SUMMARY

Over the last few years, an extensive amount of work has been reported on the complexes of ruthenium containing tertiary phosphines, tertiary arsines or acetylacetone as one of the ligands. Researchers have also taken much interest in the study of binuclear ruthenium complexes propagated by multi atom bridges. The interest in this area stems from attempts to investigate the electron transfer processes between metal centres, which are very essential to understand molecular electronic properties of transition metal complexes. Besides, these complexes have high potential to act as catalysts, starting materials for the synthesis of novel ruthenium complexes and antimicrobial agents. The present work concerns much with the reactions of some ruthenium(II) and ruthenium(III) complexes of triphenylphosphine, triphenylarsine or acetylacetone with a variety of binucleating ligands. The structures of ligand-bridged binuclear ruthenium complexes formed from these reactions have been investigated using various physicochemical methods. From the application point of view, the utility of these complexes as catalyst for oxidation or aryl-aryl coupling reaction, antibacterial and antifungal agents have also been investigated.

The synthesis and characterization of binuclear ruthenium(III) complexes of the type [{Ru(acac)2}2L] (acac = acetylacetonate; L = dicarboxylate) from the reactions of [Ru(acac)3] with various dicarboxylic acids have been reported. IR spectra revealed the bidentate coordination for all the dicarboxylato bridged complexes and these complexes were characterized by elemental analyses, spectral (IR, electronic, EPR), magnetic moment and cyclic voltammetry data. Some of the complexes and free ligands have been tested in vitro to assess their inhibitory activity against the bacteria Escherichia coli, Bacillus sp. and Psudomonas sp.

The reactions of ruthenium(II) complexes of the type [RuHX(CO)(AsPh3)3] (X = H or Cl) with various bis(β-diketones) of the general formula
[(RCO)(R'CO)CH–CH(R'′)–CH(COR)(COR')] [R = CH₃ or C₆H₅; R' = CH₃ or C₆H₅; R'′ = H, C₆H₅, 4-(CH₃)C₆H₄, 4-(OCH₃)C₆H₄ or 4-N(CH₃)₂C₆H₄] have been carried out. Based on the analytical and spectral studies an octahedral structure has been tentatively proposed for all the ligand-bridged binuclear complexes. The new complexes have been subjected to the antibacterial and catalytic activity studies.

A detailed investigation on the reactions of [RuX₃(EP₃)₃] (X = Cl or Br; E = P or As) or [RuBr₃(PPh₃)₂(MeOH)] with Schiff bases in a 2 : 1 molar ratio have been carried out. The Schiff bases used were prepared by condensing the appropriate diamine with salicylaldehyde or benzoylaceton e in a 2 : 1 molar ratio respectively. The products of the general formula [(RuX₂(EP₃)₂)₂L] (X = Cl or Br; E = P or As; L = binucleating Schiff base ligand) have been assigned an octahedral structure on the basis of various physicochemical data. The complexes have been used as catalyst in aryl-aryl coupling reaction in addition to the antifungal agent.

Further, we focussed our attention on the reactions of [RuCl₃(EP₃)₃], [RuCl₃(AsPh₃)₃], [RuBr₃(AsPh₃)₃] or [RuBr₃(PPh₃)₂(MeOH)] with thiobis(β-diketones) in a 2 : 1 molar ratio in benzene. The products obtained have been characterized on the basis of analytical, IR, electronic, EPR and cyclic voltammetric studies and formulated as [(RuX₂(EP₃)₂)₂(bis-β-dk)] (X = Cl or Br; E = P or As; bis-β-dk = thiobis(β-diketone)). An octahedral structure has been proposed for these complexes. The complexes are found to be effective catalysts for the oxidation of benzyl alcohol and cyclohexanol using N-methylmorpholine-N-oxide as co-oxidant. Some of the complexes and free ligands have also been screened for their antifungal activity studies.

In addition, the synthesis of binuclear ruthenium(II) complexes of the type [(RuCl(CO)(PPh₃)(B))₂(bis-β-dk)] (B = PPh₃, pyridine, piperidine or morpholine; bis-β-dk = thiobis(β-diketonato) ion) was accomplished by reacting [RuHCl(CO)(PPh₃)₃] (B = PPh₃, pyridine, piperidine or morpholine) with thiobis(β-
diketones). The new complexes obtained from these reactions have been characterized by elemental analyses, IR, electronic, $^1$H-NMR and $^{31}$P-NMR spectral data. In all these reactions, the bis(β-diketones) behaved as a tetradeutate binegative ligands by replacing one molecule of triphenylphosphine and a halide ion from the starting complex to afford the ligand-bridged binuclear complexes. Hence, it is inferred that the Ru–P bond is more labile than the Ru–N bond which may be due to the better σ donating ability of heterocyclic nitrogen bases than triphenylphosphine. The ruthenium(II) complexes exhibited catalytic oxidation property in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant. The free ligands and some ruthenium(II) complexes showed growth inhibitory activity against the bacteria Escherichia coli, Bacillus sp. and Pseudomonas sp. The antibacterial activity of the ligands and ruthenium complexes are compared with the standard, Streptomycin.

From the electrochemical studies, it has been observed that there is no appreciable change in the redox potentials due to variation in the lengths and nature of the bridging ligands. The replacement of triphenylphosphine by triphenylarsine has no significant influence on the oxidation and reduction potential of metal ion.

The efficiency of the ligand-bridged binuclear ruthenium(II) and ruthenium(III) complexes as catalysts for various reactions such as aerial oxidation of benzaldehyde to benzoic acid, aryl-aryl coupling reaction of phenylmagnesium bromide with bromobenzene and oxidation of benzyl alcohol, cinnamyl alcohol and cyclohexanol to benzaldehyde, cinnamaldehyde and cyclohexanone respectively have been investigated using N-methylmorpholine-N-oxide as co-oxidant. The following interesting observations have been made from the catalytic studies.
(i) While oxidising cinnamyl alcohol, only alcoholic group gets oxidised selectively without affecting the double bond.

(ii) Binuclear complexes showed better catalytic efficiency than the similar mononuclear complexes.

As for as biological activity studies are concerned, the complexes possess more toxicity than their parent ligands. Further, the toxicity of the metal chelates generally increases with increasing the concentration of the test solution.