalent of PPh_2Py in methanol yielded complexes **6.5** and **6.6** in 1:1 ratio as evidenced from ^{1}HNMR spectrum. These complexes unlike **6.4** are not soluble in chloroform but soluble in acetone and dichloromethane. ^{1}H NMR spectrum of **6.5** showed different pattern of signals compared to the spectrum of complex **6.2** *viz.* (a) an extra triplet appears for the protons of the *p*-cymene ring. (b) Two doublets were observed at 1.16 and 1.05 ppm for the $HC(\underline{Me})_2$ protons. We have previously reported the similar pattern of signals in the case of *p*-cymene ruthenium (II) schiff base complexes [13]. This observation could be due to the loss of planarity of the *p*-cymene ligand imparted by the steric influence of the rigid P, N-chelate ligand. The yellow crystals (complex **6.6**) separated from complex **6.5** do not show any signals for the *p*-cymene moiety except well-resolved signals in the aromatic region at 8.55-6.76 ppm corresponding to the PPh_2Py ligand. This type of displacement of the *p*-cymene ring by tertiary phosphines from $[(\eta^6\text{-p-cymene})RuCl_2]_2$ is well documented [14]. The ^{31}P NMR spectrum showed one sharp singlet at 1.50 ppm. The elemental data suggest the compound to be $[RuCl_2(PPh_2Py)_2]$ (**6.6**). ^{1}HNMR spectra of these three complexes are shown in next page. The far IR spectrum taken in CsI showed a band at 280 cm^{-1}, which was assigned to terminal $\nu_{Ru\text{-}Cl}$ stretching mode. The

IR data and ^{31}P NMR spectrum suggests that the complex is trans product otherwise one could expect multiplet for phosphorous and two stretching bands for Ru-Cl.

6.4.2.1 X-ray structure of [(η^6-p-cymene)RuCl$_2$(κ-P-PPh$_2$Py)] (6.4) and [(η^6-p-cymene)RuCl(κ-P,N-PPh$_2$Py)]BF$_4$ (6.5)

An ORTEP view of the complexes **6.4** and **6.5** are shown in figure 6.2 and 6.3. The complexes exist as half sandwich complex with the distorted octahedral geometry around the metal center assuming the *p*-cymene ring occupying three facial sites. The *p*-cymene ligand is π bonded to the ruthenium atom with an average Ru-C distance of 2.214 Å and 2.212 Å respectively for **6.4** and **6.5**. The distance between ruthenium and the chloride ligands are almost same 2.411 and 2.397 Å. The average C-C bond lengths in the p-cymene ring for both the complexes **6.4** and **6.5** are 1.411 Å and 1.416 Å respectively with alternate short and long C-C bond lengths. In complex **6.4,** ruthenium atom is directly coordinated to phosphorus atom of the phosphine ligand with a distance of 2.356 Å. In complex **6.5**, diphenyl-2-pyridylphosphine ligand is bonded to the ruthenium metal in a chelating fashion forming four membered ring using both P and N atoms. The bond length of Ru-P is 2.331 Å, which is shorter, as expected than that of **6.4** due to the formation of chelate ring. The bond length of Ru-N(2) is 2.104 Å with in the range of reported compounds. The bond angles P(1)-Ru-Cl(1) and P(1)-Ru-Cl(2) are 90.90 and 84.83 respectively in complex **6.4** indicating piano stool type structure. The bond angles of P-Ru-Cl and N2-Ru-Cl in complex **6.5** are 87.25 ° and 83.93 ° respectively. The narrow angle of 67.47 ° for N-Ru-P is expected due to the rigidity of the four-member chelating ligand.



[(η^6-*p*-cymene)RuCl$_2$(PPh$_2$Py)] **(6.4)**

[(η^6-*p*-cymene)RuCl(PPh$_2$Py)]BF$_4$ **(6.5)**

[RuCl$_2$(PPh$_2$Py)$_2$] **(6.6)**

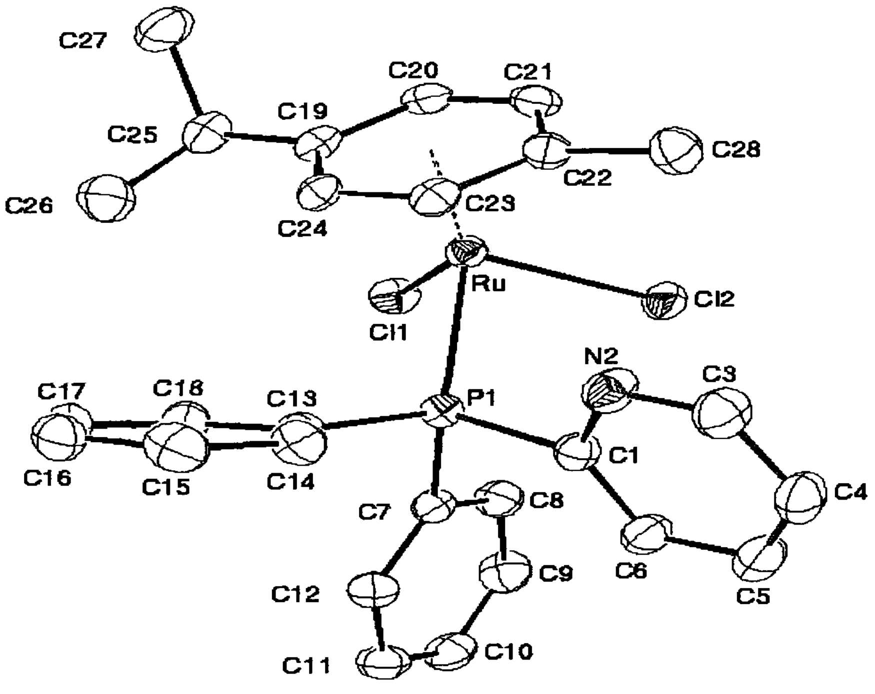


Figure 6.2 *An ORTEP perspective view of* $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa\text{-}P\text{-}PPh_2Py)]$ *(6.4) with atom numbering scheme. Hydrogen atoms are omitted for clarity.*

Table 6.2 *Selected bond lengths (Å) and angles (°) for complex* $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa\text{-}P\text{-}PPh_2Py)]$ *(6.4) with the estimated standard deviations in parentheses*

Bond lengths		***Bond angles***	
Ru-C24	2.183(3)	P1 – Ru - Cl1	90.90(3)
Ru-C23	2.160(3)	P1 – Ru – Cl2	84.83(3)
Ru-C22	2.217(3)	Cl2 – Ru - Cl1	89.41(3)
Ru-C21	2.240(3)		
Ru-C20	2.251(3)		
Ru-C19	2.238(3)		
Ru-Cl1	2.4111(8)		
Ru-Cl2	2.4107(7)		
Ru-P1	2.3565(7)		

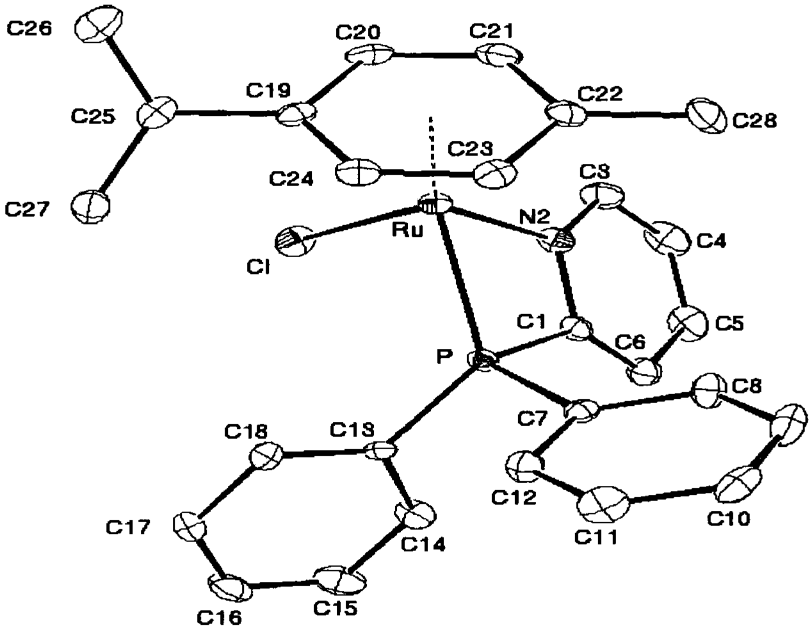


Figure 6.3 *ORTEP perspective view of $[(\eta^6\text{-}p\text{-cymene})RuCl(\kappa\text{-}P,N\text{-}PPh_2Py)]BF_4$ (6.5) with atom numbering scheme*

Table 6.3 *Selected bond lengths (Å) and bond angles (°) for complex $[(\eta^6\text{-}p\text{-cymene})RuCl(\kappa\text{-}P,N\text{-}PPh_2Py)]BF_4$ (6.5) and the estimated standard deviations are shown in the parentheses.*

Bond lengths		***Bond angles***	
Ru-C24	2.204(3)	N2-Ru-P	67.47(7)
Ru-C23	2.166(3)	N2-Ru-Cl	83.93(7)
Ru-C22	2.207(3)	P-Ru-Cl	87.25(3)
Ru-C21	2.227(3)	Ru – N2 – C1	107.2(2)
Ru-C20	2.241(3)	N2 – C1 - P	101.0(2)
Ru-C19	2.229(3)	Ru – P – C1	84.34(10)
Ru-P	2.3311(7)		
Ru-N2	2.104(2)		
Ru-Cl	2.3970(8)		
P-C1	1.826(3)		
N2-C1	1.351(4)		

Table 6.4: *Crystal data and structure refinement for 6.1, 6.4 and 6.5*

Formula	$RuC_{46}BH_{44}P_2F_4Cl$	$RuC_{27}H_{28}NPCl_2$	$RuC_{27}BH_{28}NPF_4Cl$
	6.1	**6.4**	**6.5**
CCDC	**212964**	**205909**	**205908**
Formula weight	882.08	569.44	620.80
Crystal class	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (#14)	P I (#2)	$P2_1$ (#4)
Z	4	2	2
Cell constants:			
a (Å)	12.42500(10)	10.9403(3)	9.1738(4)
b (Å)	30.1925(3)	13.3108(3)	14.0650(6)
c (Å)	11.06530(10)	10.53940(10)	10.7453(5)
α (°)		88.943(2)	
β (°)	103.1470(10)	117.193(2)	106.809(1)°
γ (°)		113.1680(10)	
V($Å^3$)	4042.26(6)	1230.39(5)	1327.22(10)
μ (cm^{-1})	5.85	9.35	7.97 cm^{-1}
crystal size (mm)	0.46x 0.38 x 0.32	0.30 x 0.25 x 0.25	0.27x0.25x 0.24
D_{calc} (g/cm^3)	1.449	1.537	1.553
F(000)	1808	580	628
Radiation:	Mo-Kα(λ=0.71069Å)		
2θ range (°)	5.2 – 54.96	5.02 – 54.98	3.96 – 58.24
hkl collected	-16≤h≤16 -39≤k≤39 -14≤l≤14	-14≤h≤14 -16≤k≤17 -13≤l≤13	-10≤h≤11 -19≤k≤19 -14≤l≤14
No. reflections measured	39833	19788	13124
No. unique reflections	9179 (R_{int}=0.0279)	5589 (R_{int}= 0.0254)	13124 (R_{int}= 0.0000)
No. obs. reflecs. (F>4σ)	8566	5351	12916
No. reflecs.	9179	5589	13124
No. parameters	500	293	329
R indices (F>4σ)	R_1= 0.0422 wR_2= 0.1066	R_1= 0.0416 wR_2= 0.1089	R_1= 0.0338 wR_2= 0.0913
R^1 indices (all data)	R_1= 0.0464 wR_2= 0.1102	R_1= 0.0436 wR_2= 0.1110	R_1= 0.0347 wR_2= 0.0927
GOF	1.104	1.074	1.090
Final Difference Peaks (e/$Å^3$)	+0.558, -0.602	+0.701, -0.707	+0.799, -0.809

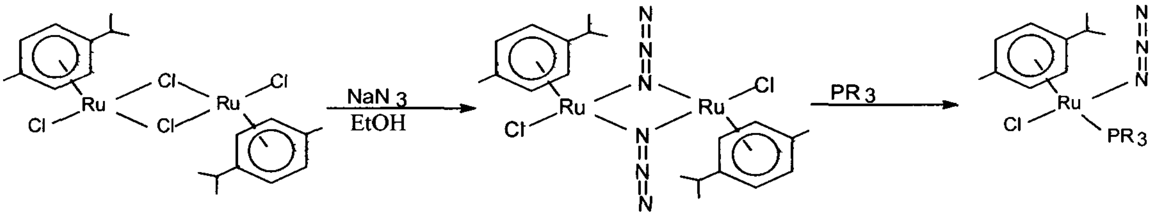
6.4.3 Azido complexes

The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with sodium azide at ambient temperature in ethanol rapidly yielded an orange colored compound which shows very strong IR absorption at 2057 cm^{-1} assignable to bridging azide ligands [15] as shown in Scheme 6.3 and this compound appears to be the same complex obtained from $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and trimethylsilyl azide by Bates *et al* [8]. Since IR and NMR data alone does not help much in determining the actual composition of this compound, we decided to carry out independently, the structural determination and it indeed proved that the compounds are identical having the formula $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ (**6.7**) as shown in Figure 6.4. One point worth mentioning is that the complete metathetical reaction of the chlorides by N_3 could not be achieved even with prolonged reaction time, large excess of the ligand, the use of halide scavengers, change of solvents or even at elevated temperature.

6.4.3.1 Mono dentate phosphines azide complexes

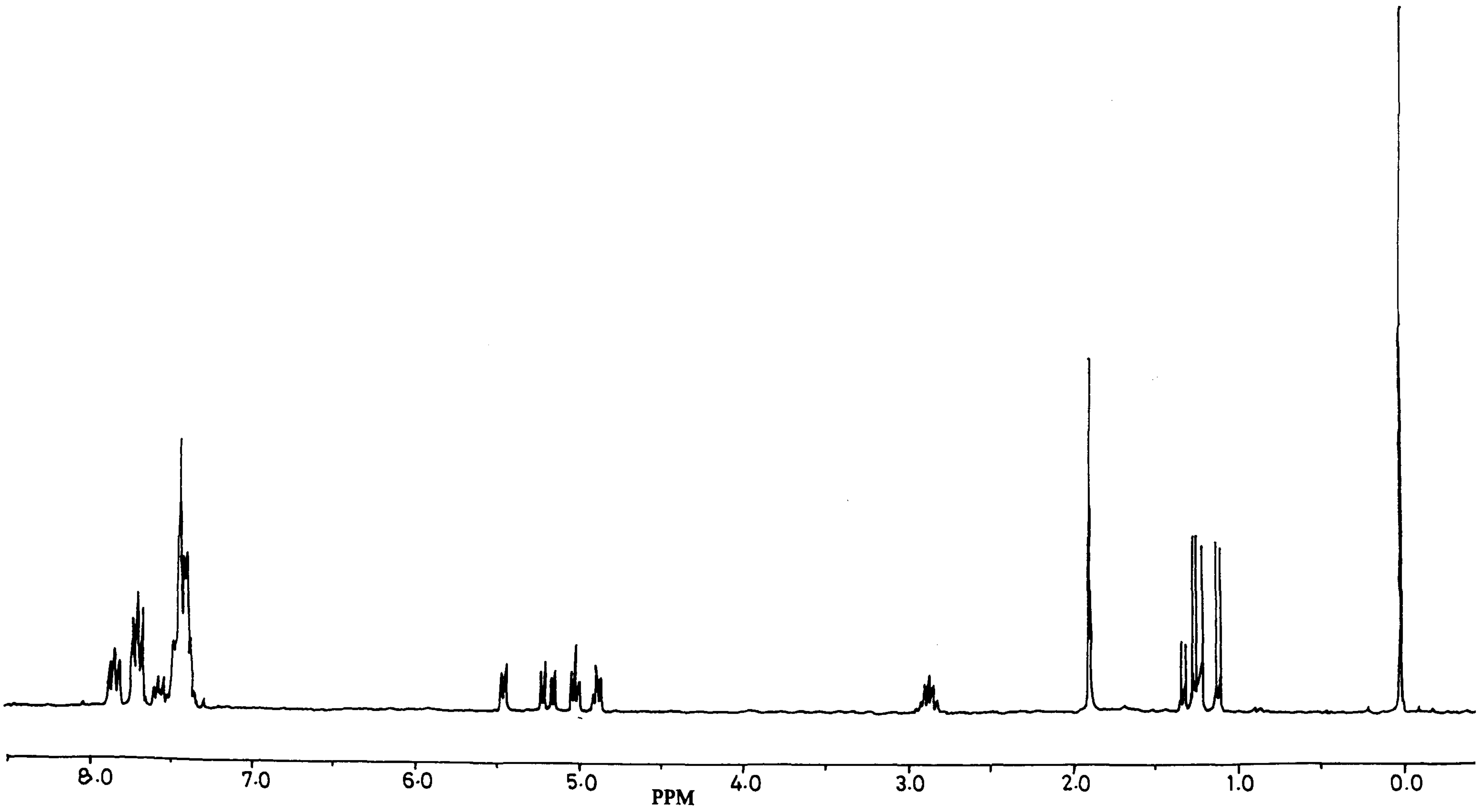
The reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)Cl]_2$ (**2**) with two equivalent of some tertiary phosphines viz, PPh_3, PMe_2Ph, $P(OPh)_3$, PPh_2Py and dppm cleanly cleave the azido-bridge to afford monomeric neutral complexes $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)(PPh_3)]$ (**6.8**), $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)(P(OPh)_3)]$ (**6.9**), $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)(PMe_2Ph)]$ (**6.10**), $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)(\kappa\text{-}P\text{-}PPh_2Py)]$ (**6.11**), $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)(dppm)]$ (**6.12**) (Scheme-1). The IR spectra clearly indicate the presence of terminally bound azide ligand in the range of 2030 – 2044 cm^{-1} which is within the range of other reported azide ligand terminally bound to the transition metal centers [15]. The ^{1}HNMR spectra showed the diasteomeric nature of these complexes due to the chiral metal center. In all the cases, the protons from the *p*-cymene group showed bunch of peaks at their usual respective positions. ^{1}HNMR spectra of **6.8** and **6.10** are shown in the next page.

The reaction of complex **6.7** with $AsPh_3$ and $SbPh_3$ under similar reaction conditions fails to cleave the azide bride as evident from IR and ^{1}HNMR spectra, our attempts by changing the reactions conditions are also unsuccessful.

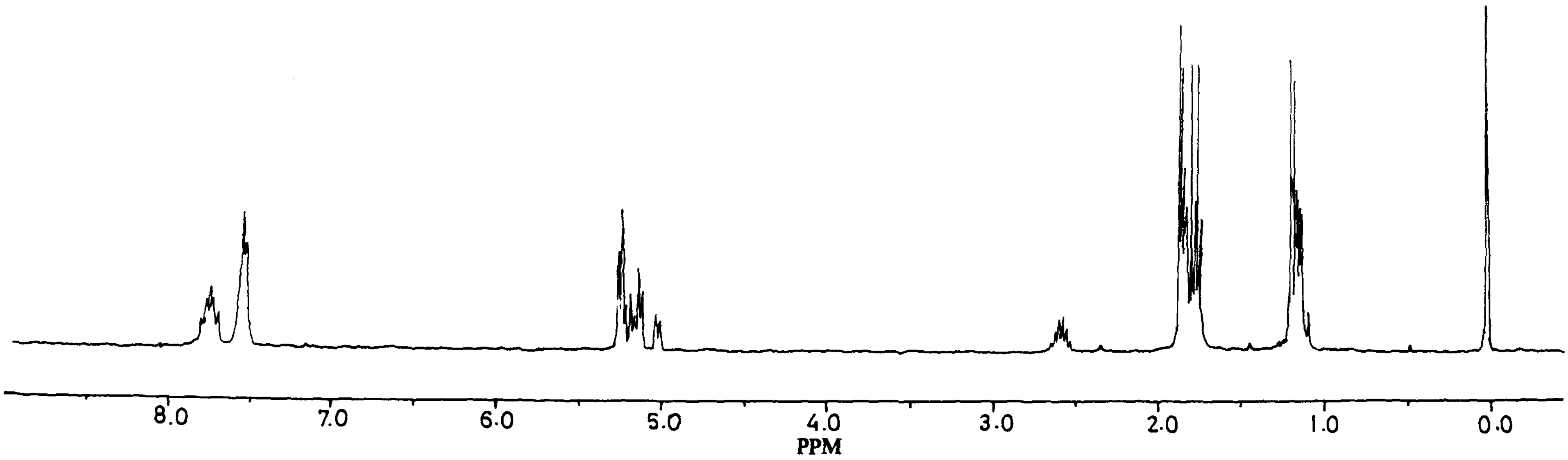


$PR_3 = PPh_3$ (**6.8**), $P(OPh)_3$, (**6.9**), PMe_2Ph (**6.10**), PPh_2Py (**6.11**), dppm (**6.12**)

Scheme 6.3



^{1}HNMR spectrum of [(η^6-*p*-cymene)RuCl(N_3)(PPh_3)] **(6.8)**



^{1}HNMR spectrum of [(η^6-*p*-cymene)RuCl(N_3)(PMe_2Ph)] **(6.10)**

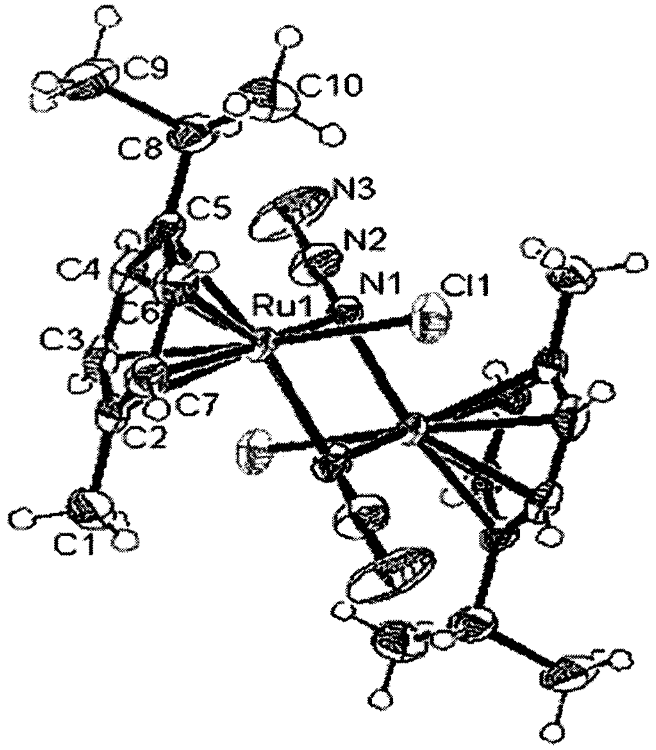


Figure 6.4: *Perspective view of the X-ray crystal structure of* $[(\eta^6\text{-cym})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ *(6.7) showing atom labelling scheme.*

Table 6.5: *Selected bond lengths (Å) and angles (°) for* $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ *(6.7) (estimated standard deviations are in parentheses)*

Bond lengths		**Bond angles**	
Ru1-N1	2.158(2)	N1-Ru1-N1#1	74.49(10)
Ru1-N1#1	2.173(2)	N1#1-Ru1-Cl1	85.42(6)
Ru1-Cl1	2.4017(7)	N1-Ru-Cl1	85.44(7)
N1-N2	1.157(3)	N2-N1-Ru1	122.07(18)
N2-N3	1.160(4)	N2-N1-Ru1#1	123.13(19)
		Ru1-N1- Ru1#1	105.51(10)
		N1-N2-N3	177.6(4)

*6.4.3.1.1 X-ray structure of [(η^6-p-cymene)RuCl(N_3)(P(OPh)$_3$)] (**6.9**)*

An ORTEP view of the complex **6.9** is shown in Figure 6.5 and selected bond length and angles are shown in Table 6.6. There is nothing very unusual from the crystallographic data except that one phenyl group of $P(OPh)_3$ has an occupancy at one place (80%) and 20 % at another place. The Ru(1)-Cl(1) bond length remain more or less the same as that of the starting dimer and as expected the Ru(1)–N(1) bond length (2.207 Å) is significantly longer. The Ru(1)–N(1)–N(2) angle of 124.5° is slightly bigger than those of **6.7** but comparable with the data obtained by Bates *et al* [8].

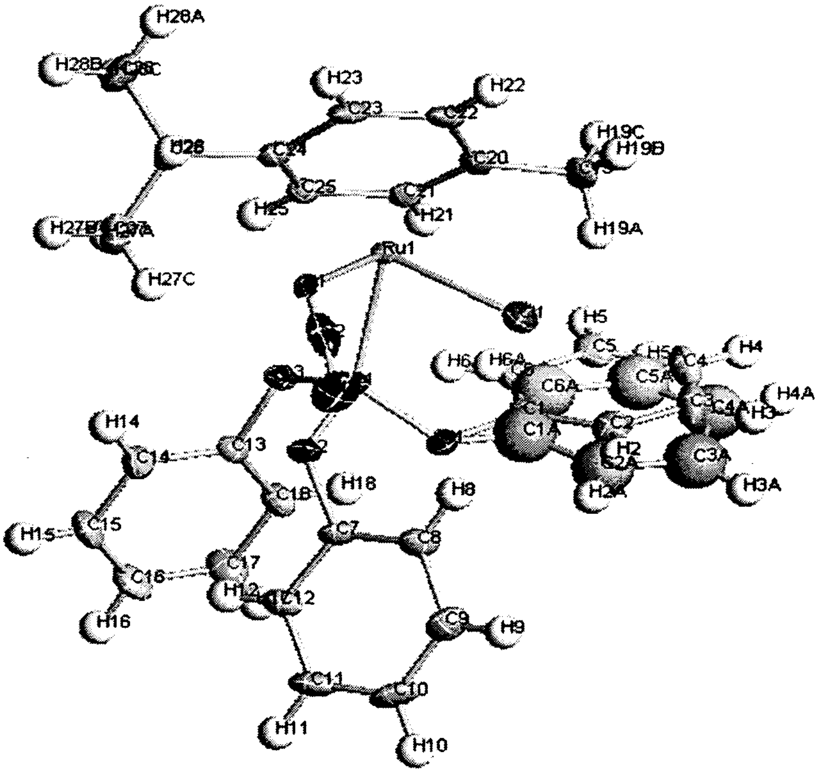


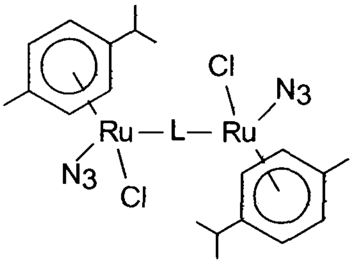
Figure 6.5: *Perspective view of the X-ray crystal structure of [(η^6-p-cymene)RuCl(N_3)P(OPh)$_3$)] (**6.9**) showing atom labelling scheme.*

Table 6.6: *Selected bond lengths (Å) and angles (°) for [(η⁶-p-cymene)RuCl(N₃)P(OPh)₃)] (6.9) (the estimated standard deviations in parentheses)*

Bond lengths		**Bond angles**	
Ru1-N1	2.207(4)	N1-Ru1-P1	90.14(9)
Ru1-Cl1	2.3977(12)	P1-Ru1-Cl1	86.01(4)
Ru1-P1	2.2523(10)	N1-Ru-Cl1	85.02(10)
N1-N2	1.004(6)	N2-N1-Ru1	124.5(3)
N2-N3	1.219(7)	N1-N2-N3	172.5(5)

6.4.3.2 Dinuclear ligand bridged azide complexes

The reaction of **6.7** and one equivalent of some potentially bridging ligands, 4,4'-bipyridine, pyrazine and dppe also cleave the azido-bridges. The IR spectra of the product isolated showed the terminally bound azide ligand at ca. 2037 cm^{-1}. These complexes are also characterized by ^{1}HNMR and some also with ^{31}P{^{1}H}NMR. Careful integration of the spectra suggest the presence of one ligand per two *p*-cymene ligands suggesting the formation of complexes with a general formula [{(η^{6}-*p*-cymene)Ru(N$_3$)Cl}$_2$(L)] as shown in Scheme-6.4. The similar reaction performed between **6.7** and one equivalent or excess of dppm unexpectedly do not yield dinuclear compound of the same type but give only chelate complex (see next section) or 'dangling' P-bound dppm complex (see previous section 6.4.3.1) and attempts to separate the product(s) isolated from the reaction between stoichiometric amount or excess dppp with **6.7** are unsuccessful.



L = 4,4'-bipyridine (**6.13**), pyrazine (**6.14**) and dppe (**6.15**)

Scheme 6.4

6.4.3.2.1 X-ray structure of $[\{(\eta^6\text{-}p\text{-cymene})RuCl(N_3)\}_2(dppe)]$ *(6.15)*

Single crystals suitable for X-ray analysis were grown from slow diffusion of hexane into concentrated solution of the compound in dichloromethane. The ORTEP diagram of half of the molecule is shown in Figure 6.6. Selected bond length and angles are shown in Table 6.7. The bond distances for Ru(1)-N(1) [2.304(9) Å] and Ru(1)-Cl(1) [2.4337(17) Å] are significantly longer than those of the complex $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)P(OPh)_3)]$ (**6.9**), while the bond angles N(1)-Ru(1)-Cl(1) [91.85(13)°] and N(1)-Ru(1)-P(1) [86.66(10)°], P(1)-Ru(1)-Cl(1) [84.54(5)°] reveal the distortion of the geometry around the metal center from the actual octahedral arrangement and these angles are quite similar to those of **6.9**.

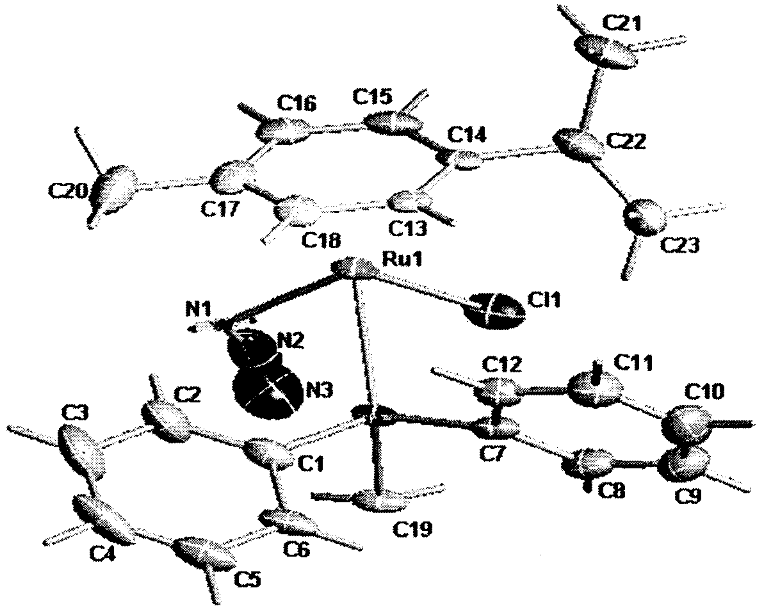


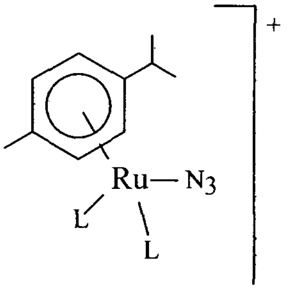
Figure 6.6: *Perspective view of half of the molecule of the X-ray crystal structure of* $[(\eta^6\text{-}p\text{-cymene})RuCl(N_3)_2(\mu\text{-dppe})]$ *(6.15) showing atom labelling scheme.*

Table 6.7: *Selected bond lengths (Å) and angles (°) for [(η⁶-p-cymene)RuCl(N₃)₂(μ-dppe)]* ***(6.15)*** *(estimated standard deviations in the parentheses)*

Bond lengths		***Bond angles***	
Ru1-N1	2.304(5)	N1-Ru1-P1	86.66(10)
Ru1-Cl1	2.4337(17)	P1-Ru1-Cl1	84.54(5)
Ru1-P1	2.3515(13)	N1-Ru-Cl1	91.85(13)
N1-N2	1.049(8)	N2-N1-Ru1	112.2(6)
N2-N3	1.253(9)	N1-N2-N3	165.6(9)

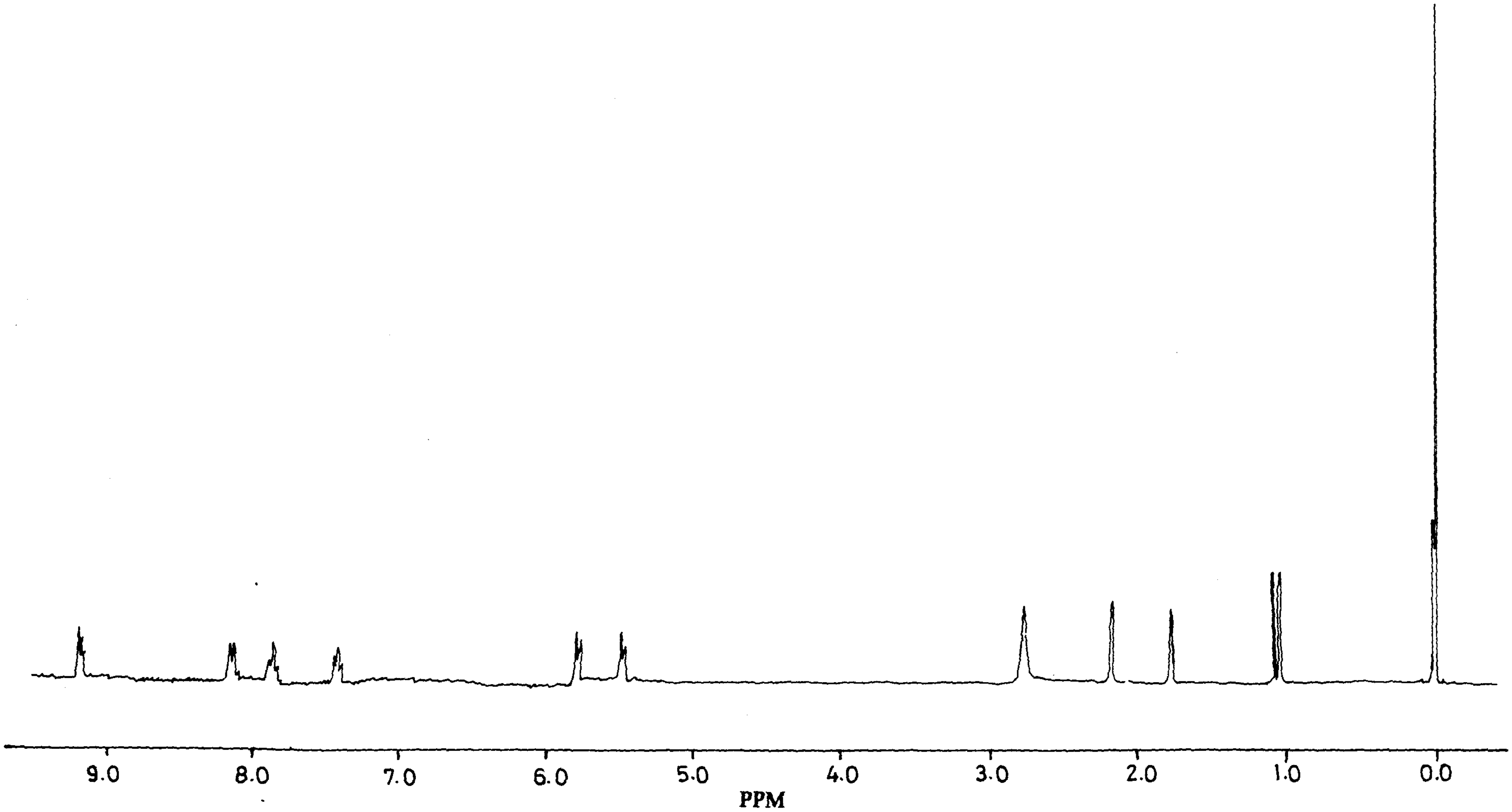
6.4.3.3 Mononuclear cationic chelate azide complexes

The reaction of **6.7** and two equivalent of some potentially chelating ligands in the presence of NH_4BF_4 or NH_4PF_6 at room temperature yielded complexes of the general formula $[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(LL)]^+$ (LL = dppm, dppe, PPh_2Py, 2,2'- bipy) as shown in Scheme 6.5. The IR spectra of these complexes showed the terminally bound azide ligand at ca. 2037 cm^{-1}. The integration of the ^1H NMR spectra of these complexes showed the presence of the ligand and *p*-cymene in 1:1 molar ratio. $^{31}P\{^1H\}$NMR spectra of the complexes **6.16** - **6.17** showed singlet at 27.9 and 68.07 δ respectively and no pendent phosphorus peaks are found from the spectra. $^{31}P\{^1H\}$NMR spectrum of the complex **6.18** shows a singlet at –10.41 δ and is comparable to that found in chelate PPh_2Py complex, $[(\eta^6\text{-}p\text{-cymene})RuCl(PPh_2Py)]BF_4$ (**6.5**). ^1H NMR spectrum of $[(\eta^6\text{-}p\text{-cymene})Ru(N_3)(2,2\text{-bipy})]BF_4$ is found in the next page.



LL = dppm (**6.16**), dppe (**6.17**), PPh_2Py (**6.18**), 2,2'-bipy (**6.19**)

Scheme 6.5



^{1}HNMR spectrum of [(η^6-*p*-cymene)Ru(N_3)(2,2'-bipy)]BF_4 **(6.19)**

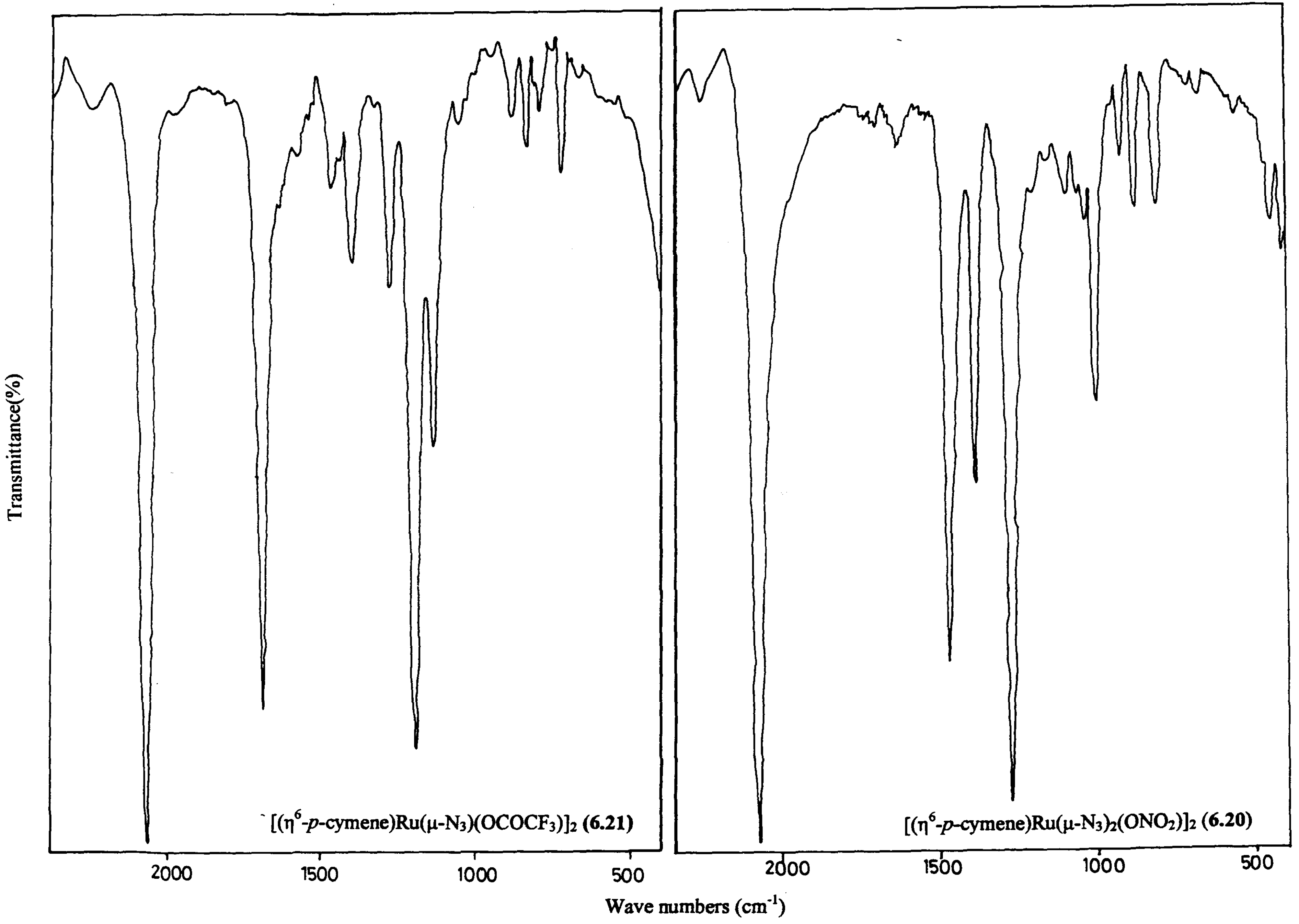
6.4.3.4 Dinuclear azide-bridged nitrato and trifluoroacetato complexes.

The filtrate from the preparation of the complex [(η^6-*p*-cymene)Ru(μ-N_3)Cl]$_2$ (**6.7**) or this compound itself when treated with Ag[NO_3] in ethanol after work up afforded orange crystals that showed very strong absorption at 2077 cm^{-1} (ca. 20 cm^{-1} higher than that of the complex **6.7** in the IR spectrum which is within the range of the stretching vibration of the bridging azido-ligand, apart from this, band at 1275 and 1003 cm^{-1} typical for monodentate nitrato absorption [16] are also observed. Since NMR spectroscopy is not a suited method to characterized this type of compound, single crystals were grown from slow evaporation of the compound in ethanol and x-ray structure determination carried out revealed the compound as binuclear azido-bridged compound having the [(η^6-*p*-cymene)Ru(μ-N_3)(ONO_2)]$_2$ **(6.20)** formed from the displacement of the terminal chloride ligands from the starting compound. As far as our knowledge is concern, this compound is the first structurally characterized arene ruthenium (II) nitrato complex even though some nitrato complexes have been reported earlier [16a].

The analogous reaction with silver trifluoroacetate resulted in the same way where the IR spectrum of the product shows very strong peaks at 2070 and 1686 cm^{-1} assignable to bridging azido group and $\nu_{C=O}$ of O_2CCF_3 [17] respectively. Its IR spectrum along with that of **6.20** is shown in the next page. In this case also, X-ray structural analysis reveal that the product as [(η^6-*p*-cymene)Ru(μ-N_3)($OCOCF_3$)]$_2$ **(6.21)**.

*6.4.3.4.1 X-ray structure of [(η^6-p-cymene)Ru(μ-N_3)(ONO_2)]$_2$ (**6.20**) and [(η^6-p-cymene)Ru(μ-N_3)($OCOCF_3$)]$_2$ (**6.21**)*

The ORTEP diagram of the complexes **6.20** and **6.21** are shown in Figure 6.7 and 6.8 respectively while the selected bond lengths and angles are shown in Table 6.8 and 6.9 respectively. In both the complexes the ligating nitrogens are pyramidally coordinated, not planar, with the angles about the nitrogens summing to 357.7° (complex **6.20**) and 363.8° (for complex **6.21**), and the ruthenium atoms and ligating nitrogens lie in a plane. In the complex [(η^6-p-cymene)Ru(μ-N_3)(ONO_2)]$_2$ (**6.20**), the distance between Ru atom and the O- bonded monodentate nitrato ligand is 2.1196(14) Å. Similarly for the complex [(η^6-p-cymene)Ru(μ-N_3)($OCOCF_3$)]$_2$ (**6.21**), the distance between the


Transmittance(%)
[(η^6-p-cymene)Ru(μ-N3)(OCOCF3)]2 (6.21)
[(η^6-p-cymene)Ru(μ-N3)2(ONO2)]2 (6.20)
2000
1500
1000
500
2000
1500
1000
500
Wave numbers (cm^-1)

ruthenium atom and ligating O atom of trifluoroacetato group is 2.1024(16) Å. The distances between ruthenium atoms and N(1) or N1#1 in both these complexes are almost the same, however they are longer than those found in the starting compound, $[(\eta^6\text{-cym})Ru(\mu\text{-}N_3)Cl]_2$ **(6.7)**.

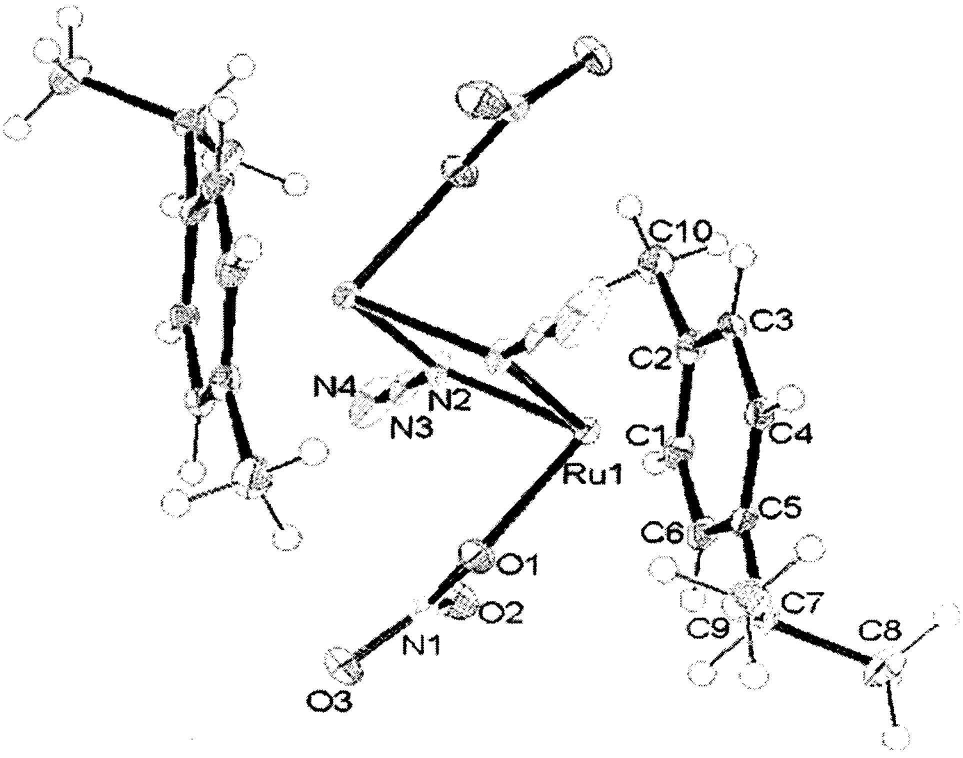


Figure 6.7: *Molecular structure of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)(ONO_2)]_2$ **(6.20)** with atom labelling scheme.*

Table 6.8: *Selected bond lengths and angles for $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)(ONO_2)]_2$ **(6.20)** and the estimated standard deviations are shown in the parentheses.*

Bond lengths (Å)		***Bond angles (°)***	
Ru1-N2	2.1210(15)	O1-Ru1-N2	83.27(6)
Ru1-O1	2.1196(14)	Ru1#-N2-Ru1	105.92(6)

N1-O1	1.303(2)	N2#-Ru1-N2	74.08(7)
N1-O2	1.234(2)	N2#-Ru1-O1	79.20(6)
N1-O3	1.229(2)	N1-N2-N3	178.9(2)
O3-N1-O1	116.67(16)	N3-N2-Ru1#	125.88(12)
O3-N1-O2	123.33(16)	O2-N1-O2	120.00(15)

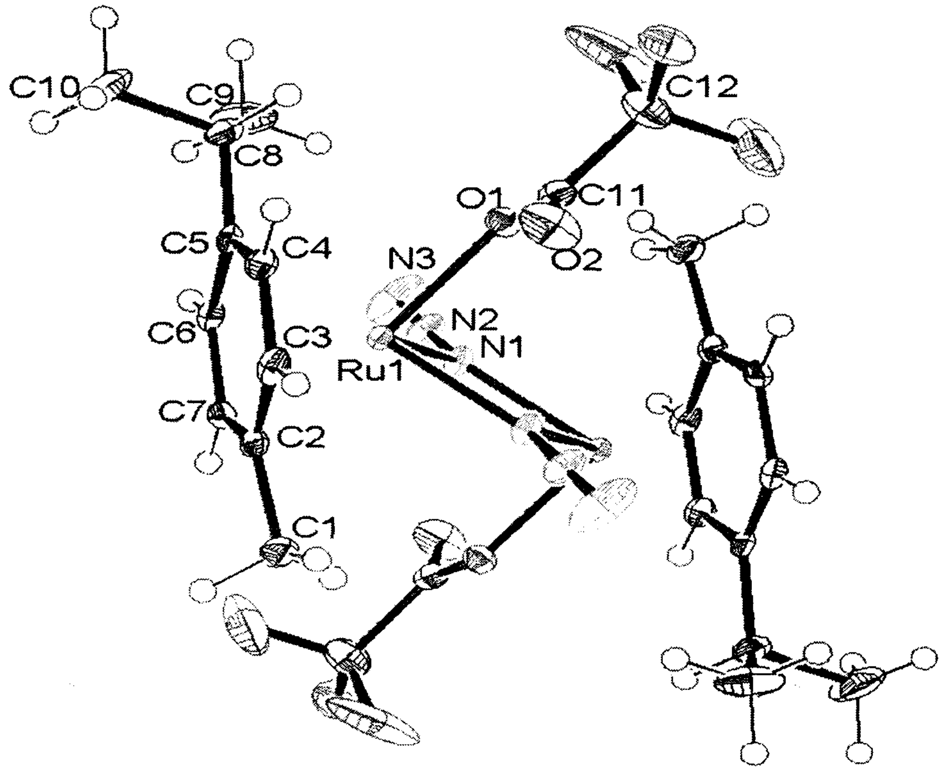


Figure 6.8: *Molecular structure of* $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)(OCOCF_3)]_2$ *(6.21)*

Table 6.9: *Selected bond lengths and angles for* $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}N_3)(\kappa^1\text{-}O\text{-}COCF_3)]_2$ *(6.21) and the estimated standard deviations are shown in the parentheses.*

Bond lengths (Å)		***Bond angles (°)***	
Ru1-O1	2.1064(16)	O1-Ru1-N1	81.66(7)
Ru-N1#1	2.1169(19)	O1-Ru1-N1#1	84.61(15)

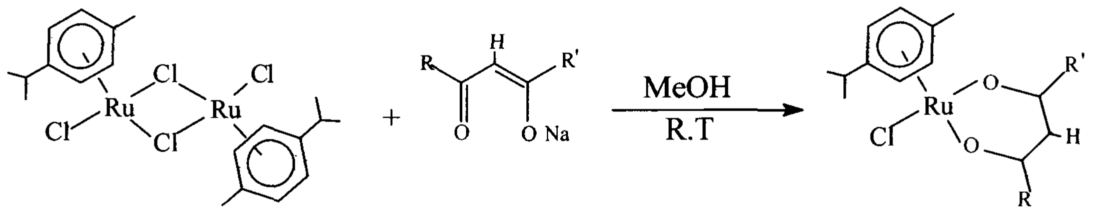
Ru1-N1	2.1144(17)	N1-Ru1-Ru1#1	128.65(15)
N3-N2	1.133(3)	Ru1-N1-Ru1#1	106.40(8)
N1-N2	1.211(3)	N1-N2-N3	178.2(2)
O2-C11	1.211(3)	O1-C11-O1	130.3(2)
O1-C11	1.272(3)		

Table 6.10: ***Crystal data and structure refinement for 6.7, 6.9, 6.15, 6.20 and 6.21***

formula	C10H14ClN3Ru	C28H29ClN3O3PRu	C23H26ClN3PRu	C10H14N4O3Ru	C12H14F3N3O2Ru
temp,	293(2)	95(2)	95(2)	95(2)	95(2)
Crystal system	triclinic	monoclinic	monoclinic	Monoclinic	Monoclinic
Space group	P-1	p2(1)/c	P2(1)/n	p2(1)/n	C2/c
a(Å)	7.5590 (6)	15.953 (2)	10.1497(14)	8.1638 (10)	17.301 (4)
b(Å)	8.384 (3)	8.3085 (11)	14.2548(19)	17.415 (2)	8.5308 (15)
c(Å)	9.6840 (11)	21.034 (3)	15.400 (2)	9.3551 (11)	20.430 (4)
α(°)	78.702 (16)				
β(°)	87.054 (8)	100.282 (2)	98.024 (3)	112.578 (2)	99.859 (6)
γ(°)	77.478 (15)				
V, Å^3	590.6 (2)	2743.1 (6)	2206.3 (5)	1228.1 (3)	2970.6 (10)
M$_r$	312.76	623.03	511.96	339.32	390.33
Z	2	4	4	4	8
ρ_{calc}, g/cm^3	1.759	1.509	1.541	1.835	1.746
rflns measd	2055	6537	14233	7838	9338
rflns unique	2055 (R$_{int}$= 0.0000)	6048 (R$_{int}$= 0.0255)	5305 (R$_{int}$= 0.0249)	2926 (R$_{int}$= 0.0219)	3523 (R$_{int}$= 0.0316)
R1, %	1.99	3.99	6.72	2.15	2.76
wR2, %	2.01	11.58	15.46	5.78	6.55
GOF	1.146	1.099	1.190	1.063	1.746

6.4.4 β-diketonato complexes

The reaction of [(η^6-*p*-cymene)RuCl$_2$]$_2$ with two eqivalent of the sodium salt of dibenzoylmethane (dbzm) or 1-benzoylacetone (bzac) (see Chart 6) at ambient temperature in methanol after two hours afforded an orange-red colored compounds of the formula [(η^6-p-cymene)Ru(LL)Cl] [LL = dbzm (**6.23**), bzac (**6.24**)] as shown in Scheme 6.6. It may be worth while mentioning here that these complexes are not formed from the reaction between the free ligands i.e. not the sodium salts and *p*-cymene dimer.

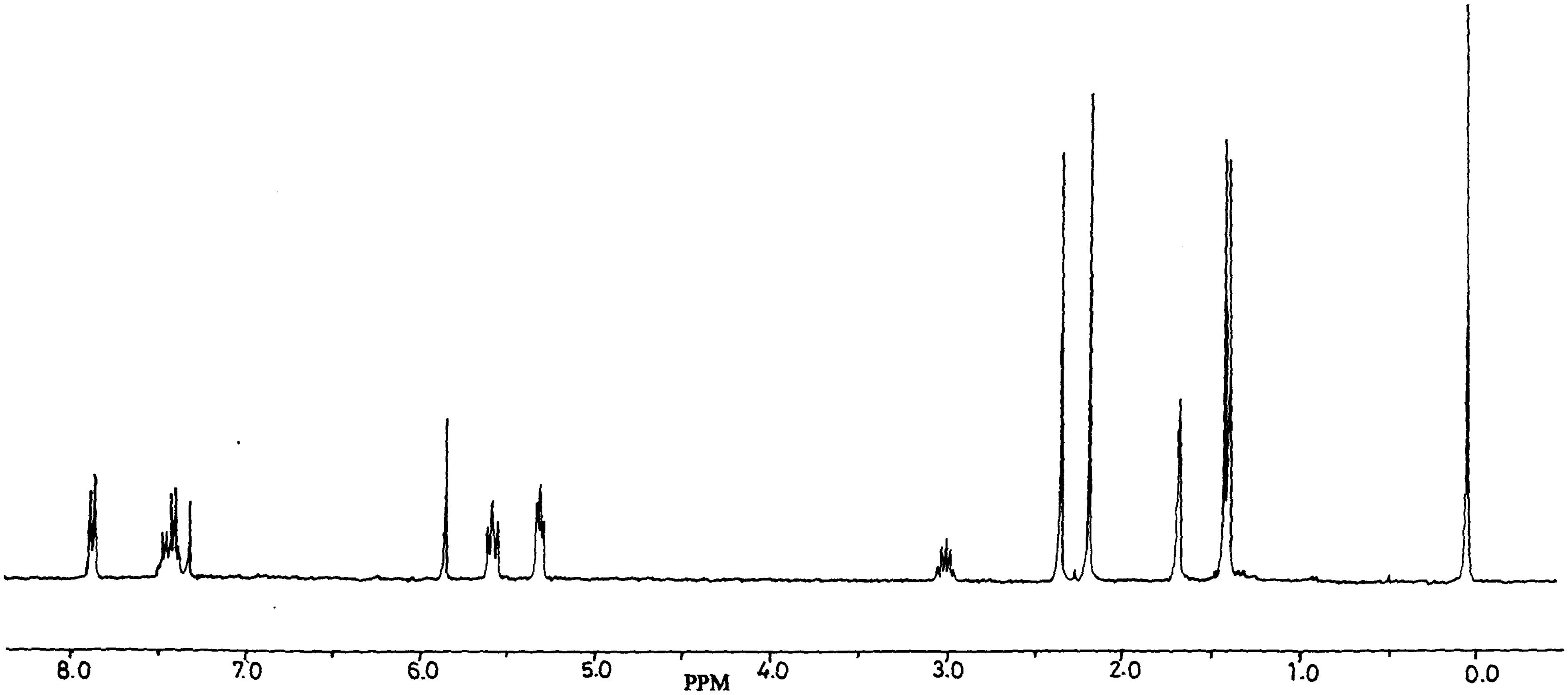


R = R' = Ph (**6.23**)
R = Me, R' = Ph (**6.24**)

Scheme 6.6

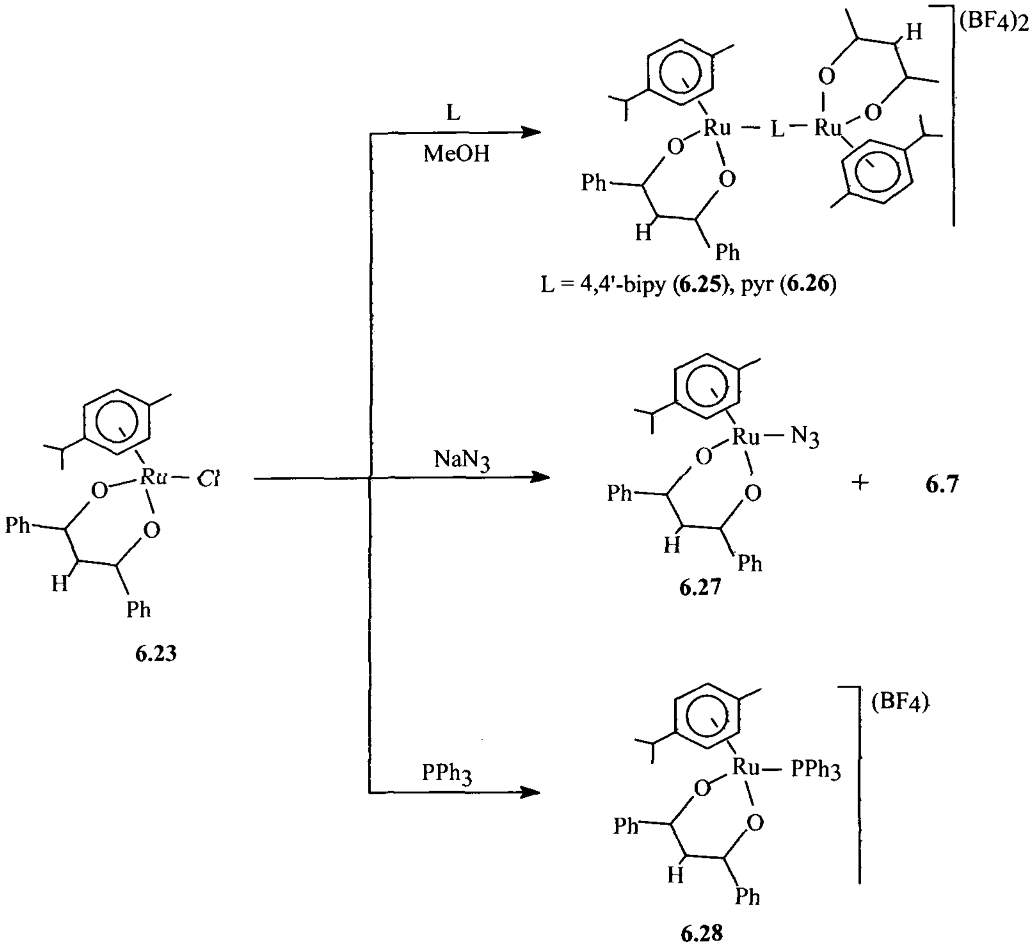
These two complexes are highly soluble in all polar solvent except water. The ^{1}H NMR spectrum of the complex [(η^6-p-cymene)Ru(dbzm)Cl] (**6.23**) showed besides the characteristic peaks corresponding to *p*-cymene ligand, ten protons multiplets in the aromatic region and one proton singlet at 6.44 δ due to phenyl groups and the γ-hydrogen of the dbzm ligand respectively. The ^{1}H NMR spectrum of the complex [(η^6-p-cymene)Ru(dbzm)Cl] (**6.24**) is also essentially similar except the γ-hydrogen resonate at relatively higher field at 5.78 δ and ^{1}H NMR spectrum of this compound is shown in the next page. Two singlets corresponding to the methyl protons appear at 2.28 δ and 2.11 δ, from comparison with the spectrum of the complex **6.23**, the latter chemical shift may be assigned to the methyl proton of the bzac ligand. The IR spectra of the complexes show bands at ca. 1590, 1550, 1520 cm^{-1} assignable to $\nu_{C=O}$ + $\nu_{C=C}$ modes of the bidentate *O,O'*-donor ligands. However, attempts to prepare the analogous complexes from dimethyl or diethyl malonate are so far unsuccessful.

Some initial studies on the reactivity of [(η^6-p-cymene)Ru(dbzm)Cl] (**6.23**) which maybe assumed to be analogous for **6.24** have also been done. Treatment with some monodenate ligands such as NaN$_3$, PPh$_3$, 4,4'-bipyridine, pyrazine in polar solvent such



^{1}HNMR [illegible] 6

as methanol in the presence of NH_4BF_4 substitute the chloride ligand (Scheme 6.7) to afford mononuclear neutral complex **6.27** or cationic **6.28** and ligand bridged binuclear complexes **6.25 and 6.26**.

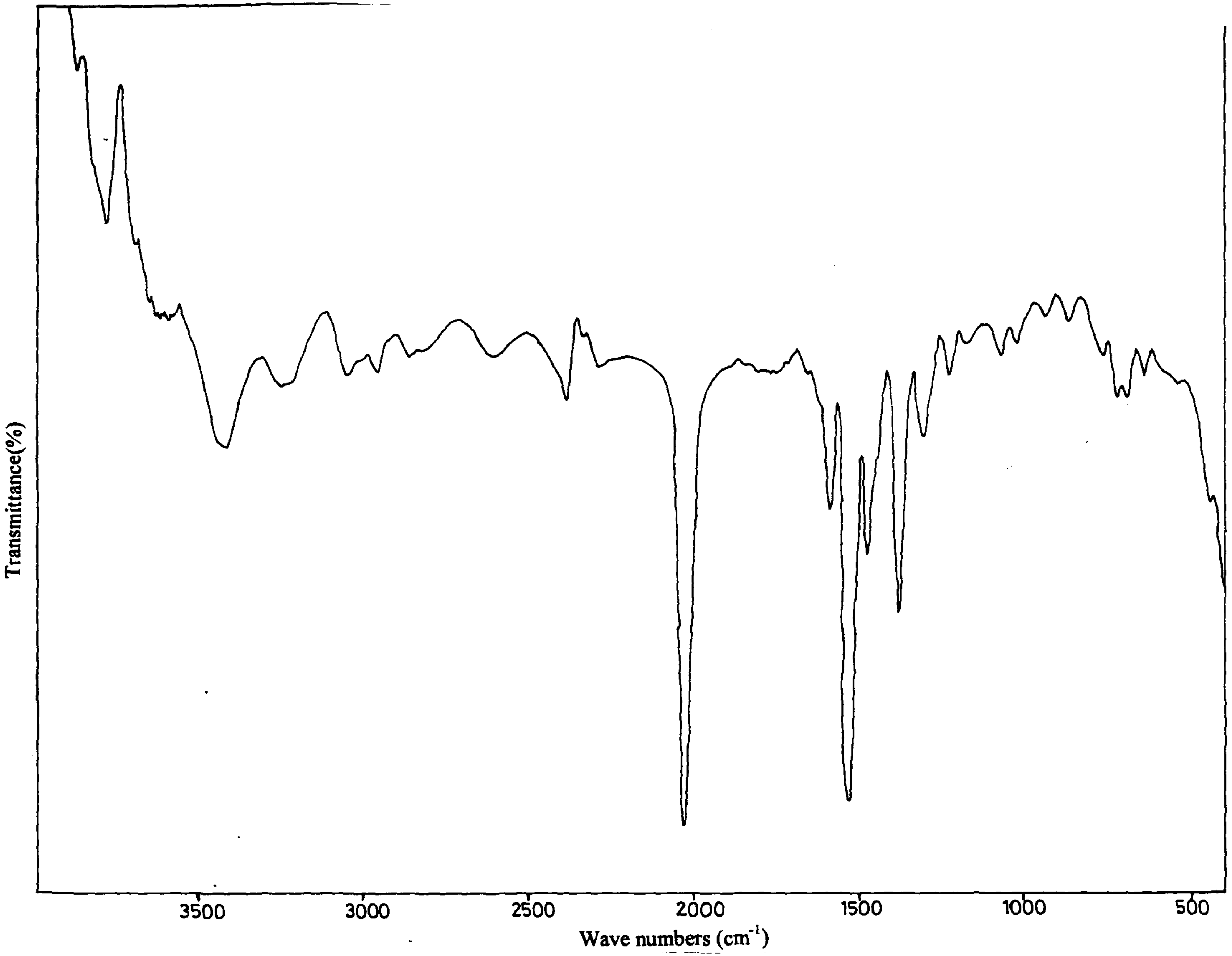


Scheme 6.7

One interesting observation is the unexpected formation of the ether insoluble byproduct (see Experimental *6.3.8.5*) which, we tentatively proposed to be same as the complex, $[(\eta^6\text{-p-cymene})RuCl(N_3)]_2$ (**6.7**). This byproduct showed very strong IR absorption band at 2056 cm^{-1} assignable to bridging azido ligand but no bands assignable to $\nu_{(C=O)}$ were observed in the range of 1590 – 1510 cm^{-1} and the ^1H NMR spectrum shows peaks corresponding to the protons of the *p*-cymene ligand but non for the dbzm ligand and the positions of the *p*-cymene peaks are also identical with those of the complex **6.7**. It is somehow difficult to explain how this complex is generated which would essentially proceed via the displacement of the dbzm ligand. ^{1}H NMR spectra of the complexes **6.25** - **6.28** show the γ-proton of the dbzm ligand in the range of 6.07 to 6.41 δ (see experimental section for detail chemical shifts) and the IR spectrum of the complexes **6.27** is shown in the next page.

6.4.4.1 X-ray structures of [(η^6-p-cymene)Ru(dbzm)Cl] (6.23) and [(η^6-p-cymene)Ru(dbzm)(N_3)] (6.27)

The ORTEP diagram of the complexes **6.23** and **6.27** are shown in Figure 6.9 and 6.10 respectively. The data collection parameters are listed in Table 4.1 and bond lengths and bond angles are listed in Table 6.11 and Table 6.12 respectively. The ruthenium atom is bonded to the two oxygen atoms of the dbzm ligand, one chloride (or azide) ligand and to a *p*-cymene group through the six carbon atoms. In complex **6.23**, the average Ru-C bond length is 2.177 Å with Ru-C(5) bond distance is found to be slightly longer than the rest. The Ru(1)-O(1) and Ru(1)-O(1) bond distances are almost the same i.e. 2.0683(18) and 2.0675(17) Å respectively, while in complex [(η^6-*p*-cymene)Ru(dbzm)(N_3)] (**6.27**) Ru(1)-O(1) bond length of 2.0795(19) Å is slightly but significantly longer than Ru(1)-O(2) distance of 2.0652(19) Å. The Ru(1)-Cl(2) bond length of 2.4173 (8) Å is not much different from those described in previous chapters. The bond distance between Ru atom and the ligating nitrogen of the azide group in complex **6.27** is 2.155 (3) Å and this is significantly shorter than those described in section 6.4.3, but the bond angles of N(2)-N(1)-Ru(1) [127.7(3)°] and N(1)-N(2)-N(3) [174.2(4)°] do not exceptionally deviate from those described in section 6.4.3.



IR spectra of [(η^6-*p*-cymene)Ru(dbzm)(N_3)] **(6.27)**

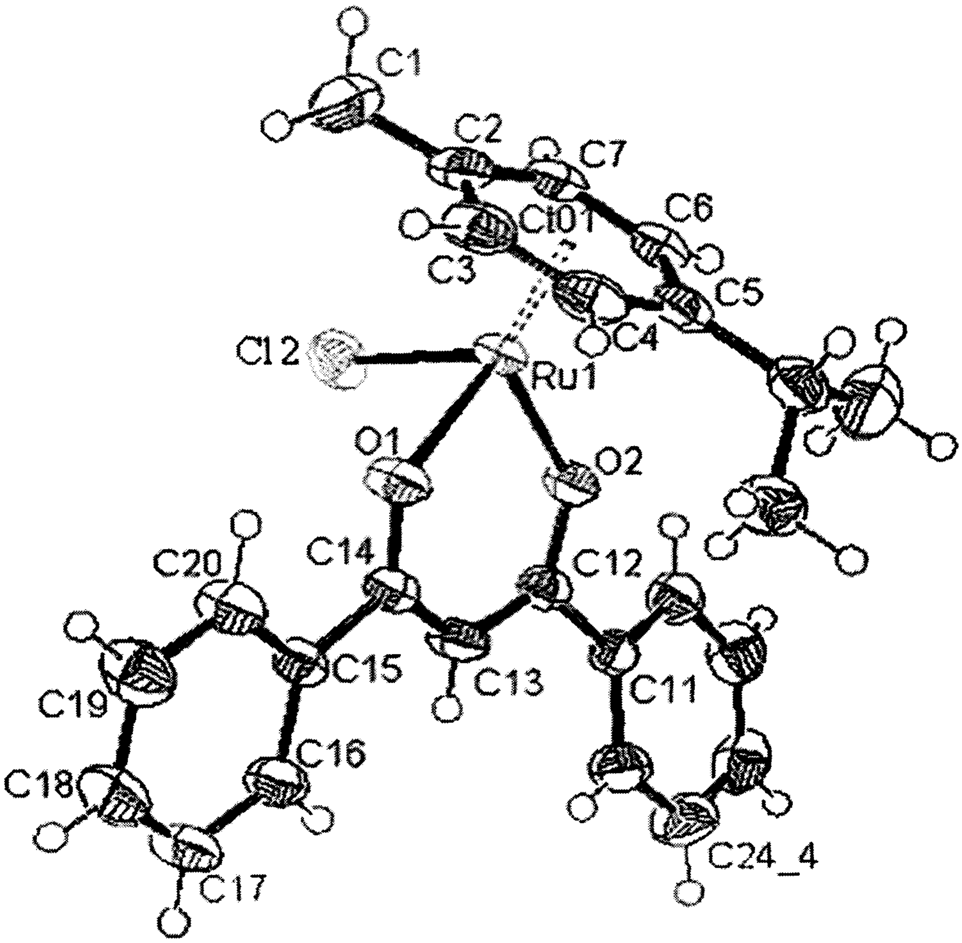


Figure 6.9 *ORTEP perspective view of the complex [(η^6-p-cymene)Ru(dbzm)Cl] (6.23) with atom numbering scheme.*

Table 6.11 *Selected Bond distances (Å) and Bond angles $(^0)$ for [(η^6-p-cymene)Ru(dbzm)Cl] (6.23) (estimated standard deviations are shown in parenthesis).*

Bond lengths

Ru(1) – O(2)	2.0675(17)	Ru(1) – C(2)	2.188(3)
Ru(1) – O(1)	2.0683(18)	Ru(1) – C(3)	2.160(3)
Ru(1) – Cl(2)	2.4173(8)	Ru(1) – C(4)	2.161(3)
O(1) – C(14)	1.272(3)	Ru(1) – C(5)	2.202(3)
O(2) – C(12)	1.277(3)	Ru(1) – C(6)	2.169(3)
C(14) – C (13)	1.391(4)	Ru(1) – C(7)	2.182(3)

C(12) – C(13)	1.389(4)		

Bond angles

O(2) – Ru(1) – O(1)	87.59(7)
O(2) – Ru(1) – Cl(2)	84.87(6)
O(1) – Ru(1) – Cl(2)	85.46(6)

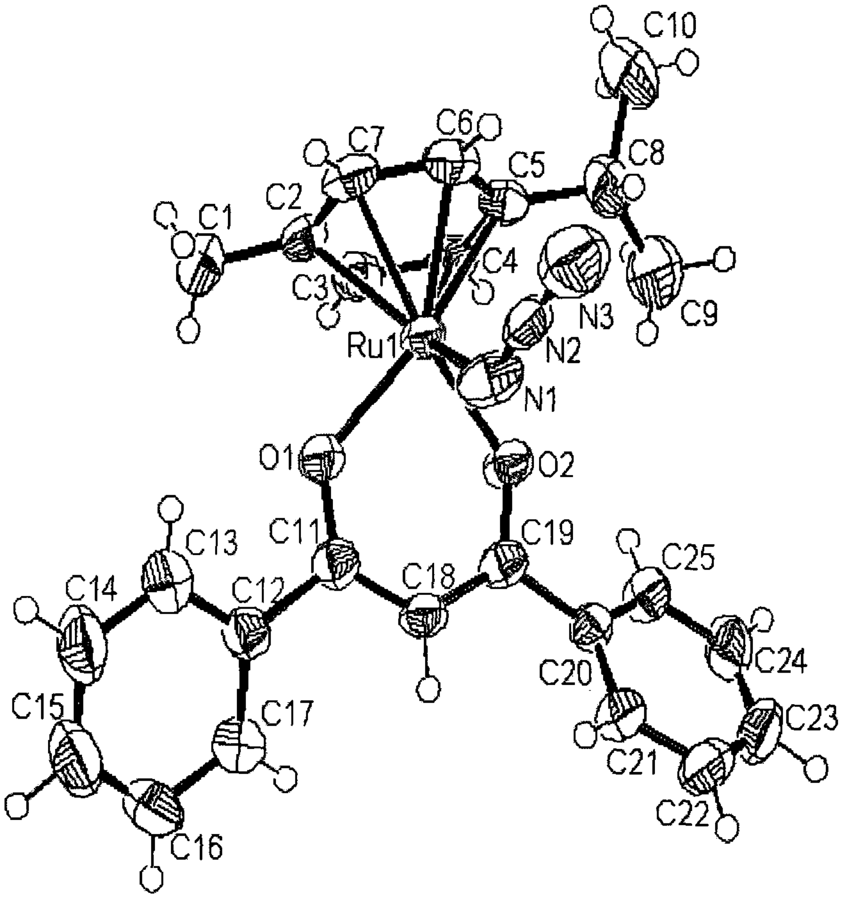


Figure 6.10 *ORTEP perspective view of the complex [(η^6-p-cymene)Ru(dbzm)Cl] (6.27) with an atom numbering scheme*

Table 6.12 *Selected Bond distances (Å) and Bond angles (^{0}) for [(η^6-p-cymene)Ru(dbzm)(N_3)]* ***(6.27)*** *(estimated standard deviations are shown in parenthesis).*

Ru(1) – O(2)	2.0652(19)	Ru(1) – C(2)	2.194(3)
Ru(1) – O(1)	2.0795(19)	Ru(1) – C(3)	2.177(3)
Ru(1) – N(1)	2.155(3)	Ru(1) – C(4)	2.154(3)
O(1) – C(11)	1.279(3)	Ru(1) – C(5)	2.183(3)
O(2) – C(19)	1.279(3)	Ru(1) – C(6)	2.147(3)
C(11) – C (18)	1.392(4)	Ru(1) – C(7)	2.190(3)
C(18) – C(19)	1.392(4)	N(1) – N(3)	1.227(5)
N(1) – N(2)	1.038(4)		

Bond angles

O(2) – Ru(1) – O(1)	87.21(8)
O(2) – Ru(1) – N(1)	80.26(10)
O(1) – Ru(1) – N(1)	83.41(10)
Ru(1) – N(1) – N(2)	127.7(3)
N(1) – N(2) – N(3)	174.2(4)

Table 6.13: ***Crystal data and structure refinement for 6.23 and 6.27***

Empirical formula	C25 H25 Cl O2 Ru	C25 H25 N3 O2 Ru
Formula weight	493.97	500.55
Temperature (K)	293(2)	293(2)
Wavelength	0.70930	0.70930
Crystal system, space group	Monoclinic, P 21/c	Monoclinic, P 21/c
Unit cell dimensions		
a (Å)	16.4040(9)	10.6790(4)
b (Å)	7.7290(10)	11.9520(11)
c (Å)	17.2040(7)	17.7020(10)
β (°)	103.094(4)	90.554(4)
Volume (A^3)	2124.5(3)	2259.3(3)
Z, Calculated density	4, 1.5444	1.472
Absorption coefficient	0.882 mm^-1	0.720

F(000)	1008	1024
Crystal size	0.25 x 0.175 x 0.20	0.35 x 0.15 x 0.10
Theta range for data collection	1.27 to 24.93	1.90 to 24.93
Index ranges	0<=h<=19 0<=k<=9 -20<=l<=19	0<=h<=12, 0<=k<=14 -20<=l<=20
Reflections collected / unique	3470 / 3470 [R(int) = 0.0000]	3526 / 3526 [R(int) = 0.0000]
Completeness to 2 θ	24.93 85.7%	24.93 84.3%
Absorption correction	Psi-scan	
Max. and min. transmission	1.000 and 0.923	1.000 and 0.994
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3470 / 0 / 363	3526 / 0 / 380
Goodness-of-fit on F^2	1.074	1.069
Final R indices [I>2σ(I)]	R1 = 0.0262, wR2 = 0.0652	R1 = 0.0266 wR2 = 0.0602
R indices (all data)	R1 = 0.0308, wR2 = 0.0684	R1 = 0.0369, wR2 = 0.0658
Largest diff. peak and hole (e.A^{-3})	0.750 and -0.609	0.325 and -0.413

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12. List of Publications:

Research Papers Published/Communicated/ under preparation.

(1) *Syntheses and characterization of arene ruthenium(II) complexes containing N,N'-donor Schiff base ligands. Crystal and molecular structure of* $[(\eta^6\text{-}C_6Me_6)Ru(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2]PF_6$. R. Lalrempuia, Mohan Rao Kollipara, Patrick J. Carroll, *Polyhedron*, 22 (2003) 605.

(2) *Synthesis and reactivity studies of cyclopentadienyl bis(triphenylphosphine) osmium(II) complexes. Crystal and molecular structure of* $[CpOs(PPh_3)(phen)]BF_4$. R. Lalrempuia, Patrick J. Carroll, Mohan Rao Kollipara, *Polyhedron*, 22 (2003) 1391.

(3) *Synthesis, characterization and molecular structure of new* (η^6*-p-cymene) ruthenium(II) amidine complexes:* $[(\eta^6\text{-}p\text{-}cymene)Ru\{NH{=}C(Me)\text{-}3,5\text{-}dmpz\}3,5\text{-}Hdmpz)][BF_4]$. K. M. Rao, P. Sarkel, S. Chakraborty, R. Lalrempuia, *J. Coord. Chem.*, 56 (2003) 1085.

(4) *Reactivity studies of* η^6*-arene ruthenium (II) dimers with polypyridyl ligands: Isolation of mono, binuclear p-cymene ruthenium (II) complexes and bis-terpyridine ruthenium (II) complexes.* R. Lalrempuia and Mohan Rao Kollipara , *Polyhedron*, 23 (2003) 3155.

(5) *The reactivity studies of p-cymene ruthenium(II) dimer towards diphenyl-2-pyridylphosphine: Synthesis, characterization and molecular structures of* $[(\eta^6\text{-}p\text{-}cymene)RuCl_2(PPh_2Py)]$ *and* $[(\eta^6\text{-}p\text{-}cymene)RuCl(PPh_2Py)]BF_4$. R. Lalrempuia, Patrick J. Carroll and Mohan Rao Kollipara, *J. Chem. Sci.*, 116 (2004) 21.

(6) *Syntheses of* $[(\eta^6\text{-}p\text{-}cymene)Ru(EPh_3)_2Cl]^+$ *complexes and molecular structure of chloro* (η^6*-p-cymene)bis(triphenylphosphine)ruthenium (II) tetrafluoroborate (E = P, As and Sb).* R. Lalrempuia, Patrick J. Carroll, Mohan Rao Kollipara, *J. Coord. Chem.*, 56 (2003) 1499.

(7) *Synthesis, characterization and molecular structures of allenylidene, vinylidene-alkylidene complexes containing $[CpOs(PPh_3)_2]^+$ fragment.* R. Lalrempuia, Hemant Yennawar, Yurij Mozharivskyj, Mohan Rao Kollipara, *J. Organomet. Chem.*, 689 (2004) 539.

(8) *Reactivity studies of cyclopentadienyl bis(triphenylphosphine) ruthenium(II) complex towards some polypyridyl ligands.* R. Lalrempuia, P. Govindaswamy, Yurij A. Mozharivskyj, Mohan Rao Kollipara, Polyhedron, 23 (2004) 1069.

(9) *Synthesis and characterization of cyano-bridged home and heterobimetallic complexes containing η^5 and η^6-cyclic hydrocarbons,* R. Lalrempuia, E. K. Rymmai, Kollipara Mohan Rao, Patrick J. Carroll, Glenn P. A. Yap, K. A. Kreisel, (*communicated*).

(10) *Bis(η^6-p-cymene)dichloro di-μ-1,1-azido diruthenium(II): a versatile starting material for p-cymene ruthenium(II) azide complexes,* R. Lalrempuia, K. S. Singh, Hemant Yennawar, Kollipara Mohan Rao, (Communicated).

(11) *Synthesis, characterization and reactivity studies of O,O'- donor β-diketonato complexes of ruthenium.* R. Lalrempuia, K. S. Singh, Kollipara Mohan Rao. (Under preparation).

(12) *Preparation of p-cymene ruthenium(II) amine complexes via hydrolysis of phenylenedimines,* (Under preparation).

(13) *Unprecedented formation and crystal structure of trans- $[Ru(MeCN)_4Cl_2]$ hydrate.* R. Lalrempuia, Glenn P. A. Yap, Kollipara Mohan Rao (under preparation).