CHAPTER 1
INTRODUCTION

Scope and objective of the work

Transition metal complexes with tertiary phosphines and arsines have gained considerable interest during the last few decades. Triphenylphosphine and triphenylarsine complexes of ruthenium(II) and ruthenium(III) have been used as catalysts in many reactions of industrial importance such as hydrogenation, hydroformylation, oxidation, carbonylation, decarbonylation, isomerisation, reduction and alkylation and some of the complexes have been used as starting materials for the synthesis of novel ruthenium(II) and ruthenium(III) complexes containing triphenylphosphine and triphenylarsine bonded to metal ion besides other ligands. Further, there has been an upsurge of interest in the chemistry of transition metal chelates containing O, O; O, N; N, S and S, S donor ligands due to their potential carcinostatic, antitumour, antifungal, antiviral and antibacterial activities. It will, therefore, be interesting to study the reactions of ruthenium(II) and ruthenium(III) complexes of tertiary phosphines and arsines with various ligands containing O, O; O, N and N, S donor atoms leading to the formation of new complexes and to investigate their structures and properties.

The present work has been undertaken with a view to study the effect of chelating ligands containing donor atoms like O, O; O, N and N, S on the substitution reactions of ruthenium(II) and ruthenium(III) triphenylphosphine and triphenylarsine complexes. The significant changes in the spectral characteristics of ruthenium(II) and ruthenium(III) complexes due to the presence of different chelating ligands are also of considerable interest. Besides, it is also equally interesting to study the effect of dibasic tetradoentate Schiff base
ligands on the substitution reactions of ruthenium(II) complexes containing triphenylphosphine and heterocyclic nitrogen bases to ascertain the labile nature of Ru—P and Ru—N bonds in these complexes towards substitution reactions. Moreover, a detailed study on the electrochemistry of the complexes containing PPh₃/AsPh₃ and other ligands will throw some light on the nature of electron transfers in such systems, leading to stabilisation of either higher or lower oxidation states of ruthenium ion. From the application point of view, it is worthwhile to investigate the antibacterial and antifungal activities of the new mixed ligand complexes of Ru(II) and Ru(III) since, the free ligands used in these systems have been shown to exhibit considerable amount of biological activities. The possibility of using the new ruthenium complexes as catalysts for various chemical reactions will also be a matter of interest to study.

Based on the above objectives, a detailed study on the reactions of ruthenium(II) triphenylphosphine complexes with 2'-hydroxychalcones has been carried out. The new complexes obtained from these reactions have been characterised on the basis of elemental analysis, IR, electronic, ¹H-NMR and ³¹P-NMR spectral data. The complexes obtained are of the type [RuCl(CO)(LL')(PPh₃)₂] or [RuCl(CO)(LL')(PPh₃)][B] (HLL' = 2'-hydroxychalcones; B = pyridine(py), piperidine(pip) or morpholine(morph)).

The reactions of 2'-hydroxychalcones with ruthenium(III) complexes of the type [RuX₃(EPh₃)₃] or [RuBr₃(PPh₃)₂(MeOH)] (X = Cl or Br; E = P or As) have been carried out in benzene medium and the new complexes have been characterised on the basis of analytical, IR, electronic, EPR spectral data, magnetic moment and electrochemical studies.

In addition to the above reactions, we focussed our attention on the synthesis of ruthenium(III) triphenylphosphine or triphenylarsine complexes containing N, S donor ligands and the biological activities of the new complexes.
formed. The in vitro studies on the antibacterial activity of some of the thiosemicarbazone ligands and that of the ruthenium(III) thiosemicarbazone complexes have been carried out.

Further, the synthesis and characterisation of some stable ruthenium(II) carbonyl complexes containing tetrade ntate Schiff bases of the general formula \([\text{Ru(CO)}(\text{L})(\text{B})]\) (\(\text{B} = \text{PPh}_3, \text{pyridine(py)}, \text{piperidine(pip)}; \text{L} = \) the dianionic tetrade ntate Schiff base) have been described. The products obtained have been characterised on the basis of elemental analysis, IR, electronic, \(^1\text{H-}	ext{NMR}\) and \(^{31}\text{P-}	ext{NMR}\) spectral studies and an octahedral structure has been tentatively proposed for the new complexes.

We have also carried out the reactions of bidentate Schiff bases with ruthenium(II) complexes of the type \([\text{RuHCl(CO)}(\text{PPh}_3)_2(\text{B})]\) (\(\text{B} = \text{PPh}_3, \text{pyridine(py)}, \text{piperidine(pip)}\)). All the new complexes have been characterised using various physico-chemical methods and an octahedral geometry has been tentatively proposed for them. The toxicity of the Schiff base ligands and their ruthenium(II) complexes have been tested in vitro against \textit{Aspergillus flavus} to evaluate the antifungal activity.

**Present status of metal-phosphorus and metal-arsenic bonds**

Many years ago, a kind of similarity has been noted between carbon monoxide, phosphorus and arsenic donors in their ability to form complexes with transition metals. According to Pauling's theory of metal carbonyl double bonding, J. Chatt summarised that phosphorus in ligands such as tertiary phosphines had vacant d-orbitals capable of accepting electrons from filled metal d-orbitals and thus forming a "dative \(\pi\)-bonds" in addition to the metal-ligand \(\sigma\)-bond. The presence of electronegative group bonded to phosphorus would promote the transfer of electron density from the metal to ligand. Chatt tested
the theory by studying the interactions of phosphorus trifluoride with platinum(II) chloride and boron trifluoride where platinum formed stable complexes and boron, which has no electrons available for dative $\pi$-bond formation did not have any significant interaction with phosphorus trifluoride. Nyholm and co-workers\textsuperscript{101,102} also introduced this suggestion of back-bonding or d$\pi$-d$\pi$ overlap between the metal and donor atoms. Much of the discussion about the nature of bond between phosphorus and metals has centered on the relative importance of $\sigma$ or $\pi$ contributions to the metal-ligand bonding and this topic still remains one of considerable controversy.

Regarding the nature of bonding between metal ion and phosphorus containing ligands, it appears to be reasonably clear that the metals in the oxidation state of +2 or higher form pure $\sigma$-bonds with alkyl or aryl phosphines. The complexes in which the metal is in zero or -1 oxidation state, there is an extensive participation of both $\sigma$ and $\pi$-bond. For intermediate situations, there is an uncertainty in the degree of $\pi$-character in metal-phosphorus bond which is either due to lack of suitable results or lack of agreement concerning their interpretation. These conclusions are based on the results of the studies carried out using various physical methods.\textsuperscript{103-121}

There are no systematic studies to understand the nature of bonding between metal to ligands containing heavier group VB donor atoms. However, it appears that the arsines as ligands behave very similar to that of the phosphines and therefore, it may be that the arsines also form $\sigma$-bonds with metals in the higher oxidation states. This assumption may not be correct as was pointed out by Pauling,\textsuperscript{122} who noted that the Co As and Mn As bonds in trans-[CoCl$_2$(diarsine)$_2$]$^+$ and [[Mn(\pi-MeC$_5$H$_4$)(CO)$_2$](diarsine)] are shorter than their respective estimated single bond distances. But, similar shortening of the metal-phosphorus bond length has also been observed for metals in quite higher
oxidation states. It has been suggested that the metal radii are quite significantly dependent on the nature of ligands.\textsuperscript{123}

Various physico-chemical studies on the Pt(II), Fe(II) and Fe(III) with arsenic and antimony donors indicated that the $\sigma + \pi$ interaction increases in the order $\text{Ph}_3\text{As} < \text{Ph}_3\text{Sb} < \text{Ph}_3\text{P}$ and the study of pentacyanato Fe(II) and Fe(III) derivatives suggested that the affinity of $\text{Ph}_3\text{As}$ and $\text{Ph}_3\text{Sb}$ are respectively similar and lower than that of $\text{Ph}_3\text{P}$.\textsuperscript{124,125}

Survey of previous work

Ruthenium(II) complexes containing tertiary phosphine/arsine and other ligands

There are voluminous reports describing the reactions of tertiary phosphine and arsine complexes of ruthenium(II) with various types of ligand systems available in the literature. Among them, some important reactions and their results which we feel related to our research have been presented in this section.

Synthesis of many hydride, carbonyl and hydridocarbonyl complexes of ruthenium(II) with tertiary phosphines and arsines have been reported.\textsuperscript{1} Some of the ruthenium(II) complexes have been used as catalysts in a variety of reactions including hydrogenation, oxidation, hydroformylation, polymerisation etc. Some important ruthenium(II) complexes showing potential catalytic properties are $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuCl}_2(\text{PPh}_3)_4]$, $[\text{RuH}(\text{PPh}_3)_3(\text{OCOCH}_3)]$ and $[\text{RuHCl}(\text{PPh}_3)_3]$.\textsuperscript{4}
[RuHCl(PPh₃)₃] is an active and much studied catalyst for hydrogenation, prepared from [RuCl₂(PPh₃)₃] and sodium borohydride in benzene solution containing a small amount of water.¹⁵⁻¹⁷ The reactions of [RuCl₂(PPh₃)₃] with nitriles, amines, β-diketones, carboxylic acids and cyclopentadiene resulted in the formation of the following type complexes, [RuCl₂(RCN)(PPh₃)₂], [RuCl₂(amine)(PPh₃)₂], [Ru(β-dk)(PPh₃)₂], [Ru(OCOR)(PPh₃)₁₂] and [RuCl₂(n-C₅H₅)(PPh₃)₂].¹²⁸

Poddar et al.¹²⁷ prepared ruthenium(II) complexes of the type [RuCl₂(py)(PPh₃)] and [RuCl₂(py)₄] (py = pyridine) by reacting [RuCl₂(PPh₃)₃] with pyridine. The reactions of¹¹ [RuCl₂(AsPh₃)(OAsPh₃)] with NO and CO gases resulted in the formation of [RuCl₂(NO)(AsPh₃)(OAsPh₃)] and [RuCl₂(CO)(AsPh₃)(OAsPh₃)]. In the nitrosyl complexes, NO is bonded to ruthenium as NO⁺.

The complexes [RuH₂(CO)(PPh₃)₃] and [RuHCl(CO)(PPh₃)₃] have been treated with 1,5- diphenylformazanes (H-dphf) in boiling 2-methoxyethanol and the resulting products were found to be cyclometalated formazane derivative of ruthenium(II) complex of the type [Ru(dphf)(CO)(PPh₃)₂]. The structure of the complex has been established by single crystal X-ray diffraction studies.⁵⁷

Mixed ligand ruthenium(II) complexes of the type [Ru(X)(CO)(PPh₃)₂(RCOCHCOCF₃)] (X = H or Cl; R = C₆H₅, 3',4'-OMeC₆H₃, 4-BrC₆H₄, 2'-ClC₆H₄, 4-(Me)C₆H₄ and 2'-(Me)C₆H₄) have been synthesised from the reactions of [RuHCl(CO)(PPh₃)₃] or [RuH₂(CO)(PPh₃)₃] with various fluorinated β-diketones in benzene medium.³⁵ The new products have been characterised by analytical and spectral studies. The reactions of [RuHX(CO)(PPh₃)₃] with monothio-β-diketones have been carried out in benzene medium and the products obtained have been characterised on the basis of analytical and spectral (IR, electronic, ¹H-NMR and ³¹P-NMR) studies and formulated as [RuX(CO)(PPh₃)₂(RCSCHCOR')] (X = H or Cl; R = R' = CH₃ or C₆H₅).⁷¹
Natarajan et al. have reported\textsuperscript{37,128} the synthesis and characterisation of several new binuclear ruthenium(II) complexes of the type \([\text{RuCl}(\beta\text{-dk})_2\text{L}_2]\) (\(\beta\text{-dk} = \beta\text{-diketonate or fluorinated } \beta\text{-diketonate; } \text{L} = \text{PPh}_3 \text{ or AsPh}_3\)) with chloride bridges. Further, the reactions of \(\beta\text{-diketones and fluorinated } \beta\text{-diketones with } [\text{RuHCl(CO)}(\text{PPh}_3)_3] \text{ and } [\text{RuH}_2(\text{CO})(\text{PPh}_3)_3] \text{ gave monomeric complexes of the type } [\text{RuH(CO)}(\text{PPh}_3)_2(\beta\text{-dk})] \text{ and } [\text{RuCl(CO)}(\text{PPh}_3)_2(\beta\text{-dk})] \text{ respectively.}\textsuperscript{34}

The complexes of the composition \([\text{RuHCl(CO)}(\text{PPh}_3)_2(B)] \) (\(B = \text{nitrogen containing heterocyclic base like pyridine, piperidine or morpholine} \)) have been reported\textsuperscript{69} from the reactions of \([\text{RuHCl(CO)}(\text{PPh}_3)_3] \text{ and heterocyclic nitrogen bases.} \text{ In these reactions, an unusual trans bond weakening effect of the hydride ligand in } [\text{RuHCl(CO)}(\text{PPh}_3)_3] \text{ has been observed which accounts for the ready substitution of a trans-phosphine by a strongly bonding heterocyclic nitrogen base.} \textsuperscript{\textit{\textdagger}}

Recently, cationic complexes of the type \([\text{RuH(CO)}(\text{PPh}_3)_2\text{L}_2]^+\)\((\beta\text{-dk})\) (\(\text{L} = \text{pyrazole or imidazole} \)) have been reported from the reactions of \([\text{RuHCl(CO)}(\text{PPh}_3)_3] \text{ with pyrazole or imidazole.} \text{ The new products obtained have been characterised on the basis of analytical and IR, electronic and } ^1\text{H-NMR spectral studies.}\textsuperscript{129}

Several new hexa-coordinated ruthenium(II) complexes of the type \([\text{RuCl(CO)}(\text{PPh}_3)_2(\text{NX})] \text{ and } [\text{RuH(CO)}(\text{PPh}_3)_2(\text{NX})] \) (\(X = \text{O}; \text{ semicarbazones and } X = \text{S}; \text{ thiosemicarbazones} \)) have been synthetised from the reaction between \([\text{RuHCl(CO)}(\text{PPh}_3)_3] \text{ or } [\text{RuH}_2(\text{CO})(\text{PPh}_3)_3] \text{ and various semicarbazones or thiosemicarbazones.} \text{ In all these reactions, it has been observed that the semicarbazones and thiosemicarbazones behave as a uninegative bidentate chelating ligand coordinating through } N, O \text{ or } N, S \text{ donor atoms.}\textsuperscript{130}
Ruthenium(II) dithiocarbazate Schiff base complexes of the type \([\text{RuX(CO)(PPh}_3\text{)}_2(\text{LL}')]\) (\(X = \text{H or Cl} \); \(\text{LL'} = \text{heterocyclic dithiocarbazates or alkyl, aryl dithiocarbazates}\)) have been reported\(^{131,132}\) from the reactions of \([\text{RuHX(CO)(PPh}_3\text{)}_3]\) with heterocyclic dithiocarbazates or alkyl, aryl dithiocarbazates. In these reactions, the Schiff bases behave as uninegative bidentate ligands.

Some ruthenium(II) chiral Schiff base complexes of the composition \([\text{Ru(PPh}_3\text{)(H}_2\text{O})(\text{L})]\) (\(\text{L} = \text{chiral Schiff bases derived from the condensation of salicylaldehyde and L - aminoacids namely L - phenylalanine, L - tyrosine and L - methionine}\)) have been synthesised. The interaction of these complexes with \(\pi\)-acceptor ligands such as 2,2' - bipyridyl and 1,10 - phenanthroline have also been carried out.\(^{133}\)

Natarajan et al. have reported\(^{73}\) the reactions of bis-\(\beta\)-diketones with \([\text{RuHCl(CO)(PPh}_3\text{)}_3]\) and \([\text{RuH}_2\text{(CO)(PPh}_3\text{)}_3]\) and the new complexes have been characterised on the basis of analytical and spectral (IR, electronic, \(^1\)H-NMR and \(^{31}\)P-NMR) data. The bis-\(\beta\)-diketone ligands act as a bridge between two metal atoms and the new complexes have been formulated as \([\text{RuX(CO)(PPh}_3\text{)}_2(\text{bis-}\beta\text{-dk})]\) (\(X = \text{H or Cl} \); \(\text{bis-}\beta\text{-dk} = \text{bis-}\beta\text{-diketonate}\)).

Gopinathan et al.\(^{70}\) have carried out the reactions of \([\text{RuHCl(CO)(PPh}_3\text{)}_3]\) with 2-hydroxypyridine(py-OH) and 6-methyl-2-hydroxypyridine(Mepy-OH) in benzene which resulted in the formation of the complexes of the type \([\text{RuCl(CO)(PPh}_3\text{)}_2(\text{pyO})]\) and \([\text{RuCl(CO)(PPh}_3\text{)}_2(\text{MepyO})]\). In the same report, it was stated that the reaction between \([\text{RuHCl(CO)(PPh}_3\text{)}_3]\) and the sodium salt of 2-hydroxypyridine(pyONa) or 6-methyl-2-hydroxypyridine (MepyONa) in tetrahydrofuran affords the products of the type \([\text{RuH(CO)(PPh}_3\text{)}_2(\text{pyO})]\) and \([\text{RuH(CO)(PPh}_3\text{)}_2(\text{MepyO})]\). All the new complexes have been characterised by analytical and spectral (IR, electronic and \(^1\)H-NMR) data.
The reaction between the sodium salt of various heterocyclic dithiocarbamates and \([\text{RuHCl(CO)(PPh}_3]_2\) or \([\text{RuHCl(CO)(PPh}_3]_2(\text{B})]\) have been reported and the resulting products have been formulated as \([\text{RuH(CO)(PPh}_3]_2(\text{LL}')]\) or \([\text{RuH(CO)(PPh}_3](\text{B})](\text{LL}')]\) (\text{LL}' = \text{morpholine dithiocarbamate, piperidine dithiocarbamate, piperazine dithiocarbamate; B = pyridine, piperidine or morpholine}). In all these reactions, the heterocyclic dithiocarbamates behaved as uninegative bidentate chelating ligands.\(^{134}\)

Ruthenium(II) mixed ligand complexes of the type \([\text{RuX(CO)(PPh}_3]_2(\text{LL})]\) (\(X = \text{H or Cl; LL}' = \alpha,\beta - \text{unsaturated-}\beta\)-ketoamine) have been synthesised from the reactions of \([\text{RuH}_2(CO)(\text{PPh}_3]_3]\) or \([\text{RuHCl(CO)(PPh}_3]_3]\) with various \(\alpha,\beta - \text{unsaturated-}\beta\)-ketoamines. In all these reactions, the \(\alpha,\beta\)-unsaturated-\(\beta\)-ketoamines replaced a hydride ion and one of the triphenylphosphine groups from the starting complexes.\(^{72}\)

Synthesis, structure and photophysical studies of novel ruthenium(II) carboxypyridine complexes have been reported.\(^{136}\) Sariego et al. have studied\(^{136}\) the synthesis of ruthenium(II) complexes containing heterocyclic nitrogen ligands and their applications in catalysis.

The interaction between \(\text{NO}^+\) and \textit{trans} \(\pi\)-donor ligands in chloro (2-methyl-8-quinolinolato)nitrosyl(8-quinolinolato) ruthenium(II) complexes have been studied.\(^{137}\) Studies on the preparation of mono- and bis(hydrazine) complexes of ruthenium(II) have been reported by Albertin and co-workers.\(^{138}\) Studies on the synthesis of tetrammine ruthenium(II) and ruthenium(III) complexes containing \(\alpha\)-benzoxquinonediimine have been reported.\(^{139}\)
Synthesis and characterisation of ruthenium(II) complexes containing NNS donor Schiff bases derived from 2-methyl-2(2-pyridyl)benzothiazoline have been reported.\textsuperscript{140} The preparation of highly active ruthenium(II) complexes with bidentate phosphine ligands for the solvent free catalytic synthesis of N,N-dimethylformamide and methyl formate have been reported.\textsuperscript{141} Studies on the chemical and electrochemical synthesis, characterisation and X-ray analysis of ruthenium(II) complexes with 1,2-cis(diphenylphosphino)ethylene have been reported by Batista and co-workers.\textsuperscript{142}

Several binary, ternary and quaternary complexes of ruthenium(II) containing triphenylphosphine and 2,6-diacetylpyridine thiosemicarbazone have been reported.\textsuperscript{143} Synthesis, electrochemistry and X-ray studies of \([\eta^5-C_5H_4R]Ru(PPh_3)_2H\) (R = H or t-bu) have been carried out by Romming et al.\textsuperscript{144} A series of new arsine dihydrido ruthenium(II) complexes of the type \([RuH_2(CO)(AsPh_3)_3]\) and \([RuH_2(CO)(AsPh_3)(LL')]\) (LL' = diars, arphos, diphos) has been synthesised and characterised. The catalytic activities of these complexes for the hydrogenation of propionaldehyde to yield propane-1-ol have been examined and compared with the catalytic activity of \([RuH_2(CO)(PPh_3)_3]\).\textsuperscript{145}

The synthesis and characterisation of some penta-coordinated ruthenium(II) complexes viz., \([RuX_2(MPh_3)_{3-5}L_2]\) (X = Cl or Br; M = P or As; L = o-HOC_6H_4CHO or p- OCH_3C_6H_4CHO) have been described. The catalytic oxidation of PPh_3 in the presence of molecular oxygen by \([RuBr_2(PPh_3)_{3-5}L_2]\) (L = o-HOC_6H_4CHO or p- OCH_3C_6H_4CHO) has also been studied.\textsuperscript{146}

An interesting array of ruthenium(II) complexes with NNS donor chelating ligands have been synthesised and characterised. The chemical and electrochemical reactivity patterns of these complexes have also been explored.\textsuperscript{147}
The reactions of $[\text{RuCl}_2(\mu-O_2CCH_3)_4]$ with indole-2-carboxylic acid, N-methyl-pyrrole-2-carboxylic acid, furan-2-carboxylic acid, thiophene-2-carboxylic acid and benzofuran-2-carboxylic acid have been reported and the structure of $[\text{Ru}_2(\mu-O_2CC_4H_3S)_4(\text{OPPh}_3)_2]\text{BF}_4\cdot 2\text{H}_2\text{O}$ has been determined by X-ray crystallography.\textsuperscript{148} The synthesis and characterisation of a series of $[(\text{trpy})\text{RuCl}_2(L)]$ (trpy = 4,4′,4′′-tri-tert-butyl-2,2′-6′,2′′-terpyridine and L = CO, PPh$_3$, PMe$_3$ and PMe$_2$Ph) complexes have also been described together with a preliminary study of their $\text{trans}$ to $\text{cis}$ thermal and photochemical isomerisation.\textsuperscript{149}

Leung et al.\textsuperscript{150} have reported the synthesis and reactivities of $[\text{Ru}(\text{Et}_2\text{dtc})(\text{PPh}_3)_2(\text{CO})\text{H}]$ (Et$_2$dtc = N,N-diethyldithiocarbamate) with ArSO$_2$N$_3$ (Ar = $p$-CH$_3$C$_6$H$_4$, $p$-t-BuC$_6$H$_4$ or 2,4,6-ipt$_3$C$_6$H$_2$). Three new dinuclear ruthenium(II) complexes bridged by a pyridine-2,6-diyl-2-acetyl-6-methyl group have been prepared by thermal reaction of 2,6-bis(chloromethyl)pyridine with $[\text{Ru}_3(\text{CO})_{12}]$ followed by treatments with methanol and triphenylphosphine respectively. The crystal structures of two of them have been determined by X-ray analysis.\textsuperscript{151}

The cychloruthenated pyri-2-yl acetyl complex $[[\text{RuCl}(\text{C}_5\text{H}_4\text{N}-2-\text{CH}_2\text{CO})\text{(CO)}_2]_2]$(1) has been obtained from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with an excess of 2-(chloromethyl)pyridine in refluxing toluene. Subsequent reaction of (1) with two equivalents of triphenylphosphine in refluxing benzene afforded $[\text{RuCl}(\text{C}_5\text{H}_4\text{N}-2-\text{CH}_2\text{CO})(\text{CO})(\text{PPh}_3)_2]$.\textsuperscript{152}

Synthesis and studies on some five coordinated ruthenium(II) complexes of the type $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$ and $[\text{Ru}(\text{MPh}_3)_2\text{(CO)}\text{Cl}_2]$ (M = P or As) have been described. Further, the reactions of $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$ with N,N-dimethylformamide, dimethyl sulphoxide and pyridine have also been described.\textsuperscript{153}
Ruthenium(III) complexes containing tertiary phosphine/arsine and other ligands

Eventhough, there has been an extensive amount of research work carried out on ruthenium(II) triphenylphosphine/arsine complexes, the study on ruthenium(III) is relatively less. Some of the reactions of ruthenium(III) triphenylphosphine and arsine complexes described in the literature have been reviewed and presented here.

Ruiz-Ramirez et al.\textsuperscript{82,154} have reported the preparations of a number of ruthenium(III) complexes from the reactions of \([\text{RuX}_3(\text{EPh}_3)_2(\text{MeOH})]\) (\(X = \text{Cl or Br} ; \ E = \text{P or As}\)) with various ligands. An interesting reaction of \([\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})]\) with cyclopentadiene in presence of Zn leading to \([\{\pi\text{-C}_5\text{H}_5\}\text{Ru}(\text{AsPh}_3)_2\text{Cl}\] has also been reported.\textsuperscript{155} The complexes \([\text{RuCl}_3(\text{PPh}_3)_2(\text{MeOH})]\) and \([\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})]\) have been used as catalysts in the homogeneous reduction of 1-hexene to n-hexane.

The ruthenium(III) carbonyl phosphine complex, \([\text{RuBr}_3(\text{CO})(\text{PPh}_3)_2]\) has been prepared by Vaska,\textsuperscript{156} along with other ruthenium(III) complexes. Another ruthenium(III) carbonyl phosphine complex, \([\text{RuCl}_2(\text{CO})(\text{acac})(\text{PPh}_3)]\) (acac = acetylacetonate) has been synthesised by Agarwala et al.\textsuperscript{157} The synthesis and characterisation of \(\beta\)-diketonato\textsuperscript{157} and fluorinated-\(\beta\)-diketonato\textsuperscript{79} complexes of ruthenium(III) with triphenylphosphine and triphenylarsine have been reported. A new isomer of \([\text{RuCl}_3(\text{AsPh}_3)_3]\) has been synthesised and characterised.\textsuperscript{81}

The reactions of S-alkyl dithiocarbazates with \([\text{RuX}_3(\text{EPh}_3)_3]\) (\(X = \text{Cl or Br} ; \ E = \text{P or As}\)) have resulted in the formation of complexes of the composition \([\text{RuX}_2(\text{EPh}_3)_2(\text{LL})]\) (\(X = \text{Cl or Br} ; \ E = \text{P or As} ; \ LL = \text{RRC=NNCSSR}\)). All the new complexes have been assigned an octahedral structure on the basis of
analytical, IR, electronic and EPR spectral data. The Schiff bases deprotonate in neutral medium and behave as uninegative bidentate NS\(^-\) donor ligands.\(^{23}\)

Ruthenium(III) complexes of the type \([\text{RuCl}_2(\text{PPh}_3)_2(L)]\) \((L = \text{the monoanions of maltol, kojic acid, tropolone and acetylacetone})\) have been synthesised and characterised by microanalytical, spectral and electrochemical studies. The catalytic oxidation of alcohols by \([\text{RuCl}_2(\text{PPh}_3)_2(\text{acac})]\) \((\text{acac} = \text{acetylacetone})\) in the presence of excess N-methylmorpholine-N-oxide has also been reported.\(^{159}\)

Several new hexa-coordinated binuclear ruthenium(III) complexes of the type \([\{\text{RuX}_2(\text{EPPh}_3)_2\}_2(\text{bis-\(\beta\)-dk})]\) \((\text{X} = \text{Cl or Br}; \text{E} = \text{P or As}; \text{bis-\(\beta\)-dk} = \text{bis-\(\beta\)-diketonates})\) have been obtained from the reactions of \([\text{RuCl}_3(\text{PPh}_3)_3]\), \([\text{RuCl}_3(\text{AsPh}_3)_3]\), \([\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]\) and \([\text{RuBr}_3(\text{AsPh}_3)_3]\) with bis-\(\beta\)-diketonates in benzene. The new bis-\(\beta\)-diketonato ruthenium(III) complexes have been characterised on the basis of elemental analysis, IR, electronic, EPR and cyclic voltammetric studies.\(^{90}\)

The reactions of ruthenium(III) triphenylphosphine and triphenylarsine complexes with a series of \(\alpha,\beta\)-unsaturated-\(\beta\)-ketoamines have been carried out\(^{160}\) and the geometry of the products have been proposed on the basis of elemental analysis, IR, electronic, EPR spectral data, magnetic moment and cyclic voltammetric data.

Natarajan et al. have studied the reactions of \([\text{RuX}_3(\text{EPPh}_3)_3]\) and \([\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]\) \((\text{X} = \text{Cl or Br}; \text{E} = \text{P or As})\) with bidentate Schiff bases such as salicylidene-aniline, salicylidene-\(\alpha\)-toluidine, salicylidene-\(m\)-toluidine and salicylidene-\(p\)-toluidine. The new complexes obtained have been characterised on the basis of elemental analysis, spectral (IR, electronic, EPR) and cyclic voltammetric studies.\(^{161}\)
Much of the reports on the reactions of ruthenium(III) triphenylphosphine and triphenylarsine complexes have come from Stephenson et al.\textsuperscript{87,162} Reactions of tetramethylammonium and tetrphenylarsonium halides with $[\text{RuX}_3\text{L}_2(\text{MeOH})]$ ($X = \text{Cl or Br}; \text{L} = \text{PPh}_3$ or $\text{AsPh}_3$) gave ionic complexes of the type $M[\text{RuX}_4\text{L}_2]$ ($M = \text{Me}_4\text{N}^+; \text{Ph}_4\text{As}^+; \text{L} = \text{PPh}_3, \text{AsPh}_3; \ X = \text{Cl or Br}$).

Several new hexa-coordinated ruthenium(III) complexes of the type $[\text{RuX}_2(\text{EPh}_3)_2(\text{LL}')]$ ($X = \text{Cl or Br}; \ E = \text{P or As}; \ \text{LL}' = \text{morpholinedithiocarbamate, piperidinedithiocarbamate and piperazinedithiocarbamate}$) have been synthesised by reacting $[\text{RuX}_3(\text{EPh}_3)_3]$ and $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ with various dithiocarbamates.\textsuperscript{163} The new complexes showed a reasonable antifungal activity against \textit{Fusarium Species}.

The treatment of the triphenylphosphine and triphenylarsine complexes of the type $[\text{RuX}_3(\text{EPh}_3)_3]$ and $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ ($X = \text{Cl or Br}; \ E = \text{P or As}$) with mono- and di- selenobis-\textbeta-diketones leads to the formation of bridged binuclear complexes having the formula $[[\text{RuX}_2(\text{EPh}_3)_2]_2\text{Se}(\text{C}_5\text{H}_6\text{O}_2)_2]$ and $[[\text{RuX}_2(\text{EPh}_3)_2]_2\text{Se}_2(\text{C}_5\text{H}_6\text{O}_2)_2]$.\textsuperscript{164}

Synthesis, spectra and electrochemistry of a series of non-electrolytic, low-spin ruthenium(III) complexes containing cage-like Schiff base ligands have been reported.\textsuperscript{165} A series of low-spin ruthenium(III) complexes of the type $[\text{RuX}(\text{EPh}_3)(\text{LL}')]$ ($X = \text{Cl or Br}; \ E = \text{P or As} \text{and LL}' = \text{Salen, salpn and saldien}$) have been synthesised by reacting $[\text{RuCl}_3(\text{PPh}_3)_3]$, $[\text{RuCl}_3(\text{AsPh}_3)_3]$, $[\text{RuBr}_3(\text{AsPh}_3)_3]$ and $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ with tetradentate Schiff bases such as bis(salicylaldehyde)ethylenediimine($\text{H}_2\text{-salen}$), bis(salicylaldehyde)propylenediimine ($\text{H}_2\text{-salpn}$) and bis(salicylaldehyde)diethylenetriimine($\text{H}_2\text{-saldien}$). All the new complexes have been characterised by elemental analysis, IR, electronic and EPR spectral studies, magnetic moment and cyclic voltammetric data.\textsuperscript{166}
Ruthenium(III) complexes containing some biologically active azomethines with N(X = S or O) donor systems have been described.\textsuperscript{167}

Bhattacharya et al.\textsuperscript{168} reported the synthesis, characterisation, redox properties and reactivities of phenolato complexes of ruthenium(III) containing tertiary phosphine. Two new binuclear \(\beta\)-diketonato ruthenium(III) complexes linked by bis(ethynyl)thiophene and bis(ethynyl)anthracene have been prepared and characterised.\textsuperscript{169} The first series of isolable (nitro)ruthenium(III) complexes have been prepared by the chemical oxidation of \(\text{trans-}[\text{Ru(NO}_2\text{)(PR}_3\text{)}_2\text{(trpy)}]^+\) (R = methyl, ethyl or n-propyl) and \(\text{trans-}[\text{Ru(NO}_2\text{)(PMe}_3\text{)(PR}_3\text{)}\text{(trpy)}]^+\) (R = ethyl or n-propyl). These complexes have been characterised by elemental analysis, UV-visible spectroscopy, cyclic voltammetry and magnetic susceptibility. A study on the decomposition reactions of these complexes in acetonitrile at 25 °C have also been undertaken.\textsuperscript{170}

Several new hexa-coordinated ruthenium(III) complexes of the type \([\text{RuX(EPh}_3\text{)(LL')}\text{(x = Cl or Br; E = P or As; HLL'}\text{H = H}_2\text{acacen, H}_2\text{bzacen, H}_2\text{acacpn or H}_2\text{bzacpn)}\) have been synthesised by reacting \([\text{RuCl}_3\text{(PPh}_3\text{)}_3\text{]}, [\text{RuCl}_3\text{(AsPh}_3\text{)}_3\text{], [RuBr}_3\text{(AsPh}_3\text{)}_3\text{] and [RuBr}_3\text{(PPh}_3\text{)}_2\text{(MeOH)}\]) with tetradeionate Schiff bases. All the new complexes have been characterised by elemental analysis, IR, electronic, EPR spectral studies and cyclic voltammetric data.\textsuperscript{171}
REFERENCES


