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

Organic and organometallic chemists have extensively investigated arene metal complexes for around 50 years. Arene ruthenium complexes play an increasingly important role in organometallic chemistry. They appear to be good starting materials for access to reactive arene metal hydrides or 16-electron metal (\( d^8 \)) intermediates that have been used recently for carbon-hydrogen bond activation. Various methods of access to cyclopentadienyl, borane and carborane arene ruthenium complexes have been reported. Recently, from classic organometallic arene ruthenium has grown an area making significant contributions to the chemistry of cyclophanes. These compounds are potential precursors of organometallic polymers that show interesting electrical properties and conductivity. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic “piano stool” structure offers the possibility to vary the additional donors via substitution of halide(s) with a variety of \( \sigma \)-donors ranging from tertiary phosphines to \( \beta \)-diketones to aliphatic as well as aromatic amines.

The primary objective of the thesis is to explore the chemistry of \( \eta^5 \) - and \( \eta^6 \)-cyclic hydrocarbon platinum group metal (Ru, Rh, Os and Ir) complexes and give reader a synthetic methodology for these classes of complexes.
The sequence of chapters reflects preparation of $\eta^5$- and $\eta^6$-cyclic hydrocarbon platinum group metal (Ru, Rh, Os and Ir) complexes and their characterization with the help of analytical and spectroscopic data. The solid-state structures of representative complexes were determined by single crystal X-ray crystallographic studies. The work of this thesis has been studied in six chapters.

Chapter 1

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

Chapter 2

This chapter deals with the reaction of $\eta^5$- and $\eta^6$-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the N₄ type ligand 3,5-bis(2-pyridyl)pyrazole (bpp-H), which posses two contiguous binding sites for metal ions forming both mono- and binuclear complexes. However, arene ruthenium complexes yielded bimetallic complexes with bpp-H, whereas ($\eta^5$-C₅Me₅)M dimers and mononuclear triphenylphosphine complexes did not yield bimetallic complexes with bpp-H, this could be due to the steric effect of $\eta^5$-C₅Me₅ and PPh₃ ligands (Scheme 1). These compounds have been characterized by IR, NMR and mass spectrometry as well as by elemental analyses. The molecular structures of representative complexes have been established by single crystal X-ray diffraction studies and some representative examples have been studied by UV-visible spectroscopy.
Chapter 3

This chapter describes the reaction of ruthenium half-sandwich complexes with tautom erized pyrazolyl-pyridazine ligands. Here, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methylypyrazole moiety and the existence of both the tautomers in a single compound is described in this chapter which are the first of its kind known in the literature. The tautom erized products were supported by $^1$H NMR and $^{13}$C NMR as well as single crystal X-ray structure. The reactions of $\eta^6$-areneruthenium complexes in methanol with the above mentioned pyrazolyl pyridazine ligands form mononuclear complexes of the type $\{[\eta^6\text{-}arene]Ru(\text{Cl}-L)(\text{Cl})]\}^+$ and $\{[\eta^6\text{-}arene]Ru(L)(\text{Cl})\}^+$; (arene = benzene and $p$-cymene;
Cl-L = Cl-L1, Cl-L2, Cl-L3; L = L1, L2, L3 (Scheme 2). All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

Scheme 2
Chapter 4

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

\begin{align*}
\text{(i)} &= [(\eta^5\text{-Cp})\text{M}_x\text{Cl}](\text{PPh}_3)_2; \text{M}_x=\text{Ru}, \text{Os} \\
\text{(ii)} &= [(\eta^5\text{-Cp}^*)\text{M}_x\text{Cl}(\mu-\text{Cl})]_2; \text{M}_x=\text{Rh}, \text{Ir} \\
\text{(iii)} &= [(\eta^5\text{-Cp}^*)\text{RuCl}(\text{PPh}_3)_2]
\end{align*}

Scheme 3
Chapter 5

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

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

The concluding chapter describes the syntheses of various dinuclear complexes arising from the reaction of \( \eta^5 \)- and \( \eta^6 \)-cyclic hydrocarbon platinum group metals (Ru, Rh, Os and Ir) with the tetradeinate nitrogen donor ligand, 1,3-bis((3-(pyridin-2-yl)-1H-pyrazol-1-yl)methyl)benzene (NN\(\text{NN}\)), in which the two pyrazolyl-pyridine units are connected by an aromatic spacer. This ligand has the ability to form both mono and dinuclear complexes with metals like Cu and Ag, but surprisingly in the case of arene ruthenium and Cp\(^*\)rhodium and Cp\(^*\)iridium systems, it only forms dinuclear complexes. The complexes are characterized by a combination of NMR spectroscopy, IR spectroscopy, mass spectrometry and UV-visible spectroscopy. The solid state structures
of representative complexes are determined by single crystal X-ray crystallographic studies. Despite the presence of two chiral centers in all the X-ray structures, only racemic mixtures were obtained, and all compounds crystallize in centrosymmetric space groups.

Scheme 5