

Synthesis, characterization and emission properties of quinolin-8-olato chelated ruthenium organometallics

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Abstract. The reaction of $\text{Ru}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$, **1**, with quinolin-8-ol (HQ) has afforded complexes of the type $[\text{Ru}(\text{RL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$, **3**, in excellent yield (RL^1 is $\text{C}_6\text{H}_2\text{O}-2\text{-CHNHC}_6\text{H}_4\text{R}(p)\text{-3-Me-5}$, RL^2 is $\text{C}_6\text{H}_2\text{OH}-2\text{-CHNC}_6\text{H}_4\text{R}(p)\text{-3-Me-5}$ and R is Me, OMe, Cl). In this process, quinolin-8-olato (Q) undergoes five-membered chelation, the iminium-phenolato function tautomerizing to the imine-phenol function. In dichloromethane solution, **3** displays a quasireversible $3^+/3$ couple near 0.50 V vs SCE (3^+ is the ruthenium (III) analogue of **3**). Coulometrically generated solutions of 3^+ display a strong absorption near 395 nm associated with a shoulder near 475 nm and rhombic EPR spectra with *g* values near 2.55, 2.13, 1.89. Solutions of **3** absorb near 415 nm and emit near 510 nm at 298 K and 585 nm at 77 K. The fluorescence is believed to originate from the $^3\text{MLCT}$ state.

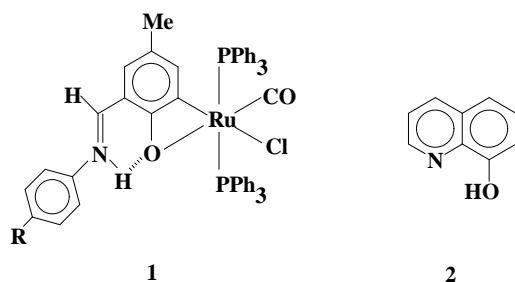
Keywords. Ruthenium organometallics; quinolin-8-olato chelation; emission properties; trivalent ruthenium.

1. Introduction

There is continuing interest in the chemistry of ruthenium,^{1–4} primarily due to the fascinating electron-transfer properties exhibited by complexes of this metal. Variation of the coordination environment around ruthenium plays a key role in modulating the redox properties of its complexes. In particular, the chemistry of orthometallated ruthenium compounds is of current interest in the context of synthesis,^{5–7} reactivity^{6,8–12} and photophysical properties.^{13,14} It was demonstrated that the decarbonylative metallation of 4-methyl-2,6-diformyl phenol by $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ in the presence of primary aromatic amines ($\text{RC}_6\text{H}_4\text{NH}_2$) is known to furnish four-membered ruthenium organometallics of type $\text{Ru}(\text{RL}^1)(\text{PPh}_3)_2$

$(\text{CO})\text{Cl}$ (**1**) juxtaposed to a hydrogen-bonded iminium-phenolato function.^{15–17} We are scrutinizing the reactivity of these compounds. Thus alkynes and isonitriles have been found to promote metallacyclic expansion,^{8,9,11,18} bidentate monoanionic *s*-donor reagents such as acetate, nitrate, nitrite, xanthate and pyridine-2-thiolate undergo four-membered chelation,^{19–22} and electroneutral *a*-diimine ligands such as bipyridine, phenanthroline furnish five-membered ruthenium organometallics.²³

The richness of this reaction chemistry has now prompted us to explore the reactivity of **1** towards quinolin-8-ol, **2**, (HQ, H stands for the dissociable phenolic hydrogen) which is suited for five-membered N, O-chelation. A facile reaction is indeed observed affording five-membered ruthenium organometallics via displacement of Ru–O and Ru–Cl bonds. Changes in the coordination mode and tautomeric state of the Schiff base ligand accompany the synthetic reaction. It may be noted here that the chemistry of ruthenium quinolin-8-olates appears to have received relatively less attention,^{24–28} but organoruthenium compounds incorporating quinolin-8-olates are unprecedented. A point of special interest is that such species are potentially luminescent in the visible region.



2. Experimental

2.1 Materials

The compounds $\text{Ru}(\text{PPh}_3)_2\text{Cl}_2^{29}$ and $\text{Ru}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}^{15}$ were prepared by reported methods. Quinolin-8-ol was obtained from Merck. The purification of dichloromethane and the preparation of tetraethyl ammonium perchlorate (TEAP) for electrochemical work were done as described in previous work.³⁰ All other chemicals and solvents were of analytical grade and were used as received.

2.2 Physical measurements

Electronic, IR and fluorescence spectra were recorded with a Shimadzu UV-1601 PC spectrophotometer, Nicolet Magna IR series II spectrometer and Perkin-Elmer model LS 55 luminescence spectrometer respectively. ^1H NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer. The numbering scheme used for the ^1H NMR is the same as shown in drawing **3**. Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer. The magnetic behaviour of the complexes was examined by a PAR 155 vibrating sample magnetometer. EPR spectra were recorded on a Varian E-109C X-band spectrometer fitted with a quartz dewar. Solution electrical conductivity was measured in acetone with a Phillips PR 9500 bridge using a platinized electrode (cell constant of 1.05). Electrochemical measurements were performed in a nitrogen atmosphere in dichloromethane solution using a CHI model 620A electrochemical analyzer. The supporting electrolyte was tetraethyl ammonium perchlorate and potentials are referenced to the saturated calomel electrode.

2.3 Synthesis of the complexes $[\text{Ru}(\text{RL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**)

$[\text{Ru}(\text{RL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**) complexes were synthesized in excellent yield (~85%) by reacting $\text{Ru}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (**1**) in $\text{MeOH-CH}_2\text{Cl}_2$ (2:1) at room temperature with excess HQ. Details of a representative case are given below. The other compounds are prepared in an analogous manner.

2.3a $[\text{Ru}(\text{MeL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**) (*Me*): To a vigorously stirred violet solution of $\text{Ru}(\text{MeL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (100 mg, 0.109 mmol) in a mixture

of 40 ml methanol and 20 ml dichloromethane was added 48 mg (0.331 mmol) of HQ. The mixture was stirred for 4 h when the colour of the solution changed from violet to yellow. The solvent was then removed under reduced pressure and the yellow solid thus obtained was washed with a little amount of methanol (removal of excess HQ). The residue was recrystallized from dichloromethane-hexane (1:3) mixture followed by drying *in vacuo*. Yield: 96 mg (86%).

Analysis: Calc. for $\text{C}_{61}\text{H}_{50}\text{N}_2\text{O}_3\text{P}_2\text{Ru}$: C, 69.13; H, 4.54; N, 2.69%. Found C, 69.08; H, 4.50; N, 2.63%.

^1H NMR (300 MHz, CDCl_3 , ppm, 298 K): 12.93 (*s*, 1H, O-H, disappeared upon shaking with D_2O), 8.05 (*s*, 1H, H7), 6.23 (*s*, 1H, H3), 1.70 (*s*, 3H, 4-Me), 2.38 (*s*, 3H, 13-Me), 8.24 (*d*, $J_{\text{HH}} = 6.3$ Hz, 1H, H16), 7.43 (*d*, $J_{\text{HH}} = 8.4$ Hz, 1H, H18), 6.36 (*d*, $J_{\text{HH}} = 7.8$ Hz, 1H, H19), 6.71 (*d*, $J_{\text{HH}} = 8.1$ Hz, 1H, H21), 6.58–6.63 (*m*, 2H, H17, H20), 6.90–7.23 (*m*, 35H, 2PPh₃, H5, H11, H12, H14, H15).

IR (KBr, cm^{-1}): 1899 (ν_{CO}), 1590 ($\nu_{\text{C=N}}$).

2.3b $[\text{Ru}(\text{MeOL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**) (*OMe*): $\text{Ru}(\text{MeOL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (100 mg, 0.107 mmol) and HQ (47 mg, 0.324 mmol) were employed. Yield: 93 mg (83%).

Analysis: Calc. for $\text{C}_{61}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{Ru}$: C, 71.68; H, 4.93; N, 2.74%. Found C, 71.63; H, 4.96; N, 2.77%.

^1H NMR (300 MHz, CDCl_3 , ppm, 298 K): 12.95 (*s*, 1H, O-H, disappeared upon shaking with D_2O), 8.04 (*s*, 1H, H7), 6.22 (*s*, 1H, H3), 1.70 (*s*, 3H, 4-Me), 3.85 (*s*, 3H, 13-OMe), 8.23 (*d*, $J_{\text{HH}} = 6.5$ Hz, 1H, H16), 7.44 (*d*, $J_{\text{HH}} = 8.5$ Hz, 1H, H18), 6.36 (*d*, $J_{\text{HH}} = 7.5$ Hz, 1H, H19), 6.71 (*d*, $J_{\text{HH}} = 7.8$ Hz, 1H, H21), 6.58–6.62 (*m*, 2H, H17, H20), 6.92–7.25 (*m*, 35H, 2PPh₃, H5, H11, H12, H14, H15).

IR (KBr, cm^{-1}): 1904 (ν_{CO}), 1609 ($\nu_{\text{C=N}}$).

2.3c $[\text{Ru}(\text{CIL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**) (*Cl*): $\text{Ru}(\text{CIL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (100 mg, 0.107 mmol) and HQ (47 mg, 0.324 mmol) were used. Yield: 90 mg (81%).

Analysis: Calc. for $\text{C}_{60}\text{H}_{47}\text{N}_2\text{O}_3\text{P}_2\text{Ru}$: C, 70.58; H, 4.85; N, 2.70%. Found C, 70.52; H, 4.81; N, 2.73%.

^1H NMR (300 MHz, CDCl_3 , ppm, 298 K): 12.69 (*s*, 1H, O-H, disappeared upon shaking with D_2O), 8.04 (*s*, 1H, H7), 6.25 (*s*, 1H, H3), 1.72 (*s*, 3H, 4-Me), 8.25 (*d*, $J_{\text{HH}} = 6.1$ Hz, 1H, H16), 7.47 (*d*, $J_{\text{HH}} = 8.2$ Hz, 1H, H18), 6.38 (*d*, $J_{\text{HH}} = 7.2$ Hz, 1H, H19), 6.73 (*d*, $J_{\text{HH}} = 7.5$ Hz, 1H, H21), 6.59–6.64 (*m*, 2H, H17, H20), 6.88–7.27 (*m*, 35H, 2PPh₃, H5, H11, H12, H14, H15).

IR (KBr, cm^{-1}): 1902 (ν_{CO}), 1602 ($\nu_{\text{C=N}}$).

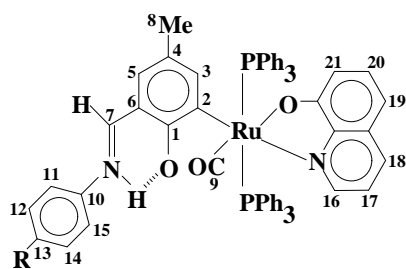
3. Results and discussion

3.1 Chelation with quinolin-8-olato

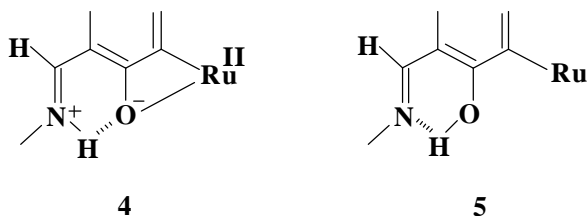
In methanol–dichloromethane solution, $\text{Ru}(\text{RL}^1)(\text{PPh}_3)_2(\text{CO})\text{Cl}$ (**1**) reacts smoothly with three-fold excess of HQ upon stirring at room temperature, according to,



The colour of the solution changes from violet to yellow, from which $[\text{Ru}(\text{RL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$ (**3**) is obtained in excellent yield. The R groups utilized in the present work are Me, OMe and Cl. Specific compounds are identified by putting R in parentheses: thus **3**(Me) stands for $[\text{Ru}(\text{MeL}^2)(\text{PPh}_3)_2(\text{CO})(\text{Q})]$. The complex **3** has been isolated in pure form in >85% yield. An isomer (because quinolin-8-ol is unsymmetrical) of **3** is possible in principle but it has never been observed. Careful examination of ^1H NMR spectra of crude sample (before recrystallization) did not reveal the presence of any extra signals apart from those characterizing **3**. We assign structure **3** to it in analogy with the stereochemistry of other Ru^{II} (quinolin-8-olato) complexes^{26,28} and also by comparing with pyridine-2-thiolate chelated ruthenium organometallics.²²



3



4

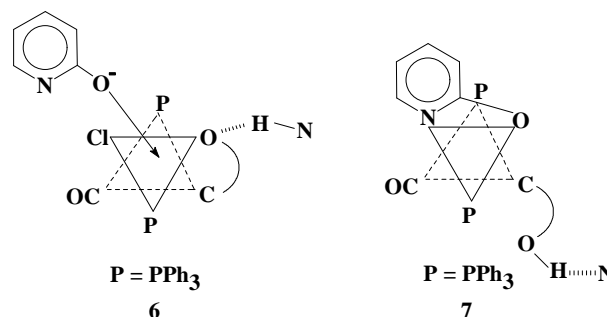
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The conversions $\mathbf{1} \rightarrow \mathbf{3}$ is attended with a prototropic shift within the salicyaldimine function. In **1** the metal is coordinated to phenolato oxygen and

the Schiff base function occurs in the zwitterionic iminium–phenolato tautomeric form **4**. Chelation of quinolin-8-olato is attended with the cleavage of the Ru–O bond and the Schiff base function becomes an imine-phenol **5**. This is fully consistent with the spectroscopic data.

Thus the C=N stretching frequency in **3** is significantly lower ($\sim 1600 \text{ cm}^{-1}$) than that in **1** ($\sim 1620 \text{ cm}^{-1}$) as expected.³¹ Also the aldimine CH signal in ^1H NMR in **3** (figure 1) occurs at lower field viz. 8.0 ppm as compared to ~ 7.5 ppm in **1**.¹⁵ The O–H resonance in **3** is a relatively sharp signal near 13 ppm having half-height width of ~ 30 Hz. In contrast, the iminium N–H resonance in **1** is broad (width, ~ 150 Hz) evidently due to the quadrupole moment of the nitrogen atom.¹⁵ The prototropic transformation between **1** and **3** has certain similarities with the imine–iminium tautomerization in rhodopsins.³¹

A plausible mechanism¹⁹ for the displacement of chloride in **1** consists of *cis* attack by Q^- is shown in **6**. The anchored ligand displaces the phenolato oxygen and halide atoms achieving Q^- chelation with concomitant prototropic shift and conformational reorganization as in **7**.



3.2 Characterization

Organometallics of type **3** are non-electrolytic in solution and are diamagnetic, consistent with a metal oxidation state of +2. The C≡O stretch is seen as a sharp band near 1900 cm^{-1} .

In ^1H NMR (figure 1) the 3-H proton of the metallated ring occur as sharp singlets near 6.2 ppm, while the C(4)-Me protons resonate near 1.7 ppm. These protons are subject to shielding by phosphine phenyl rings.^{15,19,32} The PPh_3 , Schiff base ($\text{C}_6\text{H}_4\text{R}$) aromatic protons form a complex multiplet in the region 6.80–7.30 ppm and the quinolin-8-olato aromatic protons appear in the 6.20–8.30 ppm region. Detailed assignments of the ligand protons are given

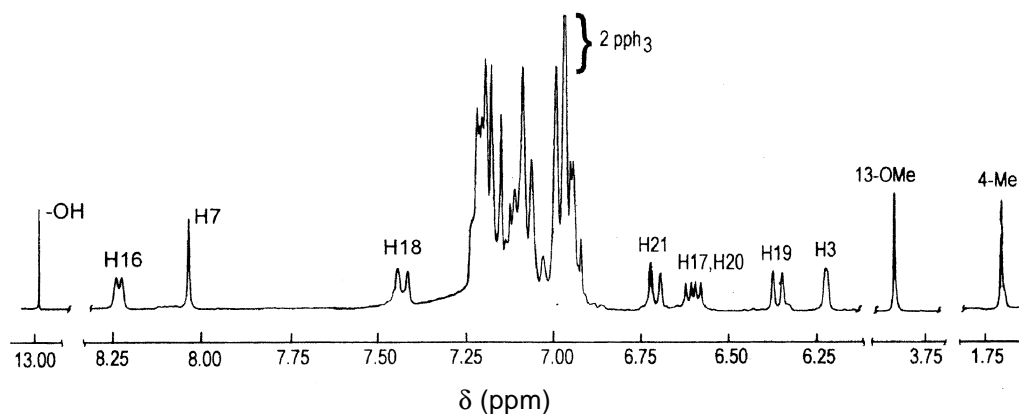


Figure 1. ^1H NMR spectrum of **3** (OMe) in CDCl_3 solution.

Table 1. Spectral and electrochemical data of **3**.

Complexes	UV-Vis data ^a		Emission data		Electrochemical data	
	I_{max} , nm (ϵ^b , $\text{M}^{-1}\text{cm}^{-1}$)		I_{max} , nm ($f_r^{a,c}$)		$E_{1/2}$, V (ΔE_p , mV) ^d	n^e
	298 K	77 K				
3 (Me)	338 (17995) 410 (9720)	507 (2.01×10^{-3})	586	0.52 (184)	1.09	
3 (OMe)	345 (21715) 420 (9800)	506 (1.74×10^{-3})	584	0.48 (102)	1.02	
3 (Cl)	342 (16085) 415 (9447)	513 (1.30×10^{-3})	587	0.58 (166)	0.96	

^aSolvent: dichloromethane; ^bmolar absorption coefficient; ^cexcitation at the higher wavelength absorption peak; ^dsolvent: dichloromethane; ΔE_p is peak-to-peak separation; ^e $n = Q/Q'$ where Q is the observed Coulomb count and Q' is the calculated Coulomb count for one-electron transfer

in the experimental section. In the previous section the chemical shifts of the imine–phenol protons were considered. The redox and photophysical properties of the complexes are examined in later sections.

3.3 Electrochemistry: Trivalent ruthenium

In dichloromethane solution **3** displays a quasireversible one-electron cyclic voltammetric response near 0.50 V (peak-to-peak separation is ~ 100 mV) vs SCE corresponding to the couple



where $\mathbf{3}^+$ represents the ruthenium(III) analogue of **3**. A representative cyclic voltammogram is shown in figure 2. As R is varied, the $E_{1/2}$ values increase in the Hammett order³³ $\text{OMe} < \text{Me} < \text{Cl}$, see table 1. The reduction potentials are systematically lower than those of the type **1** precursors¹⁵ by ~ 200 mV, indicating better stabilization of the trivalent state in **3** compared with that in **1**. The one-electron nature of the couple is consistent with the current height

data compared to those of the one-electron standard $[\text{Ru}(\text{bpy})_3]^{2+}$. The exhaustive coulometric oxidation at 0.8 V affords a Coulomb count corresponding to one-electron transfer (table 1).

Trivalent organometallics $\mathbf{3}^+$, generated coulometrically, have been examined in solution. Their cyclic voltammograms (initial scan cathodic) are virtually superimposable on those of **3** (initial scan anodic), showing that $\mathbf{3}^+$ retains the gross structure of **3**. Orange-red solutions of $\mathbf{3}^+$ are characterized by an intense band near 395 nm associated with a shoulder near 475 nm (table 2). The solutions are EPR-active when frozen into the glassy state (dichloromethane–toluene, 77 K) giving rise to well-resolved rhombic spectra consistent with the low-spin $4d^5$ configuration in a nonaxial geometry.^{24,34} A representative spectrum is shown in figure 3 and the g values are listed in table 2.

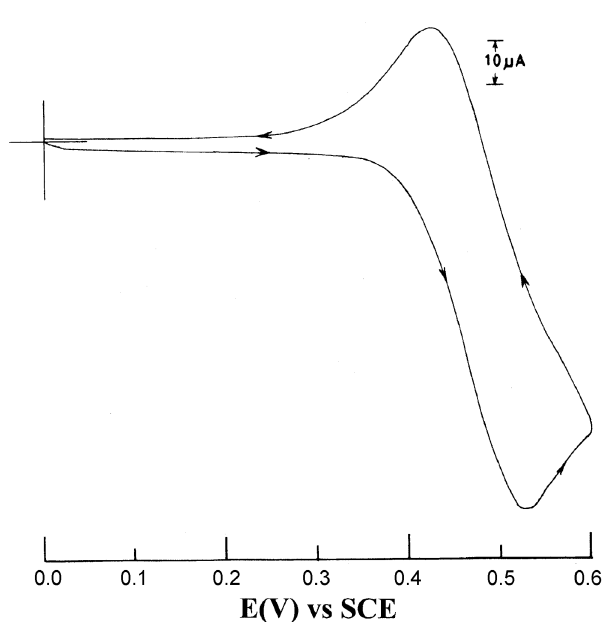
3.4 Photophysical properties

In dichloromethane solution complexes of type **3** display two allowed absorption bands in the regions

Table 2. Electronic and EPR spectral data of **3**⁺.

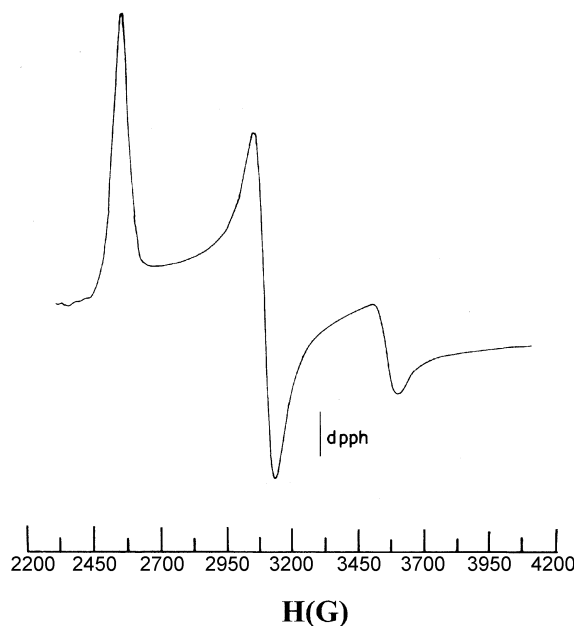
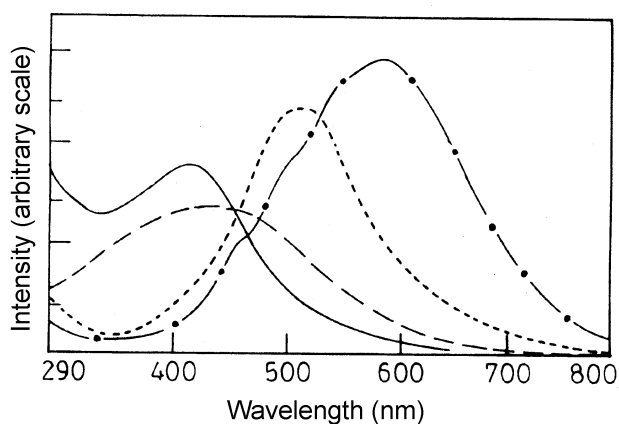
Complexes	UV-Vis data ^a I_{\max} , nm (ϵ^b , $M^{-1} \text{ cm}^{-1}$)	EPR g values ^c		
		g_1	g_2	g_3
3 (Me) ⁺	330 (28850), 394 (12903), 475 (3072)	2.529	2.124	1.895
3 (OMe) ⁺	338 (24090), 390 (12764), 477 (2542)	2.544	2.131	1.881
3 (Cl) ⁺	327 (22721), 397 (10071), 472 (2007)	2.578	2.158	1.896

^aSolvent: dichloromethane; ^bmolar absorption coefficient; ^cin 1:1 dichloromethane/toluene frozen glass (77 K)

**Figure 2.** Cyclic voltammogram of **3** (OMe) in dichloromethane solution.

330–350 and 400–420 nm. The latter band is weaker in intensity and is believed to have significant $dp(\text{Ru})-p^*(\text{Q})$ MLCT character. Selected UV-Vis spectral data are given in table 1. The solutions are fluorescent at room temperature, and also at low temperature (77 K). The peaks lying in the region 505–515 and 580–590 nm at 298 K and 77 K respectively (figure 4, table 1) makes **3** fluorescent in the visible region. Low-temperature emission spectra are red-shifted from room temperature ones. The complexes are weak emitters, as noted from their quantum yield (f_r) values which are one order of magnitude lower than that of the $[\text{Ru}(\text{bpy})_3]^{2+}$ standard³⁵ (table 1).

Quantum yields are calculated using equation (3) as described previously³⁵ where f_{std} is 0.042 at 298 K, A is the solution absorbance at the excitation wave length, I is the relative emission intensity, n are the refractive index values of the solvent for the

**Figure 3.** X-band EPR spectrum of electrogenerated **3** (Cl)⁺ in dichloromethane-toluene glass at 77 K. Instrument settings: power, 30 dB; modulation, 100 kHz; sweep centre, 3200 G.**Figure 4.** Absorption (—), excitation (---), and fluorescence spectra at 298 K (---) and at 77 K (—•—) of **3** (Cl) in dichloromethane solution.

sample (subscript *r*) and the standard reference (subscript std) respectively,

$$f_r = f_{\text{std}} (A_{\text{std}}/A_r)(I_r/I_{\text{std}}) (h_r^2/h_{\text{std}}^2). \quad (3)$$

Excitation spectral studies show that fluorescence is associated with the absorption band near 400 nm. A representative case is shown in figure 4. Assuming that the band has MLCT character as suggested above, the possible involvement of the ³MLCT state¹³ incorporating *p** (*Q*) contribution is implicated in the emission process. We also note that the parent organometallics of type **1** do not display any fluorescence in the visible region.

4. Conclusions

It is demonstrated that the metallacyclics of type **1** react smoothly with HQ furnishing aryl ruthenium organometallics of type **3**. The conversion **1** → **3** is attended with cleavage of Ru–O and Ru–Cl bonds, (N,O) chelation of quinolin-8-olate, iminium-phenolato → imine-phenol tautomerization. Ru^{III}/Ru^{II} reduction potentials are systematically lower than those of **1** and **3** is electrooxidizable to the ruthenium(III) analogue **3**⁺ characterized by rhombic EPR spectra. The Ru → Q MLCT absorption in the visible region makes **3** fluorescent with quantum yields one order of magnitude less than that of the [Ru(bpy)₃]²⁺ standard.

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