

LIGAND CONTROL OF METAL OXIDATION STATES. SYNTHESIS, CHARACTERIZATION AND CYCLIC VOLTAMMETRIC STUDIES OF A GROUP OF RUTHENIUM PHENOLATES

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Abstract—Reaction of a series of phenolic ligands with different functional groups at the 2-position with $[Ru(PPh_3)_3Cl_2]$ affords stable complexes of ruthenium(II) and ruthenium (II). The ruthenium(II) complexes are diamagnetic and show intense absorption in the visible region due to MLCT transitions. In dichloromethane solution, the complexes show redox (ruthenium(II)–ruthenium(III)) behaviour, the potential of which varies with the electronic nature of the phenolic ligand. In two of these complexes, an irreversible ruthenium(III)–ruthenium(IV) oxidation was observed near 1.2 V (vs SCE). The ruthenium(III) complexes are one-electron paramagnetic showing rhombic ESR spectra at 77 K. Intense LMCT transitions were observed in the visible region together with low-intensity ligand-field transitions at lower energies. In acetonitrile solution the ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III) the visible region together with low-intensity ligand-field transitions at lower energies. In acetonitrile solution the ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III) reduction and ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III)–ruthenium(III) complexes show both ruthenium(III)–ruthenium(III) reduction and ruthenium(III)–

The chemistry of ruthenium is dominated by electron-transfer reactions which are possible because of the different accessible oxidation states of this metal. Tuning of redox stability by ligand modification is therefore of particular interest in ruthenium chemistry. In the present work, which has emerged from our interest in the chemistry of ruthenium,¹ we have dealt with ruthenium phenolates of two general types, 1 and 2. The aim of this study has been to investigate the influence of simple modifications of these ligands (variations of R and/or R') on the stability of different oxidation states of ruthenium. The synthesis and characterization of a group of bis(phenolate) complexes of ruthenium and their spectroscopic and electrontransfer properties are described in this paper.

EXPERIMENTAL

Physical measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyser. IR spectra

were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Hitachi U-3400 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. X-band ESR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen) and the spectra were calibrated with DPPH (g = 2.0037). Solution electrical conductivity was measured with the help of a Philips PR 9500 bridge with a solute concentration of 10^{-3} M. Electrochemical measurements were made using the PAR model 370-4 electrochemistry system.^{1c} All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Materials

Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was converted to $RuCl_3$ · $3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. Triphenyl-phosphine (PPh₃), salicylaldoxime, triethylamine

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(NEt₃) and salicylaldehyde were obtained from SD, Bombay, India. 2-Hydroxynaphthaldehyde was purchased from Aldrich. All other chemicals and solvents were reagent grade commercial materials and were used as received. [Ru(PPh₃)₃Cl₂] was prepared following a reported procedure.² The Schiff-base ligands were prepared by reacting equimolar amounts of the respective aldehyde and amine in hot ethanol. Purification of acetonitrile and dichloromethane, and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.^{3,4}

Preparation of complexes

 $[Ru^{II}(PPh_3)(sal)_2]$. To a 0.5 ml solution (63 mg, 0.52 mmol) of Hsal in 30 cm³ of ethanol was added $[Ru(PPh_3)_3Cl_2]$ (200 mg, 0.21 mmol). Upon refluxing the mixture for 30 min a brownish orange product separated out. After cooling the mixture to room temperature, the precipitated solid was filtered, washed with ethanol followed by diethyl ether and dried in air; yield 130 mg, 72%.

 $[Ru^{II}(PPh_3)_2(nap)_2]$. To a mixture of [Ru

(PPh₃)₃Cl₂] (100 mg, 0.10 mmol) and Hnap (40 mg, 0.23 mmol) was added 30 cm³ of ethanol. The mixture was refluxed for 1 h to produce a deep red solution. On partial evaporation of the solvent a deep red crystalline product separated out, which was collected by filtration, washed with diethyl ether and dried in air; yield 80 mg, 79%.

 $[Ru^{II}(PPh_3)_2(saldnp)_2]$ and $[Ru^{II}(PPh_3)_2(napnan)_2]$. These two complexes were prepared by following the same procedure as above using Hsaldnp and Hnapnan, respectively, instead of Hnap. The yields of these complexes were found to be 90 mg (70%) and 100 mg (79%), respectively.

 $[Ru^{III}(PPh_3)_2(salox)(saloxH)]$. To a suspension of $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.10 mmol) in ethanol (30 cm³) was added HsaloxH (30 mg, 0.22 mmol). The resulting mixture was then refluxed for 30 min after which a bright green crystalline product started separating out. The mixture was then cooled and the precipitated solid was filtered, washed with ethanol and dried in air; yield 75 mg, 80%.

 $[Ru^{III}(PPh_3)(salan)_2Cl]$ and $[Ru^{III}(PPh_3)(salan)_2Cl]$. These complexes were prepared by reacting $[Ru(PPh_3)_3Cl_2]$ with Hsalan and H₂salen, respectively, following a published procedure.⁵

 $[Ru^{III}(PPh_3)_2(nap)_2]ClO_4$. To a solution of $[Ru(PPh_3)_2(nap)_2]$ (100 mg, 0.10 mmol) in dichloromethane (30 cm³) was added an aqueous solution (10 cm³) of ammonium ceric sulphate (80 mg, 0.13 mmol). Upon vigourous stirring for 15 min, the colour of the dichloromethane layer turned green. This green layer was then separated and diluted with an equal volume of acetonitrile. A saturated aqueous solution of sodium perchlorate was added to it. Partial evaporation of the solvents afforded a dark crystalline product, which was filtered, washed with cold water and dried *in vacuo* over P₄O₁₀; yield 85 mg, 77%.

RESULTS AND DISCUSSION

Synthesis

Seven different ligands have been used in this study, and are shown in structures 3–7. Four of the seven ligands, namely Hsal, Hnap, Hsaldnp and Hnapnan, react smoothly with $[Ru(PPh_3)_3Cl_2]$ in refluxing ethanol to afford complexes of the type $[Ru^{II}(PPh_3)_2(L)_2]$ in good yields [eq. (1)]. Reaction

 $[Ru^{II}(PPh_3)_3Cl_2] + 2HL \longrightarrow$

 $[Ru^{II}(PPh_3)_2(L)_2] + 2HCl + PPh_3$ (1)

of the remaining three ligands, namely HsaloxH, Hsalan and H₂salen with $[Ru(PPh_3)_3Cl_2]$ affords three complexes of ruthenium(III) [eqs (2)–(4)].





$$[Ru^{II}(PPh_3)_3Cl_2] + 2HsaloxH \longrightarrow$$

$$[Ru^{III}(PPh_3)_2(salox)(saloxH)] + 2HCl$$

$$+ PPh_3 + H^+ + e^- \quad (2)$$

$$[Ru^{II}(PPh_3)_3Cl_2] + 2Hsalan \longrightarrow$$

$$[Ru^{III}(PPh_3)(salan)_2Cl] + HCl$$

 $+2PPh_{3}+H^{+}+e^{-}$ (3)

 $[Ru^{II}(PPh_3)_3Cl_2] + H_2$ salen \longrightarrow

$$[Ru^{III}(PPh_3)(salen)Cl] + HCl$$

 $+2PPh_{3}+H^{+}+e^{-}$. (4)

During the course of these synthetic reactions [eqs (2)-(4)], ruthenium undergoes a one-electron oxidation. In view of the potential of the ruthenium(II)-ruthenium(III) couple displayed by these complexes (*vide infra*), oxygen in air seems to be the probable oxidant. It should be noted here that the synthesis of [Ru(PPh₃)(salen)CI] has been reported in the literature.⁵ Another ruthenium(III) complex, [Ru^{III}(PPh₃)₂(nap)₂]⁺, has been synthesized by chemical oxidation of its ruthenium(II) precursor [eq. (5)] and this cationic complex has been isolated as the perchlorate salt in the solid state.

$$[\operatorname{Ru}^{\operatorname{II}}(\operatorname{PPh}_3)_3(\operatorname{nap})_2] \xrightarrow{} [\operatorname{Ru}^{\operatorname{III}}(\operatorname{PPh}_3)_2(\operatorname{nap})_2]^+ + e^- \quad (5)$$

It is interesting to note that the reaction of a group of phenolic ligands with different functional groups at the 2-position with a single ruthenium starting material, namely $[Ru(PPh_3)_3Cl_2]$, affords air-stable complexes containing ruthenium in different oxidation states. This shows the direct influence of ligand modification on metal-centred redox processes.

Characterization

Characterization data of the complexes are presented in Tables 1 and 2. The observed elemental (C, H, N) analytical data (Table 1) agree well with the compositions of these complexes. The ruthenium(II) complexes are diamagnetic (low-spin d^6 , S = 0) while the complexes of ruthenium(III) (lowspin d^5 , S = 1/2) are one-electron paramagnetic (Table 2), as expected. Infrared spectra of all the $[Ru(PPh_3)_2(L)_2]$ complexes contain many bands of different intensities and hence are complex in nature. Assignment of all the bands has not been attempted. However, comparison with the spectrum of [Ru(PPh₃)₃Cl₂] shows that in [Ru $(PPh_3)_2(L)_2$] the v(Ru-Cl) stretch (observed at 320 cm^{-1} in [Ru(PPh₃)₃Cl₂]) is absent. Vibrations due to coordinated PPh₃ (near 520, 540, 690 and 740 cm^{-1}) are present and some new vibrations are present that are obviously due to the phenolic ligand L. The IR spectrum of $[Ru^{III}(PPh_3)_2]$ (salox)(saloxH)] shows the v(N-O) stretch at 1295 $cm^{-1.6}$ The [Ru^{III}(PPh₃)(salan)₂Cl] and [Ru^{III} (PPh₃)(salen)Cl] complexes show a sharp vibration near 360 cm⁻¹, which is assigned to the v(Ru—Cl) stretch.⁶ Besides the additional intense bands at 1100 and 622 cm⁻¹ due to ClO_4^- , the IR spectrum of [Ru^{III}(PPh₃)₂(nap)₂]ClO₄ is almost identical to that of $[Ru^{II}(PPh_3)_2(nap)_2]$, as expected.

As the phenolic ligands (L) are unsymmetrical, five geometrical isomers are possible for the $[Ru^{II}$ $(PPh_3)_2(L)_2]$ complexes. Chromatographic studies on these complexes show that they are isomerically pure. As we have no experimental evidence to distinguish between these five isomers, we assume the completely *trans* structure, **8**, for these complexes. A similar *trans* structure has indeed been determined by X-ray crystallography for complexes of similar type.⁷ Amongst the four ruthenium(III) complexes, $[Ru^{III}(PPh_3)_2(salox)(saloxH)]$ is assumed to have structure **9**. Such a structure would be stable sterically, as well as due to intramolecular hydrogen bonding.⁶ The $[Ru^{III}(PPh_3)(salen)CI]$

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Compound	Analytical data"			Electronic spectral data	Cyclic voltammetric data ^b $E_{298}^{o}, V(\Delta E_{p}, mV)$	
	%C	%H	%N	$\lambda_{\max} \operatorname{nm} (\varepsilon^{\epsilon}, \mathbf{M}^{-1} \operatorname{cm}^{-1})$	Ru ^{II/III}	Ru ^{III/IV}
$[\mathbf{Ru}^{11}(\mathbf{PPh}_3)_2(\mathbf{sal})_2]^d$	69.1	4.6				
	(69.2)	(4.6)				
$[\mathbf{Ru}^{11}(\mathbf{PPh}_3)_2(\mathbf{nap})_2]^d$	71.7	4.6		500 ^e (1300), 400(4600)	0.29(70)	1.20
	(71.9)	(4.6)				
$[Ru^{II}(PPh_3)_2(saldnp)_2]^d$	60.6	3.8	9.0	775(400), 600 ^e (2200)	0.82(60)	
	(60.6)	(3.9)	(9.1)	$500^{e}(6600), 400(13,000)$. ,	
$[\operatorname{Ru}^{II}(\operatorname{PPh}_3)_2(\operatorname{napnan})_2]^d$	69.5	4.1	4.5	$525^{e}(1300), 350^{e}(1700)$	0.25(60)	1.24
	(69.6)	(4.3)	(4.6)			
$[Ru^{111}(PPh_3)_2(salox)]$	66.8	4.5	3.0	1625(455), 700(1400),	-0.48^{h}	0.98(60)
(saloxH)] ^g	(67.0)	(4.6)	(3.1)	360°(7100)		~ /
[Ru ^{III} (PPh ₃)(salan) ₂ Cl] ^g	66.7	4.4	3.4	$1500(30), 610(910), 400^{e}(2700),$	-0.28(70)	0.73(60)
	(66.8)	(4.4)	(3.5)	350(3800)		. ,
[Ru ^{III} (PPh ₃)(salen)Cl] ^g	61.2	4.3	4.2	1300(70), 770(3900),	-0.21(70)	0.81(70)
	(61.4)	(4.4)	(4.2)	500(1300), 345(2400)		
$[Ru^{III}(PPh_3)_2(nap)_2](ClO_4)^g$	65.2	4.0		675(1100), 350 ^e (9100)	0.29(70)	1.21 ^f
	(65.3)	(4.1)				

Table 1. Characterization data

^a Calculated values are in parentheses.

^bConditions : supporting electrolyte, TEAP (0.1 M) ; working electrode, platinum ; reference electrode, SCE ; solute concentration, 10^{-3} M ; $E_{298}^{\circ} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials ; $\Delta E_{p} = E_{pa} - E_{pc}$; scan rate, 50 mVs⁻¹.

^c Extinction coefficient.

^dSolution studies in dichloromethane.

^e Shoulder.

 ${}^{f}E_{pa}$ value.

⁹ Solution studies in acetonitrile.

^{*h*} $E_{\rm pc}$ value.

complex is reported to have structure 10.⁵ Owing to the similarity in synthetic reaction and spectral and electrochemical properties (*vide infra*), a similar structure may be assumed for $[Ru^{III}(PPh_3)$ (salan)₂Cl]. The cyclic voltammetric behaviour of $[Ru^{III}(PPh_3)_2(nap)_2]^+$ (*vide infra*) indicates that the gross structure of this complex is similar to its

ruthenium(II) precursor. Hence the same *trans* structure **8** is assumed for this complex.

The four $[Ru^{II}(PPh_3)_2(L)_2]$ complexes are readily soluble in dichloromethane and much less soluble in acetonitrile. $[Ru^{II}(PPh_3)_2(sal)_2]$ is unstable in solution and this red solid instantly produces a green solution upon dissolution. The remaining

Table 2. Magnetic moment and ESR g values and derived energy parameters of the ruthenium(III) complexes

Compound	$\mu_{ m eff}$ (BM)	g values			Derived energy parameters (cm ⁻¹)	
		<i>g</i> 1	<i>g</i> ₂	g_3	ΔE_1	ΔE_2
[Ru ^{III} (PPh ₃)(salox)(saloxH)] ^a	1.86	2.491	2.167	1.820	3312	6819
$[Ru^{III}(PPh_3)(salan)_2Cl]^a$	1.91	2.252	2.159	1.891	4591	6487
[Ru ^{III} (PPh ₃)(salen)Cl] ^a	1.88	2.270	2.123	1.903	4526	7825
$[Ru^{III}(PPh_3)_2(nap)_2]ClO_4^b$	1.94	2.401	2.007	1.890	3471	15,951

"ESR spectrum in 1:1 dichloromethane/toluene at 77 K.

^bESR spectrum in 1:1 acetonitrile/toluene at 77 K.



Fig. 1. Electronic spectra of (a) $[Ru(PPh_3)_2(nap)_2]$ and (b) $[Ru(PPh_3)_2(saldnp)_2]$ in dichloromethane solution.

three ruthenium(II) complexes are stable in solution and electronic spectra recorded in dichloromethane solution show several intense absorptions in the visible region (Table 1, Fig. 1). These are probably due to allowed metal-to-ligand chargetransfer transitions. In the $[Ru(PPh_3)_2(saldnp)_2]$ complex a low-intensity transition is observed at 775 nm which is assigned to the d-d transition $({}^{1}A_{1} \rightarrow {}^{1}T_{1}).^{8}$ The other possible *d*-*d* transition $({}^{1}A_{1} \rightarrow {}^{1}T_{2})^{8}$ could not be detected due to the presence of intense absorption at higher energies. No d-d transition is observed in the other two complexes. The ruthenium(III) complexes are soluble in both acetonitrile and dichloromethane, except [Ru^{III}(PPh₃)₂(nap)₂]ClO₄, which is much less soluble in dichloromethane. Conductivity measurements on $[Ru^{III}(PPh_3)_2(nap)_2]ClO_4$ in acetonitrile solution show that it behaves as a 1:1 electrolyte $(\Lambda_{\rm M} = 140 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm M}^{-1})$, as expected. Electronic spectra recorded on the green solution of these ruthenium(III) complexes show intense absorptions in the visible region and weak absorptions at lower energies (Table 1, Fig. 2). The intense absorptions are assigned to ligand-to-metal chargetransfer transitions and the origin of the lower energy absorptions is discussed below.

ESR spectra for the four ruthenium(III) complexes have been recorded in either 1:1 dichloromethane/toluene solution or in 1:1 acetonitrile/



Fig. 2. Electronic spectra of (a) [Ru(PPh₃)₂(salox) (saloxH)] and (b) [Ru(PPh₃)(salen)Cl] in acetonitrile solution.

toluene solution at 77 K. All the complexes show rhombic ESR spectra with three distinct g values (Table 2, Fig. 3). The rhombic nature of the ESR spectra indicates the asymmetry of electronic environment around ruthenium in these com-



Fig. 3. ESR spectra of (a) [Ru(PPh₃)₂(salox)(saloxH)]
and (b) [Ru(PPh₃)(salen)Cl] in 1:1 dichloromethane/ toluene solution at 77 K.

plexes. As a result of this lowering of symmetry, and spin-orbit coupling, the three t₂ levels are well separated. Hence, two electronic transitions [transition energies ΔE_1 and ΔE_2 , $\Delta E_2 > \Delta E_1$] are probable within these three levels. Using the observed qvalues, the g tensor theory of low-spin d^5 complexes⁹ and a reported method,¹⁰ these transition energies have been calculated¹¹ (Table 2). In the case of $[Ru^{III}(PPh_3)_2(salox)(saloxH)]$, the ΔE_1 transition falls in the IR region and could not be detected. However, the ΔE_2 transition is indeed observed as a low-intensity absorption (Table 1, Fig. 2) at 1625 nm, which is close to the predicted value. In the [Ru^{III}(PPh₃)(salan)₂Cl] and [Ru^{III} (PPh₃)(salen)Cl] complexes, the ΔE_2 transition is observed at 1500 and 1300 nm, respectively (Table 1, Fig. 2), which is in good agreement with the theoretically calculated values (Table 2). The ΔE_1 transition in these complexes, which is predicted to occur near 4500 cm⁻¹, could not be identified because the solvent itself is not transparent in this region. In $[Ru^{III}(PPh_3)_2(nap)_2]ClO_4$, the ΔE_1 transition again falls in the IR region and hence could not be detected. The ΔE_2 transition in this complex, has shifted into the visible region (Table 2) and could not be identified separately due to the presence of intense charge-transfer transitions at similar energy (Table 1).

Cyclic voltammetric studies

Electron-transfer properties of all the complexes except $[Ru(PPh_3)_2(sal)_2]$ have been studied in dichloromethane or acetonitrile solution by cyclic voltammetry. Voltammetric data are presented in Table 1 and selected voltammograms are shown in Fig. 4. The three ruthenium(II) complexes, which are stable in dichloromethane solution, show a



Fig. 4. Cyclic voltammograms of (a) $[Ru(PPh_3)_2(nap)_2]$ in dichloromethane and (b) $[Ru(PPh_3)(salen)Cl]$ in acetonitrile. The scan rate and solute concentration were 50 mV s^{-1} and 10^{-3} M respectively.

reversible one-electron oxidation on the positive side of SCE (Table 1) which is assigned to the ruthenium(II)-ruthenium(III) oxidation [eq. (6)].

$$[\operatorname{Ru}^{II}(\operatorname{PPh}_3)_2(L)_2] \Longrightarrow [\operatorname{Ru}^{III}(\operatorname{PPh}_3)_2(L)_2]^+ + e^-$$
(6)

The one-electron nature of this couple is established by comparing its current heights with those of the standard ferrocene–ferrocenium couple ($\Delta E_{p} = 70$ mV) under identical experimental conditions. The potential of this oxidation is very sensitive to the nature of ligand L. For L = nap this oxidation takes place at 0.29 V (all potentials are referenced to SCE) while the same oxidation occurs at 0.25 V for L = napnan. The ruthenium(II)-ruthenium(III) couple usually shifts towards the negative when an aldehydic oxygen is replaced by an imine nitrogen. For example, in tris(salicylaldehydato)ruthenium (III), the ruthenium(III)-ruthenium(II) couple occurs at -0.48 V¹² and at -0.83 V in tris(salicylaldiminato)ruthenium(III).13 In the present case the difference in potential between $[Ru(PPh_3)_2(nap)_2]$ and $[Ru(PPh_3)_2(napnan)_2]$ is only 40 mV. This is due to the electron-withdrawing nitro groups in the aniline fragment of the two napnan ligands, which almost compensate the expected negative shift due to the imine function. In $[Ru(PPh_3)_2(saldnp)_2]$ the same ruthenium(II)-ruthenium(III) oxidation takes place at a much higher potential (0.82 V), primarily due to the two nitro groups in the hydrazine fragment of the saldnp ligand. In $[Ru(PPh_3)_2]$ (sal)₂] the ruthenium(II)-ruthenium(III) oxidation probably occurs at a much more negative potential relative to that for $[Ru(PPh_3)_2 (nap)_2]$ and therefore undergoes immediate oxidation in solution followed by some unidentified chemical reaction which is responsible for its instability in solution. In the case of $[Ru(PPh_3)_2(nap)_2]$ and $[Ru(PPh_3)_2(napnan)_2]$, a second irreversible oxidation is observed near 1.2 V (Table 1, Fig. 4), which is assigned to the ruthenium(III)-ruthenium(IV) oxidation [eq. (7)].

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{PPh}_3)_2(\operatorname{L})_2]^+ \longrightarrow$$
$$[\operatorname{Ru}^{\operatorname{IV}}(\operatorname{PPh}_3)_2(\operatorname{L})_2]^{2+} + e^- \quad (7)$$

The irreversibility indicates that $[Ru^{IV}(PPh_3)_2(L)_2]^{2+}$, formed during the anodic scan, undergoes fast chemical transformation. The ruthenium(III)-ruthenium(IV) oxidation, in $[Ru(PPh_3)_2(saldnp)_2]$, which is expected to occur at a much higher potential, has not been observed, probably as a result of solvent cut-off.

All four ruthenium(III) complexes show both ruthenium(III)-ruthenium(II) reduction and ruthenium(III)-ruthenium(IV) oxidation (Table 1, Fig. 4). The cyclic voltammetric behaviour of $[Ru^{III} (PPh_3)_2(nap)_2]^+$ is almost identical to that of $[Ru^{II} (PPh_3)_2(nap)_2]$, as expected. The other three ruthenium(III) complexes show ruthenium(III)–ruthenium(III) reduction on the negative side of SCE. This indicates that the +3 state of ruthenium is much more stable in these complexes. In $[Ru (PPh_3)_2(salox)(saloxH)]$ this reduction is irreversible while in the other two complexes it is reversible. The ruthenium(III)–ruthenium(IV) oxidation occurs reversibly and at less positive potentials than in the $[Ru(PPh_3)_2(L)_2]$ complexes (Table 1), indicating the enhanced stability of ruthenium(IV) in these three complexes.

CONCLUDING REMARKS

Reaction of phenolic ligands with different functional groups at the 2-position with $[Ru(PPh_3)_3Cl_2]$ affords complexes of ruthenium in two different airstable oxidation states, +2 and +3. The influence of the ligand modification is also reflected in the shift of metal-centred redox potentials. This shows that the stability of the different oxidation states of ruthenium can be tuned by proper modification of the phenolic ligands.

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