CHAPTER 1

Introduction

1.1 Metal complexes of Schiff base ligands

Schiff base ligands as described by Hugo Schiff in 1864 as condensation between an aldehyde and an amine are considered, as privileged ligands are attractive due to their stability and the ease by which modified variations can be obtained are once again topical in connection with a diverse range of applications such as, in organic synthesis,2,3 as liquid crystals4 and as molecular switches in logic or memory circuits,5 ultraviolet stabilizers6,7 and as laser dyes.8 This class of ligands are used to make a combinatorial library of ligands9 and are flexible in terms of both size and charge.10 Schiff base complexes of transition metal11,12 having O, N donors has shown an exponential increase as inorganic catalysts for various organic transformations. Schiff base ligands have also proven to be very useful in constructing supramolecular architectures such as coordination polymers, double helixes and triple helicates.13,14 Schiff bases can accommodate different metal centres involving various coordination modes allowing successful synthesis of homo- and hetero- metallic complexes with varied stereochemistry.15 This feature is employed for modelling active sites in biological systems.16,17

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest18,19 because of their ability to possess unusual configurations, be structurally labile and their sensitivity to molecular environments.20 Schiff base complexes are also known for their significant biological activities such as photosynthesis and transport of oxygen in mammalian and other respiratory systems.21,22 The crucial role of Schiff bases in the biological function of bacteriorhodopsin has also been proven.23 The retinal chromophore is bound covalently to the protein via a protonated Schiff base.24 Further, the Schiff base complexes have been studied for their dioxygen uptake25 and oxidative catalysis.26
The steric and electronic effects around the metal core can be fine tuned by an appropriate selection of bulky and/or electron withdrawing or electron donating substituents incorporated into the Schiff bases. The two donor atoms O and N of the chelated Schiff bases exert two opposite electronic effects: the phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the metal atom whereas imine nitrogen is soft donor and accordingly, will stabilize the lower oxidation state of the metal.\textsuperscript{27} Ruthenium(II) complexes have been characterized by their high stability mainly when ligands with donor atoms such as N, P, S, As or O are present in the coordination sphere. From a practical point of view, the aspects involved in the preparation of Schiff base metal complexes are spread out in the literature.

**Different bonding modes of Schiff bases**

The Schiff bases co-ordinate to the metal ion as

(i) Monodentate

The basic strength of the C=N group is not sufficient to obtain stable complexes by coordination of the imino nitrogen atom to a metal ion.\textsuperscript{12} Hence the presence of at least one other donor atom suitably near the nitrogen atom, should stabilize the metal-nitrogen bond through formation of chelate rings.

(ii) Bidentate

The Schiff bases can co-ordinate to the metal atom through

(a) N, N donor atom
(b) N, S donor atom
(c) N, O donor atom

2
Bidentate Schiff bases having N, O donor atoms have been widely studied.

(iii) Tridentate

Many tridentate Schiff bases have been utilized as anionic ligands with different donor sets.

(a) ONO donors

(b) ONS donors

(c) ONN donors

(d) NNS donors

(iv) Tetradentate

Schiff bases coordinating to the metal as N₂S₂, N₂O₂ and N₄ donor sets have been widely studied for their ability to coordinate metal ions.

(a) N₂S₂ donor
(b) N₂O₂ donor

\[
\begin{array}{c}
\text{CH=N} \\
\text{N=HC} \\
\text{O} \\
\text{O}
\end{array}
\]

Where \( W = (\text{CH}_2)_n, \text{C}_n\text{H}_4 \)

(c) N₄ donor

\[
\begin{array}{c}
\text{N} \\
\text{M} \\
\text{N} \\
\text{C=N}
\end{array}
\]

(v) Pentadentate

Metal complexes of the potentially pentadentate ligands have also been studied.

(vi) Hexadentate

The dianion of the Schiff bases is known to act as a hexadentate ligand in a variety of metal complexes, thereby forming a distorted octahedral arrangement around the metal ion.
1.2 Metal complexes of arylazo ligands

Metal complexes containing azo dyes and pigments may be conveniently divided into two classes: those in which the azo group is involved in coordination to the metal and those in which it is not. Metal complexes in which the azo group is involved in coordination are derived from chelating diarylazo compounds having at least one donor function ortho to the azo group. The stability of the complexes depend upon factors including the size of the chelate ring, the formation of annelated chelate rings, the basicity of the ligand and nature of the metal. The metal complex so formed may be five or six membered chelates which depends upon the number of atoms involved in coordination.

Transition-metal chelates incorporating azo ligands have drawn much attention in recent years. Among these, complexes of arylazooximes,\textsuperscript{28} arylazoimines,\textsuperscript{29} ary lazophenols,\textsuperscript{30} sulf enylazobenzenes\textsuperscript{31} and alkylthioazobenzenes,\textsuperscript{32} are some notable examples. The arylazo ligands are potentially able to form M-C bonds or metallacycles due to its acidic nature of the azo function.\textsuperscript{33} Particularly, the azo (-N=N-) group due to its strong π-acid character stabilizes ruthenium in lower oxidation states while phenolate oxygen being a hard base stabilizes the higher oxidation states of the metal ion.\textsuperscript{34}

The five membered chelates formed by the tridentate azo compounds in which it behaves as a C,N,O dianionic tridentate donors is more stable than the six membered chelates where it acts as a O, N monoanionic bidentate donor. However, under forced conditions these ligands undergo C-H activation by transition metal ions and leads to the formation of cyclometalated compounds. As a rule, the most basic ligand forms the most stable complex and the most acidic the least stable complex. Transition metal mediated C-H activation of arylazo ligands is of significant importance and it leads to the formation of reactive organometallic complexes. In particular, the organometallic compounds of ruthenium derived from arylazo ligands has been well developed primarily due to the wide range of oxidation states, the stability and interconvertibility of which is directed by the coordination environment around the metal ion. Also, a variety of azo compounds find important applications in other fields, particularly colour photography and
reprography analyse, catalysis, biology and some modern high technology industries such as electronics. Metal complexes of arylazo ligands undergo different organic transformations at the pendant aryl ring such as hydroxylation, thiolation, C-N coupling reaction with aromatic amines.\textsuperscript{35}

**Nature of bonding by the azo group**

The donor properties of the azo group are weak and its involvement in coordination to a metal ion was originally inferred from the observation that whereas those azobenzenes having a hydroxy or amino group ortho to the azo group form metal complexes, those having such groups in \textit{meta} or \textit{para} position don't. However, it was not clear whether the bonding between the azo group and the metal involved the sp\textsuperscript{2} lone pair of electrons of one of the nitrogen atoms or the \pi electrons of the azo groups. The mode of coordination of the azo group to a metal ion was not fully resolved until X-ray data on several metal azo compounds were established which inferred only one nitrogen atom of the azo group is involved in bonding to the metal.

**Different bonding modes of azo compound**

(i) Bidentate azo compounds (NO; NN)

\[
\begin{array}{c}
\text{X} \\
\text{\textbullet} \quad \text{N=N} \quad \text{\textbullet} \\
\text{\textbullet} \\
\end{array}
\]

Where, X = OH, NH\textsubscript{2}

(ii) Tridentate azo compounds (ONO; NNO)

\[
\begin{array}{c}
\text{Y} \\
\text{\textbullet} \quad \text{N=N} \quad \text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \quad \text{OH} \\
\end{array}
\]

Where, X = COOH, OH; Y = OH, NH
The most important azo compounds of this type are those containing the \( o,o' \)-dihydroxyazo-, \( o \)-hydroxy-\( o' \)-carboxyazo and \( o \)-hydroxy-\( o' \)-aminodiarylanzo systems.

(iii) Tetradentate azo compounds (ONOO; NNNN)

\[
\begin{array}{c}
\text{XH} \\
N=N
\end{array}
\quad
\begin{array}{c}
H_X \\
M
\end{array}
\]

Where \( X = O, N \)

(iv) Pentadentate azo compounds

Pentadentate azo compounds capable of forming metal complexes containing annelated chelate rings are reported and are stable compounds.

(v) Hexadentate azo compounds

Hexadentate azo compounds, which contain two annelated six membered, chelate rings involving the azo group are also reported.
1.3 Metal complexes of tripodal ligands

A key feature of the coordination chemistry of tripodal ligand is their ability to divide the metal-ligand coordination sphere into no-labile sites and reactive sites. The rich coordination chemistry of tripodal ligands was first demonstrated by Saconni and Florence school.\(^{36}\) The chemistry of tripodal ligands has undergone a renaissance in 1990s. Among the various tripodal ligands, N,N-bis(2-pyridylmethyl)amine (Scheme 1) and related ligands are well known and have been used for synthesis of metal complexes.\(^{37}\) The flexibility of the N-coordinating arms of the tridentate ligand allows them to act as meridional and also as facial ligands when coordinating to transition metal complexes.

![Scheme 1](image)

(R = alkyl (or) aryl)

Further, phenolate containing ligands are valuable in modeling the active sites of metal-tyrosine centers in metalloproteins\(^{38}\) and homogenous and heterogenous catalysts.\(^{39}\) Koch et. al., have reported polyphenolate amine tripod ligands.\(^{40}\) Polypridyl tripod ligands provide thermodynamic stability to ruthenium complexes with TPA derivatives\(^{41}\) (TPA = tris(2-pyridylmethyl)amine) ligands due to their chelate effect and the extensive Ru\(^{11}\) back-bonding to pyridyl groups. Transition metal complexes which use tris(pyridyl)tripod display significant differences in overall charge, solubility and redox properties from the analogous complexes which contain tris(pyrazolyl) tripod ligands. Tris(2-pyridyl) tripod ligand are classified based on the central binding atom either nitrogen, phosphorus, arsenic or carbon (Scheme 2).

![Scheme 2](image)

<table>
<thead>
<tr>
<th>X</th>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>tpm</td>
</tr>
<tr>
<td>COH</td>
<td>tpmOH</td>
</tr>
<tr>
<td>N</td>
<td>tpN</td>
</tr>
<tr>
<td>P</td>
<td>tpP</td>
</tr>
<tr>
<td>As</td>
<td>tpAs</td>
</tr>
</tbody>
</table>
Schutte et al., isolated a ruthenium complex containing tpP ligand, namely \([\text{RuCl}_2(\text{PPh}_3)(\text{tpP})]\). The facial tridentate coordination of the ligand has been confirmed by single crystal X-ray diffraction. Cis-oriented labile positions in metal complexes containing tripodal ligands, are quite important in hydrolases model complexes, metal-DNA interaction studies and catalyst ruthenium complexes.

1.4 Cyclometalation Reactions

The term “cyclometalation” was first introduced by Trofimenko to describe those reactions in which a ligand undergoes an intramolecular (or more rarely, intermolecular) metalation with formation of metal-carbon \(\sigma\) bond. Metalations of phenyl-substituted ligands have been most frequently described, and termed ortho-metalation, but the wider scope of these reactions are recognized as cyclometalation (Scheme 3). One way of obtaining a cyclometalated complex is by the intramolecular activation or C-H activation of coordinated ligands by transition metals. Ever since, the first cyclometalated complex was synthesized, cyclometalation has become an important part of organometallic chemistry and several reviews covering the subject have appeared.

\[
\text{H—C—E} \quad \text{M} + \text{HX}
\]

Scheme 3. Cyclometalation, \(E = \text{donor atom}, \text{M} = \text{transition metal, X = leaving group}\)

In general, formation of the metal-carbon \(\sigma\) bond occurs more or less readily by direct interaction of the ligand and metal substrate, and elimination of the hydrogen by combination with a suitable leaving group. In most cases, an intermediate ligand-metal complex without a metal-carbon \(\sigma\) bond is formed, which may or may not be isolable. The cyclometalation reaction is facilitated by choice of a good leaving group in the metal complex, which combines with the hydrogen atom displaced from the metalated carbon atom. These complexes have provided a stimulating area of research and they can be found in uses such as in organic synthesis, liquid crystals,
photochemistry, catalysts and as antitumour agents toward some forms of cancer.

1.5 Present status of Metal Carbonyl and Metal-Phosphorus/Arsenic bonds

The coordination chemistry of transition metal complexes with carbonyl, phosphine and arsine ligands is rich and interesting. Metal carbonyls are an intensively investigated chapter in transition metal organometallic compounds in which carbon monoxide is attached through a metal-carbon bond to a transition metal atom in a low oxidation state (usually zero or ±1) include binary compounds, hetero bimetallic carbonyls and many substituted derivatives in which carbon monoxide is replace by other organic groups for example allyl, cyclobutadiene, cyclopentadienyl, arenes, etc. The binding of carbonyl ligands to metal center in the biological systems has renewed interest in metal carbonyls. The metal carbonyl bonding includes the \(\sigma\)-donation from the filled orbital to the empty \(\pi\)-back bonding from the filled metal orbital to the empty \(\pi^*\) orbital of CO. The \(\sigma\)-interaction makes the carbon in carbonyl relatively acidic that is susceptible to attack by nucleophiles. The nucleophilic addition reactions are important in catalysis for synthesizing organic chemicals and the search for alternative energy. Such reactions also play an important role in biological systems.

A kind of similarity was noted between carbon monoxide, phosphorus and arsenic donors in their ability to form complexes with transition metals in the middle of 20th century. Based on Pauling’s theory of metal carbonyl double bonding J. Chatt summarized that phosphorus, in ligands such as tertiary phosphines has vacant \(d\)-orbitals capable of accepting electrons from filled metal \(d\)-orbitals and thus forming a “dative \(\pi\)-bonds” in addition to the ligand metal \(\sigma\)-bond. The transfer of electron density from the metal to ligand should be promoted by electronegative group bonded to phosphorus. Much of the discussions about the nature of bond between phosphorus and metal have centered on the relative importance of \(\sigma\) or \(\pi\) contribution to the metal ligand bonding and this topic still remains one of considerable controversy.

Ruthenium chemistry of triphenylphosphine and triphenylarsine has been enriched with various ligand types and their role as potential catalysts for many organic synthesis is well documented. These ligands modify the
oxidation chemistry of ruthenium-oxo complexes due to their variety of steric and electronic properties. Further, the availability of large number of phosphines with varying steric and electronic properties provides many possibilities for future catalyst development. Triphenylphosphine also favors the lower oxidation states of a metal dσ-dπ interaction. The predominant coordination chemistry of group 15 donors with ruthenium concerns metal oxidation state of ≤2. For the +3 oxidation state limited examples have been reported in recent years.

1.6 Emission property of Metal complexes

In recent years there have been concerted efforts to design electrochemical and optical sensing devices based on transition metal based receptors. The study of photoinduced electron or energy transfer between donor and acceptor molecule is an interesting subject of learning, about the factors controlling primarily photochemical event in chemistry and biology and for designing of new artificial systems for photonic applications. The metal complexes of lowest electronic excited state, which is based on metal-to-ligand charge transfer (MLCT) transition is able to transfer energy to aromatic ligands. The particular character of the lowest excited state MLCT or σ-π*-is largely determined by the structure of the metal complex fragments in which the excited electron originates.

Transition metal complexes exhibit an enormous potential for the discovery of photo redox processes for solar energy conversion, information storage systems, laser materials, biosensors and complexes with antitumour activity have already been explored or are currently under investigation. In particular the photophysical and the excited state chemistry of Ru(II) diimine complexes has been extensively studied. The complex tris(bipyridyl)ruthenium(II) has been studied in great detail and is one of the most used sensitizers in research laboratories due to the very favourable photochemical, photophysical and redox properties.

In addition, the π-conjugated metal complexes have found applications in many areas of chemistry and materials science. Gratzel et. al., have demonstrated the use of novel ruthenium(II) complexes as sensitizers and their application in dye-sensitized solar cells. In comparision to the
photophysical properties of polypyridyl complexes the luminescent chemistry of Schiff base complexes are not well developed. Recently two Schiff base aluminium complexes have been proposed as luminescent biolabels thanks to their high fluorescence intensity. Photoluminescence spectroscopy technique used to monitor molecular recognition processes offers great advantages in terms of sensitivity and versatility. As a consequence, this technique could also be used to monitor some of the events occurring in the catalytic processes in which Schiff base complexes play a so-important role, since the nature of the coordination sphere could be monitored by changes in the luminescence properties.

Most of transition metal complex have partially filled d-orbital. To a considerable extent the ordering and occupancy of these orbitals determine emissive properties (Scheme 4) shows a schematic orbital and state diagram for a representative octahedral MX₆ d⁶ metal complex where M is the metal and X is a ligand that coordinate at one site. The d⁶ notation indicates that the complex have six-electron. This configuration because of its central role in current transition metal luminescence.

Scheme 4. Simplified orbital and state diagram for a d⁶ metal complex in an octahedral environment showing the d and σ bonding and antibonding orbitals. Each arrow represents an electron with its associated spin. A strong crystal field is assumed so that all the t₂ orbitals are filled. Ligand to metal charge transfer states are ignored.
In addition, luminescent metal complexes are a fascinating class of molecule that have found applications in many areas such as Light Emitting Devices (LED), among which luminescent ruthenium complexes with nitrogen containing ligands have been considerably investigated as potential luminescent materials. Particularly ruthenium(II) polypyridyl complexes have been researched extensively for decades as photochemical molecular devices due to their excellent chemical stability, facial electron transfer, strong luminescence and relatively long-lived excited states. Recently, polypyridine containing ruthenium(II) complexes whose luminescent properties can be tuned, one of particular interest as pH-induced sensitizers and luminescent sensors. In contrast to the considerable growth of literature on the chemistry of polypyridyl complexes, the luminescent chemistry of ruthenium carbonyl complexes containing Schiff bases ligands are not well developed.

1.7 Catalytic application

1.7.1 Oxidation of organic substrates

Oxidation of organic substrates as catalyzed by coordination complexes of transition metals in resemblance of enzymatic oxidations is an intriguing area of current research and plays a central role in organic chemistry, hence a wide variety of methods have been developed. Transition metals in combination with cooxidants used as sacrificial agents (NaIO₄, NaClO₄, t-BuOOH, N-oxides, S-oxides, etc) are known to perform catalytic oxidation. Ruthenium compounds are intensively studied transition metal compounds towards the oxidation of primary and secondary alcohols to their corresponding carbonyl compounds (Scheme 5) due to their wide range of chemically accessible oxidation states.

![Scheme 5.](image-url)
Many methods for specific catalytic oxidation of various organic substrates such as alcohols, amines, amides and hydrocarbons have been studied extensively using low-valent metal complex catalysts. In particular the oxidation of primary and secondary alcohols to corresponding aldehydes and ketones is of tremendous importance in organic synthesis and many transition metal compounds have been used for this purpose. \(^87\) It is to be noted that ruthenium compounds are intensively studied transition metal compounds and many methodologies have been developed with them. \(^88\) In addition to the higher economy of ruthenium compared to the other group eight transition metals such as rhodium and palladium, there is a larger availability of ruthenium complexes which have proven to serve as highly efficient reagents and catalyst for a variety of organic transformations.

A central idea concentrate oxidation catalysis with ruthenium complex is that: i) "by varying the oxidation state and also nature of the co-ligands the oxidizing power of the complexes can be fine tuned". \(^89\) In addition, ii) once the oxidation mechanism has been identified, one can modify the reaction conditions in order to accelerate the desired conversion and thereby enhance the process selectivity, Finally, iii) instead of varying the structural properties of the Ru complex one can modify those of the material entrapping the catalytic activity. "In the field of alcohol, ruthenium-based catalysts belong to the state of the art in their field and bear great potential for application in the fine chemical synthesis". Ruthenium complexes can be synthesized by the judicious choice of the auxiliary ligands with appropriate steric bulkiness and \(\sigma\)-and/or \(\pi\)-donor properties.

Ruthenium mediated oxidations are finding application due to the unique properties of this extremely versatile transition metal, whose oxidation state can vary from -II to +VIII. \(^90\) High-valent metal-oxo complexes such as Ru-porphyrin, in fact, are analogues to monooxygenase enzymes such as cytochrome P450. The high valent metal-oxo (Scheme 6) species have been considered as active intermediates in various oxidation process catalyzed by transition metal complexes. \(^91\) The high valent iron-oxo intermediates in the
Scheme 6. Proposed catalytic cycle for the oxidation of organic substrates by metal complexes

enzyme catalyzed by hemeproteins play an important role for oxidative transformation of bio-related compounds. In this regard ruthenium-oxo species (Ru(IV, V or VI)) generated through the reaction of low valent ruthenium complexes (Ru(II) or Ru(III)) and various oxidants are widely utilized.

1.7.2 Transfer hydrogenation of ketones

The synthesis of secondary alcohols by catalytic reduction of the corresponding ketone remains a pivotal transformation in organic synthesis. The three different catalytic procedures which have emerged in recent years are: (i) hydride reduction; (ii) hydrogenation; (iii) transfer hydrogenation. Some of the most successful and general catalysts for hydride reduction were developed by Corey. Hydrogenation catalysts derived from BINAP and DuPHOS ligands, amongst others, are capable of hydrogenating functionalized ketones. A major drawback of such catalytic systems is the need for an adjacent heteroatom in the substrate to coordinate to the metal centre. The third major method for carbonyl reduction involves transfer hydrogenation has recently emerged as a powerful, practical and versatile system for the title transformation which provides practical simplicity, mild reaction conditions, relatively non-hazardous reagents and high selectivities from which this method benefits is unparalleled by most other synthetic processes in synthetic organic chemistry.
Transfer hydrogenation in general is defined as “the reduction of multiple bonds with the aid of a hydrogen bond in the presence of catalyst” as depicted in Scheme 7.

\[
\begin{align*}
\text{C} & \quad \text{X} \quad + \quad \text{DH}_2 \quad \xrightarrow{\text{Catalyst M}} \quad \text{C} & \quad \text{H} \quad + \quad \text{D} \\
\text{Where X = O, NR} \\
\text{DH}_2 = \text{hydrogen donor}
\end{align*}
\]

Scheme 7.

In the classical Meerwein-Ponndorf-Verley reduction, aluminium iso-propoxide is required in stoichiometric amounts. Transfer hydrogenation of ketones, for example with 2-proponol, referred to as the Meerwin - Ponndorf - Verley reduction, is effected by metal alkoxides, typically aluminium 2-propoxides, as promoters (Scheme 8).

\[
\begin{align*}
\text{R}_1\text{R}_2\text{O} & \quad + \quad \text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{Metal} & \quad \text{promotor} \quad \text{H} & \quad \text{OH} \\
\text{R}_1\text{H} & \quad \text{R}_2\text{OH} \quad + \quad \text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{O} & \quad \text{K} & \quad \text{O}
\end{align*}
\]

Scheme 8.

Recent studies revealed that some lanthanide salts also catalyze the same type of reaction. In these cases, hydrogen transfer between the donor and acceptor molecules is thought to occur via metal alkoxides through a six-membered cyclic type 1 transition state (TS) (M= metallic species). Within the different catalytic approaches developed for instance addition of organometallic reagents to carbonyl compounds, hydrogenation of olefins, functionalization reactions of epoxides, the hydrogenation of ketones or
aldehydes is the most powerful tool with respect to industrial applications. Many efforts have been made for designing highly efficient catalysts for selective transformations, but for large-scale application increasing activity and productivity of catalytic reactions is still a target of primary importance.\(^\text{96}\)

In particular transfer hydrogenations represent a potent strategy, because of high atom efficiency, no need of pressure and economic as well as environment advantages.\(^\text{97}\) In more detail, a broad scope of alcohols is accessible by transfer hydrogenation using non-toxic hydrogen donors under mild conditions in the presence of various metal catalysts, such as Ir, Rh or Ru. These catalysts utilize 2-propanol or hydrogen as the terminal reductant, providing "green" alternatives to stoichiometric reducing agents such as Li\(\text{AlH}_4\) and Na\(\text{BH}_4\).\(^\text{98}\) Historically, it is interesting to note that the first ruthenium-catalyzed hydrogen transfer reaction of practical use was reported by Sasson and Blum.\(^\text{99}\)

Most reactions are promoted with an inorganic base such as KOH, NaOH, or K\(_2\)CO\(_3\) as an essential co-catalyst. The currently accepted putative mechanism for the standard catalytic process is outlined in Scheme 8, in which MX is a transition metal complex acting as a catalytic precursor (X = anionic ligand, typically a halide; for clarity, supporting ligands are omitted).\(^\text{100}\) This pathway involves a metal hydride intermediate, although the possibility of direct hydrogen delivery via 1 (Scheme 8) could not be eliminated.

The mechanism begins with displacement of X from MX by 2-propoxide to give the transition metal 2-propoxide 2.\(^\text{101}\) Elimination of acetone from 2 by way of 3 forms the transition metal hydride 4.\(^\text{102}\) Subsequently, insertion of a ketonic linkage to M-H bond occurs via 5,\(^\text{103}\) resulting in the secondary alkoxide 6. Finally, ligand exchange between 6 and 2-propanol, giving the alcoholic product and 2, completes the catalytic cycle.
Scheme 9. Transition Metal catalyzed Transfer hydrogenation

The removal of acetone from the metal alkoxide 2 is viewed as an analogue of the β-hydride elimination of transition metal alkyls, and hence this step would require generation of a vacant cis coordination site at the metallic center. The key issues concerning this mechanism are the capability of M to carry alkoxide and hydride ligands and the Lewis acidity to accommodate ketones. The role of an alkaline base is believed to involve an increase in the concentration of 2-propoxide anion and also the deprotonation of 2-propanol coordinated to M to form 2, thereby facilitating the overall reaction. All of the elementary steps have been well established with model compounds and are therefore viable under catalytic conditions. Thus, Scheme 9 reasonably explains the previously reported transfer hydrogenation catalyzed by transition metal complexes that normally possess tertiary phosphine or sp²-hybridized amine ligands.

1.8 Literature Review

Literature review on the synthesis of ruthenium(II)/(III) complexes of Schiff bases, arylazo and tripodal ligands along with their catalytic and biological properties are given in this section.

A number of ruthenium(II) complexes, [Ru(PPh₃)₂L₂] (L = monoanion of Schiff bases formed from 2,3-dihydroxybenzaldehyde, 3,5-dibromosalicylaldehyde and salicylaldehyde with aniline or its p-
substitutents) have been prepared. They were characterized by spectroscopic techniques and investigated by cyclic voltammetry. The effective catalytic oxidation of alcohols by these complexes in the presence of N-methylmorpholine-N-oxide or molecular oxygen as co-oxidants is reported.\textsuperscript{106}

Ruthenium complexes catalyze the oxidation of alcohols to the corresponding ketones or aldehydes when \( \text{t-BuOOH} \) (70\% aq.) is used as an oxidant. The reactions proceed at room temperature to give the products in excellent to fairly good yields. Among the transition metal catalysts used, dichlorotris(triphenylphosphine)ruthenium (\( \text{RuCl}_2(\text{PPh}_3)_3 \)) showed the highest catalytic activity. 3,5-Di-t-butylcatechol and 4-t-butylicatechol are also effectively oxidized to the corresponding 1,2-benzoquinones in the presence of a catalytic amount of \( \text{RuCl}_2(\text{PPh}_3)_3 \) at room temperature with 1.1 equiv. of \( \text{t-BuOOH} \), in quantitative yields. Hydrogen peroxide (30\% aq.) can also be employed as an oxidant to give 1,2-benzoquinones in excellent yields.\textsuperscript{107}

The reaction of ruthenium trichloride with 2-(arylazo)phenyl thioethers (\( \text{ArNNC}_6\text{H}_4\text{SR} \); \( \text{Ar} = \text{Ph}, \text{p-tolyl}; \text{R} = \text{Me}, \text{CH}_2\text{Ph} \)) (HL) in methanol affords blue violet \( \text{Ru(HL)}(\text{L})\text{Cl} \) and red violet \( \text{RuL}_2 \), the former being the major product. Both complexes contain pseudooctahedral ruthenium(II); HL is bidentate, coordinating via thioether sulphur and an azonitrogen, but L is meridionally tridentate (coordination at sulphur, nitrogen and the \textit{ortho} carbon of the Ar). All chelate rings are five membered.\textsuperscript{108}

\( \text{RuCl}_2(\text{PPh}_3)_3 \) acts as a homogeneous catalyst for the condensation reaction between long-chain terminal alcohols and secondary amines to give tertiary amines. Supporting evidence is presented for a pathway involving an intermediate aldehyde which undergoes Schiff base formation with the secondary amine. Small amounts of amine side product are formed from catalyzed alkyl group transfer reactions between the amines in the solution. A secondary pathway involving decarbonylation of the aldehyde leads to the formation of alkane and \( \text{RuHCl(CO)(PPh}_3)_3 \). Mechanistic probes are presented and discussed, and the scope of the reaction with secondary alcohols and ketones is presented.\textsuperscript{109}

Long chain alcohols such as octanol, dodecanol and hexadecanols are oxidized to the corresponding aldehydes and carboxylic acids in the presence of the homogeneous catalyst tris(triphenylphosphine) ruthenium dichloride. The known oxidizing agent \( \text{N-methylmorpholine-N-oxide (NMO)} \) has been
compared with a new system involving N-methylmorpholine (NM) and hydrogen peroxide. With the system NM/H$_2$O$_2$ simple recycling of the ruthenium catalyst and of the oxygen transmitter MM is possible by a simple phase separation process. A mechanism is proposed in which the oxygen of the NMO formed \textit{in situ} serves to convert a dihydrido-ruthenium complex into the catalytically active ruthenium species.$^{110}$

Mono- and binuclear complexes of Ru(III) were synthesized using Schiff base ligands obtained by condensation of 2-pyridinecarboxaldehyde with 1,2- and 1,3- or 1,1-phenylenediamine, respectively. The complexes were characterized by analytical, spectral, conductance, cyclic voltammetry, and ESR studies. The epoxidation of alkenes was studied using these complexes as catalysts and iodosylbenzene as an oxidant. The complexes were found to be remarkably stable under the reaction conditions. Rates of the epoxidation of \textit{cis}-cyclooctene using binuclear complexes were found to be nearly twice those using the mononuclear ones, indicating participation of both the metal centers of the former in the reaction.$^{111}$

Mono and binuclear complexes of Ru(III) were synthesized using Schiff base ligands obtained by condensation of 2-pyridinecarboxaldehyde with 1,2- and 1,3- or 1,4-phenylenediamine, respectively. The complexes were characterized by analytical, spectral, conductance, cyclic voltammetry, and ESR studies. The epoxidation of alkenes was studied using these complexes as catalysts and iodosylbenzene as an oxidant. The complexes were found to be remarkably stable under the reaction conditions.$^{112}$

Hydrogen transfer from 2-propanol to prochiral ketones with several new chiral ruthenium complexes has been examined. Optical yields up to 62 % were achieved.$^{113}$

Ruthenium complexes generated \textit{in situ} from [Ru(C$_6$H$_5$Cl)$_2$]$_2$ and chiral Schiff bases [derived from(1R,2R)-diaminocyclohexane] catalyse asymmetric hydrogen-transfer reduction of alkyl aryl ketones by 2-propanol to give the (S)-alcohol in up to 40% ee.$^{114}$

The degradation-resistant ligand tri-2-pyridylamine (tripyam) (1) forms a variety of stable ruthenium complexes. Reaction of (1) with RuCl$_3$(PPh$_3$)$_3$ yields the complex RuCl$_2$(PPh$_3$)(tripyam) (2) and, upon prolonged heating in pyridine, forms RuCl$_2$(py)(tripyam) (3). Complexes (2) and (3) display unusual thermal stability, resisting degradation at temperatures of 270 °C. Reaction of
(2) with two equivalents of AgSbF₆ in water yields the solvento complex [Ru(PPh₃)(tripyam)(OH)₂] (SbF₆)₂ (2a). Reaction of (1) with RuCl₃·H₂O also yields the trichloro complex RuCl₃(tripyam) (4). The organometallic precursor [RuCl₂(p-cymene)] reacts with (1) and either two or four equivalents of AgSbF₆ to yield [RuCl(p-cymene)(η²-tripyam)]SbF₆ (5) and [Ru(p-cymene)(η³-tripyam)][SbF₆]₂ (6), respectively. Each of these complexes has been characterized by spectroscopic techniques and, in the case of (5), by single-crystal X-ray diffraction.¹¹⁵

The complexes [RuCl₃(PPh₃)(L)] in which L is a tridentate ligands with P, N, and O donor atoms are very efficient catalysts for the transfer hydrogenation of cyclic ketones and acetophenone have been reported (turnover ≤ 118800 h⁻¹) in basic media.¹¹⁶

Transfer hydrogenation of alkyl aryl ketones as well as a representative dialkyl ketone with isopropanol catalyzed by Ru complexes of chiral phosphinoxazolines were found to proceed with excellent turnover at a substrate/catalyst mole ratio of 1000:1 to yield products with upto 94 % enantiomeric excess.¹¹⁷

The reaction of mono-Schiff bases of 4-methyl-2,6-diformylphenol and primary amines (p-XC₆H₄NH₂, X = OMe, Cl, CO₂Et and NO₂) with Ru(PPh₃)₃Cl₂ in boiling ethanol afforded violet diamagnetic complexes, [Ru(η²-p-XC₆H₄L)(PPh₃)₂(CO)Cl]η²-p-XC₆H₄L = [4-methyl-6(N-p-Xphenyliminoethyl)phenolato-C₂,O] incorporating the unprecedented orthoruthenated phenolato function, which is hydrogen-bonded with the uncoordinated imine nitrogen. The spectral (IR, UV-vis and ¹H NMR) features of the complexes and the effect of the X substituent on electronic and ¹H NMR spectra are scrutinized. The effect of PPh₃ ring currents on the chemical shifts of the metallated ring protons is semiquantitatively estimated. In these complexes different types of novel intramolecular N...O interaction and the conformational orientation of p-XC₆H₄L ligands are noted. The redox behaviour of these complexes is reported. The E₁/₂ values of Ru³⁺/Ru²⁺ couple correlate linearly with the Hammett constants (σ) of X substituent in the halo complexes. A spectroelectrochemical correlation in these complexes is also reported.¹¹⁸

The new complexes [RuII(bpy)L](PF₆) and [RuIII(bpy)₂Cl₂]X (bpy = 2,2'-bipyridine; HL = acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, dibenzylmethane or tropolone ; X = IO₄ and PF₆) have been prepared and
characterized by spectroscopic measurements and also investigated by cyclic voltammetry. They effectively catalyze the oxidation of alcohols, 3,5-di-t-butylcatechol and alkane in the presence of t-butyl hydroperoxide or N-methylmorpholine-N-oxide as co-oxidants.\textsuperscript{119}

The reaction of \([\text{Ru}^{II}(\text{PPh}_3)_3\text{X}_2] (\text{X} = \text{Cl, Br})\) with \(\sigma-(\text{OH})\text{C}_6\text{H}_4\text{C}(\text{H})=\text{N}-\text{CH}_2\text{C}_6\text{H}_5 (\text{HL})\) under aerobic conditions affords \([\text{Ru}^{III}\text{L}_2(\text{PPh}_3)_2] 1\), in which both the ligands \(\text{L}\) are bound to the metal center at the phenolic oxygen (deprotonated) and azomethine nitrogen and \([\text{Ru}^{III}\text{L}_1(\text{L}_2)(\text{PPh}_3)]\) 2, in which one \(\text{L}\) is in bidentate N, O form like in complex 1 and the other ligand is in tridentate C, N, O mode where cyclometalation takes place from the ortho carbon atom (deprotonated) of the benzylamine fragment.\textsuperscript{120}

The Schiff bases \((\text{LL'})\) formed from pyridine-2-carboxaldehyde or 2-acetyl pyridine and S-1-phenylethylamine react with \([\text{Ru}(\text{mes})\text{Cl}_2]\) (mes = \(\eta^6\)-C\(_6\)H\(_3\)Me\(_3\)-1,3,5) to form diastereomeric salts \([\text{Ru}(\text{mes})\text{Cl}(\text{LL'})][\text{BF}_4]\). Crystallisation gives a single diastereomer, \((S_{\text{Ru}}S_{\text{Cl}})\) in each case, which have been characterised by X-ray diffraction; the conformation of the phenylethyl group is different to related \(\eta^6\)-benzene complexes. The configuration at the metal is solvent dependent, it is stable in CDCl\(_3\) but epimerisation occurs in D\(_2\)O.\textsuperscript{121}

The reaction of 1-methyl-2-(p-chlorophenylazo)imidazole \((\text{L}_1')\) and 2-(phenylazo)pyridine \((\text{L}_2')\) with \([\text{Ru}(\text{H})(\text{X})(\text{CO})(\text{PPh}_3)_3]\) \((\text{X} = \text{Cl, Br})\) have afforded the green paramagnetic \((S = 1/2)\) and EPR-active \((g \approx 2.00)\) title anion radical complexes \([\text{Ru}(\text{L}_1')(\text{Cl})(\text{CO})(\text{PPh}_3)_2]\) and \([\text{Ru}(\text{L}_2')(\text{Br})(\text{CO})(\text{PPh}_3)_2]\) in which the N-N bond lengths lie near 1.35 Å.\textsuperscript{122}

New tetradentate \((\text{O}_2\text{N}_2, S_2\text{N}_2 \text{and } P_2\text{N}_2)\) Schiff base ruthenium (II)(III) complexes were prepared and their properties were investigated. The Schiff base ruthenium(II) complexes containing soft sulfur donor atoms cause photosubstitution of the axial ligands under room light. Thus, \([\text{RuCl}_2(\text{btb-en})]\) \((\text{btb-en} = \text{N,N}'-\text{bis}(2\text{-tert-butylthiobenzilidene})-1,2\text{-ethanediamine})\) in acetonitrile under room light yields \([\text{RuCl}_2(\text{CH}_3\text{CN})(\text{btb-en})]\)Cl. The analogous photosubstitution reaction of \([\text{RuCl}_2(\text{ppb-}\{\text{RR}\}-\text{chxn})]\) \((\text{ppb-}\{\text{RR}\}-\text{chxn} = \text{N,N}'-\text{bis}(2\text{-diphenyl- phosphinobenzilidene})-1,2\text{-cyclohexanediadmine})\) was also observed in acetonitrile. On the other hand, the photosubstitution reaction of \([\text{RuCl}(\text{PPh}_3)(\text{sal-}\{\text{RR}\}-\text{chxn})]\) \((\text{H}_2\text{sal-}\{\text{RR}\}-\text{chxn} = \text{N,N}'-\text{disalicylidene}(R,R\text{-}1,2\text{-cyclohexanediadmine})\) did not occur under the same conditions. The single-
crystal diffraction studies revealed the following crystal data: monoclinic, \( \text{C}2/c \), \( a = 16.092(4) \) Å, \( b = 9.699(2) \) Å, \( c = 20.618 \) (4) Å, \( \beta = 109.20(2)^\circ \), \( Z = 4 \) for [RuCl\(_2\)btb-tn] (btb-tn = \( N,N'\)-bis(2-tert-butylthiobenzilidene)-1,3-propanediadmine); monoclinic, \( \text{P}2_1/n \), \( a = 9.688(3) \) Å, \( b = 16.795(3) \) Å, \( c = 18.086(3) \) Å, \( \beta = 101.10(2)^\circ \), \( Z = 4 \) for [RuCl\(_2\)(CH\(_3\)CN)(btb-en)]Cl.\(^{123}\)

Novel Ru(II) and Ru(III) complexes having TPA (tris(2-pyridylmethyl)amine, \( L1 \)) and 5-Me\(_3\)-TPA (tris(5-methyl-2-pyridylmethyl)amine, \( L2 \)) were prepared to establish their synthetic routes and to elucidate coordination geometry and interactions between tightly bound tripodal tetradeinate ligands and RuII/RuIII centers. They include mononuclear Ru(II) complexes [RuCl(DMSO)(L)](C\(_2\)O\(_4\)) \( (1 \ (L1), \ 2 \ (L2)) \), dinuclear bis-i-chloro Ru(II) complexes [RuCl(L)]\(_2\)(C\(_2\)O\(_4\)) \( (3 \ (L1), \ 4 \ (L2)) \), and mononuclear Ru(III) complexes [RuCl\(_2\)(L)]ClO\(_4\) \( (5 \ (L1), \ 6 \ (L2)) \). They were characterized by X-ray crystallography (for \( 2, \ 3, \) and \( 5 \)), \(^1\)H-NMR spectroscopy, and cyclic voltammetry. Electrochemical measurements on \( 1-6 \) in CH\(_3\)CN revealed that the methyl groups on pyridyl rings exert electron-donating effects onto the Ru centers to lower each redox process and such effect strengthens the Ru-S bonding in \( 2 \) compared with that in \( 1 \), accommodating \( \delta \)-back-bonding from Ru(II) center to other \( \delta \)-acceptors such as DMSO in \( 2 \) enough to prevent isomerization of DMSO binding mode. The dinuclear complexes \( 3 \) and \( 4 \) showed relatively large comproportionation constants, which suggest mixed-valent Ru(II)/Ru(III) states would be stabilized.\(^{124}\)

The reaction of dodecacarbonyltriruthenium (Ru\(_3\)(CO)\(_{12}\)) with tris(2-pyridylmethyl)ammonium perchlorate (tpa\(\cdot\)3HClO\(_4\)) in toluene, in the presence of acetic acid has been carried out and a new ruthenium(II) complex of tpa \[ Ru(CH\(_3\)CO\(_2\))(CO)(tpa)ClO\(_4\)C\(_6\)H\(_5\)CH\(_3\) \( (1) \) \] has been reported. A similar reaction of Ru\(_3\)(CO)\(_{12}\) with 2-pyridylcarboxylic acid \( (pyCO\(_2\))H \) in toluene yielded a ruthenium(II) complex Ru[pyCO\(_2\)]\(_2\)(CO) \( (2) \). A related ruthenium(III) compound, \[ [Ru(pyCO\(_2\))]_3\cdot\text{H}_2\text{O} \ (3) \], was obtained from the reaction of RuCl\(_3\)\(\cdot\)nH\(_2\)O and sodium 2-pyridinecarboxylate in a mixture of water and ethanol (1:1 by volume). The reaction of Ru\(_3\)(CO)\(_{12}\), benzoic acid and pyridine \( (py) \) in toluene resulted in the formation of a dinuclear ruthenium(I) complex \[ [Ru_2(C_\(_6\)H\(_5\)CO\(_2\))]_2(CO)\(_4\)(py)\(_2\)]\(_0.5\)C\(_6\)H\(_5\)CH\(_3\) \( (4) \). Compounds \( 1-4 \) have been characterized by IR, NMR and X-ray crystallography.\(^{125}\)

23
Cationic \([\text{Ru}^\text{III}(\text{app})(\text{pic})(\text{H}_2\text{O})]^+\) complex (Happ = N-(hydroxyphenyl)pyridine-2-carboxaldimine; Hpic = picolinic acid) has been synthesized and characterized by physio-chemical methods and employed as catalyst in the oxidation of both saturated and unsaturated hydrocarbons using tert-butylhydroperoxide (t-BuOOH). A mechanism involving formation of and transfer from a reactive high valent Ru(V)-oxo species as catalytic intermediate is proposed for the catalytic processes.\(^{126}\)

The reaction of ruthenium trichloride with 2-(arylazo)phenyl thioethers (ArNNC\(_6\)H\(_4\)SR; Ar = Ph, \(p\)-tolyl; R=Me, CH\(_2\)Ph) (HL) in methanol affords blue violet \(\text{Ru}(\text{HL})(\text{L})\text{Cl}\) and red violet \(\text{RuL}_2\), the former being the major product. Both complexes contain pseudoctahedral ruthenium(II); HL is bidentate, coordinating via thioether sulphur and an azonitrogen, but L is meridionally tridentate (coordination at sulphur, nitrogen and the \textit{ortho} carbon of the Ar). All chelate rings are five membered.\(^{127}\)

The electronic character of the ruthenium complexes with tripodal polypyridine ligands, which is controlled by the substituted groups at pyridine 6-position, gives rise to differences in the reactivity for the ruthenium catalyzed hydroxylation of adamantine and epoxidation of cyclohexene with PhIO as an oxidant.\(^{128}\)

The synthesis, characterizations, and photochemical reactions of the nitrosyl ruthenium(III) complexes \([\text{Ru}(\text{salen})(\text{ONO})(\text{NO})]\) (salen = N,N'-ethylenebis(salicylideneiminato) dianion), [\(\text{Ru}(\text{salen})(\text{Cl})(\text{NO})\)], [\(\text{Ru}(\text{Bu}_4\text{salen})(\text{Cl})(\text{NO})\)] (\(\text{Bu}_4\text{salen} = \text{N,N'}\text{-hexamethylenebis}(3,5\text{-di-tert-butylsalicylideneiminato})\) dianion), [\(\text{Ru}(\text{Bu}_4\text{salen})(\text{ONO})(\text{NO})\)] and [\(\text{Ru}(\text{Bu}_4\text{salophen})(\text{Cl})(\text{NO})\)] (\(\text{Bu}_4\text{salophen} = \text{N,N'}\text{-hexamethylenebis}(3,5\text{-di-tert-butylsalicylideneiminato})\) dianion) are described. Upon photolysis, these \([\text{Ru}(\text{X})(\text{L})(\text{NO})]\) compounds undergo NO dissociation to give the ruthenium(III) solvento products \([\text{Ru}(\text{X})(\text{L})(\text{Sol})]\).\(^{129}\)

The reaction of N,N'-bis[\(\text{o-(diphenylphosphino0benzylidene)-1,2-diaminoethane}\)] with one equivalent of \(\text{RuCl}_2(\text{PPh}_3)_3\) in dichloromethane at room temperature gave trans-\(\text{RuCl}_2(\text{PPh}_3)(\kappa^3-\text{L})\) \(2\) in high yield. Catalytic studies show that \(2\) is an effective catalyst for the oxidation of alkanes, alkenes and alcohols with air or \textit{tert}-butylhydroperoxide.\(^{130}\)

Mononuclear and binuclear carbonylruthenium(II) complexes with N\(_2\)O\(_2\) Schiff base ligands based on 3,5-di-tert-butylsalicyaldehyde and three
different o-diamines have been prepared. The electrochemical studies revealed that the central tetraamino linker regulates the communication between the two metal centers of the binuclear complexes.\textsuperscript{131}

Some ruthenium complexes, $[\text{Ru}^{\text{II}}(\text{bhabp})(\text{dms})][\text{L}]$, with a square planar ligand, $\text{H}_2\text{BABP}$, and axial ligands, $\text{L}$ ($\text{L} = \text{dms}$, imidazole, or pyridine derivatives), have been prepared as catalysts for oxygen-transfer reactions. The catalytic activity and selectivity of the metal oxo species derived from these complexes and PhIO have been affected by the axial ligands $\text{L}$, in which active species has been interpreted in terms of contribution of both characters of $\text{Ru(V)}=\text{O}$ and $\text{Ru(IV)}=\text{O}$.\textsuperscript{132}

Efficient aerobic oxidation of alcohols was developed via a biomimetic catalytic system. The principle for this aerobic oxidation is reminiscent of biological oxidation of alcohols via the respiratory chain and involves selective electron/proton transfer. A substrate-selective catalyst (ruthenium complex 1) dehydrogenates the alcohol, and the hydrogens abstracted are transferred to an electron-rich quinone (4b). The hydroquinone thus formed is continuously reoxidized by air with the aid of an oxygen-activating Co-salen type complex (6). Most alcohols are oxidized to ketones in high yield and selectivity within 1-2 h, and the catalytic system tolerates a wide range of $\text{O}_2$ concentrations without being deactivated. Compared to other ruthenium-catalyzed aerobic oxidations this new catalytic system has high turnover frequency (TOF).\textsuperscript{133}

Three methods are described, in the context of the guiding principles of green chemistry, for the catalytic oxidation of alcohols. The first employs a recyclable oligomeric TEMPO catalyst (PIPO) and sodium hypochlorite as the oxidant in a bromide-free and chlorinated hydrocarbon solvent-free system. The second involves a ruthenium/TEMPO catalyst and oxygen as the oxidant. The third consists of a recyclable water-soluble palladium-diamine complex in conjunction with air as the oxidant in an aqueous biphasic system. The mechanisms of the ruthenium/TEMPO- and palladium-catalyzed oxidations are discussed, and the mechanism of the former is compared with that of the analogous copper/TEMPO catalyst.\textsuperscript{134}

The reaction between $[\text{RuCl}_2(\text{PPPh})_3]$ and one or two equivalent amounts of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (1) in dichloromethane gave $[\text{RuCl}_2(\text{PPPh})(\text{1})]$ (2) or $[\text{RuCl}_2(\text{1})_2]$ (3), respectively, in good yields. Activation of propargylic alcohol derivatives by 3 in refluxing
dichloromethane and in the presence of NaBPh₄ lead to the new allenylidene ruthenium complexes \([\text{RuCl}(1)2(C=C\text{CPhCH}_3)][\text{BPh}_4]\) ([4][BPh₄]) and \([\text{RuCl}(1)2(C_2C\text{CPh2})][\text{BPh}_4]\) ([5][BPh₄]). The reaction between 3 and phenylacetylene in dichloromethane and in the presence of KPF₆ affords the vinylidene complex \([\text{RuCl}(1)2(C=\text{CPh})][\text{PF}_6]\) ([6][PF₆]). The X-ray diffraction studies of 2, 3, and [5][BPh₄] are reported.¹³⁵

The cycloruthenation of 2-phenylimidazole(phim) by \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)(\text{n-CIJC1J2}) \text{in acetonitrile in the presence of NaOH has been carried out. The unstable intermediate [Ru(phim)(MeCN)₄]PF₆ formed has been converted into the complexes [Ru(phim)(4,4'-Me bpy)(MeCN)₂]PF₆ and [Ru(phim)(LL)₂]PF₆ (LL=phen, bpy, 4,4'-Me₂bpy), which were characterized by mass-spectrometry, \(^1\text{H NMR spectroscopy, UV-Vis spectrophotometry, and cyclic voltammetry. Complexes were used as mediators for the fabrication of enzyme electrodes by simple co-adsorbing with Glucose Oxidase (GO) or horseradish peroxidase on graphite electrodes.¹³⁶}

The reactions of hydrated \(\text{RuCl}_3\) and tetradeutate Schiff bases (\(L=\text{paen, papn and pabn}\) derived from 2-pyridine-carboxaldehyde and linear diamines such as 1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane in boiling methanol afford complexes of general formula trans-[\text{RuLCl}_3]. The molecular structures of trans-[\text{Ru(papn)Cl}_2] and trans-[\text{Ru(pabn)Cl}_2] in the solid state have been determined by X-ray crystallography. In each molecule, the ruthenium (II) centre is in distorted octahedral \(\text{N}_4\text{Cl}_2\) coordination sphere. Electronic spectra of the complexes in dichloromethane solutions display intense metal-to-ligand charge transfer bands in the range 595-656 nm. Cyclic voltammograms of the complexes in acetonitrile solutions display a reversible oxidation response.¹³⁷

Reaction of 2,5-diphenylphospholide anion with 2-chloromethylpyridine affords the 1-(2-methylpyridine) phosphole ligand. The corresponding cationic Ru-(cymene)Cl chelate complex catalyzes the hydrogen transfer process of ketones with very high TON and TOF numbers.¹³⁸

A novel oxalate-bridged binuclear ruthenium(III) complex, ([\text{Ru(acac)}₂]\(\mu\text{-ox}) [acac” = acetylacetonate and ox²⁻ = oxalate), has been prepared via self-dimerization of K[\text{Ru-(acac)}₂(ox)] in aqueous solutions containing ferric salts as catalyst. The \(\text{Ru}^{\text{III,II}}\) mixed-valence species generated electrochemically with \(K_c = 10^{5.0}\) for the comproportionation constant exhibits
a weak intervalence charge transfer (IVCT) band at 1430 nm. The IR spectra from spectroelectrochemistry indicate a partially localized mixed-valence state (Class II-III behavior).  

Mixed-chelate complexes of ruthenium have been synthesized using tridentate Schiff base ligands (TDLs) derived by condensation of aldehydes (Salicyaldehyde, 2-pyridinecarboxaldehyde) with 2-aminobenzoic acid and bidentate ligands (2,2'-bipyridine or picolinic acid). The complexes were characterized by analytical, spectral (IR and UV-Vis), conductance, magnetic moment and electrochemical studies. Catalysis of hydrocarbon oxidation for cyclohexene, cyclohexane, cyclohexanol, toluene, benzyl alcohol and tetrahydrofuran has been studied using various O-atom transfer agents (t-BuOOH, H₂O₂, NaOCl, KHSO₅ and pyridinium-N-oxide. A mechanism involving intermediacy of a high valent Ru(V)-oxo species is proposed for the catalytic oxidation processes.

Catalytic aerobic oxidations with photoactivated nitrosyl ruthenium-salen complexes, including asymmetric oxidation of secondary alcohols to ketones (kinetic resolution), enantioselective oxidative coupling of 2-naphthols to binaphthols and oxygen-radical bicyclization of 2,2'-dihydroxystilbene, chemoselective oxidation of primary alcohols to aldehydes and diols to lactols, and asymmetric desymmetrization of meso-diols to lactols have been reported.

The bis(isocyanide)-ruthenium(II) complexes trans,cis,cis-[RuX₂(CNR)₂(dppf)] (X = Cl, R = CH₂Ph (2a), Cy (2b), tBu (2c), 2,6-C₆H₃Me₂ (2d), (S)-(-)-C(H)MePh (2e); X = Br, R = CH₂Ph (3a), Cy (3b), tBu (3c), 2,6-C₆H₃Me₂ (3d), (S)-(-)-C(H)MePh (3e)) have been prepared by reaction of the bis(allyl)-ruthenium(II) derivative [Ru(ti₃-2-C₃H₄Me)₂(dppf)] (1) with the appropriate isocyanide ligand, in CH₂Cl₂ at room temperature and in the presence of the corresponding hydrogen halide HX. The structure of the compound trans,cis,cis-[RuCl₂(CNCH₂Ph)₂(dppf)] (2d) has been confirmed by X-ray crystallography. The catalytic activity of complexes 2a-e and 3a-e in the transfer hydrogenation of acetophenone by propan-2-ol has been studied, and the most active complex, trans,cis,cis-[RuCl₂(CNCH₂Ph)₂(dppf)] (2a), has been also tested as a catalyst in the transfer hydrogenation of a large variety of ketones. The hydride derivatives cis,cis-[RuHCl(CN-2,6-C₆H₃Me₂)₂(dppf)] (4) and cis,cis,cis-[RuH₂(CN-2,6-
C₆H₃Me₂J₂[dppf] (5) have been isolated and characterized. Although both hydride complexes catalyze the transfer hydrogenation of acetophenone in the absence of base, the reactions proceed ca. 5 times faster with 5 than with 4, pointing out that the real active species are dihydride-ruthenium complexes.¹⁴²

A new type of chiral Ru(II) complex, prepared from a conformationally rigid, sterically bulky ‘roofed’ cis-diamine and [RuCl₂(benzene)]₂, functions as an efficient catalyst for the asymmetric transfer hydrogenation of a wide variety of aryl ketones, including sterically bulky ketones, when the reaction is conducted in the presence of 5HCO₂H.₂NEt₃.¹⁴³

The free carbene 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene reacts with trans,cis-RuHCl(PPh₃)₂(ampy) (ampy = 2-(aminomethyl)pyridine) affording an orthometalated N-heterocyclic carbene complex characterized by an X-ray diffraction study. This compound in presence of NaOH shows very high catalytic activity for the transfer hydrogenation of several ketones to alcohols using 2-propanol as hydrogen source, affording TOF values up to 120,000 h⁻¹ (at 50% conversion).¹⁴⁴

The reactions between [M₃(CO)₁₂], M = Ru and Os, and salicylideneimine-2 thiophenol Schiffs base in THF under reflux gave [Ru(CO)₄(satpH)] and [Os(CO)₃(satpH₂)] complexes. Structures of the two complexes were proposed on the basis of spectroscopic studies. Magnetic study of [Ru(CO)₄(satpH)] suggested that a change in oxidation state of the ruthenium atom from zero to +1 was achieved via oxidative addition of the SH group with a proton displacement to give a low-spin d⁷ electronic configuration. UV-Vis spectra of the two complexes in different solvents exhibited visible bands due to metal-to-ligand charge transfer. Electrochemical investigation of the free ligand and complexes showed some cathodic and anodic irreversible peaks due to interconversions through electron transfer.¹⁴⁵

Air-stable, mononuclear orthometallated ruthenium(III) 2-(arylazo)phenolate complexes of the general composition [RuX(AsPh₃)₂(L)] (X=Cl or Br; L= CNO donor of the 2-(arylazo)phenolate ligands) have been synthesized and characterized by IR, UV-Vis and EPR as well as by elemental analysis. One of the complexes [RuBr(AsPh₃)₂(azo-OMe)], was structurally characterized by X-ray analysis and was found to be an efficient catalyst for
the transfer hydrogenation of ketones with excellent conversion in the presence of isopropanol at 80 °C in 1 h.\textsuperscript{146}

A series of mononuclear organoruthenium complexes of the type [RuX(PPh\textsubscript{3})\textsubscript{2}(L)] (X = Cl or Br; L = 2-(arylazo)phenolate ligand) have been synthesized from the reaction of five 2-(arylazo)phenol ligands with ruthenium(III) precursors viz. [RuCl\textsubscript{3}(PPh\textsubscript{3})\textsubscript{3}] and [RuBr\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{3}OH)] in benzene under reflux. The 2-(arylazo)phenol ligands behave as dianionic tridentate C, N, O donors and coordinated to ruthenium by dissociation of the phenolic proton and the phenyl proton at the ortho position of the phenyl ring. The complexes have been characterized by elemental analysis, magnetic susceptibility measurement, FT-IR, UV-Vis and EPR spectral data. The structural conformation of the complex 1 has been carried out by X-ray crystallography. The redox behavior of the complexes has been investigated by cyclic voltammetry and the potentials are observed with respect to the electronic nature of substituents(R) in the 2-(arylazo) phenolate ligands. These complexes catalyze transfer hydrogenation of benzophenone to benzhydrol with up to 99.5% in the presence of i-prOH/KOH. Further, these complexes have shown great promise in inhibiting the growth of both gram +ve and gram –ve bacteria viz. \textit{Stap. aureus NCIM 2079} and \textit{E. coli NCM 2065} and fungus \textit{Candida albicans NCIM 3102}.\textsuperscript{147}

Stable ruthenium(III) Schiff base complexes of general formula [RuX(EPh\textsubscript{3})(LL')] (X = Cl or Br; E = P or As; LL' = \{ONNO\} donor of the heterocyclic Schiff base ligands) were accessible via simple and convenient synthesis. The complex [RuCl(PPh\textsubscript{3})(DHAphen)] is found to be efficient catalyst in the transfer hydrogenation of ketones in excellent conversion up to 99% in the presence of isopropanol/KOH.\textsuperscript{148}

Diamagnetic ruthenium(II) complexes [Ru(CO)(B)(L)] (where B= PPh\textsubscript{3}, AsPh\textsubscript{3}, py (or) pip ; L = dianion of tetradeutate Schiff bases) were synthesized from the reaction of tetradeutate Schiff bases derived from 2-hydroxy-1-naphthaldehyde and appropriate diamines with monomeric metal precursors [RuHCl(CO)(EPh\textsubscript{3})\textsubscript{2}(B)] (Where E = As, B = AsPh\textsubscript{3}; E = P, B = PPh\textsubscript{3}, py (or) pip). Elemental analyses and spectral (FT-IR, UV-Vis and \textsuperscript{1}H-NMR) studies of all the new synthesized complexes suggest the presence of octahedral environment around Ru(II) ion. All the metal complexes exhibit characteristic MLCT absorption and luminescence bands in the visible region. The
luminescence efficiency of ruthenium(II) complexes was explained based on the ligand environment around metal ion. Cyclic voltammogram of all the complexes display quasi-reversible oxidation (RuIII/RuII) in the range 0.76 to 1.04 V and an irreversible reduction peaks (RuII/RuI) in the range −0.70 to −0.95 V. The observed redox potentials vary with respect to the size of the chelate ring of Schiff base ligands. Further, the catalytic activity of complex 1 has been found to be high towards the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant. The formation of high valent RuIV =O species as a catalytic intermediate is proposed for the catalytic process.149

A concise overview has been given on mononuclear and dinuclear, bidentate Schiff base ruthenium complexes with different additional ligands and on their applications in various chemical transformations such as Kharasch addition, enol-ester synthesis, alkyne dimerization, olefin metathesis and atom transfer radical polymerization. These new ruthenium complexes, conveniently prepared from commonly available ruthenium compounds, are very stable, exhibit a good tolerance towards organic functionalities, air and moisture and display high activity and chemoselectivity in chemical transformations. Relevant features of coordination chemistry connected with the reaction mechanism and chemoselectivity are also fully described. Since the nature of Schiff bases can be changed in a variety of ways, appealing routes for designing and preparing novel ruthenium complexes can be foreseen in the future.150

Five novel ruthenium complexes, RuCl2[MOTPP]2[(S,S)-DPEN] [MOTPP = tris(4-methoxyphenyl)phosphine] (1), RuCl2[TFTPP]2[(S,S)-DPEN] [TFTPP = tris(4-trifluoromethylphenyl)phosphine] (2), RuCl2(PPh3)2[(S,S)-DPEN] (3), RuCl2(BDPX)[(S,S)-DPEN] [BDPX = 1,2-bis(diphenylphosphinomethyl)benzene] (4), RuCl2(BISBI)[(S,S)-DPEN][BISBI = 2,2'-bis((diphenylphosphino)methyl)-1,1'-biphenyl]] (5) have been synthesized and used for the hydrogenation of aromatic ketones. The complexes showed high catalytic activities, especially that the catalytic activity of complex 5 containing the diphosphine with large bite angle and complex 1 containing triarylphosphine with electron donating group were higher than the other three complexes. The enantioselectivities of products were almost not influenced by the electron factors of phosphine.151
The synthesis of various Schiff base mononuclear and binuclear ruthenium complexes, whose additional ligands around the metal core have been selected from an array of motifs, was described. These types of ruthenium complexes, conveniently prepared from commonly available ruthenium sources, are rather stable, display good tolerance towards diverse organic functionalities and also to air and moisture. Remarkably, they exhibit a high activity and chemoselectivity in a variety of catalytic processes such as ring-closing metathesis (RCM), Kharasch addition, alkyne dimerization, enol ester synthesis, ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP). This review covers both homogeneous and heterogeneous hybrid Schiff base-ruthenium complexes.\textsuperscript{152}

The dihydride ruthenium N-heterocyclic carbene complex $[\text{Ru(IMes)}(\text{PPh}_3)_2\text{CO(H)}_2]$ (1) (IMes$^4$:1,3-dimesityl-1,3-dihydro-2H-imidazol-2-ylidene) is an efficient catalyst for both direct hydrogenation and transfer hydrogenation of ketones and imines, in the absence of base.\textsuperscript{153}

Keppler-type ruthenium(III) complexes exhibit promising antitumor properties. A study of 2-aminothiazolium$[\text{transtetrachlorobis(2-aminothiazole)ruthenate(III)}]$, both in the solid state and in solution has been reported. The crystal structure has been solved and found to exhibit classical features. Important solvatochromic effects were revealed. Notably, introduction of an amino group in position 2 greatly accelerates chloride hydrolysis compared to the thiazole analogue; this latter finding may be of interest for a fine-tuning of the reactivity of these novel metallodrugs.\textsuperscript{154}

The reactions of $[\text{Ru(PPh}_3)_3\text{Cl}_2]$ and $N$-[aryloyl]-$N$-(pyridinylimidene)hydrazines (HL), derived from 2-pyridinecarbaldehyde and 4-substituted aroylhydrazines in boiling methanol provide mixed-ligand complexes having the general formula $\text{trans-[RuL(PPh}_3)_2\text{Cl}]$. The complexes were characterized by analytical, spectroscopic and electrochemical measurements. The $+2$ oxidation state of the metal ions in these complexes is confirmed by their diamagnetic nature in the solid state and electrically non-conducting behavior in solution. The X-ray structure of a representative complex has been determined. The metal ion is in a distorted octahedral $N_2O_2P_2Cl$ coordination sphere. Electronic spectra of the complexes in dichloromethane solution display several bands due to metal-to-ligand charge transfer and intraligand transitions.\textsuperscript{155}
Oxidation of N,N-disubstituted hydroxylamines by N-methylmorpholine N-oxide (NMO) and catalytic amounts of tetra-n-propylammonium perruthenate (TPAP) at room temperature occurs very rapidly to give the corresponding nitrones, has been investigated.\textsuperscript{156}

The synthesis, characterization and \textit{in vitro} antiamoebic activity of 5-nitrothiophene-2-carboxaldehyde thiosemicarbazones (TSC), 1–5, and their bidentate complexes [Ru(η^4-C_8H_{12})(TSC)Cl_2] 1a–5a have been reported. The biological study of these compounds were investigated against \textit{HK-9} strain of \textit{Entamoeba histolytica} and the concentration causing 50\% cell growth inhibition (IC\textsubscript{50}) was calculated in the micromolar range. The ligands exhibited antiamoebic activity in the range (2.05–5.29 \textmu M). Screening results indicated that the potencies of the compounds increased by the incorporation of ruthenium(II) in the thiosemicarbazones. The complexes 1a–5a showed antiamoebic activity with an IC\textsubscript{50} of 0.61–1.43 \textmu M and were better inhibitors of growth of \textit{E. histolytica}, based on IC\textsubscript{50} values.\textsuperscript{157}

The complex trichloro(phenylazo)bis(triphenylphosphine)ruthenium(II) shows a longest-wavelength absorption at \(\lambda_{\text{max}} = 520\) nm due to Ru(II) \(\rightarrow\) phenyldiazonium\(^+\) MLCT transition has been reported. MLCT excitation leads to the oxidation of the metal and reduction of the diazonium cation which decays to nitrogen and phenyl radical.\textsuperscript{158}

The reaction of the [RuCl\(_2\)(PPh\(_3\))] complex with picolines has been examined. New ruthenium(II) complexes – [RuCl\(_2\)(C\(_6\)H\(_7\)N\(_4\))] have been obtained and characterized by IR, \(^1\)H NMR and UV–Vis measurements. The crystal structure of the [RuCl\(_2\)(\beta\text{-pic})\(_4\)] complex has been determined. The electronic spectra of the complexes have been calculated by the TDDFT method.\textsuperscript{159}

The mono anionic bidentate Schiff base ligands of N, O bonding system has been employed to synthesize a series of new stable ruthenium(III) complexes of general composition [RuX(EPh\(_3\))(L)\(_2\)] (where, E = P or As, X = Cl or Br and L = O, N donor of Schiff bases). All the complexes have been fully characterized by elemental analyses, magnetic susceptibility measurements, FT-IR, UV-Vis, EPR and cyclic voltammetric techniques. The catalytic reactivity explored proving these complexes to be efficient in the transfer hydrogenation of imines to amines with moderate to high conversions.\textsuperscript{160}
The discovery and optimization of the highly enantioselective asymmetric hydrogenation of an α-alkoxy substituted ketone has been described. The use of a ruthenium (phosphinoferrocenyl)oxazoline catalyst and the appropriate choice of a solvent and a base is the key to the success of this transformation.\(^\text{161}\)

The asymmetric transfer hydrogenation of fluoroalkyl ketones mediated by \([\text{Ru}(\eta_6\text{-arene})((S,S)-\text{R}_2\text{NSO}_2\text{DPEN})]\) catalysts using \(\text{HCO}_2\text{H-Et}_3\text{N}\) afforded the corresponding alcohols with high ee’s and in excellent yields.\(^\text{162}\)

The complex \([\text{Ru}(4,4’-\text{Me}_2\text{bpy})_2(\text{AsPh}_3)(\text{H}_2\text{O})][\text{ClO}_4]_2\) (\(4,4’\)-dimethyl-2,2′-bipyridine) has been prepared and their spectral and redox properties has been investigated. The catalytic activity of the complex has been investigated at pH 7.0 in the homogeneous electrooxidation of benzyl alcohol, 1-phenylethanol and cyclohexene. The reactivity was found to decrease in the order 1-phenylethanol > benzyl alcohol > cyclohexene. The higher reactivity of this complex compared to the analogous complex \([\text{Ru}(4,4’-\text{Me}_2\text{bpy})_2(\text{PPh}_3)(\text{H}_2\text{O})][\text{ClO}_4]_2\) is attributed to the higher hydrophobic character of the arsine ligand.\(^\text{163}\)

An interesting series of mononuclear organoruthenium complexes of formulation \([\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{ap-R})]\) (Where ap-R= -H, -Cl, -Me, -OMe, -OEt) have been synthesized from the reaction of five 2-(arylazo)phenol ligands with ruthenium(II) precursor \([\text{RuH(Cl)(CO)(PPh}_3)_3]\) in benzene under reflux. These complexes have been characterized by elemental analysis, FT-IR, \(^1\text{H}\) NMR and UV-visible spectroscopy. In dichloromethane solution all the metal complexes exhibit characteristic metal-to-ligand charge transfer (MLCT) absorption and emission bands in the visible region. A distorted octahedral geometry has been proposed for \([\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{ap-H})]\) and \([\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{ap-Cl})]\) based on X-ray crystallography. Cyclic voltammetric data of all the complexes show a \(\text{Ru}^{II}/\text{Ru}^{III}\) oxidation and reduction \(\text{Ru}^{II}/\text{Ru}^{I}\) within the range 0.74 V to 0.84 V and –0.38 V to –0.50 V Vs saturated calomel electrode (SCE) respectively. The potentials are observed with respect to the electronic nature of substituents (R) in the 2-(arylazo)phenolate ligands. Further, the free ligands and their ruthenium complexes have also been screened for their antibacterial and antifungal activities.\(^\text{164}\)

The optical absorption and luminescence spectra, the electrochemical behavior, and the X-ray crystal structure of a series of three heteroleptic Ru(II)
complexes in comparison to \([\text{Ru(bipy)}_3]^{2+}\) have been reported. The complexes examined are of the type \([\text{Ru(bipy)}_2(\text{bipy'})][\text{PF}_6]_2\) with BIPY=2,2'-bipyridine and bipy'=5,5'-diamino-2,2'-bipyridine (4), diethyl-2,2'-bipyridine-5,5'-dicarboxylate (5) or 5,5'-bis(ethoxycarbonylamino)-2,2'-bipyridine (6). Absorption bands and redox waves are fully assigned. The position of bands or half-wave potentials can be correlated with the electron-withdrawing/donating properties of the bipy' ligand. The relative emission intensities of complexes with 4 and 6 can be modulated through the hydrogen-bonding capabilities of the solvent (MeOH and H_2O). The cyclic voltammograms between +1.5 and -2.2 V show a reversible metal-oxidation wave and two to four reduction waves, attributed to successive reductions of the different ligands. Ligand 4 can only be oxidized. Correlations between spectroscopical and electrochemical data give a linear relation for \(h\nu_{\text{max}}^{\text{abs}}\), \(h\nu_{\text{max}}^{\text{em}}\) versus \(\Delta E_{1/2}\). A comparison with complexes with the analogous 4,4'-disubstituted-2,2'-bipyridine ligands reveals pronounced differences in the position of the MLCT-absorption and emission bands due to the 5- or 4-position of the substituent.\(^{165}\)

A series of cationic, half-sandwich ruthenium complexes with the general formula \([\text{[(n}_6^-\text{-p-cymene})\text{RuCl(MeS-C}_6\text{H}_4-2-\text{N=CHAr})][\text{PF}_6]_2\) (3a-h), have been prepared from the reaction of \([\text{[(n}_6^-\text{-p-cymene})\text{RuCl}_2]_2\) with various N,S-donor Schiff base ligands derived from 2-(methylthio)aniline and several substituted benzaldehydes. The related aniline complex \([\text{[(n}_6^-\text{-p-cymene})\text{RuCl(MeS-C}_6\text{H}_4-2-\text{NH}_2)][\text{PF}_6]_2\) (4) was synthesized from 2-(methylthio)aniline. All of the ruthenium complexes were characterized by IR, \(^1\text{H}-\text{NMR},\) and UV/Vis spectroscopies. The molecular structure of complex 4 was determined by X-ray crystallography.\(^{166}\)

Reaction of 2-(arylazo)phenols with \([\text{Ru(PPh}_3)_2(\text{CO})_2\text{Cl}_2]\) affords a family of organometallic complexes of ruthenium-(II) of type \([\text{Ru(PPh}_3)_2(\text{CO})(\text{CNO-R})]\), where the 2-(arylazo)phenolate ligand (CNO-R; R) OCH_3, CH_3, H, Cl, and NO_2 is coordinated to the metal center as tridentate C,N,O-donor. Another group of intermediate complexes of type \([\text{Ru(PPh}_3)_2(\text{CO})(\text{NO-R})(\text{H})]\) has also been isolated, where the 2-(arylazo)phenolate ligand (NO-R) is coordinated to the metal center as bidentate N,O-donor. Structures of the \([\text{Ru(PPh}_3)_2(\text{CO})(\text{NO-OCH}_3)(\text{H})]\) and \([\text{Ru(PPh}_3)_2(\text{CO})(\text{CNO-OCH}_3)]\) complexes have been determined by X-ray crystallography.\(^{167}\)
The utility of Grubbs' 2nd generation metathesis catalyst has been expanded by the development of two tandem olefin metathesis/oxidation protocols. These ruthenium-catalyzed processes provide cis-diols or trans-hydroxy ketones from simple olefinic starting materials.168

The chirality of an "achiral" benzophenone-based complex can be controlled. The chiral benzophenone-based ruthenium complex has been found to possess high enantioselectivity in the catalytic asymmetric ketone hydrogenation (up to 99% ee >99% yield).169

Novel ruthenium carbene complexes have been in situ generated and tested for the transfer hydrogenation of ketones. Applying Ru(cod)(methylallyl)_2 in the presence of imidazolium salts in 2-propanol and sodium-2-propanolate as base, turnover frequencies up to 346 h\(^{-1}\) have been obtained for reduction of acetophenone. A comparative study involving ruthenium carbene and ruthenium phosphine complexes demonstrated the higher activity of ruthenium carbene complexes.170

A new series of neutral organometallic building blocks based on piano-stool ruthenium(II) complexes, RuCl_2(p-cymene)Ph_2PCH_2Y \( [Y = \text{NHC}_6\text{H}_4(2-\text{CO}_2\text{H}) \text{ (2a)}, \text{NHC}_6\text{H}_4(3-\text{CO}_2\text{H}) \text{ (2b)}, \text{NHC}_6\text{H}_3(3-\text{CO}_2\text{H})(6-\text{OCH}_3) \text{ (2c)}, \text{NHC}_6\text{H}_4(4-\text{CO}_2\text{H}) \text{ (2d)}, \text{NHC}_6\text{H}_3(2-\text{CO}_2\text{H})(4-\text{OH}) \text{ (2e)}, \text{NHC}_6\text{H}_3(3-\text{OH})(4-\text{CO}_2\text{H}) \text{ (2f)}, \text{NHC}_6\text{H}_3(2-\text{CO}_2\text{H})(5-\text{CO}_2\text{H}) \text{ (2g)} \text{ and -OH (2h)}] \), were synthesised in high yields (>88%) from \{RuCl_2(p-cymene)\}_2 and the appropriate phosphines la-lh. The new tertiary phosphine 1b was prepared by Mannich condensation of NH_2C_6H_4(3-CO_2H) with Ph_2PCH_2OH in MeOH. Solution NMR \(^{31}\text{P}{^1}\text{H}, {^1}\text{H}), FT-IR and microanalytical data are in full agreement with the proposed structures. Single crystal X-ray studies confirm that, in each case, compounds 2a, 2b and 2d–2h have pianostool arrangements with typical Ru–P, Ru–Cl and Ru–Ccentroid bond lengths. Head-to-tail dimer pairs through classical intermolecular O–H...O hydrogen bonding is observed in isomer 2d but dimer pairs are further associated to give a 1-D chain through assisted intermolecular N–H...Cl hydrogen bonding. In contrast the isomeric compound 2f does not show head-to-tail O–H...O hydrogen bonding but instead O–H...Cl and N–H...O intermolecular hydrogen bonding is observed. Depending on the choice of solvent (MeOH or DMSO), 2g forms extended networks based on chains (2g.DMSO.1.5MeOH) or tapes
In 2h, a single intramolecular O–H.....Cl hydrogen bond is observed for each independent molecule.\textsuperscript{171}

The enantioselective intramolecular cyclopropanation of cis-substituted allylic diazoacetates catalyzed by the chiral ruthenium Schiff base complexes [Ru(Schiff base)(PPh\textsubscript{3})\textsubscript{2}] (I) has been described. Among this class of complexes examined, [Ru(2-Br-salen)(PPh\textsubscript{3})\textsubscript{2}] (1a) is the most effective, catalyzing intramolecular cyclopropanation of cis-allylic diazoacetates cis-(CR\textsubscript{2}H\textsubscript{2}CH)OCC(0)CHN\textsubscript{2} (R) alkyl, aryl) in CHCl\textsubscript{3} solution to give [3.1.0]-bicyclic lactones with yields and ee values up to 71 and 90 \%, respectively. The analogous reactions of cis-alkenyl diazoacetates using [Ru(Schiff base)(CO)] (2) as catalyst gave comparable enantioselectivities (up to 91 \% ee) but lower product yields of 20-38\%.\textsuperscript{172}

The reaction of the chelating ligands (obtained by the condensation of 2-hydroxy-1-naphthaldehyde with various primary amines) with [RuHCl(CO)(EPh\textsubscript{3})\textsubscript{2}(B)] (where E = P; B = PPh\textsubscript{3}, py or pip; E = As; B = AsPh\textsubscript{3}) in benzene afforded new stable ruthenium(II) carbonyl complexes of the general formula [Ru(Cl)(CO)(EPh\textsubscript{3})(B)(L)] (L = anion of bidentate Schiff bases). The structure of the new complexes was investigated using elemental analyses, spectral (FT-IR, UV-Vis and \textsuperscript{1}H-NMR) and electrochemical studies and is found to be octahedral. All the metal complexes exhibit characteristic MLCT absorption and luminescence bands in the visible region. The luminescence efficiency of the ruthenium(II) complexes was explained based on the ligand environment around the metal ion. These complexes catalyze oxidation of primary and secondary alcohols into their corresponding carbonyl compounds in the presence of \textit{N}-methylmorpholine-\textit{N}-oxide (NMO) as the source of oxygen. The formation of high valent Ru\textsuperscript{IV} =O species as a catalytic intermediate is proposed for the catalytic process.\textsuperscript{173}

A simple and convenient synthesis of a new class of air-stable mononuclear cyclometallated ruthenium(II) carbonyl 2-(arylazo)phenolate complexes bearing triphenylarsine [Ru(ap-R)(AsPh\textsubscript{3})\textsubscript{2}(CO)] has been described. The 2-(arylazo)phenolate ligands behave as dianionic tridentate ligand and are coordinated to ruthenium through C, N and O by dissociation of the phenolic and phenyl proton at the ortho position of the phenyl ring forming two five-membered chelate rings. These complexes have been characterized by elemental analysis, FT-IR, \textsuperscript{1}H-NMR and UV-Visible spectroscopy. In
dichloromethane solution all the metal complexes exhibit characteristic metal-to-ligand charge transfer (MLCT) absorption and emission bands in the visible region. One of the complexes \([\text{Ru}(\text{ap-Cl})\text{AsPh}_3\text{]CO}]\) was successfully characterized by X-ray crystallography. Cyclic voltammetric data of all the complexes show a Ru\(^{III}/\)Ru\(^{II}\) oxidation and reduction Ru\(^{II}/\)Ru\(^{I}\) within the range +0.75 to +0.86 V and -0.50 to -0.57 V with respect to Ag/AgCl respectively. The potentials are observed with respect to the electronic nature of substituents (R) in the 2-(arylazo)phenolate ligands. Further, one of the complex (2) was tested as a new catalyst in the oxidation of primary and secondary alcohols in presence of NMO as a more viable oxidant with moderate to high conversion.\(^{174}\)

Three stereoisomers of a Ru(II) complex bearing a chiral bisphenanthroline Tröger's base analogue, TBphen\(_2\) (1), have been isolated from the reaction of the enantiomerically pure precursor complex \(\Lambda\)- (or \(\Delta\)-) cis-\([\text{Ru}([\text{phen}]_2[p\text{y}])_2]^{2+}\) (phen = 1,10-phenanthroline, py = pyridine) with the racemic mixture of 1. Each stereoisomer of \([\text{Ru}[\text{phen}]_2\text{TBphen}_2]^{2+}\) (2) has been characterized by \(^1\text{H}\) NMR and CD spectroscopy. Electrochemical studies revealed that the redox properties of 2 are not influenced by the stereochemistry, however, the electrochemical oxidation of the metallic center is irreversible because of the diazocine bridge of the TBphen\(_2\) ligand. Steady-state emission measurements in the presence of calf thymus DNA showed that the DNA binding of \([\text{Ru}[\text{phen}]_3\text{TBphen}_2]^{2+}\) depends on the stereoisomer and is mainly controlled by the absolute configuration of the metal center of the complex. The affinity constant for the stereoisomer \(\Lambda\)-S-2 is \(10^2\) higher than that for \(\Lambda\)-S-2 and rac-\([\text{Ru}[\text{phen}]_3]^{2+}\).\(^{175}\)

Four ruthenium (II) complexes of general formula \(\text{Ru}(\text{PPhi}_3)_2(L)_2\) have been synthesized and characterized. The spectroscopic and cyclic voltammetric studies of these complexes are also reported. X-ray crystal structure determination of two of the complexes reveal that Ru(II) occupies trans,trans,trans-(t,t,t) \(\text{N}_2\text{O}_2\text{P}_2\) centrosymmetric octahedral environments, with the ligand pair occupying the equatorial plane. \(^{31}\text{P}\) NMR confirms the presence of two trans-PPhi\(_3\) groups in all the complexes. The transformation of the complexes in dichloromethane solution is studied by spectrophotometry and \(^{31}\text{P}\) NMR spectroscopy.\(^{176}\)
The reaction of Ru(PPh$_3$)$_3$(CO)H$_2$ with excess Et$_3$N·3HF at elevated temperature affords the hydride fluoride complex Ru(PPh$_3$)$_3$(CO)HF (1). This reacts with a series of N-heterocyclic carbenes (NHCs) at ambient temperature to form the mono-NHC products Ru(NHC)(PPh$_3$)$_2$(CO)HF (NHC = IMe$_4$ (2), lEt$_2$Me$_2$ (3), ICy (4), l'Pr$_2$Me$_2$ (5)). Complexes 2-4 convert from the trans- to cis-phosphine isomers in solution over weeks (relative rates 2 > 3 > 4), while 5 undergoes both isomerization and disproportionation to yield cis-Ru(l'Pr$_2$Me$_2$)(PPh$_3$)$_2$(CO)HF (6), 1, and Ru(l'Pr$_2$Me$_2$)$_2$(PPh$_3$)(CO)HF (7) in a matter of hours. The molecular structures of compounds 1-4 have been determined by X-ray crystallography.¹⁷⁷

The complexes RuHCl((R)-binap)(L-NH$_2$) with L-NH$_2$ = (S)-histidine-Me-ester (1), histamine (3), (S)-histidinol (4) or 1-Me-(S)-histidine-Me-ester (5), and RuHCl((S)-binap)(L-NH$_2$) with L-NH$_2$ = (S)-histidine-Me-ester (2) have been prepared in 60-81% overall yields in a one-pot, three-step procedure from the precursor RuCl$_2$(PPh$_3$)$_3$. Their octahedral structures with hydride trans to chloride were deduced from their NMR spectra and confirmed by the results of a single crystal X-ray diffraction study for complex 3. Under H$_2$ and in the presence of KOfBu, complexes 1-5 in 2-propanol form moderately active catalyst precursors for the asymmetric hydrogenation of acetophenone to 1-phenylethanol. Complex 5 is more active and enantioselective than complexes 1-4, allowing complete conversion to 1-phenylethanol in 46% e.e. (R) in 72 h at 20 °C under 1 MPa of H$_2$ with substrate : catalyst : base = 2000 : 1 : 30. Complex 5, when activated, also catalyzes the hydrogenation of trans-4-phenyl-3-buten-2-one to exclusively the allyl alcohol 4-phenyl-3-buten-2-ol under 2.7 MPa of H$_2$ at 50 °C in 2-propanol.¹⁷⁸
1.9 References


