This chapter provides the motivation for the research presented in this thesis and is intended to situate the reader in the field of Coordination Chemistry and Organometallic Chemistry. The general aspects and recent advances of the half-sandwich platinum group metal complexes are discussed in this chapter. Platinum group metal complexes find applications in most of the areas where coordination and organometallic chemistry present. The last section of this chapter provides the information for the starting materials and physical techniques which are used in this study.
1.1 Organometallic and coordination chemistry

Organometallic compounds are defined as materials which possess direct, more or less polar bonds between metal and carbon atoms.\(^1\) Zeise synthesized in 1827 the first organometallic compound, \(\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]\), since then the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. Some of the key points in the fast expansion of organometallic chemistry are the selectivity of organometallic complexes in organic synthesis (discovered with Grignard reagents at the end of the 19\textsuperscript{th} century),\(^2,3\) and the interesting role that metals play in biological systems (e.g. enzymes, haemoglobin, \textit{etc.}).\(^4\)

Since Werner’s pioneering work, coordination chemistry has maturated in a continuous way, being bioinorganic and bio-metallic chemistry and the growing interest in materials its latest driving forces. Now days, coordination compounds are involved in an unbelievable wide range of applications that can be divided in the following areas: (i) use of coordination complexes in all types of catalyses: (ii) applications related to the optical properties of coordination complexes, which cover fields as diverse as solar cells, non linear optics, display devices and pigments, dyes and optical data storage devices; (iii) hydrometallurgical extraction; (iv) medicinal and biomedical applications of coordination complexes, including both image and therapy and (v) use of coordination complexes as precursors to semiconductor films and nanoparticles. If nothing else, such an extensive list of applications can be employed, as suggested by Professor Ward in the last edition of \textit{Comprehensive Coordination Chemistry}\(^5\) as a suitable answer to the eternally irritating question that everyone involved in the field get asked at parties when we reveal what we do for a living. “But what’s it for?”

1.2 \(\eta^6\)-arene ruthenium chemistry and half- sandwich piano stool complexes

The first arene ruthenium complex was obtained from the reaction of \(\text{RuCl}_3\cdot\text{nH}_2\text{O}\) with 1,3-cyclohexadiene (scheme 1.1) and reported by Winkhaus and Singer in 1967 as a polymeric material, \([(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_n\).\(^6\) Later studies by Zelonka and Baird\(^7\) and by Bennett and Smith\(^8\) showed this complex is to be a dimer, \([(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2\). Since these early reports, the chemistry of arene ruthenium complexes has been steadily developed.\(^9,10,11\)
Within this large family of $\eta^6$-arene ruthenium complexes, piano-stool complexes are undeniably the most studied ones. They have found applications as catalysis, supramolecular assemblies, molecular devices and have shown antiviral, antibiotic, and anticancer activities. These piano stool complexes are resulted by the reaction of the dimeric complexes with coordinating solvents such as CH$_3$CN, DMSO and some of the monodentate ligands such as CO, pyridine, triphenylphospine etc. (Scheme 1.2) due to the presence of more labile chloro bridges in dimeric complexes. These three-legged piano-stool complexes possess a pseudo-octahedral geometry at the ruthenium(II) center, the arene ligand occupying three coordinating sites (the seat) where as other coordination sites occupied by with other three ligands (the legs) (figure 1.1). Therefore, the octahedral geometry can be viewed as pseudo-tetrahedral, thus limiting the number of possible isomers.
The arene ligands are relatively inert towards substitution reactions and consequently are often considered as spectator ligands. However, the arene moiety which is strongly coordinated to the ruthenium atom can be customised by simply attaching different substituents (Scheme 1.3). These functionalised substituents can be modified to tune the properties of the arene-ruthenium complexes. The three remaining coordination sites opposite to the arene ligand can be used to introduce a wide variety of ligands such as N-, O-, S- or P- donor atoms. The resulting complexes are neutral, mono- or dicationic, and often these ligands are labile. This tendency to exchange ligands in solution is crucial in self-assemblies\textsuperscript{12} and catalytic processes.\textsuperscript{13}
possible to provide a fully survey of this area. However, it is hoped that the discussion that follows will give some important entry into the literature. More recently, Gimeno et al., found that catalytic efficiency of compounds \([\{(\eta^6\text{-arene})\text{Ru}(\mu-\text{Cl})\text{Cl}\}_2\}\] is strongly dependent on the arene ligand. The rate order observed, \textit{i.e.} \(C_6H_6 (\text{TOF} = 500 \text{ h}^{-1}) > p\text{-cymene} (\text{TOF} = 333 \text{ h}^{-1}) > C_6\text{Me}_6 (\text{TOF} = 125 \text{ h}^{-1})\), indicates clearly that the less sterically demanding and electron-rich arene exhibit the higher performance, also found that these arene ruthenium complexes are much more active than the classical ruthenium(II) catalysts \([\text{RuCl}_2(\text{PPh}_3)_3]\) and \([(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}]\].\(^{14}\) Furthermore, Finke et al., reported that arene-ruthenium monometallic complexes are only heterogeneous catalysts and pentamethylcyclopentadienyl-rhodium compounds are homogeneous catalysts.\(^{15}\)

1.2.1. Applications of \(\eta^6\)-areneruthenium chemistry

1.2.1.1 Biological applications

The monodentate ruthenium(II) arene complexes of the type \([\{(\eta^6\text{-arene})\text{Ru(II)}(\text{en})\text{X}\}[\text{PF}_6]\], where \text{en} is ethylenediamine and \text{X} is chloride or iodide (see Chart 1.1), constitute a group that is believed to exert an antitumor action \textit{via} mechanisms different from those of other ruthenium(III) complexes such as NAMI-A or KP1019.\(^{16-19}\) DNA appears to be a target for these compounds, which bind preferentially to the guanine residues and also interact "non-covalently" \textit{via} both arene intercalation and minor groove binding.\(^{21,22}\) \([(\eta^6\text{-toluene})\text{Ru(II)}(\text{pta})\text{Cl}_2]\) (RAPTA-T), where \text{pta} is 1,3,5-triaza-7-phosphaadamantane (see chart 1.1), is the parent compound from which a group of water-soluble selective DNA-binding antimetastatic drugs was synthesized.\(^{23,24}\) The RAPTA compounds exhibit pH dependent DNA binding, almost no toxicity towards cancer cells \textit{in vitro} and no toxicity at all towards healthy cells, also \textit{in vitro}. However, RAPTA-T was found to inhibit lung metastases in mice bearing a mammary carcinoma, again with only mild effects on the primary tumours. The mechanism of action of the RAPTA compounds is only starting to be investigated.\(^{25,26}\)
Chart 1.1: Structures of ruthenium-based anticancer drug candidates.

1.2.1.2 Catalytic applications

(a) Homogeneous catalysis:

A catalytic system in which the substrates for the reaction and the catalyst are mixed together in one phase, most often the liquid phase, is known as homogenous
catalysis. Ligand effects are crucial in homogeneous catalysis by metal complexes.\textsuperscript{27} The catalytic properties of a given transition metal can be tuned through the nature of ligands bonded to the metal centre. Therefore, one metal can give a variety of products from a single substrate simply by changing the ligands around it. As example, Figure 1.2 shows the different products that can be obtained from styrene with various ruthenium catalysts.

Figure 1.2: Ruthenium catalyzed reactions of styrene

(b) \textit{Water oxidation by ruthenium dimers}

In the past decade, mankind has begun to appreciate more fully the delicate balance between his existence and his environment. This awareness has taken several forms. One form is the realization that current energy resources will not be sufficient to provide for rapidly expanding population and emerging economies. Most important in
this regard is the finite limitation of fossil fuel resources. These resources were accumulated over millions of years and thus are not renewable in any realistic sense. Another major emerging concern is the effect that our current utilization of natural resources, such as petroleum, is having on the atmosphere and general environment of our planet.\textsuperscript{28,29,30}

In this respect the eventual movement to a hydrogen-based economy is particularly promising. Hydrogen is generally considered the best fuel for the future due to its ease of application in fuel cells and clean burning properties. This fuel could be used to replace oil as the source of electricity, heat and transportation to give us a \textit{hydrogen economy}.\textsuperscript{31}

In view of this; producing hydrogen from water would offer several benefits over current methods, including steam reforming of natural gas, which produces carbon dioxide along with the hydrogen. Heat derived from fossil-fuel combustion is currently used to drive the steam reforming process, resulting in even more carbon dioxide as a byproduct, all of which contributes to global warming. Making hydrogen by splitting water would not add carbon dioxide to the atmosphere.

In view of all these things, designing and syntheses of water oxidation catalytic complexes has been receiving continuous attention for the last few decades. Especially the ruthenium complexes have been showing most promising feature for the catalytic activities. For nearly 15 years 1 (blue dimer) (see figure 1.3) was the only ruthenium complex known to catalyze water to oxygen. Following that, many groups are working on this theme, but only few research groups have been succeeded with the prospect; they are Llobet and co-workers synthesized\textsuperscript{32,33} complex 2 (figure 1.3) and a more substantial structural change has come from the laboratory of Thummel\textsuperscript{34} with the synthesis of complex 3 (see figure 1.2). However, the stability of the complex is only modestly improved and turnover increases to 20 with \( k_o \) rising by a factor of six to \( 1.4 \times 10^2 \cdot s^{-1} \), in later the rate increases to \( k_o = 7.7 \times 10^2 \cdot s^{-1} \).\textsuperscript{35}
1.3 Arene-ruthenium polypyridyl compounds

Reactions of dimeric complex $\{(\eta^6\text{-arene})\text{RuCl}_2\}_2$ (arene = $\text{C}_6\text{H}_{6}$, $p$-cymene and $\text{C}_6\text{Me}_6$) with various mono, bi and polydentate nitrogen bases gave neutral and cationic substitution complexes of formulation $\{(\eta^6\text{-arene})\text{RuCl}(L)_1\}$ or dinuclear complexes of formulation $\{(\eta^6\text{-arene})\text{RuCl}_2(\mu-L)_2\}^{2+}$ ($L =$ polypyridyl ligands, L_1 to L_15) (Chart 1.2) by cleavage of chloride bridges. In the case of polydentate nitrogen bases co-ordinates as a bidentate manner. Reactions with 1,10-phenanthroline (L_1) or with its 5-nitro or 5-amino derivatives to give quantitatively the cationic chloro complexes $\{(\eta^6\text{-arene})\text{Ru(NN)}\text{Cl}\}\text{Cl}$ containing the corresponding N,N-donor as chelating ligand. All these complexes $\{(\eta^6\text{-C}_6\text{Me}_6\text{Ru}(L_1)\text{Cl}\}$ have shown the catalytic property for the hydrogenation of acetophenone with formic acid in aqueous solution to give phenylethanol and carbon dioxide. Reactions with two equivalents of 5,6-diphenyl-3-(pyridine-2-yl)-1,2,4-triazine (L_2), 4,6-bis(2-pyridyl)pyridazine (L_3), 4,6-bis(2-pyridyl)4-phenylpyridazine (L_4), 4,6-bis(pyrazolyl)pyridazine (L_5) in the presence of KPF_6 to form the cationic mononuclear arene ruthenium complexes where as some of the polypyridyl ligands yielded both mono and dinuclear complexes based on their molar ratios, for example 2,2'-bipyridine (L_6), 3,5-bis(2-pyridyl)pyrazole (L_7), 2,3-bis(2-pyridyl)pyrazine (L_8), 2,4,6-tris(2-pyridyl)1,3,5-triazine (L_9), pyridine-2-carbaldehyde azine (L_10) etc. Interestingly few ligands yielded only dinuclear complexes upon reaction of arene ruthenium dimers, for example p-phenylene-
bis(picoline)-aldamine (L_{11}), p-biphenylene-bis(picoline)-aldamine (L_{12})^{47} and 3,6-bis(2-pyridyl)bithiazole (L_{13}), 3,6-bis(2-pyridyl)1,2,4,5-tetrazine(L_{14}) (Chart 1.2).^{44}

![Diagram of molecular structures](image)

Chart 1.2

Bruno et al reported^{48} a hexa-nuclear metal grid \([(\eta^6-p^3\text{PrC}_6\text{H}_4\text{Me})_6\text{Ru}_6(\mu_3-\text{tpt-}
\kappa\text{N})_2(\mu_2\text{O}_2\kappa\text{O})_3]^6+\) with the reaction of tpt ligand (figure 1.4) as well as a tetra nuclear arene ruthenium complexes with porphyrin ligand (figure 1.5).^{49,50}
1.4 $\eta^5$-Pentamethylcyclopentadienyl (Cp*) rhodium(III) and iridium(III) chemistry

The discovery of [(η$^5$-Cp*)MCl$_2$]$_2$ (M = Rh and Ir) (scheme 1.4) by Maitlis$^{51,52}$ has provided a relevant milestone on the development of organometallic chemistry and homogeneous catalysis for nearly four decades, resulting in major advances in the understanding of these areas. The η$^5$-pentamethylcyclopentadienyl group is an excellent protecting ligand towards rhodium and iridium, whilst substitution of the chloride ligands occurs very easily, with a marked tendency to form mononuclear complexes.

\[
\text{MCl}_3 \text{ nH}_2\text{O} + \text{Cp*} \rightarrow \text{M} = \text{Rh and Ir}
\]

1.4.1 Application of pentamethylcyclopentadienyl rhodium and iridium complexes

Ir(III) and Rh(III) metal centres are reactive and have the potential to catalyse a range of other transformations not reliant on oxidative addition. Recent work by Crabtree
et al. has utilised an Ir(III) hydride complex to catalyse the intramolecular hydroamination and hydroalkoxylation of alkynes.\textsuperscript{53} \([\text{Cp}^*\text{IrCl}_2]_2\) is effective as a catalyst for the hydroborylation of styryl sulfonamides,\textsuperscript{54} the N-alkylation of amines with alcohols\textsuperscript{55} and also the transfer hydrogenation of ketones\textsuperscript{56} and quinolines.\textsuperscript{57} Rh(III) complexes are known to be effective in catalysing carbon-carbon bond formation,\textsuperscript{58} and \([\text{Cp}^*\text{RhCl}_2]_2\) has been shown to effect transfer dehydrochlorination of aryl chlorides.\textsuperscript{59}

For example the complex \([(\text{Cp}^*)\text{RhCl}(\text{N-N})_t]^{+} (\text{N-N} = 2,2'-\text{bipyridine})\), was shown to occur as a crucial intermediate\textsuperscript{60} in hydride transfer catalysis schemes intended at \(\text{H}_2\) production\textsuperscript{60} or NADH regeneration (Scheme 1.5). Related compounds could be generated from photolysis of olefin-containing precursors.\textsuperscript{61}

Treatment of hydroquinone with \([\text{Cp}^*\text{M(solvent)}_3][\text{OTf}]_2\) (\(\text{M} = \text{Rh, Ir}\)) in acetone afforded the \(\pi\)-bonded complexes \([\{\text{Cp}^*\text{M}(\eta^5\text{-semiquinone})][\text{OTf}]_n\}) (\(\text{M} = \text{Rh, Ir}\))\textsuperscript{62}.

\[\begin{align*}
\text{Cp}^* &= \eta^5\text{-C}_5\text{Me}_5 \\
\text{Scheme 1.5}
\end{align*}\]

1.5 Rhodium and iridium polypyridyl compounds

The chemistry of rhodium(III) and iridium(III) is very similar to the chemistry of arene ruthenium(II) since all these metals are with isoelectronic (d\(^6\)) configuration. As is typical within the d\(^6\) configuration, many of the organometallic reactions studied with arene ruthenium(II) are often equally valid for \(\text{Cp}^*\) rhodium(III) and iridium(III). Pentamethylcyclopentadienyl (\(\text{Cp}^*\)) is ubiquitous as a ligand in organometallic complexes. Many complexes incorporating this ligand are important as active catalysts, largely due to the electron-rich nature of the \(\text{Cp}^*\) group and also the ability of \(\text{Cp}^*\) to
completely block one face of the complex, imparting steric bulk and structural rigidity. Rh(III) and Ir(III) complexes incorporating both the Cp* ligand and bidentate sp\(^2\)-nitrogen donor ligands have been synthesised previously.\(^{63-70}\) In particular, the complex [Cp*Ir(bipy)(H\(_2\)O)]SO\(_4\) (bipy = 2,2’-bipyridine) was found to be active as a catalyst for the hydration of phenylacetylene in water,\(^71\) and the complex [Cp*Rh(\(^{(i}Pr\)-pymox)]\(^{2+}\) (pymox = pyridyloxazoline) was found to promote the enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene.\(^66\)

The reactions of Cp* Rh and Ir complexes with N donor ligands with a series of bidentate ligands with sp\(^2\) N-donors such as bis(pyrazolyl)-methane (L\(_{16}\)), bis(1-methylimidazolyl)methane (L\(_{17}\)), bis(3,5-dimethylpyrazolyl)methane (L\(_{18}\)), bis(1-methylimidazolyl)ketone (L\(_{19}\)), bis(2,4,6-trimethylphenylimino)-acenapthene (L\(_{20}\)) (Chart 1.3) resulted a series of complexes of the formulations [Cp*MCl(N–N)][X] (M = Rh and Ir), where N–N (L\(_{16}-L_{21}\))\(^72\) (Chart 1.3).

![Chart 1.3](image)

1.6 Materials and physical measurements

1.6.1 Materials

All solvents were dried and distilled prior to use. The chemicals which were used in the present research were purchased from Aldrich, Fluka, Mercury and Rankem Companies and were used as received. The metal chlorides RuCl\(_3\), RhCl\(_3\) and IrCl\(_3\) were purchased from Arora Matthey Ltd. [(\(\eta^5\)-C\(_6\)H\(_6\))Ru(\(\mu\)-Cl)Cl]\(_2\), [(\(\eta^6\)-P-\(i\)PrC\(_6\)H\(_4\)Me)Ru(\(\mu\)-Cl)Cl]\(_2\), [(\(\eta^6\)-C\(_6\)Me\(_6\))Ru(\(\mu\)-Cl)Cl]\(_2\), [(\(\eta^5\)-C\(_6\)H\(_5\))Ru(\(\mu\)-Cl)Cl]\(_2\)\(^73-75\) [(Cp*)M(\(\mu\)-Cl)Cl]\(_2\) (M = Rh, Ir),\(^76-78\) [(Cp)Ru(PPh\(_3\))\(_2\)Cl]\(_2\),\(^82\) [(Cp*)Ru(PPh\(_3\))\(_2\)Cl] and [(\(\eta^5\)-C\(_6\)H\(_5\))Ru(PPh\(_3\))\(_2\)Cl]\(_2\)\(^78,80,81\) were prepared according to literature methods. The synthetic procedure for the ligands which
were used in the present research was mentioned on proceeding chapters and their structures are shown in Chart 1.4.

Chart 1.4: Ligands used in the present study: polypyridyl and polypyrazolyl bridging and terminal ligands.
1.6.2 Synthesis of the starting materials

1.6.2.1 Synthesis of \[\{(\eta^6-\text{p-cymene})\text{RuCl}_2\}_2\]

The \[\{(\eta^6-\text{p-cymene})\text{RuCl}_2\}_2\] was prepared according to well established synthetic procedure.\(^7\) A solution of hydrated ruthenium trichloride (approximating \(\text{RuCl}_3 3\text{H}_2\text{O}\), containing 38-39% Ru) (1 g, 3.85 mmol) in 80 ml ethanol is treated with 5 ml of \(\alpha\)-phellandrene and heated under reflux in a 150 ml round-bottomed flask for 4 hours. The solution is allowed to cool to room temperature, and the red-brown, microcrystalline product is filtered off. Additional product is obtained by evaporating the orange-yellow filtrate under reduced pressure to approximately half-volume and cooling over night to 4 °C. After drying in \textit{vacuo} the yield is 1.10 g (81%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.48\) (d, 2H, \(3J = 6.4\) Hz, Ar\(_{\text{p-cy}}\)), 5.34 (d, 2H, \(3J = 6.4\) Hz, Ar\(_{\text{p-cy}}\)), 2.95 (sept, 1H, \(3J = 6.2\) Hz, CH(CH\(_3\))\(_2\)), 2.15 (s, 3H, Ar\(_{\text{p-cy}}\)-Me), 1.28 (d, 6H, \(3J = 6.4\) Hz, CH(CH\(_3\))\(_2\)).

1.6.2.2 Synthesis of \[\{(\eta^6-\text{C}_{6}\text{H}_{6})\text{RuCl}_2\}_2\]

Preparation of \[\{(\eta^6-\text{C}_{6}\text{H}_{6})\text{RuCl}_2\}_2\] followed Bennett method.\(^7\) Hydrated \(\text{RuCl}_3\) (2 g) in 100 ml of ethanol was heated under reflux with 10 ml of cyclohexadiene (either 1,3- or 1,4-) for 4 hours. The brown precipitate was filtered off, washed with methanol, and dried in \textit{vacuo} (1.83g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.07\) (s, 6H, C\(_6\)H\(_6\))

1.6.2.3 Synthesis of \[\{(\eta^6-\text{C}_{6}\text{Me}_{6})\text{RuCl}_2\}_2\]\(^7\)

To the dimer \[\{(\eta^6-\text{p-cymene})\text{RuCl}_2\}_2\] (200 mg, 0.33 mmol) taken in sealed glass vial of 5 ml capacity, a three fold excess of hexamethylbenzene (0.98 mmol) was added and mixed properly. The reaction was carried out fixing the microwave at 170° C and a pressure of 5 bar. With the 200 W microwave system, this temperature was reached within a few minutes, and the reaction completed in 10 min. Excess hexamethylbenzene was recovered by washing with hexane through a silica gel column using hexane as eluent. The orange red band \[\{(\eta^6-\text{p-cymene})\text{RuCl}_2\}_2\] was collected by passing a mixture of methanol- acetone in 1:1 ratio. The solvent was removed on a rotary evaporator. The resulting solid was washed with hexane and diethylether and dried in vacuum. Yield (175 mg, 96%), \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.07\) (s, 18H, C\(_6\)Me\(_6\))
1.6.2.4 Synthesis of \( [(\eta^5-C_{p}^*)\text{RhCl}_2]_2 \) and \( [(\eta^5-C_{p}^*)\text{IrCl}_2]_2 \)

The \( [(\eta^5-C_{p}^*)\text{MCl}_2]_2 \) (M = Rh and Ir) was prepared according to well established synthetic procedure.\(^7^8\) A solution of hydrated metal trichloride (1 g) in 80 ml methanol is treated with 0.8 ml of pentamethylcylopentadiene and heated under reflux in a 100 ml round-bottomed flask for 48 hours. The solution is allowed to cool to room temperature, and the red-brown, microcrystalline product is filtered off. The crystalline product was filtered and washed with cold methanol, diethyl ether and after drying in \( \text{v}_{\text{acu}} \) the yield is 1.1 g (78%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.62 \) (s, 15H, C\(_3\)Me\(_3\))

1.6.2.5 Synthesis of \( [(\eta^5-C_{5}H_5)\text{Ru}(P\text{Ph}_3)_2\text{Cl}] \)

The compound hydrated ruthenium trichloride (1 g, 4.82 mmol) in dry ethanol (20 ml) was added rapidly to the refluxing solution of triphenylphosphine (5 g) in ethanol 100 ml, followed immediately afterward by a solution of freshly distilled cyclopentadiene (10 ml) in ethanol (20 ml). The mixture was then refluxed until the color change from dark brown to orange was completed (60 min to 90 min), and then cooled in a refrigerator overnight. The orange crystalline product was filtered, washed with cold ethanol, water, ethanol and petroleum ether and dried to give pure product (2.50 g, 86%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 4.52 \) (s, 5H, C\(_3\)H\(_5\)),

\(^{13}\)P \( \{^1\text{H}\} \) NMR (162 MHz, CDCl\(_3\)): \( \delta = 46 \)

1.6.2.6 Synthesis of \( [(\eta^5-C_{5}Me_5)\text{Ru}(P\text{Ph}_3)_2\text{Cl}] \)

The compound RuCl\(_3\) 3H\(_2\)O (1 g, 4.82 mmol) and C\(_5\)Me\(_5\) (131 ml, 9.64 mmol) were dissolved in ethanol (60 ml) and refluxed for 90 min after which a solution of PPh\(_3\) (5 g, 20 mmol) and NaOEt (92 mg of Na in 4 ml ethanol) in ethanol (40 ml) was added dropwise. The solution was then refluxed for 18 hours. The orange yellow precipitate was collected and washed with ethanol and hexane to give pure product (2.6 g, 70%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.62 \) (s, 55H, C\(_3\)Me\(_5\))

\(^{13}\)P \( \{^1\text{H}\} \) NMR (162 MHz, CDCl\(_3\)): \( \delta = 48 \)

1.6.3 Physical measurements

Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 FT-IR spectrophotometer in the 4000 - 400 cm\(^{-1}\). Elemental analyses of the complexes were performed on a Perkin-Elmer-2400 CHN/S analyzer. NMR spectra were recorded on
Bruker AMX-400 MHz FT-NMR spectrometer using TMS as the internal standard. Mass spectra were obtained from Waters ZQ 4000 mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV/Visible spectrophotometer.

1.7 Crystallographic data collection and structure analyses

Single crystal X-ray diffraction measurements were carried out on a Bruker Smart Apex CCD diffractometer. The crystals were mounted on a Stoe Image Plate Diffraction system equipped with a \( \phi \) circle goniometer, using Mo-K\( \alpha \) graphite monochromated radiation (\( \lambda = 0.71073 \, \text{Å} \)) with \( \phi \) range 0–200°. The structures were solved by direct methods using the program SHELXS–97.\(^2\) Refinement and all further calculations were carried out using SHELXL–97.\(^3\) The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on \( F^2 \). The structures were drawn with the softwares ORTEP\(^4\) and MERCURY.\(^5, 6\)

The crystal data for the representative complexes can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. The CCDC numbers of the crystal structures are mentioned in corresponding chapters with a heading under supplementary material.

References


General Introduction

Chapter 1


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Chapter 1