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 $\eta^6$-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, $[(\eta^6$-arene)RuCl(YZ)] where YZ is a chelating diamine such as ethylenediamine are cytotoxic to cancer cells including cisplatin-resistant cell lines and $[(\eta^6$-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 $[(\eta^6$-arene)RuCl$_2$]$_2$ (arene = p-cymene, hexamethylbenzene). Apart from these, another materials namely, [CpM(PPh$_3$)$_2$X] (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(PPh₃)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(PPh₃)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(PPh₃)₂Br] with monodentate anion or neutral ligands such as CH₃CN, 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(PPh₃)₂Br] but with [CpOs(PPh₃)₂(CH₃CN)]⁺ to give cationic complexes of the formula [CpOs(PPh₃)(L₂)]⁺ resulting from the substitution of one of the PPh₃ as well as the acetonitrile ligand. The reaction of [CpOs(PPh₃)₂Br] with diphenylpropargylic alcohol HC≡C(Ph)₂(OH)
afforded cationic osmiumallenylidene complex [CpOs(C≡C=CH)(PPh3)2]+, but with HCC≡CMe2(OH), unexpected dimerization product, a dicationic diosmium vinylidene-alkylidene complex of the formula [(CpOs)2(μ-C10H12)(PPh3)4]2+ was obtained as shown in the figure below. The X-ray crystal structures of these complexes as well as that of [CpOs(PPh3)(phen)]BF4 are also presented in this chapter.

Chapter three described the synthesis and characterization of the complexes resulting from the reaction of [(η6-arene)RuCl2]2 with N, N'-donor Schiff bases viz, para-substituted N-(2-pyridinylmethylene)phenylamines and N-(2-pyridinylmethylene)cyclohexylamine (arene = hexamethylbenzene, p-cymene). The X-ray structure of a representative complex [(η6-C6Me6)Ru(C5H4N-2-CH=N-C6H4-p-NO2)Cl]PF6 has revealed that the complex adopt usually expected distorted octahedral geometry around the metal center. Another part of this chapter described the hydrolysis
of phenylimine ligands during its reaction with $p$-cymene dimer aided presumably by moisture to afford amine complexes as shown below,

![Diagram of complex formation](image)

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 $[(x$-pterpy)$_2$Ru]$^{2+}$ under mild condition, starting from the reaction between $[(\eta^6$-arene)RuCl$_2$] and substituted phenylterpyridines ($x$-pterpy). This method provides a general route for the bis terpyridine complexes instead of starting from the usual ruthenium(III) precursors such as $[(terpy)$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 $[(\eta^6$-arene)RuCl(N,N)]$^+$, confirmed by X-ray crystallographic studies on two of these compounds.

Chapter four 'B' encompasses the results obtained from the reaction of [CpRu(PPh$_3$)$_2$Cl] with some terpyridine-like, N,N',N''-donor as well as two potentially bridging N,N'-donor ligands. The results are in contrast to with those observed in part
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(PPh3)(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 -C≡N- 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 EPh3 (E = P, As, Sb), PPh2Py, Sodium azide and β-diketonate (bzac, dbzm) ligands and p-cymene dimer. These could be very briefly summarized as,

(i) [(η^6-p-cymene)RuCl2]2 with excess of EPh3 (ca. five fold excess in the case of PPh3) afforded cationic [(η^6-p-cymene)RuCl(EPh3)]+ 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.

(ii) PPh2Py reacts with [(η^6-p-cymene)RuCl2]2 to afford P-bound neutral complex, P, N-chelate complex and trans-[(PPh2Py)2RuCl] resulting from displacement of p-cymene (the first two complexes are fully characterized).

(iii) The reinvestigated preparation of [(η^6-p-cymene)Ru(μ-N3)Cl]2 from Na[N3] 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.

(iv) Sodium salt of dibenzoylmethane (dbzm), 1-benzoylaceton (bzac) when treated with $p$-cymene dimer afforded $O,O'$-bound $p$-cymene complexes. Some initial studies on the reactivity of a fully characterized complex, $[(\eta^6-p$-cymene)Ru(dbzm)Cl]$, has been done.