Chemistry of some ruthenium phenolates: synthesis, structure and redox properties

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Received 16 March 2000; accepted 28 April 2000

Abstract

Reaction of three phenolate ligands, viz. 2,4,6-tribromophenol (HL 1, where H stands for the phenolic proton), 2-nitrophenol (HL 2) and 2,4,6-trinitrophenol (HL 3O), with [Ru(PPh 3) 3Cl 2] in a 2:1 molar ratio in the presence of a base gives complexes of type [Ru(PPh 3) 2(L) 2] (L = L 1, L 2 and L 3). The 2,4,6-tribromophenolate ligand (L 1) binds to ruthenium as a bidentate O,Br-donor, while the 2-nitrophenolate ligand (L 2) acts as a bidentate O,O-donor. 2,4,6-Trinitrophenol (HL 3O) undergoes oxygen loss from one nitro group at the ortho position and coordinates to ruthenium in the 2-nitroso-4,6-dinitrophenolate (L 3) form through the nitroso nitrogen and phenolate oxygen. The structures of the [Ru(PPh 3)(L 1)] 2 and [Ru(PPh 3)(L 3)] 2 complexes have been solved by X-ray crystallography. In [Ru(PPh 3)(L 1)] 2 the coordination sphere around ruthenium is O 2P2Br 2 with a trans–cis–cis disposition of the three sets of donor atoms, respectively. In [Ru(PPh 3)(L 3)] 2 ruthenium has a N 2O 2P 2 coordination sphere with a cis–cis–trans arrangement of the three sets of donor atoms, respectively. The [Ru(PPh 3)(L 1)] 2 complexes are diamagnetic (low-spin d 6, S = 0) and in acetonitrile solution show intense MLCT transitions in the visible region. Cyclic voltammetry on the [Ru(PPh 3)(L) 2] complexes shows a reversible ruthenium(II)–ruthenium(III) oxidation within 0.63–0.71 V versus SCE followed by an irreversible ruthenium(III)–ruthenium(IV) oxidation near 1.5 V versus SCE. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium; Phenolic ligands; Synthesis; Structure; Redox properties

1. Introduction

There is much current interest in the chemistry of ruthenium [1–10], most of which is due to the fascinating electron-transfer and energy-transfer properties displayed by the complexes of this metal. The coordination environment around the metal primarily dictates properties of the ruthenium complexes. Complexation of ruthenium by ligands of different types has thus been of particular interest. In the present work, which has emerged from our continued interest in the chemistry of ruthenium in different coordination environments [11–25], our objective has been to explore the chemistry of ruthenium bound to phenolate oxygens. Phenolate oxygen is a recognized hard donor and hence coordination of ruthenium by phenolate oxygen is of particular importance with regard to stabilization of the higher oxidation states of this metal [26–29]. The initial goal of the present study was to investigate the coordinating ability of simple phenols with no additional donor atoms. As a source of ruthenium, [Ru(PPh 3) 3Cl 2] has been used, which is well known for its efficiency in binding to ligands of different types via dissociation of PPh 3 and chloride ligands [29–33]. However, we have observed that until a second donor site is incorporated at the ortho position of the phenyl ring, no tractable phenolate complex is formed.
When phenols of type 1 (abbreviated in general as HL, where H stands for the dissociable phenolic proton) are used, where D is the second donor atom linked to the ortho carbon directly or via one intervening atom, stable complexes of general formula \([\text{Ru}^0(\text{PPh}_3)_2(L)_2]\) are formed. The chemistry of these complexes is described in this paper with special reference to synthesis, structure and redox properties.

2. Experimental

2.1. Materials

Commercial ruthenium trichloride was purchased from Arora Matthey, Calcutta, India and was converted to RuCl\(_3\)·3H\(_2\)O by repeated evaporation with concentrated hydrochloric acid. Triphenylphosphine, triethylamine, 2,4,6-tribromophenol (HL\(_1\)), 2-nitrophenol (HL\(_2\)) and 2,4,6-trinitrophenol (HL\(_3\)O) were obtained from SD Fine Chemicals, Mumbai, India. [Ru(PPh\(_3\))\(_2\)Cl\(_2\)] was prepared following a reported procedure [34]. Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature [35,36]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Preparation of complexes

2.2.1. [Ru(PPh\(_3\))\(_3\)Cl\(_2\)]

[Ru(PPh\(_3\))\(_3\)Cl\(_2\)] (100 mg, 0.10 mmol) and 2,4,6-tribromophenol (85 mg, 0.26 mmol) were taken up in 30 cm\(^3\) methanol and triethylamine (42 mg, 0.42 mmol) was added. The resulting mixture was stirred for 2 h. A dark-red microcrystalline solid separated out, which was collected by filtration, washed with methanol and dried in air. Recrystallization from dichloromethane–benzene afforded shiny red crystals of [Ru(PPh\(_3\))\(_3\)Cl\(_2\)]. The yield was 34 mg (30%).

2.2.2. [Ru(PPh\(_3\))\(_2\)L\(_1\)\(_2\)]

This compound was prepared by the same above procedure using 2-nitrophenol instead of 2,4,6-tribromophenol. The yield was 70 mg (75%).

2.2.3. [Ru(PPh\(_3\))\(_2\)L\(_2\)\(_2\)]

To a solution of 2,4,6-trinitrophenol (50 mg, 0.22 mmol) in ethanol (30 cm\(^3\)) was added [Ru(PPh\(_3\))\(_3\)Cl\(_2\)] (100 mg, 0.10 mmol) and triethylamine (42 mg, 0.42 mmol). The resulting mixture was heated at reflux for 2.5 h to produce a red solution. Upon cooling the solution to room temperature, a dark red crystalline solid separated out, which was collected by filtration, washed with ethanol and dried in air. Recrystallization from dichloromethane–benzene afforded shiny red crystals of [Ru(PPh\(_3\))\(_2\)L\(_2\)\(_2\)]. The yield was 94 mg (75%).

2.3. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin–Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV 240 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker scientific L75FBAL magnet. Electrochemical measurements were made using a PAR model 273 potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a thre electrode configuration. A RE 0089 X-Y recorder was used to trace the voltammograms. Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.4. Crystallography

Single crystals of [Ru(PPh\(_3\))\(_3\)L\(_1\)\(_2\)] were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 25 centered reflections (11.4 ≤ θ ≤ 25.5°). Data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo K\(_\alpha\) radiation (λ = 0.71073 Å) by ω scans within the angular range 2.15 < θ < 27.49°. Three standard reflections were used to check the crystal stability towards X-ray exposure and they showed no significant intensity variation over the course of data collection. X-ray data reduction, structure solution and refinement were done using the SHELXS-97 and SHELXL-97 packages. The structure was solved by the direct method.

Single crystals of [Ru(PPh\(_3\))\(_2\)L\(_2\)\(_2\)] were grown by slow diffusion of benzene into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 25 centered reflections (10.84 < θ < 19.80°). Data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo K\(_\alpha\) radiation (λ = 0.71073 Å) by θ–2θ scans within 20 max 50.0°. Three standard reflections, used to check the crystal stability towards X-ray exposure, showed no significant
intensity variation over the course of data collection. X-ray data reduction, and structure solution and refinement were done using the NRCVAX package. The structure was solved by the direct method.

<table>
<thead>
<tr>
<th>Crystallographic data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>[Ru(PPh₃)₂(L)₂]</strong></td>
</tr>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a (Å)</td>
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<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
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<tr>
<td>β (°)</td>
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<tr>
<td>V (Å³)</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
</tr>
<tr>
<td>T (K)</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
</tr>
<tr>
<td>R indices</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>GOF</td>
</tr>
</tbody>
</table>

a = R₁ = Σ|Fᵢ|–|Fᵢ'|/Σ|Fᵢ|, where M is the number of reflections and N is the number of parameters refined.

b = wR₂ = [Σw(Fᵢ²–Fᵢ'²)]/Σw(Fᵢ²)]²/2.
c = R₁ = Σ|Fᵢ|–|Fᵢ'|/Σ|Fᵢ|, where M is the number of reflections and N is the number of parameters refined.
d = R_e = [Σw(Fᵢ²–Fᵢ'²)]/2Σw(Fᵢ²)]²/2.
e = GOF = [Σw(Fᵢ²–Fᵢ'²)(M–N)]²/2, where M is the number of reflections and N is the number of parameters refined.
f = GOF = [Σw(Fᵢ²–Fᵢ'²)]²/(M–N)]²/2, where M is the number of reflections and N is the number of parameters refined.

3. Results and discussion

Three phenolic ligands have been used in the present study which are shown, along with their individual abbreviation and coordination mode, in Fig. 1. The phenolic ligands react smoothly with [Ru(PPh₃)₃Cl₂] in the presence of a base to afford complexes of type [Ru(PPh₃)₂(L)₂]Cl₂. It may be noted here that unlike in the reactions of the first two phenolic ligands, heating of the reaction mixture at reflux was necessary in the reaction of 2,4,6-trinitrophenol with [Ru(PPh₃)₂Cl₂] for obtaining the phenolate complex. It is also interesting to note that 2,4,6-trinitrophenol undergoes oxygen loss from one nitro group during the course of the synthetic reaction and coordinates in the nitrosophenolate fashion. Hence 2,4,6-trinitrophenol is abbreviated as HL₃O (see Fig. 1) to underline this oxo-transfer reaction. Mechanism of this oxygen loss reaction is not yet clear. However, oxygen from the nitro group is probably transferred to the PPh₃, dissociated from [Ru(PPh₃)₂Cl₂]. Indirect evidence of this oxo-transfer comes from detection of OPPh₃ in the residue of the synthetic reaction (after isolation of [Ru(PPh₃)₂(L)₂]), identified by its characteristic infrared spectrum (ν_P–O observed at 1185 cm⁻¹). Triphenylphosphine is well known to act as an oxygen-scavenger in many oxo-transfer reactions [37–40]. The role of [Ru(PPh₃)₂Cl₂] in this oxo-transfer reaction is not yet clear, but that it does not act as a mere supplier of PPh₃ is clear from the fact that a mixture of PPh₃ and 2,4,6-trinitrophenol is unable to bring about any oxo-transfer reaction. Prior coordination of the 2,4,6-trinitrophenolate ligands to ruthenium in the nitrophenolate fashion followed by oxo-transfer from the metal-bound ligands appears to be probable. It may also be noted here that the yield of 2[Ru(PPh₃)₂Cl₂] + 2HL₃O
→ [Ru(PPh₃)₂(L)₂] + 2HCl + 2OPPh₃ + [Ru(PPh₃)₂Cl₂]

(1)

[Ru(PPh₃)₂(L)₂] is rather low, which might be attributed to the fact that [Ru(PPh₃)₂Cl₂] dissociates in solution yielding free PPh₃ and an unstable [Ru(PPh₃)₂Cl₂] species [41,42]. Hence 2 mol of [Ru(PPh₃)₂Cl₂] (which supply 2 mol of PPh₃) are required for the reduction of 2 mol of 2,4,6-trinitrophenol. The 2 mol of reduced ligand (L²) utilize only 1 mol of [Ru(PPh₃)₂Cl₂] for complex formation (Eq. (1)). The other mole of [Ru(PPh₃)₂Cl₂] probably undergoes decomposition [41,42]. Some characterization data of the complexes are given in Table 2. Elemental (C, H, N) analytical data agree well with the compositions of the [Ru(PPh₃)₂(L)₂] complexes. All three complexes are diamagnetic, which corresponds to the bivalent state of ruthenium (low-spin d⁶, S = 0) in these complexes.
Table 2
Microanalytical, electronic spectral and cyclic voltammetric data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Microanalytical data a</th>
<th>Electronic spectral data b</th>
<th>Cyclic voltammetric data c</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
<td>%N</td>
</tr>
<tr>
<td>[Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(L&lt;sup&gt;1&lt;/sup&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>44.82</td>
<td>2.68</td>
<td>0.71</td>
</tr>
<tr>
<td>[Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(L&lt;sup&gt;2&lt;/sup&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>63.94</td>
<td>4.16</td>
<td>3.06</td>
</tr>
<tr>
<td>[Ru(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(L&lt;sup&gt;3&lt;/sup&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>54.91</td>
<td>3.24</td>
<td>7.98</td>
</tr>
</tbody>
</table>

a Calculated values are in parentheses.
b Dichloromethane solution.
c Solvent, acetonitrile; Supporting electrolyte, TEAP; reference electrode, SCE; E<sub>1/2</sub> = 0.5(E<sub>pa</sub> + E<sub>pc</sub>), where E<sub>pa</sub> and E<sub>pc</sub> are anodic and cathodic peak potentials, respectively; ΔE<sub>p</sub> = E<sub>pa</sub> − E<sub>pc</sub>; scan rate, 50 mV s<sup>-1</sup>.
d E<sub>pa</sub> value.

From the composition of the complexes and also from the fact that ruthenium(II) prefers to be hexacoordinated, the phenolic ligands appear to have served as bidentate ligands. Five geometrical isomers (2–6) are then possible for the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>] complexes.

To sort out the problem of stereochemistry and also to authenticate coordination mode of the phenolic ligands, molecular structures of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>] and [Ru(PPh<sub>3</sub>)<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>] have been solved by X-ray crystallography [43]. The structures are shown in Fig. 2 and selected bond parameters are given in Table 3. In [Ru(PPh<sub>3</sub>)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]. 2,4,6-tribromophenol is coordinated to ruthenium via loss of the phenolic proton, as a bidentate O,Br-donor ligand forming a five-membered chelate ring with a bite angle of 80.55°. While the phenolate oxygens are mutually trans, the PPh<sub>3</sub> ligands are mutually cis and the two bromines are also mutually cis. Hence the O<sub>2</sub>P<sub>2</sub>Br<sub>2</sub> coordination sphere around ruthenium has a trans–cis–cis geometry (6) with regard to mutual dispositions of the three pairs of donor atoms. The coordination sphere around ruthenium is distorted octahedral in nature, which is reflected in the bond parameters around ruthenium. While the Ru–O and Ru–P distances are quite normal [18,21,44,45], the Ru–Br lengths are a bit longer than is usually observed [46–48]. The C–Br lengths corresponding to the coordinated bromines are slightly longer than the other two C–Br distances in the same ligand and this may be attributed to coordination of the bromine to ruthenium(II). The phenolate C–O lengths are also quite usual [44,45]. The [Ru(PPh<sub>3</sub>)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>] complex could not be characterized crystallographically [43]. However, the 2-nitrophenolate ligand is known to coordinate as bidentate O,O-donor forming a six-membered chelate ring [49] as shown in Fig. 1. The same coordination mode of the 2-nitrophenolate ligand is assumed in [Ru(PPh<sub>3</sub>)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>].
Structure determination of [Ru(PPh₃)₂(L³)₂] shows that 2,4,6-trinitrophenol is coordinated, via loss of the phenolic proton and reduction of one nitro group at the ortho position, as a 2-nitroso-4,6-dinitrophenolate anion. Chelation takes place from the nitroso nitrogen and phenolate oxygen forming a five-membered chelate ring with a bite angle of 80.85°. The coordinated nitrogens are mutually cis, the phenolate oxygens are also mutually cis and the two coordinated PPh₃ ligands are mutually trans. The coordination sphere around ruthenium is slightly distorted octahedral N₂O₂P₂ with a cis–cis–trans geometry, respectively (3). While the Ru–P distances are normal [50,51], the bond distances within the N–O chelates are rather unusual. The Ru–N bonds are significantly shorter than usually observed [15,16,18]. Such a short Ru–N distance is known to result only from very strong π-interaction [52]. The Ru–O bonds are longer than usually observed [21,45]. The observed C–O lengths are shorter than usual phenolate C–O distances [44,45]. The unusual nature of observed bond distances in [Ru(PPh₃)₂(L³)₂] appears to result from the combined effect of the possible resonance in the nitrosophenolate ligand (7) and the π-bonding interaction [52–54] between ruthenium(II) and the imine-oxo moiety of the nitrosophenolate ligand.

Fig. 2. View of the (a) [Ru(PPh₃)₂(L¹)₂] and (b) [Ru(PPh₃)₂(L³)₂] molecules.
This strong π-interaction is also reflected in the cis disposition of this imine nitrogens [53, 54]. In complexes containing the Ru(II)(PPh₃)₂ moiety, the two triphenylphosphines usually take up cis positions [15, 18, 44, 45], which has also been observed in [Ru(PPh₃)₂(L)₂] (vide supra). In [Ru(PPh₃)₂(L)₂] the imine-oxo group appears to be a stronger π-acceptor than PPh₃ and thus forces the bulky PPh₃ ligands to take up trans positions for less steric hindrance.

The IR spectra of these complexes show many sharp bands of different intensities in the 1700–400 cm⁻¹ region due to vibrations arising from the coordinated PPh₃ and phenolic ligands and are therefore complex in nature. No attempt has been made to assign individual vibrations near 520, 700, and 740 cm⁻¹; however, the strong vibrations due to vibrations arising from the coordinated PPh₃ ligands [15, 18, 44, 45]. The [Ru(PPh₃)₂(L)₂] complexes are soluble in polar solvents like acetonitrile, dichloromethane, chloroform, etc, producing intense red solutions. Electronic spectra of the complexes have been recorded in dichloromethane solution. All these complexes show several intense absorptions in the visible and ultraviolet region. Spectral data are presented in Table 2. The intense absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals and those in the visible region are probably due to allowed metal-to-ligand charge-transfer transitions. Multiple charge-transfer transitions in such mixed-ligand complexes are known to result from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling [57–60].

Electrochemical properties of all the complexes have been studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. A selected voltammogram is shown in Fig. 3 and the voltammetric data are presented in Table 2. Each complex shows two oxidative responses on the positive side of SCE. The first oxidative response is observed within 0.63–0.71 V versus SCE and is assigned to the ruthenium(II)–ruthenium(III) oxidation (Eq. (2)). This oxidation is reversible in nature with a peak-to-peak separation (ΔEₚ) of 60–70 mV, which does not change when the scan rate is changed.

\[
[Ru^{II}(PPh_{3})_{2}(L)_{2}] \rightarrow [Ru^{III}(PPh_{3})_{2}(L)_{2}]^{2+} + e^{-} \quad (2)
\]

\[
[Ru^{III}(PPh_{3})_{2}(L)_{2}]^{2+} \rightarrow [Ru^{IV}(PPh_{3})_{2}(L)_{2}]^{3+} + e^{-} \quad (3)
\]

The anodic peak current (iₚa) is also equal to the cathodic peak current (iₚc) as expected for a reversible electron-transfer process. The one-electron nature of this oxidation has been verified by comparing its current heights with those of the standard ferrocene–ferrocenium couple under identical experimental conditions. The second oxidative response, which appears near 1.5 V versus SCE, is irreversible and is tentatively assigned to ruthenium(III)–ruthenium(IV) oxidation (Eq. (3)). One-electron stoichiometry of the oxidation is verified by comparing its current height (iₚa, calculated after deduction of solvent contribution from the observed current at Eₚa) with that of the ruthenium (II)–ruthenium(III) oxidation.

Table 3

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(PPh₃)₂(L)₂]</td>
<td></td>
</tr>
<tr>
<td>Ru-O(1)</td>
<td>2.091(6)</td>
</tr>
<tr>
<td>Ru-O(2)</td>
<td>2.086(6)</td>
</tr>
<tr>
<td>Ru-Br(1)</td>
<td>2.635(13)</td>
</tr>
<tr>
<td>Ru-Br(4)</td>
<td>2.634(12)</td>
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<tr>
<td>Ru-P(1)</td>
<td>2.282(3)</td>
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<tr>
<td>Ru-P(2)</td>
<td>2.299(2)</td>
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<tr>
<td>O(1)–C(1)</td>
<td>1.281(10)</td>
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<tr>
<td>O(2)–C(7)</td>
<td>1.299(10)</td>
</tr>
<tr>
<td>C(2)–Br(1)</td>
<td>1.914(9)</td>
</tr>
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<td>1.899(11)</td>
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<tr>
<td>C(6)–Br(3)</td>
<td>1.895(11)</td>
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<tr>
<td>C(8)–Br(4)</td>
<td>1.906(8)</td>
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<td>C(10)–Br(5)</td>
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</tr>
<tr>
<td>O(2)–Ru–Br(4)</td>
<td>1.382(9)</td>
</tr>
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</table>

Fig. 3. Cyclic voltammogram of [Ru(PPh₃)₂(L)₂] in acetonitrile solution (0.1 M TEAP) at a scan rate of 50 mV s⁻¹.
4. Conclusions

The present study shows that coordination of phenols to ruthenium as simple monodentate oxygen donor ligands is probably not possible, but phenols having a second donor site linked to the ortho position can bind to ruthenium as a bidentate ligand affording stable complexes.

5. Supplementary data

Copies of supplementary data can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the deposition numbers CCDC 141332 and CCDC 141333.

Acknowledgements

Financial assistance received from the Council of Scientific and Industrial Research, New Delhi [Grant No. 01(1408)/96/EMR-II] and the Directorate General for Higher Education (Spain) under Grant PB98-1593 is gratefully acknowledged. Thanks are also due to the Third World Academy of Sciences for financial support enabling the purchase of an electrochemical cell system.

References

[43] Single crystals of [Ru(Ph3P)2(L2)2] could not be grown.