Preface

One of the most interesting and important areas in which contemporary inorganic chemists could contribute profitably is organometallic chemistry, a broad interdisciplinary field whose sphere of interest includes all compounds wherein metal usually in a low valence state is bonded through carbon of an organic molecule, radical or ion. Since the publication of the synthesis of Zeise salt (1848), and Victor Grignards’ organomagnesium halides (1900), there have been spasmodic references to the syntheses of such novel compounds as ferrocene, ruthenocene etc. But from the middle of the twentieth century and particularly after the syntheses of the cyclopentadienyl, its analogue’s and arene transition metal complexes are came a vast blossoming of Organic-Transition Metal Chemistry which has led into the development of a large number of new areas like homogeneous catalysis, etc.

Organic and organometallic chemists have extensively investigated Arene metal complexes for over four decades. The organometallic complexes of \( \eta^6 \)- and \( \eta^5 \)- half-sandwich complexes of ruthenium, rhodium and iridium have attracted considerable current interest especially from the catalytic prospective, is the design of Ru=O functional groups and analogues capable of reversibly accepting multiple electrons and protons within a relatively small potential range. This capacity to modify the environment in order to induce electronic as well as steric effects gives scope for the design and fabrication of tailored catalysts for specific reactions. The arene ruthenium or Cp* rhodium or iridium dimers appear to be good starting materials for access to reactive arene metal hydrides and have been used for carbon-hydrogen bond activation. Recently, from classic organometallic arene ruthenium has grown an area making significant contributions to the chemistry of cyclophanes and metal grids. 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 monodentate ruthenium(II) arene complexes of the type \([(\eta^6\text{-arene})\text{Ru}(\text{en})\text{X}]PF_6\), where \text{en} is ethylenediamine and \text{X} is chloride or iodide, constitute a group that is believed to exert an antitumor action via mechanisms different from those of other ruthenium(III) complexes such as NAMI-A or KP1019. 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 \([(\eta^6\text{-arene})\text{Ru}(\mu-\text{Cl})\text{Cl}]_2\) (arene = benzene, \(p\)-cymene and hexamethylbenzene). Apart from these, another materials with similar isoelectronic metal d\(^6\) systems namely \([(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu-\text{Cl})\text{Cl}]_2\) (\(\text{C}_5\text{Me}_5 = \text{pentamethyl cyclopentadienyl}; \ M = \text{Rh or Ir}\)) are also chosen as a starting materials.

The primary objective of the thesis is to explore the chemistry of arene ruthenium and pentamethylcyclopentadienyl rhodium or iridium complexes and main objective is to synthesize or frame the ligand, in which it can coordinate to two metal centers and preparation of mono and dinuclear complexes by using nitrogen bases. Final aim is to place the reader in a synthetic methodology for these classes of complexes.

The sequence of chapters reflects preparation of a wide range of half sandwich arene ruthenium and pentamethylcyclopentadienyl rhodium or iridium complexes and their characterization with help of analytical and spectroscopic data. The solid state structure of representative complexes were also studied using single crystal X-ray crystallography.

This thesis carries syntheses of arene ruthenium, and pentamethylcyclopentadienyl rhodium and iridium complexes of polypyridyl, polypyrazolyl, thiazolyl and Schiff base ligands.
Graphical Abstracts

Chapter 1: General Introduction (pages 1-21)

This chapter provides the motivation for the research presented in this thesis and is intended to situate the reader in the field of study, Coordination Chemistry and Organometallic Chemistry. General aspects and recent advances in the half-sandwich platinum group metal complexes are discussed. Platinum group metal complexes find applications in most of the areas where coordination and organometallic chemistry present.

Chapter 2: Mono and dinuclear half-sandwich platinum group metal complexes bearing pyrazolyl-pyrimidine ligands: Syntheses and structural studies (pages 22-50)

In this chapter, we focus on the synthetic methodology applied for the development of homogeneous and immobilized half-sandwich ruthenium, rhodium and iridium complexes bearing bis(pyrazolyl)pyrimidine, as a specific N,N-bidentate bridging ligand
Chapter 3: Spectral, structural and DFT studies of platinum group metal 3,6-bis(2-pyridyl)-4-phenylpyridazine complexes and their ligand bonding modes (pages 51-81)

New mononuclear half-sandwich platinum group metal (Ru, Rh and Ir) complexes were obtained by the reaction of arene or pentamethylcyclopentadienyl metal (Ru, Rh and Ir) complexes with 3,6-bis(2-pyridyl)-4-phenylpyridazine \((L_{ph})\), yielding two sets of complexes. In one set \((type-A)\), the metal bonds to the N1 and N2 atoms of the \((L_{ph})\) ligand, and in the other \((type-B)\), the metal bonds to the N3 and N4 atoms. The structures of these complexes were confirmed through X-ray crystallography and density functional theory calculations.

Chapter 4: Cationic half-sandwich complexes (Rh, Ir, Ru) containing 2-substituted-1,8-naphthyridine chelating ligands: Syntheses, X-ray structure analyses and spectroscopic studies (pages 82-103)

In this chapter, we describe the synthesis of twelve \(\eta^5-C_5Me_5\) rhodium, iridium and \(\eta^6-C_6H_6, \eta^6-p-^3PrC_6H_4Me\) ruthenium complexes incorporating 2-substituted-1,8-naphthyridine ligands; \(2-(2-pyridyl)-1,8\)-naphthyridine (pyNp), \(2-(2-thiazolyl)-1,8\)-naphthyridine (tzNp) and \(2-(2-furyl)-1,8\)-naphthyridine (fuNp).
Chapter 5: Half-sandwich mono and dinuclear complexes of platinum group metals bearing pyrazolyl-pyridine analogues: Synthesis and spectral characterization (pages 104-125)

The chelating ligands $pp$-$Cl$ and $bppp$ were synthesized and their reactions with arene ruthenium, Cp* rhodium and Cp* iridium dimers resulted in the formation of mono and dinuclear complexes. However reactions with the $bppm$ ligand which is having Pyrimidine Bridge between pyrazolyl-pyridine units resulted only in the formation of mononuclear complexes.

Chapter 6

Part A: Mono and dinuclear complexes of half-sandwich platinum group metals (Ru, Rh and Ir) bearing a flexible pyridyl-thiazole multidentate donor ligand (pages 126-150)

In this chapter, we have synthesized new mononuclear and dinuclear complexes with arene ruthenium, rhodium and iridium complexes with polypyridyl ligand as thiazolyl rings backbone. All these new complexes were characterized by elemental analyses, $^1$H-NMR, UV-Visible and mass spectrometry as well as X-crystallographic analyses for some representatives.
Part B: New series of platinum group metal complexes bearing \( \eta^5 \)- and \( \eta^6 \)-Cyclichydrocarbons and Schiff base derived from 2-acetylthiazole: syntheses and structural studies. (Pages 151-168)

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

Chapter 7: Syntheses and characterization of mono and dinuclear complexes of platinum group metals bearing benzene-linked bis(pyrazolyl)methane ligands. (Pages 169-190)

In this chapter, we have synthesized homogeneous and immobilized half-sandwich rhodium, iridium and ruthenium complexes bearing bis(pyrazolyl)methanes bridged by benzene-linker, as bidentate or tetradentate bridging ligands \( (L) \). The \( \text{Cp}^* \) rhodium and iridium complexes with ligands \( L \) give both mono and dinuclear complexes, while only dinuclear complexes are obtained with arene ruthenium complexes.