Abstract

Platinum metals complexes with different mono and multidentate ligands have aroused considerable interest because of their structural novelty, reactivity and catalytic activity. Homogeneous catalysis by platinum metals complexes has become a major synthetic tool in industrial processes. The potential of such catalytic reactions are due to the fact that most of these reactions are highly selective, low energy processes and show high rate of conversion. As the efficiency of the complexes is dictated primarily by coordination environment around the metal center, complexation of these metals by selected ligands is of great significance. Unsymmetrical phosphines functionalized with oxygen, sulfur or selenium donor ligands often show hemilabile behaviour depending on the metal atom and its environment, and in many cases they show efficient catalytic activities in organic transformations. Thus, proper design of metal complexes and their utilization as catalysts in industrially important reactions like production of pharmaceuticals, agrochemicals, flavours etc. have added a new dimension to inorganic chemistry.

Therefore, research work relating to the synthesis of new and novel Rh(I), Ir(I) and Ru(II) complexes with various functionalized phosphine and nitrogen donor ligands, and their catalytic activity to produce value added products has been undertaken in the context of current scenario of research and development. The main objectives of the present work are given below:
➢ To synthesize and characterize Rh(I), Ir(I) and Ru(II) complexes of symmetrical / unsymmetrical chelating functionalized phosphine and nitrogen donor ligands like P-P, P-X (X = O, S, Se) and N,O.

➢ To study the reactivity [OA reactions, kinetics] of the suitable metal complexes with the small molecules like CO, O₂, CH₃I, C₂H₅I, C₆H₅CH₂Cl etc.

➢ To study the hemilabile nature of different P-X (X = O, S) donor chelating ligands.

➢ To evaluate the catalytic efficiency of the synthesized complexes for carbonylation of methanol and transfer hydrogenation of aldehydes and ketones.

**Outline of the thesis**

The thesis has been divided into seven chapters with appropriate references at the end of each chapter.

**Chapter 1:**

In this introductory chapter, the review of literature of the chemistry of platinum metals complexes containing chelated and non-chelated P–O, P–S and P–Se donor ligands has been carried out. Prime attention has been given to the rhodium, iridium and ruthenium complexes of functionalized phosphine ligands (P–X), activation of small molecules (CO, H₂, CH₃I etc.) and catalytic applications like carbonylation and hydrogenation reaction. Finally, the aim and objectives of the thesis are outlined briefly.

**Chapter 2:**

This describes the synthesis of different starting rhodium(I), iridium(I) and ruthenium(II) complexes and the instrumental techniques adopted to characterize the different ligands and metal complexes. It also describes different analytical procedures
like estimation of rhodium and chlorine, general procedure of catalytic reactions such as carbonylation of methanol and transfer hydrogenation of aldehyde and ketones, kinetic studies of OA reactions etc.

Chapter 3:

In this chapter, the syntheses of the synthesis of a series of mono-, di-, tri- and tetradeutate phosphines functionalized with oxygen, sulfur and selenium donor ligands like Ph₂PC₅H₆-2-OCH₃, Ph₂PC₅H₆-2-CH₂OCH₃, xantphos(S), DPEphos(S), xantphos(O₂), DPEphos(O₂), CH₃C(CH₂P(X)Ph₂), P(X)(CH₂CH₂P(X)Ph₂)₃ (X = O, S, Se) etc. have been described. The characterizations of the synthesized ligands with spectroscopic techniques like FT-IR, ¹H, ¹³C, ³¹P and ⁷⁷Se NMR together with elemental analyses and mass spectrometric methods have also been highlighted. In addition, structural characterization by single crystal X-ray diffraction of a few synthesized ligands is embodied in this part.

Chapter 4:

This chapter contains synthesis and reactivity of rhodium carbonyl complexes of different mono and multidentate ligands and their activity in catalytic carbonylation of methanol. Depending on the type and nature of the ligands, this chapter is divided into four sections.

Section 4.1: This section discusses the synthesis of Rh(I) complexes of the type [RhCl(CO)(η²-P,O-L)] and [RhCl(CO)(η¹-P-L)₂] {L = Ph₂PC₅H₆-2-OCH₃ and Ph₂PC₅H₆-2-CH₂OCH₃} by the reaction of the dimer [RhCl(CO)₂]₂ with appropriate mol equivalents of the ligands (L). All the complexes are characterized by elemental
analyses, mass spectrometry, IR and multinuclear NMR ($^1$H, $^{31}$P and $^{13}$C) spectroscopy. The OA reactions of the complexes and kinetic studies with CH$_3$I have been described. The catalytic activities for carbonylation of methanol using the synthesized complexes are also demonstrated, which show higher TOF 689–1808 h$^{-1}$ than the well-known Monsanto’s catalytic species [RhI$_2$(CO)$_2$]$^-$ (TOF = ~ 464 – 1000 h$^{-1}$) under similar experimental conditions.

**Section 4.2:** This section describes the reaction of dimeric precursor [RhCl(CO)$_2$]$_2$ with two mol equivalents of the bidentate phosphine ligands L {L = xantphos and DPEphos} and their corresponding dioxide analogues L' {L' = xantphos(O$_2$) and DPEphos(O$_2$)} to afford mono- and dicarbonyl complexes of the type [RhCl(CO)(L)] and [RhCl(CO)$_2$(L')] respectively. The complexes are characterized by elemental analyses, IR and multinuclear NMR ($^1$H, $^{31}$P and $^{13}$C) spectroscopy. The effect of phosphorus and oxygen donor bidentate phosphines on the reactivity of Rh(I) complexes is described. The complexes undergo OA reactions with different electrophiles such as CH$_3$I, C$_2$H$_5$I and I$_2$ to yield Rh(III) complexes of the types [RhCl(COR)(I)L], [RhCl(CO)(COR)(I)L'] {R = -CH$_3$, -C$_2$H$_5$} and [RhCl(CO)$_2$L]. The catalytic activities of the complexes for carbonylation of methanol under different CO pressure are also highlighted.

**Section 4.3:** This section deals with the reaction of dimeric precursor [RhCl(CO)$_2$]$_2$ with two mol equivalents of chalcogen functionalized tridentate phosphines like P$_3$X$_3$, where X = O, S and Se, to afford complexes of the type [RhCl(CO)$_2$(P$_3$X$_3$)]. The complexes are characterized by elemental analyses, mass spectrometry, IR, $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy. The OA reactions of the
complexes with different electrophiles such as CH$_3$I, C$_2$H$_5$I and C$_6$H$_5$CH$_2$Cl, and the kinetic studies with CH$_3$I have been described. Catalytic carboxylation of methanol to produce acetic acid and its ester using the Rh(I) complexes of P$_3$X$_3$ is also evaluated and compared with the results generated by the well-known Monsanto’s catalytic species [Rh$_2$(CO)$_2$]$.^-$

Section 4.4: This section describes the reaction of [RhCl(CO)$_2$]$_2$ with different mol equivalents of tetradeutate ligands $P^3P_3$ and $P^3P_3X_4$ {where X = O, S and Se} to afford complexes of the type [Rh(CO)($P^3P_3$)]Cl and [Rh$_6$(CO)$_8$Cl$_4$(P$P^3P_3$)$_4$]. The characterization of the complexes by elemental analyses, mass spectrometry, IR and multinuclear NMR spectroscopy, and their reactivities with CH$_3$I are also discussed.

Chapter 5:

This chapter discusses the synthesis, reactivity and catalytic activity of Ir(I) carbonyl complexes containing phosphine and nitrogen donor ligands. Depending on the type of the ligands and reactivity, this chapter is divided into three sections.

Section 5.1: This section deals with the synthesis of electron rich Vaska type complexes viz. trans-[IrCl(CO)(2-Ph$_2$PC$_6$H$_4$COOMe)$_2$] and trans-[Ir(CO)Cl(2-Ph$_2$P-C$_6$H$_4$OMe)$_2$] by the reaction of in-situ generated dimeric precursor [IrCl(CO)$_2$]$_2$ with four mol equivalents of the ligands 2-Ph$_2$PC$_6$H$_4$COOMe and 2-Ph$_2$PC$_6$H$_4$OMe. Spectroscopic and crystallographic characterizations of the complexes are demonstrated which show interesting Ir$^-$-O secondary interactions to generate pseudo hexacoordinated complexes. The reactivity of the complexes with small molecules
like O$_2$, CH$_3$I and I$_2$ as well as kinetic studies is highlighted. The comparative studies of the rate of dioxygen addition to the synthesized Vaska type complexes and Vaska’s complex are also discussed with special reference to steric and electronic factors.

Section 5.2: This section describes the reaction of [IrCl(CO)$_2$]$_2$ with two mol equivalents of the pyridine-ester ligands (L) like methyl picolinate, ethyl picolinate, methyl nicotinate and ethyl nicotinate to afford tetra coordinated neutral complexes of the type [IrCl(CO)$_2$L]. Synthesized complexes are characterized by elemental analyses, IR, and multinuclear NMR spectroscopy and one of the complexes is structurally determined by single crystal X-ray diffraction. Finally, the structural diversities of Ir(I) carbonyl complexes of nitrogen versus phosphine donor ligands are drawn briefly.

Section 5.3: This section describes the catalytic activity relating to carbonylation of methanol to produce acetic acid and methyl acetate of a set of Ir(I) carbonyl complexes of mono- and bidentate phosphine donor ligands. The Ir(I) complexes show higher TOF compared to the simple iridium precursor [Ir(COE)$_2$Cl]$_2$. The recycling experiments using the recovered catalysts have also been highlighted.

Chapter 6:

This chapter contains synthesis, spectroscopic and structural characterization, and catalytic activity of ruthenium(II) carbonyl complexes containing mono-, bi- and trifunctionalized phosphine donor ligands. Depending on the type of the ligands, this chapter is divided into three sections.
Section 6.1: This section describes the reaction of P,P and P,S type bidentate ligands with [Ru(CO)₂Cl₂]ₙ to generate hexa-coordinated chelate complexes of the type [RuCl₂(CO)₂(P∩P)] and [RuCl₂(CO)₂(P∩S)], where P∩P = DPEphos, xantphos and P∩S = DPEphos(S) and xantphos(S). The spectroscopic as well as single crystal X-ray structural characterizations together with the catalytic activity towards transfer hydrogenation of aldehyde and ketones of the synthesized complexes have been discussed. The hemilabile behaviour of the complex [RuCl₂(CO)₂{DPEphos(S)}] in solution during catalytic reaction is also explained with experimental evidences.

Section 6.2: In this section, synthesis, spectroscopic as well as X-ray structural characterization of a mononuclear complex [RuCl₂(CO)₂{xantphos(O₂)}] has been described. Interesting intramolecular O·O interaction between one of the P=O groups and backbone O in the mononuclear unit and intermolecular non-covalent interactions of the complex in solid state are also highlighted.

Section 6.3: This section deals with the reaction of polymeric ruthenium(II) precursor, [RuCl₂(CO)₂]ₙ with [P₃X₃], X = O, S and Se, in 1:1 (metal : ligand) mol ratio to afford hexa coordinated complexes of the type [RuCl₂(CO)₂(η²-X·X·P₃X₃)]. Elemental analyses, mass spectrometry and spectroscopic characterization of the complexes have been discussed. The thermal stability of the complexes has also been studied.

Chapter 7:

This chapter contains the general comments and conclusions along with future scope of the research.