Chapter 1

Introduction
1. **Introduction**

1.1. **Overview**

Organometallic chemistry, which involves metal complexes containing direct metal-to-carbon bonds, has grown since the early 1950s at an almost exponential rate, mostly owing to the development of an impressive array of highly sophisticated apparatus of which in particular NMR and single-crystal X-ray equipments have been invaluable [1]. Theoretical studies of the bonding in metal compounds and of the course of reaction pathways have not only contributed to new knowledge, but also to the purposeful design of complexes and their use in stoichiometric and catalytic reactions.

Platinum metal complexes of unsymmetrical chelating ligands such as functionalized phosphines have aroused much interest in recent time because of their structural novelty, reactivity and catalytic applications, namely carbonylation [2–4], hydrogenation [2c,5,6] and hydroformylation [2c,7,8] reactions. Homogeneous catalysis by transition metal complexes has become a major synthetic tool in industrial processes [2–8]. The potential of such catalytic reactions is due to the fact that most of these reactions are highly selective, low energy processes and show high rate of conversion. Among the platinum metals, rhodium, iridium and ruthenium complexes have been given special attention in this thesis due to their versatile catalytic activity and unique character.

1.2. **Rhodium**

Rhodium is one of the rarest and expensive precious metals. It has a typical
electronic configuration \((\text{[Kr]}4d^{8}5s^{1})\) and exhibits mainly the principal oxidation states of +1 and +3. \(\text{RhCl}_3.\text{xH}_2\text{O}\) is a versatile starting material for the synthesis of different rhodium(I) complexes. One of the most famous rhodium(I) complexes is the Wilkinson’s catalyst, \([\text{RhCl(PPh}_3)_3]\) [9a]. Great varieties of rhodium complexes are prepared from \(\text{RhCl}_3.\text{xH}_2\text{O}\) and the methods for preparation of some selected starting rhodium complexes are shown in Scheme 1.1.

**Scheme 1.1.** Important preparative routes for starting rhodium complexes

The primary use of rhodium is in automobiles as a catalyst converter, which converts harmful emission like CO, unburned hydrocarbon (HC) and oxide of nitrogen (NO\(_x\)) from the engine into less harmful gases like CO\(_2\), N\(_2\) and H\(_2\)O [10]. Rhodium(I)-complexes play an important role as industrial homogeneous catalysts for the synthesis of value added products. A few important examples are: (i) Synthesis of L-DOPA (a drug for curing Parkinson’s disease) [11], (ii) Production of acetic acid by
Monsanto’s process [12,13] (iii) hydroformylation of alkene to synthesize highly selective linear to branch aldehydes [8,14], (iv) hydrosilylation crosslinking of silicone rubber [15] and many other organic transformations [16].

1.3. Iridium

Iridium is the most corrosion-resistant metal, even at temperatures as high as 2000 °C. The electronic configuration of iridium is \([Xe]4f^{14}5d^76s^2\), which exhibits different oxidation states ranging from -3 to +6 and the most stable oxidation states are +3 and +4 [5d]. Iridium forms a number of organometallic compounds used in industrial catalysis, and in research [5d]. Some organometallic iridium(I) compounds are notable enough to be named after their discoverers. Two important examples are:

(i) Vaska's complex, \([\text{IrCl(CO)(PPh}_3])_2\], which has the unusual property of binding to the dioxygen molecule, \(\text{O}_2\) [17], and (ii) Crabtree's catalyst, \([\text{Ir(COD)(Pcy}_3)(\text{Py})]\)^+PF_6^–, a homogeneous catalyst for hydrogenation reactions [18]. These compounds are both square planar, \(d^8\) complexes, with a total of 16 valence electrons, which accounts for their reactivity [19]. Although iridium complexes are less frequently used than their rhodium analogues, in some processes they may be more effective— the \(\text{Cativa}\) process for carbonylation of methanol being an excellent example in the arena of bulk chemistry [3a,b]. Perhaps the most important catalytic applications of iridium complexes, however, are in the manufacture of fine chemicals, most notably in areas of chemoselective and enantioselective hydrogenation [5d]. Great varieties of iridium complexes are prepared from \(\text{IrCl}_3\cdot x\text{H}_2\text{O}\) and the methods of preparation of a few selected starting iridium complexes are shown in Scheme 1.2.
1.4. Ruthenium

Ruthenium is a rare transition metal belonging to the platinum group of the periodic table. It has an electronic configuration 
\[\text{[Kr]}4d^75s^1\] and can show a much wider scope of oxidation states e.g. -2, 0, +2, +3, +4, +5, +6 and +8 valence states in 
[\text{[Ru(CO)]}_2^-], [\text{[Ru(CO)]}_5], [\text{[Ru(H}_2\text{O)}_6]^{2+}, [\text{[Ru(NH}_3)_6]^{3+}, [\text{[RuO}_2]], K[\text{[RuF}_6]], [\text{[RuF}_6]] and 
[\text{[RuO}_4]^{-2}] respectively and various coordination geometries in each electronic configurations [21]. For instance, in the principal oxidation states of +2 and +3, ruthenium complexes normally prefer trigonal-bipyramidal and octahedral structures respectively. Due to this variable oxidation states and higher economy of ruthenium compared to the other platinum metals, ruthenium catalyzed processes have become
one of the most important and interesting methodologies in organic synthesis [21b,22–24]. In particular, ruthenium complexes catalyzed hydrogenation reaction is one of the most appealing routes for the reduction of various organic substrates [23]. The development of Noyori’s transfer hydrogenation catalysts has attracted the attention of the researchers towards the use of ruthenium catalysts in asymmetric hydrogenation reactions [21b,22a,24c,25]. The ruthenium complexes also exhibit a variety of suitable characteristics like high Lewis acidity, high electron transfer ability, low redox potentials, stabilities of different reactive species etc. RuCl₃·xH₂O can be utilized for the synthesis of ruthenium complexes of different ligands and the methods for preparation of some selected starting ruthenium complexes [25d] are shown in Scheme 1.3.

1.5. Carbon monoxide (CO) ligand

Carbon monoxide is the most common π-acceptor ligand in organometallic and coordination chemistry. It plays a key role in many catalytic processes. Over the last few decades, transition metal carbonyl complexes have become one of the most important families of compounds in organometallic chemistry [27]. Rhodium and iridium carbonyls are very active catalysts for carbonylation and hydroformylation reactions to synthesize industrially important products [2,3,8,28]. Some prominent examples are: (i) Rhodium catalyzed Monsanto’s process [12,13] for producing acetic acid from methanol, (ii) A recent industrial catalytic process called ‘Cativa’ [3] where [IrI₂(CO)₄]⁺ species with ruthenium-complex activator are used for carbonylation of
methanol with high efficiency and (iii) Hydroformylation of alkenes to synthesize highly selective linear to branch aldehydes [8,14].

Scheme 1.3. Some important preparative routes for ruthenium complexes [25d].

1.6. Functionalized phosphine

Tertiary phosphines functionalized with chalcogen donors like oxygen [29], sulfur [30] and selenium [31] containing ‘Soft’ phosphorus and ‘Hard’ oxygen donors or ‘Soft’ phosphorus and relatively less ‘Softer’ sulfur and selenium donor ligands with distinctly different π-acceptor strength [5a] form a variety of metal complexes
due to their different bonding abilities. Oxygen being a ‘Hard’ donor is capable of stabilizing metal ions in higher oxidation states which can be ascribed due to the absence of dπ-back bonding. On the other hand, ‘Soft’ phosphorus donors stabilize metal ion in low oxidation state by dπ–σ* back bonding. The metal-oxygen bond is weak and may dissociate reversibly to generate a vacant site for substrate binding and such ligands are called ‘Hemilabile’. The M–S/Se bonds are comparatively labile than the M–P bonds in the chelated complexes of P–S and P–Se donors ligands and thus may permit facile generation of a ‘Vacant site’ at the metal centre [5a,32] and may show interesting dynamic stereo-chemistry. Creation of such vacant coordination site through a reversible ‘Opening and Closing’ mechanism [32b] is useful for coordination and activation of the small molecules for further reaction with other organic substrates (Scheme 1.4).

\[
\text{M = Metal centre, } L_n = \text{Ligand, } X = \text{Inert group, } \ Y = \text{Labile group, } S = \text{Solvent,}
\]

**Scheme 1.4.** Ring “Opening and Closing” mechanism (Hemilabile)

A thermodynamically stable metal complex will have the substitutionally inert ligand group (X) binding to soft metals if X is a soft base, such as the case with phosphorus based hemilabile ligands, or to hard metals if X is a hard base such as oxygen or fluorine. These ligands were first described in a kinetic context as ‘Hemilabile ligands’ in 1979 by Jeffrey and Rauchfuss [32c].
1.7. Rhodium, iridium and ruthenium complexes of functionalized phosphine: A brief summary of the prior art.

Platinum metals particularly rhodium, iridium and ruthenium form a wide variety of complexes with functionalized phosphine ligands. A brief summary of different potential metal complexes are highlighted below:

1.7.1. Complexes of mono- and bidentate phosphines

A large number of coordination metal complexes of the first row transition metals [33], lanthanides [34] and actinides [35] with phosphine-chalcogenide ligands have been reported. However, the platinum metals like rhodium, iridium and ruthenium complexes have got less attention. A few interesting neutral rhodium(I) complexes of the type [Rh(COD)ClL] (L = Me₃PS, Me₂PhPS, Me₂PhPSe, Me₃AsS [36]), [RhCl(CO)₂(Cy₃PO)] (Cy = C₆H₁₁) [37] and [RhCl(CO)₂Ph₃PX] (X = O, S, Se) [38], and cationic complexes of the type [Rh(COD)(OER₃)₂]ClO₄ and [Rh(CO)₂-(OER₃)₂]ClO₄ (E = P, As; R = Ph, p-MeC₆H₄, p–MeOC₆H₄) [39] have been reported. There are also some reports on the rhodium(III) phosphineoxide complexes such as [RhCl(ylide)₂(OPR₃)] [40], [Rh(dimethylglyoximate)₂(OPPh₃)] [41] etc. Reports on the iridium complexes of chalcogen functionalized phosphines are limited except a series of Vaska type complexes, [IrX(CO)L₂], where X = Cl, Br, I and L = substituted PPh₃ [42]. The interesting monodentate ruthenium complexes reported so far are [RuCl₂(DMSO)₃(PPh₃O)] [43] and [RuCl₂(CO)₂(Ph₃PX)₃], (X = O, S, Se) [44].

During last two decades, increasing attention has been focused on the complex chemistry of hemilabile ligands, particularly, bidentate tertiary phosphines
functionalized with oxygen [5b,32a,45], sulfur [46,47] and selenium [48] donors. Reports on catalytic reactions of complexes containing sulfur or selenium donor are scanty because of metal poisoning by sulfur atom [49a] and deseleniumation of selenide under the reaction condition [49b]. However, a few metal complexes containing P–S / P–Se ligands have been reported to exhibit efficient catalytic activity in potential organic synthesis [4e,50]. A few interesting metal complexes of unsymmetrical chalcogen functionalized phosphines have been discussed with special emphasis on bidentate phosphines.

There are different types of hemilabile P–O donor ligands such as ester-phosphine [51], ether-phosphine [52], keto-phosphine [53], phosphine-acids [54], diphosphine-monoxide [55] etc. An outstanding feature of these ligands is their capability of coordinating to the metal centre either through a monodentate ($\eta^1$-P) or bidentate ($\eta^2$-P,O) coordinated fashion depending upon the metal and its environment.

The complexes [RhCl(CO)($\eta^2$-P,O-BPMO)] (BPMO = dppmO, dppeO, dpppO, and dppbO) [56a] and the iodo dppmO analogue [56b] are prepared by reacting [RhX(CO)$_2$]$_2$ (X = Cl, I) with corresponding BPMOs (Eqn. 1). The five-membered complex [RhCl(CO)($\eta^2$-P,O-Ph$_2$PCH$_2$P(O)Ph$_2$)] does not react with CO under low pressure (1 atm.), however, on increasing the pressure to 3 atm., a trace amount of dicarbonyl complex $cis$-[RhCl(CO)$_2$($\eta^1$–P-Ph$_2$PCH$_2$P(O)Ph$_2$)] is formed [56c]. On the other hand, the six-membered complex [Rh(CO)Cl($\eta^2$-P,O-Ph$_2$PCH$_2$-CH$_2$P(O)Ph$_2$)] can reversibly be cleaved by CO even at low pressure (1–3 bar) to give $cis$-[RhCl(CO)$_2$($\eta^1$–P-Ph$_2$PCH$_2$P(O)Ph$_2$)] (Scheme 1.5).
Scheme 1.5. ‘Hemilabile’ behaviour of P,O donor ligand.

Two complexes of the types $[\text{RhCl(CO)(2-Ph}_2\text{PC}_6\text{H}_4\text{COOMe})] \ (\eta^2-P,O$ chelate) and trans-$[\text{RhCl(CO)(2-Ph}_2\text{PC}_6\text{H}_4\text{COOMe})_2] \ (\eta^1-P$ coordinated) are reported [4a]. The X-ray structure (Figure 1.1) of the latter complex indicates the presence of ‘Secondary’ Rh–O interactions with the ester groups of the phosphines, which exhibits $\nu$(CO) band at 1949 cm$^{-1}$ indicating the lowest value so far reported of such complexes.

P,S ligands show an interesting feature as $[\text{RhCl(CO)}_2]_2$ reacts with $\text{Ph}_2\text{PCH}_2\text{SCH}_3$ to produce a binuclear complex $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{Ph}_2\text{PCH}_2\text{SCH}_3)_2]$, while with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SCH}_3$ it yields a mononuclear complex $[\text{RhCl(CO)}(\text{Ph}_2\text{P}-\text{CH}_2\text{CH}_2\text{SCH}_3)]$ (Scheme 1.6) [57a].
Figure 1.1. X-ray structure of *trans*-\([\text{RhCl(CO)}(2\text{-Ph}_2\text{PC}_6\text{H}_4\text{COOCH}_3)_2]\) [Ref. 4a]

Scheme 1.6. Mono and binuclear rhodium carbonyl complexes of P,S donor ligands

Unsymmetrical phosphine–phosphine monoselenide ligands react with \([\text{RhCl(CO)}_2]\) to form chelate \([\text{RhCl(CO)}(\eta^2\text{-P,Se}-\text{Ph}_2\text{PCH}_2\text{P(Se)Ph}_2)]\), \([\text{RhCl(CO)}-(\eta^2\text{-P,Se}-\text{Ph}_2\text{PN(CH}_3\text{)P(Se)Ph}_2)]\) [4d] and non-chelate \([\text{RhCl(CO)}_2(\eta^1\text{-P}-\text{Ph}_2\text{P-(CH}_2)_n\text{P(Se)Ph}_2)]\) \(n = 2–4\) complexes depending on the nature of the ligands [4e].
The molecular structure of [RhCl(CO)(η²-P,Se-Ph₂PN(CH₃)P(Se)Ph₂)] (Figure 1.2) shows a stable five-member heterocyclic (Rh, P, N, P and Se) ring.

**Figure 1.2.** X-ray structure of [RhCl(CO){η²-P,Se-Ph₂PN(CH₃)P(Se)Ph₂}] [Ref. 4d].

In addition to the several rhodium carbonyl complexes of unsymmetrical phosphine-phosphine chalcogenides, the complexes of symmetrical phosphine-phosphine chalcogenides are also reported [57b]. The preparation of rhodium carbonyl complex [Rh(CO)₂(dppmS₂)][ClO₄], where dppmS₂ = Ph₂P(S)CH₂P(S)Ph₂ is reported [57b] and the molecular structure of which was established by single crystal X-ray diffraction studies.

Some interesting complexes [Rh(CO)(PPh₃){η²-P, O-Ph₂PNP(O)Ph₂}], [Rh(CO)₂{η²-Se,Se'-Ph₂P(Se)NP(Se)Ph₂}] and [Rh(CO)(PPh₃){η²-Se,Se'-Ph₂P(Se)-NP(Se)Ph₂}], are synthesized by stepwise reactions of CO and PPh₃ with [Rh(COD){η²-P, O-Ph₂PNP(O)Ph₂}] and [Rh(COD){η²-Se,Se'-Ph₂P(Se)NP(Se)Ph₂}] respectively [57c]. The structure of the complex [Rh(CO)(PPh₃){η²-Se,Se'-Ph₂P(Se)NP(Se)Ph₂}] (Figure 1.3) exhibits a slightly distorted boat ring conformation.
Figure 1.3. The structure of [Rh(CO)(PPh₃)(ƞ²-Se,Se-){Ph₂P(Se)₂N}] [Ref. 57c].

Iridium also forms interesting complexes by the reaction of [IrL₂]Cl (L = Ph₂PCH₂CH₂PPh₂) with S₈ or Se₈ to yield [IrS₂L₂]Cl or [IrSe₂L₂]Cl, respectively; where S₂ and Se₂ act as bidentate ligands [58a].

The neutral complex [IrCl(COD)(ƞ¹⁻P-L)] (I) (L = dicyclohexyl(2-methoxy-ethyl)phosphine), obtained from the reaction of [Ir(μ-Cl)(COD)]₂ with L, reacts with AgBF₄ to undergo Cl⁻ abstraction and subsequent occupation by the ether O atom at the empty coordination site to produce cationic complex, [Ir(COD)(ƞ²-P,O-L)]Cl (II) In the presence of H₂ and L, the reactive Ir–O bond in II is cleaved with formation of cis-[H₂Ir(COD)L₂] (III) (Figure 1.4) [58b].

A few more interesting iridium complexes are obtained by the reaction of trans-[IrI(CO)(PEt₃)₂] with Y(SiH₃)₂ (Y = O, S, Se) in benzene to give [IrI(CO)H-(PEt₃)₂(SiH₂YSiH₃)] or [IrI(CO)H(PEt₃)₂(SiH₂)]₂Y, although when Y = O the formation of the former species is difficult to detect. The reaction of the complexes with P(SiH₃)₃ leads to the formation of IrI(CO)H(PEt₃)₂[SiH₂P(SiH₃)₂], [IrI(CO)H(PEt₃)₂(SiH₂)]₂PSiH₃, or [IrI(CO)H(PEt₃)₂(SiH₂)]₃P, depending on the proportions of the reactants used [58c].
Figure 1.4. Synthesis of different neutral and anionic iridium complexes of P,O donor ligand.

Ruthenium forms various types of complexes containing chalcogen functionalized phosphines as coordinating ligands. The polymeric complex [RuCl₂(CO)₂]ₙ reacts with Ph₃PX; X = O, S and Se in an appropriate Ru : Ligand mole ratio to yield five- and six-coordinated complexes of the types [RuCl₂(CO)₂(Ph₃PX)] and [RuCl₂(CO)₂(Ph₃PX)₂] respectively (Scheme 1.7) [44]. The ν(PX) bands of the complexes show significantly lower wavenumber than the corresponding free ligands indicating the formation of Ru–X bonds.

The reactions of [η⁶-C₆Me₆]RuCl₂]₂ and [(η⁵-C₅Me₅)RhCl₂]₂ with the ligands L = Ph₂PCH₃PPh₂ or Ph₂PCH₃P(Se)Ph₂ in benzene yield neutral complexes [(ring)RuCl₂(η¹-L)], [ring = (η⁶-C₆Me₆) or (η⁵-C₅Me₅)] [59]. However, cationic complexes of the type [(ring)RuCl(η²-L)]ClO₄ can be prepared using acetone as solvent in the presence of NaClO₄ [59].
Scheme 1.7. The reactions between $[\text{RuCl}_2(\text{CO})_2]_n$ and $\text{Ph}_3\text{PX}$ ($X = \text{O, S, Se}$)

Interesting complex is formed by the reaction of diphosphine, oxygen-functionalized diphosphine ligands and RuCl$_3$ in the presence of formaldehyde (Figure 1.5) [60], where the Ru–P bond trans- to oxygen is considerably shorter (222 pm) than the other two Ru–P bonds. The complex $[\text{RuCl}_2(\text{P∩O})(\text{P~O})_2]$, formed by the reaction between $[\text{RuCl}_2(\text{PPh}_3)_2]$ and P,O ligands, shows fluxional behaviour (Scheme 1.8) [61].

Figure 1.5. Ruthenium complexes of P,P and P,O donor ligands [Ref. 60]

The bisphosphine monoxides ($R$)- and ($S$)-BINAPO(O), prepared by the monooxidation of ($R$)- and ($S$)-BINAP respectively, form $[(p$-cymene$)\text{RuCl}[\eta^2-P,O$-BINAPO(O)$)]\text{Cl}$ and $[(p$-cymene$)\text{Ru}[\eta^2-P,O$-BINAPO(O)$)](\text{SbF}_6)_2$ complexes [62]. The BINAPO(O) ligand binds diastereo selectively, and form a single thermo-
dynamically stable diastereomer of the two possible isomers. The compound \([(p\text{-cymene})Ru(\eta^2-P,O-BINA(O))]\)(SbF\textsubscript{6})\textsubscript{2} is an efficient catalyst for the Diels-Alder reaction of methacrolein and cyclopentadiene in moderate ee.

**Scheme 1.8.** Fluxional behaviour of trans-, cis-, cis- [RuCl\textsubscript{2}(P\cap O)(P\sim O)\textsubscript{2}]

The hexa-coordinated chelate complex cis-[RuX\textsubscript{2}(CO)\textsubscript{2}(P\cap S)] \{P\cap S= \eta^2-P,S-coordinated, X = Cl, I\} and penta-coordinated non-chelate complexes cis-[RuCl\textsubscript{2}-(CO)\textsubscript{2}(P\sim S)] \{P\sim S = \eta^1-P-coordinated\} are synthesized [63a,b] by the reaction of [RuX\textsubscript{2}(CO)\textsubscript{2}]\textsubscript{n} with equimolar quantity of the ligands Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}P(S)Ph\textsubscript{2} (n = 1–4) at room temperature (Scheme 1.9, 1.10). The bidentate nature of the ligand Ph\textsubscript{2}PCH\textsubscript{2}P(S)Ph\textsubscript{2} in the complex leads to the formation of five-member chelate ring which confers extra stability to the complex. While, the reaction with 1:2 (Ru:L) mol ratio affords the hexa-coordinated non chelate complexes cis-[RuX\textsubscript{2}(CO)\textsubscript{2}(P\sim S)\textsubscript{2}] irrespective of the ligands.

Scheme 1.10. Synthesis of chloro carbonyl ruthenium(II) complexes of P,S ligands.
Neutral and cationic half-sandwich complexes of ruthenium, rhodium and iridium with chiral [(S)-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethyl]di-2-butyl phosphine selenide (L) are reported [64]. The ligand L is the first example of a chiral bisphosphine monoselenide prepared by direct monoselenation of a commercially available chiral bisphosphine.

1.7.2. Complexes of poly-phosphines

Polyphosphines as ligands show several advantages like (i) excellent bonding ability to metal, (ii) create high electron density at the metal centre (high nucleophilicity), (iii) formation of stable metal-complexes, (iv) stabilize different oxidation states of metals, (v) provide structural and bonding information due to the metal-phosphorus and phosphorus-phosphorus coupling constants. Metal complexes of such ligands are thermodynamically more stable than monophosphine analogues.

Tripod, HC(PPh₂)₃ with least steric constraints forms small rhodium cluster having metal-metal bond (Figure 1.6) [65a].

Figure 1.6. Rhodium complex of HC(PPh₂)₃ containing Rh–Rh bond.

In metal-tripod [tripod: MeC(CH₂PPh₂)₃] complex based catalytic reactions like hydroformylation, one of the metal-ligand bonds dissociate to create vacant site
for substrate binding (Figure 1.7) [65b].

![Figure 1.7. Reversible dissociation of Rh–P bond [Ref. 65b]](image)

Though a large number of rhodium complexes of polyphosphine ligands have been reported [65], there are only a few reports of rhodium complexes containing chalcogen functionalized polyphosphine ligands (P–X). The cationic complex [Rh(COD){η³–P,S,S-(CH(PPh₂)(P(S)Ph₂)₂)}] is prepared as fluoroborate salts by the reaction of the ligand CH(PPh₂)(P(S)Ph₂)₂ with chlorobridged complex [Rh₂Cl₂(COD)₂] under mild conditions in presence of NaBF₄ [66a]. The structure of the complex is assigned by ³¹P NMR spectroscopic studies indicating the formation of tripodal η³–P,S,S coordinated ligand.

The conventional oxidation of triphos with H₂O₂ is nonselective, but the ligand can be mono-oxidized selectively [66b] in the form of its η²–P,P-triphos metal complex (Eqn. 2). The dicarbonyl rhodium complex that is originally formed loses a molecule of CO upon bubbling argon through its solution.

The cationic complexes [(arene)RuCl{η²–L}]A are synthesized by the reaction between triphosphine CH(PPh₂)₃ or its mono / bichalcogenide derivatives with suitable η⁶-arene-Ru(II) species, where, arene = C₆Me₆, p-MeC₆H₄/Pr; L = CH(PPh₂)₃, CH(PPh₂)₂{P(E)Ph₂} (E = S, Se), CH(PPh₂){P(S)Ph₂}₂ and A = PF₆⁻, BF₄⁻ [67a]. An
interesting complex [(arene)Ru{$\eta^3$-S,S-S\{-P(S)Ph$_2$\}_3C}]BF$_4$; is prepared by deprotonation of the coordinated ligand [{P(S)Ph$_2$}_3CH], where the ligand is coordinated to the ruthenium centre by tridentate $\eta^3$-S mode (Figure 1.8).

Figure 1.8. Synthesis of [(arene)Ru{$\eta^3$-S,S-S\{-P(S)Ph$_2$\}_3C}]BF$_4$ [arene = $p$-MeC$_6$H$_4$Pr] [Ref. 67a]

The complex [RuCl$_2$(CO)$_2]$$_n$ reacts with one mol equivalent of triphos to afford [RuCl$_2$(CO)$_2$({$\eta^2$-P$_2$-triphos})] (Scheme 1.11). However, the complex on setting aside for about two weeks in DCM solution undergoes decarbonylation to yield a tridentate monocarbonyl complex [RuCl$_2$(CO)($\eta^3$-P$_3$-triphos)] (Scheme 1.12) [67b].
1.8. Activation of small molecules

One important general problem in organometallic chemistry is the binding and activation of the small molecules of nature. Thus, it is an interesting area to carry out research to activate the less reactive molecules like CO, CO₂, O₂, H₂, alkane etc. with a goal to convert these relatively common compounds into useful organic chemicals.
For example, natural gas (methane) is wasted by being flared off in certain oil fields, for lack of an economic method of transport. A method of turning this methane into easily transportable liquids, such as methanol or higher alkanes, would be very valuable. Therefore, much fundamental chemistry research has therefore been aimed to address couple of questions such as:

- How do metal ions coordinate to and modulate the reactivity of small, often rather inert molecules?
- What is the basis for the selectivity of natural and synthetic metal-containing systems for specific small-molecule substrates?
- Can one use knowledge of metal/small-molecule chemistry for the development of new catalytic processes useful in the laboratory and / or in industry?

The activation of small molecules such as CO, CH$_3$I, H$_2$, O$_2$, etc., by metal complexes [69] is important and interesting due to their catalytic reactions; for instance, OA of CH$_3$I is an important step in the rhodium-catalyzed Monsanto [12,13] and iridium-based Cativa [3a,b] process for acetic acid production. Activation of molecular oxygen by metal complexes has attracted great interest in recent years for producing model oxidation catalysts for chemical processes in terms of cost, atom economy and the potential for limited by-products [69e, 70]. Similarly, the activation of dihydrogen by metal centers is a fundamental step in nearly all metal catalytic hydrogenation reactions [71].
1.9. Catalytic applications

Rhodium, iridium and ruthenium-catalyzed reactions have made a significant contribution to the recent growth of organic synthesis particularly in carbonylation, hydrogenation, hydroformylation, carbon-carbon bond formation etc. [3,5,11–14,16, 21–23]. In this section, two potential catalytic reactions, namely, carbonylation and hydrogenation have been highlighted.

1.9.1. General aspects of carbonylation catalysis

Acetic acid is an important industrial commodity chemical, with a worldwide demand of about 7–8 million tons per year. One of the largest and fastest growing uses of acetic acid is in the production of vinyl acetate, an important industrial monomer. The major part of the remaining acetic acid production is used to manufacture other acetate esters. Cellulose acetate is used extensively in the preparation of fibers and photographic films. Inorganic acetates are used in the textile, leather and paint industries. Acetic acid is also used in the manufacture of chloroacetic acid and terephthalic acid [72].

The synthesis process of acetic acid has changed over the years with changing technologies and several problems are associated due to their lack of selectivity and formation of many byproducts. Novel acetic acid processes and catalysts have been introduced, commercialized and improved continuously since the 1950s. The objective of the development of new acetic acid processes has been to reduce raw material consumption, energy requirements and investment costs. Significant cost advantages resulted from the use of carbon monoxide (derived from
natural gas) and of low-priced methanol (from synthesis gas) as feedstock. A few carbonylation processes and their recent advances are highlighted below:

1.9.1.1. The cobalt-based BASF process

The first methanol-to-acetic acid carbonylation process was commercialized in 1960 by BASF. It used an iodide-promoted cobalt catalyst and required high pressures (600 atm) as well as temperatures (230 °C), but gave acetic acid in ca. 90% selectivity [73]. The process generates a few by-products like methane, acetaldehyde, ethanol and ethers. The proposed mechanism of the process (Scheme 1.13) indicated that [HCo(CO)₄] is the active catalytic species to propagate the cycle. However, the postulated intermediates are not well characterized [73].

![Scheme 1.13. BASF catalytic cycle for the synthesis of acetic acid from methanol.](image)

It is interesting to note that slightly lower CO pressures are possible in the presence of Ru, Ir, Pd, Pt, or Cu salts as activators [74]. Cobalt catalysts can also be used for the carbonylation of higher alcohols, such as benzyl alcohol [75].
1.9.1.2. Nickel-based processes

Nickel carbonyl, as well as a variety of nickel compounds, is also catalytically active for the carbonylation of methanol in the presence of iodine. \( \text{Ni(CO)}_4 \) is formed from \( \text{NiI}_2 \) according to Eq. 3.

\[
\text{NiI}_2 + \text{H}_2\text{O} + 5\text{CO} \rightarrow \text{Ni(CO)}_4 + 2\text{HI} + \text{CO}_2 \quad \text{[Eq. 3]}
\]

The hydrogen iodide formed in Eq. 3 is used to transform the alcohol into an alkyl halide, which adds oxidatively to nickel, as described in Scheme 1.14 [76].

![Scheme 1.14](image)

**Scheme 1.14.** Catalytic cycle of the nickel-catalyzed methanol carbonylation.

Nickel catalysts usually operate under high pressures and temperatures [77], but with high methyl iodide concentrations, carbonylation occurs readily under milder conditions [78]. Molar ratios of \( \text{CH}_3\text{I}:\text{CH}_3\text{OH} \) at least 1:10, pressures as low as 35 bar can be applied at 150 °C, using \( \text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O} \) and \( \text{Ph}_4\text{Sn} \) as catalyst systems [79]. Although nickel systems can approach the reaction rates and selectivities of rhodium based catalytic systems, and nickel is much cheaper than rhodium, commercialization
of these systems has not been achieved to date, which may be due to the very toxic and volatile nature of the Ni(CO)$_4$ compound.

1.9.1.3. The rhodium-based Monsanto process

The Monsanto acetic acid process is commercially an important process since it produces over 50% of the world’s annual acetic acid demand, i.e. 7 million metric tons [80]. The process involves the homogeneous catalysis in the carbonylation of ethanol to yield acetic acid (Scheme 1.15).

![Scheme 1.15. Catalytic cycle of the rhodium-catalyzed methanol carbonylation](image)

Furthermore, the effect of the rhodium metal centre on the catalytic system is very high, since the metal centre facilitates both the OA and reductive elimination steps. The key reaction in the Monsanto process is the facial OA of methyl iodide, (step A), to the square planar rhodium(I) metal centre to form the octahedral
rhodium(III) species. Carbon monoxide insertion (step B) into the cis- CH$_3$–Rh bond yields a five-coordinated acyl intermediate, which undergoes addition of carbon monoxide (step C), reductive elimination of the acetyl iodide (step D) to yield the original rhodium(I) complex. Hydrolysis of the acetyl iodide by water in the aqueous-methanol feed gives acetic acid and HI, the latter reacts with methanol to regenerate methyl iodide and the cycle repeats itself.

The mechanism presented, including all intermediates, was resolved after extensive research [81] into the area and as recently as 1991 by Maitlis et al. [82], the existence of the intermediate (after step A) was confirmed in low concentrations utilizing FT-IR and FT-NMR spectroscopy.

1.9.1.4. Heterogenized rhodium catalysts

An important additional requirement for all homogeneous processes is that the dissolved catalyst must be separated from the liquid product and recycled to the reactor without significant catalyst loss [83]. In order to overcome the need for a separation catalyst recycle step, the active rhodium complex was made heterogeneous by using different support [80a,84]. Although the activity of these catalysts in the liquid phase was comparable to Monsanto’s homogeneous catalyst, there were problems with rhodium metal leaching from the support and the decomposition of the support during operation at elevated temperature. Such problem was overcome by Chiyoda by introducing a novel catalytic system containing pyridine resins where the catalysts exhibited high activity, long catalyst life, and no significant rhodium loss [85]. Based on this heterogeneous rhodium catalyst, Chiyoda and UOP (Universal Oil
Products) have jointly developed an improved methanol carbonylation process, called ‘Acetica process’, for the production of acetic acid. Until the recent development of a commercial heterogeneous rhodium catalyst system by Chiyoda, no successful demonstration of such a catalyst had been known [80a]. The heterogeneous catalyst commercialized for the ‘Acetica process’ consists of rhodium complexes on a novel polyvinyl pyridine resin [86] which is tolerant of elevated temperatures and pressures.

Very recently, Haynes et al. reported an alternative strategy for catalyst immobilization, using ion-pair interactions between ionic catalyst complexes and polymeric ion exchange resins [83]. These results demonstrated that the same sequence of organometallic reactions occur for the polymer-supported rhodium catalyst as already established for the homogeneous system.

1.9.1.5. The iridium-based Cativa process:

In 1996, BP chemicals introduced a new carbonylation process called ‘Cativa’ to produce acetic acid using iridium/iodide based catalyst, in combination with a promoter metal such as ruthenium [3,87]. This catalytic system has high rates at low water concentrations and exhibits high stability which allows for a wide range of process conditions. The Cativa catalytic process is shown in Scheme 1.16.

The OA of CH$_3$I to the activated iridium complex is faster than for similar rhodium complexes. The equilibrium of this OA favors the Ir(III) state. Therefore the OA is not the rate-determining step of the Cativa process. Instead the migratory insertion of the methyl group to the co-ordinated CO has been found to be the slow rate-determining step. The metal-to-carbon σ-bonds of third row metals are stronger, more localized and more covalent than those in second-row metal complexes. A larger
amount of iridium is required to achieve an activity comparable to the rhodium catalyst based processes, however the catalyst system is able to operate at lower water levels (less than 8 wt.%). Hence, there is lower side-product formation and improved carbon monoxide efficiency is achieved while the steam consumption is also decreased.

Scheme 1.16. Iridium based Cativa process for the synthesis of acetic acid from methanol.

The high stability of the iridium catalyst is one of its major advantages. It is robust at low water concentrations (0.5 wt.%), which is significant and ideal for the optimization of the methanol carbonylation process. The catalyst remains stable under a wide range of experimental conditions that would cause similar rhodium analogues to decompose completely to an inactive and largely unrecoverable rhodium salt. Iridium is much more soluble than rhodium in the reaction medium which allows the
use of greater catalyst concentrations, making much higher reaction rates obtainable [3c].

There are two groups of promoters which affect the reaction, namely simple iodide complexes of zinc, cadmium, mercury, indium and gallium, and carbonyl complexes of ruthenium, osmium, rhenium and tungsten [88]. The promoters are highly successful when combined with iodide salts such as lithium iodide at low water concentration [89]. The best rate is found at low water conditions. The selectivity of acetic acid is greater than 99% based on methanol and there are fewer side products than the Monsanto process.

1.9.1.6. Ligand-accelerated carbonylation of methanol

The migratory insertion reaction of CO into metal-alkyl bonds is a fundamental step in the metal iodide-catalyzed carbonylation of methanol to acetic acid (and also in hydroformylation reactions) [90]. The original \([\text{RhI}_2(\text{CO})_2]^-\) catalyst, developed at the Monsanto laboratories and studied in detail by Forster and co-workers, [13] is largely used for the industrial production of acetic acid and anhydride. However, the conditions used industrially (30–60 bar pressure and 150–200 °C) [91] have spurred the search for new catalysts, which could work in milder conditions [92]. The rate-determining step of the rhodium-based catalytic cycle is the OA of CH$_3$I, so that catalyst design focused on the improvement of this reaction. The basic idea was that ligands which increase the electron density at the metal should promote OA, and consequently increase the overall rate of the reaction. For this purpose, other rhodium
compounds have been synthesized in the last few years, which show comparable or better performance as compared to the Monsanto’s catalyst [92, 93].

**1.9.2. Hydrogenation**

The two important terms ‘Hydrogenation’ and ‘Transfer Hydrogenation’ have distinct features i.e. in the former, hydrogen gas (H₂) is involved while in the latter, the hydrogen source must be different from H₂.

The study of homogeneous hydrogenation reactions catalyzed by transition metal complexes has been far more extensive than that of any other catalytic process in solution [94]. One of the most popular homogeneous catalysts for hydrogenation reaction is Wilkinson’s catalyst, [RhCl(PPh₃)₃] [9a,95]. Recent survey shows that the use of asymmetric hydrogenation for the production of fine chemicals is limited, but expanding [96]. Two major factors that hamper its use are the cost of the catalysts, and in particular the ligands that are often prepared in a multistep synthesis. However, the demand for enantiomerically pure compounds with a desired biological activity is growing rapidly in fine-chemical synthesis. An obvious reason for this development is that one of the enantiomers of a chiral pharmaceutical or chemical has at best no activity, or worse, causes side effects. One of the important success stories is the synthesis of fine chemicals like *L-DOPA* (Scheme 1.17) by an asymmetric hydrogenation of prochiral substrates with rhodium(I)-complexes containing optically active ligand DiPAMP [16]
Environmental concerns in chemistry have increased the demand for more selective chemical processes with a minimum amount of waste (Green Chemistry). Hydrogen transfer reactions are mild methodologies for reduction of ketones or imines and oxidation of alcohols or amines in which a substrate-selective catalyst transfers hydrogen between the substrate and a hydrogen donor or acceptor, respectively [97]. Furthermore, the donor (e.g. 2-propanol) and the acceptor (e.g. a ketone or a quinone) are environmentally friendly and also easy to handle. Two main pathways have been proposed for hydrogen transfer to ketones or aldehydes depending on the type of metal used. Direct hydrogen transfer is claimed to occur with main group element and was proposed for the Meerwein-Ponndorf-Verley reduction [98]. This is a concerted process involving a six-member transition state, in which both the hydrogen donor and the hydrogen acceptor are coordinated to the metal centre. The hydridic route includes transition metal catalysts and gives rise to a characteristic metal hydride that involves in the hydrogen transfer reaction [99].

Scheme 1.17. Synthesis of L-DOPA

1.9.2.1. Transfer hydrogenation

Conversion: 100%
Selectivity: 99.5%

[L-DOPA or S-DOPA]
Bäckvall et al. reported that the hydridic route can be further divided into metal monohydride and metal dihydride pathways depending on the catalyst used [100,101]. In the monohydride mechanism, the metal hydride arises purely from the $\alpha$-C–H of the hydrogen donor (e.g. 2-propanol), and this M–H is only transferred to the carbonyl carbon of the substrate and thereby the hydride keeps its identity (Scheme 1.18, path A). In the dihydride pathway the metal hydride arise from both $\alpha$-C–H and the OH of the hydrogen donor, and therefore the catalyst does not distinguish between the proton and the hydride (Scheme 1.18, path B).

**Scheme 1.18.** Hydridic routes of metal catalyzed transfer hydrogenation

There are two types of catalysts operating through the monohydride mechanism that have been suggested to operate differently. The formation of the metal monohydride from the hydrogen donor may involve the formation of a transition metal alkoxide followed by $\beta$-elimination to give the M–H. Alternatively, it may proceed through a concerted pathway with simultaneous transfer of proton and hydride from 2-propanol to a basic site of the ligand and to the metal, respectively, without coordination of the alcohol to the metal. In both pathways the metal hydride gives rise to the $\alpha$-C–H.
In the pathway via a transition metal alkoxide a coordinated carbonyl inserts into the metal hydride 1 and forms metal alkoxide 2 (Scheme 1.19). This insertion should proceed via $\pi$-bonded ketone (metal bound to the double bond). 2-Propanol exchanges the alkoxide and releases the product. The metal isopropoxide then undergoes $\beta$-elimination forming the metal hydride.

Scheme 1.19. Catalytic cycle via a metal alkoxide.

There is ample support for this alkoxide mechanism [102] and it has been shown that transition metal hydrides are obtained from $\beta$-elimination of the corresponding alkoxide complexes [103]. Even ligand assisted versions of this transformation have been reported [104]. Many transition metal catalysts are operating via a metal alkoxide in transfer hydrogenation, for example the Wilkinson
catalyst [RhCl(PPh\textsubscript{3})\textsubscript{3}] [101]. A common feature of catalysts that are proposed to operate through a concerted mechanism is that one of the donor atoms of the ligand acts as a basic centre and activates the substrate. This mechanism was first proposed by Noyori for 16-electron Ru complexes such as 3 (Scheme 1.20) [105,106].

Scheme 1.20. Catalytic cycle via a concerted six-member transition state.

The reaction cycle involves a simultaneous transfer of the proton and the hydride from 4 to the carbonyl in a cyclic six-member transition state forming the alcohol and 3. Then the proton and the hydride from 2-propanol are delivered to
the ligand and the metal, respectively, in the same fashion forming 4 and acetone. It is worth to note that the reaction is proposed to proceed without coordination of either alcohol or ketone (aldehyde) to the metal (Scheme 1.20).

1.10. Aim and objectives of the Thesis

The literature survey presented here reveals that basic as well as applied science of organometallic chemistry of platinum group metals particularly rhodium, iridium and ruthenium have aroused much interest and importance in recent time. The catalytic processes of carbonylation and hydrogenation reaction find tremendous importance in industrial production of bulk and fine chemicals. Newer concepts of ligand design and coordination of metal complexes proceeded promisingly in respect of catalyst precursors. It is therefore important to synthesize and characterize novel metal complexes and to determine their reactivities, kinetics of reactions and applications in different catalytic processes. The specific objectives of the thesis are:

- 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.
1.11. References


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