CHAPTER III
Several low-spin d⁵ complexes of second and third row transition metal ions with tertiary phosphines and arsines as ligands have been reported in the literature.¹⁻⁶ However, only a few ruthenium(III) complexes with a tertiary arsine as one of the ligands are known.⁷⁻¹⁰ Though mixed ligand complexes of ruthenium(III) containing β-diketones and other related ligands have been reported,¹¹⁻¹³ the study of the reactions of tertiary phosphine or arsine complexes of ruthenium(III) with 2'-hydroxychalcones have not been reported. In view of the growing interest of mixed ligand complexes as catalysts in many reactions,¹⁴⁻¹⁶ we report in this chapter, the synthesis and characterisation of some stable ruthenium(III) complexes containing the anion of 2'-hydroxychalcones as one of the ligands.

The 2'-hydroxychalcones used in this study are of the following type.

![Chemical structure of 2'-hydroxychalcone](image-url)
where

\[
\begin{align*}
R & \quad = C_6H_5 \quad ; \quad [HL = H-C_{15}H_{11}O_2] \\
& \quad = 4-(OMe)C_6H_4 \quad ; \quad [HL = H-C_{16}H_{13}O_3] \\
& \quad = 3,4-(OMe)_2C_6H_3 \quad ; \quad [HL = H-C_{17}H_{15}O_4]
\end{align*}
\]

**EXPERIMENTAL**

Commercially available ruthenium trichloride trihydrate was used without further purification. All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures. Microanalysis of the complexes have been performed at the Research and Development Laboratory, Hindustan Photo Film Industry, Udhagamandalam. Infrared spectra of the ligands and complexes have been recorded in Perkin-Elmer 597 spectrophotometer as KBr pellets in the range 4000 - 200 cm\(^{-1}\). Electronic spectra of the complexes have been recorded in methylene chloride using Hitachi Perkin-Elmer 20/200 instrument in 900 - 200 nm range. EPR spectra of the powdered samples were recorded with a Bruker ER-200D-SRC EPR spectrometer, internally calibrated with diphenylpicrylhydrazyl (DPPH) at X-band frequencies. The magnetic susceptibility measurements were recorded on an EG & G - PARC vibrating sample magnetometer at room temperature. The cyclic voltammetric studies have been carried out in acetonitrile using a glassy carbon working electrode and all the potentials were referenced to a saturated calomel electrode (SCE). Melting points were determined using a Mettler FP 51 instrument and are uncorrected.

The starting complexes \([\text{RuCl}_3(\text{PPh}_3)_3]^2, \quad [\text{RuCl}_3(\text{AsPh}_3)_3]^1, \quad [\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]^4, \quad [\text{RuBr}_3(\text{AsPh}_3)_3]^{10}\) and the chalcones\(^{19}\) have been prepared according to the literature methods.
PREPARATION OF THE NEW COMPLEXES

(i) Preparation of ruthenium(III) complexes of the type [RuCl₂(L)(PPh₃)₂]
(HL = 2'-hydroxychalcones)

To a solution of [RuCl₃(PPh₃)₃] (0.150 g, 0.150 mmol) in benzene (20 cm³), the appropriate 2'-hydroxychalcone (0.033 - 0.044 g, 0.150 mmol) was added (molar ratio of ruthenium complex : 2'-hydroxychalcone is 1:1). The resulting solution was heated under reflux on a water bath for about 4 hr. After concentrating the solution to about 3 cm³, the new complexes were precipitated by the addition of a small quantity of petroleum ether(60 - 80 °C). The product was filtered, washed with petroleum ether(60 - 80 °C) and recrystallised from CH₂Cl₂/petroleum ether(60 - 80 °C) mixture and dried in air.

Yield : 62 - 67 %.

(ii) Preparation of complexes of the type [RuCl₂(L)(AsPh₃)₂]
(HL = 2'-hydroxychalcones)

To a solution of [RuCl₃(AsPh₃)₃] (0.150 g, 0.133 mmol) in benzene (20 cm³), the appropriate 2'-hydroxychalcone (0.030 - 0.038 g, 0.133 mmol) was added (molar ratio of ruthenium complex : 2'-hydroxychalcone is 1:1). The resulting solution was heated under reflux on a water bath for about 4 hr. After concentrating the solution to about 3 cm³, the new complexes were precipitated by the addition of a small quantity of petroleum ether(60 - 80 °C). The product was filtered, washed with petroleum ether(60-80 °C) and recrystallised from CH₂Cl₂/petroleum ether( 60 - 80 °C) mixture and dried in air.

Yield : 65 - 70 %.
(iii) **Preparation of complexes of the type [RuBr₂(L)(PPh₃)₂]**

(ΔL = 2'-hydroxychalcones)

To a solution of [RuBr₃(PPh₃)₂(MeOH)] (0.150 g, 0.167 mmol) in benzene (20 cm³), the appropriate 2'-hydroxychalcone (0.038 - 0.048 g, 0.167 mmol) was added (molar ratio of ruthenium complex : 2'-hydroxychalcone is 1:1). The resulting solution was heated under reflux on a water bath for about 4 hr. After concentrating the solution to about 3 cm³, the new complexes were precipitated by the addition of a small quantity of petroleum ether (60 - 80 °C). The product was filtered, washed with petroleum ether (60 - 80 °C) and recrystallised from CH₂Cl₂/petroleum ether (60 - 80 °C) and dried in air.

Yield : 60 - 70 %.

(iv) **Preparation of complexes of the type [RuBr₂(L)(AsPh₃)₂]**

(ΔL = 2'-hydroxychalcones)

To a solution of [RuBr₃(AsPh₃)₃] (0.150 g, 0.120 mmol) in benzene (20 cm³), the appropriate 2'-hydroxychalcone (0.027 - 0.034 g, 0.120 mmol) was added (molar ratio of ruthenium complex : 2'-hydroxychalcone is 1:1). The resulting solution was heated under reflux on a water bath for about 4 hr. After concentrating the solution to about 3 cm³, the new complexes were precipitated by the addition of a small quantity of petroleum ether (60 - 80 °C). The product was filtered, washed with petroleum ether (60 - 80 °C) and recrystallised from CH₂Cl₂/petroleum ether (60 - 80 °C) and dried in air.

Yield : 61 - 65 %.
RESULTS AND DISCUSSION

Air and light stable complexes of the general formula \([\text{Ru}X_2(L)(E\text{Ph}_3)_2]\) (\(X = \text{Cl} \text{ or Br}; \, \text{HL} = 2'-\text{hydroxychalcones}; \, E = \text{P or As}\)) have been obtained from the reactions of \([\text{RuCl}_3(\text{PPh}_3)_3]\), \([\text{RuCl}_3(\text{AsPh}_3)_3]\), \([\text{RuBr}_3(\text{PPh}_3)(\text{MeOH})]\) or \([\text{RuBr}_3(\text{AsPh}_3)_3]\) with the respective chalcones in 1:1 molar ratio in benzene as shown by the equation below.

\[
\begin{align*}
[\text{RuX}_3(\text{EPh}_3)_3] \\
\text{or} \\
[\text{RuBr}_3(\text{PPh}_3)(\text{MeOH})] \\
\end{align*}
\begin{align*}
\text{+} \\
\text{CH} \\
\text{CHR} \\
\text{C} \\
\text{=O} \\
\text{OH} \\
\end{align*}
\]

\[(X = \text{Cl or Br; } E = \text{P or As; } R = \text{C}_6\text{H}_5, \, 4-(\text{OMe})\text{C}_6\text{H}_4, \, 3,4-(\text{OMe})_2\text{C}_6\text{H}_3).\]
Table III. 1 Analytical data of new ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Melting point (°C)</th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₂(C₅H₁₁O₂)(PPh₃)₂]</td>
<td>Brown</td>
<td>125</td>
<td>66.32 (66.61)</td>
<td>4.91 (4.45)</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₁O₂)(AsPh₃)₂]</td>
<td>Brown</td>
<td>160-62</td>
<td>61.20 (60.80)</td>
<td>4.12 (4.07)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₁O₂)(PPh₃)₂]</td>
<td>Brown</td>
<td>154</td>
<td>60.42 (60.74)</td>
<td>4.01 (4.06)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₁O₂)(AsPh₃)₂]</td>
<td>Brown</td>
<td>135</td>
<td>55.47 (55.87)</td>
<td>3.95 (3.74)</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₃O₃)(PPh₃)₂]</td>
<td>Red brown</td>
<td>182</td>
<td>65.92 (65.77)</td>
<td>4.38 (4.53)</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₃O₃)(AsPh₃)₂]</td>
<td>Yellow brown</td>
<td>132-35</td>
<td>60.53 (60.20)</td>
<td>4.45 (4.15)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₃O₃)(PPh₃)₂]</td>
<td>Red brown</td>
<td>151-53</td>
<td>60.45 (60.14)</td>
<td>4.61 (4.14)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₃O₃)(AsPh₃)₂]</td>
<td>Brown</td>
<td>142</td>
<td>55.80 (55.45)</td>
<td>4.20 (3.82)</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₅O₄)(PPh₃)₂]</td>
<td>Brown</td>
<td>162</td>
<td>65.25 (64.99)</td>
<td>5.02 (4.59)</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₅O₄)(AsPh₃)₂]</td>
<td>Yellow brown</td>
<td>120</td>
<td>59.50 (59.64)</td>
<td>4.32 (4.22)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₅O₄)(PPh₃)₂]</td>
<td>Red brown</td>
<td>108-10</td>
<td>59.87 (59.85)</td>
<td>3.84 (4.21)</td>
</tr>
<tr>
<td>[RuBr₂(C₅H₁₅O₄)(AsPh₃)₂]</td>
<td>Brown</td>
<td>135</td>
<td>55.41 (55.05)</td>
<td>3.51 (3.89)</td>
</tr>
</tbody>
</table>
In all these reactions, the chalcones behave as an uninegative bidentate chelating ligand similar to β-diketones by replacing one of the halide ions and a molecule of triphenylphosphine or arsine or methanol from the starting complexes. The analytical data obtained for the new complexes (Table III. 1) agree very well with the above molecular formula.

IR Spectra

The important infrared frequencies of the new ruthenium(III) complexes are given in Table III. 2. An intense band observed around 1620 - 1630 cm\(^{-1}\) in the IR spectra of the free chalcones due to \(\nu_{\text{C=O}}\) has been shifted to lower wavenumber in the spectra of the complexes suggesting the coordination of the chalcones to the ruthenium ion through the carbonyl oxygen atom.\(^{20}\) The phenolic \(\text{C} - \text{O}\) stretching absorption of the free chalcones occurs as a doublet in the region 1330 - 1360 cm\(^{-1}\), but in the spectra of the complexes, this band has been shifted to higher wavenumber by 5 - 20 cm\(^{-1}\) and appears as a singlet, indicating that the other coordination site is the phenolic oxygen atom. This has been further supported by the disappearance of the broad \(\nu_{\text{OH}}\) band in the spectra of the complexes. Based on these facts, it is inferred that both the carbonyl and phenolic oxygen atoms are involved in the coordination of the chalcones to the ruthenium ion in all these complexes. The absorption due to \(\nu_{\text{C=C}}\) appears as a separate band in the infrared spectra of some complexes and in some other complexes it could not be identified because of its possible merger with the strong \(\nu_{\text{C=O}}\) band.\(^{21,22}\) Another band observed in the region 1540 - 1570 cm\(^{-1}\) in the spectra of free ligands is assigned to the phenylalkene vibration and is shifted to lower wavenumbers by 10 - 20 cm\(^{-1}\) in the spectra of ruthenium complexes.\(^{23}\) The \(\nu_{\text{Ru-Cl}}\) and \(\nu_{\text{Ru-Br}}\) absorption bands appeared around 320 cm\(^{-1}\) in the spectra of all the complexes. All other characteristic bands due to triphenylphosphine, arsine and chalcones were also present in the expected region.
Table III. 2 Infrared and electronic spectral data of the new ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν &lt;sub&gt;C=O&lt;/sub&gt;</th>
<th>ν &lt;sub&gt;C=C&lt;/sub&gt;</th>
<th>ν &lt;sub&gt;Ph-C=C&lt;/sub&gt;</th>
<th>ν &lt;sub&gt;C-O&lt;/sub&gt;</th>
<th>λ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>-</td>
<td>1540</td>
<td>1370</td>
<td>340, -</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1610</td>
<td>1580</td>
<td>1540</td>
<td>1380</td>
<td>360, 270</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>1575</td>
<td>1530</td>
<td>1365</td>
<td>340, 280</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>-</td>
<td>1530</td>
<td>1370</td>
<td>360, 280</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>-</td>
<td>1520</td>
<td>1360</td>
<td>390, -</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>1580</td>
<td>1540</td>
<td>1380</td>
<td>380, 260</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>1570</td>
<td>1530</td>
<td>1360</td>
<td>380, 280</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>1580</td>
<td>1535</td>
<td>1370</td>
<td>375, 260</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>-</td>
<td>1530</td>
<td>1370</td>
<td>390, 270</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1610</td>
<td>1570</td>
<td>1530</td>
<td>1380</td>
<td>380, 270</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>-</td>
<td>1535</td>
<td>1375</td>
<td>390, 275</td>
</tr>
<tr>
<td>[RuBr&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;)(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1600</td>
<td>1570</td>
<td>1530</td>
<td>1370</td>
<td>380, 270</td>
</tr>
</tbody>
</table>

ν in cm<sup>-1</sup>; λ max in nm.
Electronic Spectra

The ground state of Ru(III) is $^{2}T_{2g}$ and the first excited doublet levels in the increasing order of energy are $^{2}A_{2g}$ and $^{2}T_{1g}$ which arise from the $t_{2g}^{4}e_{g}^{1}$ configuration. In most of the ruthenium(III) complexes the UV and visible spectra show only charge transfer bands. In a d$^{5}$ system, and especially in ruthenium(III) which has relatively high oxidising properties, the charge transfer bands of the type $L_{v} \rightarrow t_{2g}$ are prominent in the low energy region which obscure the weaker d - d transition bands. The electronic spectra of all the new ruthenium(III) chalconato complexes in methylene chloride solution showed two bands in the region 390 - 260 nm (Table III. 2). On the basis of very high extinction coefficients, these bands have been assigned to charge transfer transitions of the type $L_{v} \rightarrow t_{2g}$. These bands are very characteristic of an octahedral ruthenium(III) complexes and, hence, an octahedral geometry has been proposed tentatively for all the new complexes.

Magnetic Moment Studies

The magnetic moments of the complexes [RuBr$_2$(C$_{15}$H$_{11}$O$_2$)(PPh$_3$)$_2$] and [RuCl$_2$(C$_{16}$H$_{13}$O$_3$)(PPh$_3$)$_2$] have been measured at room temperature using a vibrating sample magnetometer and diamagnetic corrections have been applied. The values are 1.74 and 1.81 BM, respectively, corresponding to one unpaired electron indicating a low-spin d$^{5}$ configuration for the ruthenium(III) ion in all these complexes.

EPR Spectral Studies

The nature and extent of the distortions of grossly octahedral environment of low-spin d$^{5}$ systems can be studied by EPR spectra. A general distortion of the octahedron is expressed as the sum of axial and rhombic distortions. The axial...
distortions which can be tetragonal (or trigonal) splits the one electron $t_2$ representation into 'b' and 'e' representations (small letters are used for one electron representation and capital letters for state representation). The rhombic components split ‘e’ further into two non-degenarate orbitals. The axial splitting parameter ($\Delta$) is said to be positive when ‘b’ lies above ‘e’ as in Fig. 1. In the $d^5$ system, the spin orbit coupling parameter ($\lambda$) is positive.

Fig. 1

In a tetragonal system with Z as the tetragonal axis, $d_{xy}$ lies above $d_{xz}$ and $d_{yz}$ when $\Delta$ is positive and $d_{yz}$ lies above $d_{xz}$ when the added rhombic splitting $V$ is positive. In a trigonal system (here z is the trigonal axis) $\Delta$ is positive when $d_{z^2}$ lies highest.
The ground state of ruthenium(III) is $^2T_{2g}$ in the strong cubic field. In a tetragonal field it is split into two states, namely, a doubly degenerate $^2B_2$ state and a four fold degenerate $^2E$ state. These two states have a total energy separation of $\delta$ which is defined as the tetragonal field strength. First order spin orbit coupling within these states further splits the $^2E$ states into two doubly degenerate spin states. As a result of these interactions and the interactions in the magnetic field, it can be shown in an octahedral with tetragonal distortion, $g_x = g_y \neq g_z$ and one should, thus, expect two values for 'g'.\textsuperscript{26} A mathematical expression to calculate the values of $g_\perp$ and $g$ for low spin d\textsuperscript{5} system having an octahedral symmetry with tetragonal distortion has been given.\textsuperscript{27} The presence of three 'g' values suggests an octahedral geometry with rhombic distortion in which case $g_x \neq g_y \neq g_z$.\textsuperscript{26}

The solid state EPR spectra at X-band frequencies for some new ruthenium(III) 2'-hydroxchalconato complexes have been recorded at room temperature. Most of the complexes exhibit spectra characteristic of an axially symmetric system with $g_\parallel$ around 2.28 to 2.49 and $g_\perp$ around 2.02 to 2.30 (Table III. 3. Fig. III. 1). Two different 'g' values indicate tetragonal distortion in these complexes, since for an octahedral field with tetragonal distortion $g_x = g_y \neq g_z$. However, four of the complexes showed only one signal with 'g' values between 2.26 - 2.30 indicating a very high symmetry around the metal ion. Such isotropic lines are usually observed either due to the intermolecular spin exchange which can broaden the EPR lines or due to the occupancy of the unpaired electron in a degenerate orbital. The observed 'g' values are similar to those observed for other octahedral ruthenium(III) complexes.\textsuperscript{11,28-30}
Table III. 3  EPR spectral data of some ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$\langle g \rangle^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₂(C₁₅H₁₆O₂)(PPh₃)₂]</td>
<td>2.28</td>
<td>2.28</td>
<td>2.02</td>
<td>2.19</td>
</tr>
<tr>
<td>[RuCl₂(C₁₅H₁₆O₂)(AsPh₃)₂]</td>
<td>2.43</td>
<td>2.43</td>
<td>2.26</td>
<td>2.37</td>
</tr>
<tr>
<td>[RuCl₂(C₁₆H₁₉O₃)(PPh₃)₂]</td>
<td>-</td>
<td>2.27</td>
<td>-</td>
<td>2.27</td>
</tr>
<tr>
<td>[RuCl₂(C₁₆H₁₉O₃)(AsPh₃)₂]</td>
<td>2.46</td>
<td>2.46</td>
<td>2.25</td>
<td>2.39</td>
</tr>
<tr>
<td>[RuBr₂(C₁₆H₁₉O₃)(AsPh₃)₂]</td>
<td>2.49</td>
<td>2.49</td>
<td>2.30</td>
<td>2.43</td>
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<td>[RuCl₂(C₁₇H₁₈O₄)(PPh₃)₂]</td>
<td>-</td>
<td>2.26</td>
<td>-</td>
<td>2.26</td>
</tr>
<tr>
<td>[RuBr₂(C₁₇H₁₈O₄)(PPh₃)₂]</td>
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<td>2.26</td>
<td>-</td>
<td>2.26</td>
</tr>
<tr>
<td>[RuBr₂(C₁₇H₁₈O₄)(AsPh₃)₂]</td>
<td>-</td>
<td>2.30</td>
<td>-</td>
<td>2.30</td>
</tr>
</tbody>
</table>

$$\langle g \rangle^* = \left[ \frac{1}{\frac{1}{g_x^2} + \frac{1}{g_y^2} + \frac{1}{g_z^2}} \right]^{1/2}$$

DPPH was used as field marker ($g = 2.0036$) and was internally calibrated.
[RuCl₂(C₁₅H₁₁O₂)(PPh₃)₂]

FIG. III-1 (i) EPR spectra

[RuCl₂(C₁₅H₁₁O₂)(AsPh₃)₂]

FIG. III-1 (i) EPR spectra
FIG. III. 1(ii) EPR spectra
FIG. III-1 (iii) EPR spectra
Cyclic Voltammetric Studies

In an electrochemical redox experiment, electrons are usually transferred heterogeneously between the electrode surface and the dissolved electroactive substance. In the case of ruthenium complexes, the two types of processes can be represented as,

\[
\begin{align*}
\text{RuL} + e^- & \rightarrow \text{[RuL]} \\
\text{RuL} + e^- & \rightarrow \text{Ru[L]}
\end{align*}
\]

where,

L is a general ligand. In each case, the box schematically represents the primary nature of the redox orbital, i.e., the orbital occupied by the transferred electron. The orbital is essentially metal in character in equation (1) and ligand in character in equation (2). The oxidation state of the metal changes in equation (1) while that of the ligand changes in equation (2).

We have studied cyclic voltammetry for some of the ruthenium(III) complexes presented in this thesis by the consideration of metal centered redox reactions only. Ruthenium spans all oxidation states in the range -2 to +8 with the exception of -1.\textsuperscript{31} In terms of the number of known compounds and the amount of available chemistry, a three tier classification can be made as, uncommon, common and very common. These classifications are set out in the following table. The two very common oxidation states belong to the medium level while the high and very low (-2) oxidation states are uncommon.
Classification of oxidation states of ruthenium

A. Degree of oxidation

<table>
<thead>
<tr>
<th>Type</th>
<th>Oxidation States</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) high</td>
<td>+5, +6, +7 and +8</td>
</tr>
<tr>
<td>b) medium</td>
<td>+2, +3 and +4</td>
</tr>
<tr>
<td>c) low</td>
<td>-2, 0 and +1</td>
</tr>
</tbody>
</table>

B. Occurrence

<table>
<thead>
<tr>
<th>Type</th>
<th>Oxidation States</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) uncommon</td>
<td>-2, +5, +6, +7 and +8</td>
</tr>
<tr>
<td>b) common</td>
<td>0, +1 and +4</td>
</tr>
<tr>
<td>c) very common</td>
<td>+2 and +3</td>
</tr>
</tbody>
</table>

As the ligands used in our work are not reversibly reduced or oxidised within the potential limit employed, we assumed that the redox processes observed for the complexes are metal centered only. Fast electron transfer processes are expected for low-spin six coordinate ruthenium(III) complexes, since electrons can be added to or removed from \(t_{2g}\) orbitals. These orbitals are sterically more accessible than the \(e_g\) orbitals and electron changes within the \(t_{2g}\) set requires less reorganisation energy than changes within \(e_g\) orbitals. In general, the charge transfer process for the Ru\(^{III}\) - Ru\(^{II}\) couple is not as rapid as in the case for Ru\(^{IV}\) - Ru\(^{III}\) couple.\(^{32}\)

Cyclic voltammetric studies have been carried out for some of the new ruthenium(III) complexes in acetonitrile solution at a glassy carbon working electrode at the scan rate of 100 mVs\(^{-1}\). The supporting electrolyte (tetrabutyl ammonium perchlorate) used was 0.05 M. The concentration of the ruthenium complex was 0.001 M. The solution was degassed with a current of nitrogen before scanning. The cyclic voltammogram data are given in Table III. 4 and the representative cases are displayed in Fig. III. 2. The redox processes observed for these complexes within the potential limit of +1.0 V to -1.0 V are metal centered only. Cyclic voltammograms of all the complexes showed reversible
Table III. 4 Cyclic voltammetric data of some ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \text{Ru}^{IV} ) - ( \text{Ru}^{III} )</th>
<th>( \text{Ru}^{III} ) - ( \text{Ru}^{II} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{pa}(V) ) ( E_{pc}(V) ) ( E_f(V) ) ( \Delta E_p(mV) )</td>
<td>( E_{pc}(V) ) ( E_{pa}(V) ) ( E_f(V) ) ( \Delta E_p(mV) )</td>
</tr>
<tr>
<td>([\text{RuCl}<em>2(\text{C}</em>{15}\text{H}_{11}\text{O}_2)(\text{PPh}_3)_2])</td>
<td>0.66 0.60 0.63 60</td>
<td>-0.32 -0.40 -0.36 80</td>
</tr>
<tr>
<td>([\text{RuBr}<em>2(\text{C}</em>{15}\text{H}_{11}\text{O}_2)(\text{PPh}_3)_2])</td>
<td>0.76 0.66 0.71 100</td>
<td>-0.24 -0.30 -0.27 60</td>
</tr>
<tr>
<td>([\text{RuBr}<em>2(\text{C}</em>{15}\text{H}_{11}\text{O}_2)(\text{AsPh}_3)_2])</td>
<td>0.69 0.61 0.65 80</td>
<td>-0.25 -0.32 -0.29 70</td>
</tr>
<tr>
<td>([\text{RuCl}<em>2(\text{C}</em>{16}\text{H}_{13}\text{O}_3)(\text{AsPh}_3)_2])</td>
<td>0.67 0.61 0.64 60</td>
<td>-0.36 -0.42 -0.39 60</td>
</tr>
<tr>
<td>([\text{RuBr}<em>2(\text{C}</em>{16}\text{H}_{13}\text{O}_3)(\text{AsPh}_3)_2])</td>
<td>0.68 0.62 0.65 60</td>
<td>-0.32 -0.38 -0.35 60</td>
</tr>
<tr>
<td>([\text{RuBr}<em>2(\text{C}</em>{17}\text{H}_{15}\text{O}_4)(\text{PPh}_3)_2])</td>
<td>0.71 0.65 0.68 60</td>
<td>-0.29 -0.35 -0.32 60</td>
</tr>
</tbody>
</table>

\(^a\) Supporting electrolyte: 0.05 M \([\text{NBu}_4]\text{ClO}_4\); concentration of the complex is 0.001 M; all potentials are referenced to saturated calomel electrode(SCE); \( E_f = 0.5 \left( E_{pa}+E_{pc} \right) \) where \( E_{pa} \) and \( E_{pc} \) are the anodic and cathodic peak potentials respectively; scan rate is 100 mVs.\(^1\)
FIG. III-2 (i) Cyclic Voltammograms
FIG. III-2 (ii) Cyclic Voltammograms

\[ \text{[RuCl}_2 (\text{C}_{16}\text{H}_{13}\text{O}_3)(\text{AsPh}_3)_2] } \]

\[ \text{[RuBr}_2 (\text{C}_{17}\text{H}_{15}\text{O}_4)(\text{PPh}_3)_2] } \]

V vs SCE

FIG. III-2 (ii) Cyclic Voltammograms
redox couples. The oxidation and reduction potentials of all the complexes are characterised by well defined waves with $E_f$ values in the range 0.63 V to 0.70 V ($\text{Ru}^{IV} - \text{Ru}^{II}$) and -0.27 V to -0.39 V ($\text{Ru}^{III} - \text{Ru}^{II}$) versus a saturated calomel electrode (SCE). The observed electrochemical data of these complexes showed a reversible redox couple with peak to peak separation values ($\Delta E_p$) ranging from 60 to 100 mV, characteristic of a single step, one-electron transfer process, which is similar to that observed for other similar ruthenium(III) complexes. From the electrochemical studies it is evident that,

(i) There is not much variation in the redox potentials of the complexes due to various substitution in the 2'-hydroxychalcone ligands.

(ii) There is a decrease in the redox potentials of chloro complexes as compared to that of bromo complexes which may be due to the greater electronegativity of chloride ligand compared to bromide.

Based on the analytical, spectroscopic and electrochemical data, the following octahedral structure has been tentatively proposed for all the new ruthenium(III) complexes.

\[
\text{EPh}_3 \quad \text{Ru} \quad \text{EPh}_3
\]

\[
\begin{array}{c}
\text{CHR} \\
\text{CH} \\
\end{array}
\]

\[
(X = \text{Cl or Br}; \text{E} = \text{P or As}; \text{R} = \text{C}_6\text{H}_5, 4-(\text{OMe})\text{C}_6\text{H}_4 \text{ or } 3,4-(\text{OMe})_2\text{C}_6\text{H}_3).
\]
REFERENCES


