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# Two Novel Reactions of a Ruthenium-Coordinated Phenazine – Oxidative Aromatic Ring Hydroxylation and Dimerization via a New C-N Bond Formation

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The reaction of  $[Ru(CH_3OH)_2(N \land N)_2]^{2+}$   $[N \land N = 2,2'$ -bipyridine (bpy) and 1,10-ortho-phenanthroline(phen)] with the phenazine ligand,  $[HL^1 = 6-p-anisyl-2-(p-anisylamino)-$ 3(4H)-*p*-anisylimine-9-methoxyphenazine] in the presence of a base (NEt<sub>3</sub>) afforded two mononuclear ruthenium complexes,  $[Ru(L^1)(N \wedge N)_2]X$  (2), and  $[Ru(LO)(N \wedge N)_2]X_2$  (3), [LO = 7-methoxy-5-(4-methoxyphenyl)-2,3-bis(4-methoxyphenylimino)-3,5-dihydro-2H-phenazin-1-one] together with a diruthenium complex [ $(N \land N)_2 RuL^2 Ru(N \land N)_2$ ]X<sub>3</sub> (4), [L<sup>2</sup> = 7,8'dimethoxy-5,10'-bis(4-methoxyphenyl)-2,3'-bis(4-methoxyphenylamino)-3,2'-bis(4'-methoxyphenylimino)-3,5,2',10'tetrahydro-[1,5']biphenazinyl-5'-ylium], (X =  $ClO_4^-$  or  $CF_3SO_3^{-}$ ). The complexes 3 and 4 were also obtained from the pure complex 2 under two different experimental conditions. Oxidative aromatic ring hydroxylation of the complex 2 produced 3 while the diruthenium complex, 4, was formed by dimerization of 2 via a new C-N bond formation. The products were thoroughly characterized with the help of <sup>1</sup>H

## Introduction

Transition-metal mediated functionalization of C-H bonds is one of the most vigorously pursued<sup>[1-4]</sup> areas of current synthetic research. In many instances these reactions lead to the synthesis of unusual molecules, which otherwise are difficult or even impossible to synthesize using conventional procedures. In recent years we have been working<sup>[5-6]</sup> on transition-metal promoted aromatic amine fusion reactions, via C-H functionalization, for the synthesis of new organic ligands whose coordination chemistry is rich with novel features. One such example<sup>[7]</sup> is the ferric

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412

chloride-mediated oxidative polymerization of *p*-anisidine, which produces N-substituted 2-amino-3-iminophenazines via a multiple C-N bond fusion reaction (Scheme 1). NH FeCl<sub>3</sub> OCH:  $+8H^{+}+8e^{-}+NH_{3}+CH_{3}OH$ H-CO осн ÓСН,  $HL^1$ 

NMR and ESI-MS spectral measurements. Final authentica-

tion of the two complexes of the transformed phenazine li-

gands viz. 3 and 4 were made by single-crystal X-ray struc-

ture determination of the two representative complexes.

These compounds are intensely colored and show transitions

in the visible region, which are ascribed as metal-to-ligand

charge transfer (MLCT). Notably, intensities of the two

MLCT of the compound 4 are significantly higher than those

of 2 and 3. Redox properties of the complexes are reported.

Electrochemical oxidation of compound 2, even in the pres-

ence of trace moisture, produced compound 3. Cyclic voltam-

metry of compound 3 shows a reductive response near

-0.35 V. Its one-electron reduced product is blue and shows

an intense EPR signal at g = 2.001. The voltammogram of the

diruthenium complex 4 consists of two responses near 0.70

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Our interest<sup>[6]</sup> in the coordination chemistry of 1,2-diimine ligands and their redox partners prompted us to explore the ligand chemistry of [HL<sup>1</sup>]. We have shown<sup>[7]</sup> that





and 0.85 V.

Germany, 2007)

the deprotonated phenazine ligand coordinates to the [Ru- $(pap)_2$ <sup>2+</sup> moiety [pap = 2-(phenylazo)pyridine] spontaneously. The redox behavior of the resultant complex  $[Ru(L^1) (pap)_2$ <sup>+</sup> (1) was of particular interest, since it seemed to follow<sup>[7]</sup> the EC-type pathway to produce a new ruthenium complex, following the oxidation of complex 1. In practice, however, chemical oxidation of complex 1 resulted in a mixture of several products from which no pure compound could be isolated. The ESI-MS spectrum of the above crude mixture showed the presence of a moderately intense peak at m/z = 1041 amu. For comparison we note here that the parent complex, 1, showed a strong ESI-MS signal at m/z= 1026 amu due to the  $[Ru(L^1)(pap)_2]^+$  ion. The difference in mass between the two compounds indicates the addition of an oxygen atom to the parent complex 1. Subsequently, we have found that the similar ruthenium complexes of  $[L^1]^-$ ,  $[Ru(L^1)(N \land N)_2]^+$   $[N \land N = 2,2'$ -bipyridine (bpy) or 1,10-ortho-phenanthroline (phen)] also undergo similar chemical transformations upon oxidation. In these cases the transformed compounds are stable and suitable for following the above-mentioned metal-mediated redox reactions.

In this paper we report the results of the reaction of the 2-amino-3-iminophenazine, HL<sup>1</sup> and [Ru(CH<sub>3</sub>OH)<sub>2</sub>- $(N \wedge N)_2$ <sup>2+</sup>. The chemical reaction resulted in the formation of the three products 2-4, of which the complexes 3 and 4 are formed due to an unprecedented type of chemical transformation of the coordinated ligand  $[L^1]^-$  in the complex 2. While oxidative hydroxylation of the ligand produced a ruthenium complex 3 of the oxidized phenazine ligand (LO), dimerization of it, on the other hand, produced a diruthenium complex 4 of a diphenazine bridge  $[L^2]^-$ . The latter reaction is associated with a new C-N bond fusion process. In the present context it is relevant to add that the coordination chemistry of the phenazine ligands, in general, has been developed in recent years; however, this work is confined<sup>[8]</sup> mostly to the complexes of pyridyl-containing phenazines. Some of these bind DNA and RNA and are an important class of molecular probes.<sup>[9]</sup> In contrast, the coordination chemistry of the related 2-amino-3-iminophenazine or its redox partners is not available in the literature. Thus, the reference reactions are noteworthy in the context of understanding the metal-mediated redox processes that are operative in amino-imino-phenazine<sup>[10]</sup> and related systems.

## **Results and Discussion**

The synthetic reaction involved refluxing a methanolic solution of  $[\text{Ru}(N \land N)_2(\text{CH}_3\text{OH})_2]^{2+}$ , generated in situ,<sup>[11]</sup> with an equimolar quantity of HL<sup>1</sup> in the presence of a base (NEt<sub>3</sub>) for 6 h. The initial red brown color of the solution mixture gradually turned bluish-violet and finally it became blue. The complexes were precipitated as their perchlorate or triflate salts. The crude mass, so formed, was a mixture of three major products: blue **2**, violet **3** and blue **4**, which were successfully separated on a preparative alumina TLC plate. The first blue complex 2 was unstable and with time slowly converted into the violet product 3 in air even at room temperature. The  $2 \rightarrow 3$  conversion was much faster in boiling aqueous methanol.

Prolonged boiling of compound 2 in a dry and inert atmosphere, on the other hand, produced a stable blue compound 4 as the major product (vide infra). Schematic presentation of the reaction along with compound identification numbers are summarized in Scheme 2.

The sum total of the yields of the above three products exceeded 85%. There were a few minor fractions, which could not be purified and their identities remain uncertain.

The complexes gave satisfactory elemental analyses (see Exp. Sect.). These showed characteristic infrared stretches of the phenazine and coordinated ancillary ligands viz. bpy and phen. The most notable feature in the infrared spectra of 3a and 3b is the appearance of a sharp band at ca. 1680 cm<sup>-1</sup>, which confirms the presence of a carbonyl function<sup>[12]</sup> (vide infra). These complexes are diamagnetic and displayed <sup>1</sup>H NMR resonances in the normal range. The spectral patterns in the aromatic region ( $\delta = 5-9$ ) are complex in nature (see Figure S1, supporting information) owing to the presence of a large number of unique protons. The methyl resonances were, however, diagnostic and useful for assessing their preliminary identities (Figure 1). For example, while the compounds 2 and 3 showed four -OMe signals each in the range  $\delta$ , 3.38–3.75, compound 4 displayed eight –OMe resonances in the range  $\delta = 3.25 - 3.80$ . For comparison, the uncoordinated ligand,  $[L^1]^-$ , displayed four<sup>[7]</sup> such resonances at  $\delta$  = 3.55–3.85. Thus, the <sup>1</sup>H NMR spectrum of complex 4 indicated the presence of two phenazine moieties. Electrospray mass spectra of the complexes were found to be informative for the identification of the complexes. The charge state distributions of these ranging from (+1) to (+3) are clearly observed, which exactly corroborated with the ionization of the respective complexes in the acetonitrile solution. For example an abundant peak, called a base peak, was observed for  $[2a-ClO_4^-]^+$  at m/z =971 amu. The complex **3a** showed a weak signal at m/z =1085 amu, and was accompanied by a strong signal at m/z= 493 amu. These were ascribed to the  $[3a - ClO_4^-]^+$  and  $[3a - 2ClO_4^{-}]^{2+}$  ions, respectively. The compound 4a exhibited peaks at 1020 and 647 amu, respectively. The peak at 647 amu was most intense and ascribed to the [4a - $3ClO_4^{-1}^{3+}$  ion. Similarly, the substituted complexes viz. **2b**, **3b** and **4b** displayed peaks at expected m/z values (Exp. Sect.). From the ESI-MS spectral nature it is inferred that complex 4 is a dimetallic compound with a relatively high molecular weight. Notably, the experimental ESI-MS spectral features of the above compounds exactly corresponded to simulated patterns for the given formulations. Three representative ESI-MS spectra of 2-4, are submitted as supplementary materials (Figure S2). Electrolytic natures of dilute acetonitrile (1 mm) solutions of the complexes were of different type: 2, 1:1, 3, 1:2 and 4, 1:3.

Preliminary characterization of the above compounds was made from their physicochemical data. However, Xray crystal analyses of the two complexes (3 and 4) of the



Figure 1. Segmented <sup>1</sup>H NMR spectra of (a)  $HL^1$ , (b) 2a, (c) 3a, and (d) 4a  $CD_3CN$  at 298 K.

transformed ligands were indeed necessary for authentication of their formulations and structures.

The solutions of the complexes **2a** and **2b** were found to undergo chemical transformations to **3a** and **3b**, respectively, hence X-ray quality crystals of the parent complex,  $[\operatorname{Ru}(N \wedge N)_2(L^1)](X)$  (2) could not be grown. However, a complete characterization was obtained (vide supra) from the physicochemical data. The two representative complexes of the transformed ligands viz. **3b** and **4a** formed single crystals suitable for X-ray structure determination.

Scheme 2.

#### $[Ru(phen)_2(LO)](CF_3SO_3)_2 \cdot 2H_2O$ (3b)

A view of the cationic part of the molecule [Ru(phen)<sub>2</sub>-(LO)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O is shown in Figure 2 and selected bond lengths and angles are collected in Table 1. In this complex, two bidentate 1,10-ortho-phenanthroline (phen) ligands and a neutral phenazine ligand [LO], formed via successive hydroxylation and oxidation of the coordinated ligand  $[L^1]^-$ , surround a ruthenium(II) center. The complex as a whole is dicationic and the crystallographic asymmetric unit also contains two triflate anions and two water molecules. Hydroxylation of the phenazine ligand occurred at the  $\alpha$ -carbon (C13) to a N-aryl imine function [C(12)– N(11)]. The C(13)–O(130) bond length, 1.209(4) Å, indicates a localized double bond. The two C-N (imine) bond lengths, 1.300(4) Å [C(12)–N(11)] and 1.290(6) Å [C(25)– N(26)], respectively confirm<sup>[6a,13]</sup> their double bond character. The six Ru-N lengths are similar, and lie in the range 1.997-2.083 Å. The average of chelate bite angles of the phen ligand is  $79.1(2)^\circ$ , while the corresponding N(11)-Ru(1)-N(26) angle of the phenazine ligand has a value of 76.71(12)°.



Figure 2. ORTEP and atom numbering scheme for **3b**. Hydrogen atoms are omitted for clarity.

#### $[(bpy)_2RuL^2Ru(bpy)_2](ClO_4)_3$ (4a)

Figure 3 shows the ORTEP and atom numbering scheme for the cationic complex  $[4a]^{3+}$  and its bond parameters are collected in Table 1. Herein, two [Ru<sup>II</sup>(bpy)<sub>2</sub>] moieties are bridged across a dimeric phenazine ligand  $[L^2]^-$ , formed via an unusual type of C-N fusion between the two [Ru(bpy)<sub>2</sub>-L<sup>1</sup>]<sup>+</sup> units. In this reaction a new C–N bond is formed between the free pyrazine nitrogen N(9) of one unit and the  $\alpha$ -carbon C(36) of the second unit. The bridging ligand,  $[L^2]^-$ , is a zwitterion with two anionic chelating sites and a cationic pyrazine nitrogen. The bridging ligand is thus mono-negative and coordinates to two ruthenium(II) centers in a bis chelating tetradentate fashion. The resulting diruthenium complex as a whole is tri-cationic and the asymmetric unit contains three perchlorate counterions. The C–N lengths viz. C(35)–N(5) 1.387(4) Å, C(40)–N(6) 1.314(4) Å, C(71)-N(11) 1.343(4) Å and C(72)-N(12)1.348(4) Å are all longer than the corresponding distances in coordinated LO in the compound **3b** (Table 1). Notably, the C(35)–N(5) length is appreciably longer than C(40)– N(6) suggesting that the anionic charge in this part of the bridging ligand is localized on N(5). In contrast the two C-N lengths of the other part viz. C(71)-N(11) and C(72)-N(12) are nearly identical indicating effective charge delocalization over the N(11)-C(71)-C(72)-N(12) skeleton. The average of the above C-N lengths of L<sup>2</sup> lies in between a single and a double C-N bond length. The five-membered chelate rings of the bridging ligand have the expected bite angles, N(5)-Ru(1)-N(6) 76.12(9)° and N(11)-Ru(2)-N(12) 76.94(11)°.

The two reference chemical transformations, viz.  $2 \rightarrow 3$ and  $2 \rightarrow 4$ , occur due to induced C-H activation<sup>[6,14]</sup> at the ortho carbon of the coordinated phenazine. The plausible initial step for the formation of 3 is the oxidation reaction,  $2 \rightarrow 2^+$ . The oxidized product  $2^+$  is then converted to 3 in the presence of water and aerial oxygen. Water adds to the polarized phenazine ring and the hydroxo-intermediate, so formed, is oxidized to 3 in air. Exposure of an aqueous methanolic solution of 2 to air thus produces the com-

Table 1. Selected bond lengths [Å] and angles [°] for the complexes 3b and 4a.

$[Ru(phen)_2(LO)](CF_3SO_3)_2 \cdot 2H_2O (3b)$ Bond lengths				[(bpy) <sub>2</sub> RuL <sup>2</sup> Ru(bpy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub> (4a) Bond lengths			
Ru(1)–N(26)	2.053(3)	C(12)-C(13)	1.523(5)	Ru(1) - N(6)	2.056(2)	C(39) - C(40)	1.389(4)
Ru(1) - N(61)	2.082(5)	C(12) - C(25)	1.457(5)	Ru(2) - N(11)	2.034(3)	C(35)-C(40)	1.393(4)
Ru(1) - N(72)	2.038(4)	N(26)-C(25)	1.290(6)	Ru(2) - N(12)	2.050(3)	C(70)–C(71)	1.396(5)
Ru(1)–N(81)	2.042(3)	C(25)-C(24)	1.369(6)	N(6)-C(40)	1.314(4)	C(71) - C(72)	1.388(5)
Ru(1) - N(92)	2.066(4)	C(13)–O(130)	1.209(4)	N(9)-C(36)	1.470(4)	C(72)–C(73)	1.395(5)
				N(11)-C(71)	1.343(4)	C(35)–N(5)	1.387(4)
				N(12)–C(72)	1.348(4)		
Bond angles				Bond angles			
N(11)-Ru(1)-N(26)	76.71(12)	N(72)–Ru(1)–N(61)	78.6(2)	N(1)-Ru(1)-N(2)	78.27(10)	N(3)-Ru(1)-N(4)	78.14(9)
N(92)-Ru(1)-N(81)	79.64(15)			N(5)-Ru(1)-N(6)	76.12(9)	N(11)-Ru(2)-N(12)	76.94(11)
	. ,			N(13)-Ru(2)-N(14)	77.80(13)	N(15)-Ru(2)-N(16)	79.52(13)



Figure 3. ORTEP and atom numbering scheme for 4a. Hydrogen atoms are omitted for clarity.

pound 3 in almost quantitative yield. The plausible steps of this transformation<sup>[15]</sup> are shown in Scheme 3. Since the oxidation potential of complex 2 is low (vide infra), the aerial oxidation,  $2 \rightarrow 2^+$  is reasonable and is believed to be the key step for the formation of 3 from 2. Furthermore, the fact that electrochemical oxidation of the complex 2 (vide infra) produces the compound 3, also supports our proposition. The conversion of 2 to 4 occurs only in dry and boiling methanol. Nucleophilic attack of the phenazine nitrogen of one molecule of 2 at the activated *ortho* C–H of another molecule followed by (-H<sup>+</sup> – 2e<sup>-</sup>) transfer produces the compound 4.

Hence, we conclude that  $2 \rightarrow 3$  conversion is facilitated by the initial oxidation of the ruthenium(II) center of 2. However, if the initial oxidation of 2 is arrested, dimerization of the phenazine occurs preferably so as to initiate the formation of the dimetallic complex 4. The results are summarized in Scheme 4.

The electronic spectroscopic data of all the complexes are collected in Table 2 and their representative spectra are displayed in Figure 4. The visible range spectra of these complexes consisted of strong absorptions. For example, the mononuclear complexes **2a** and **3a** each showed an allowed transition at 585 nm ( $\varepsilon = 16385 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 565 nm ( $\varepsilon =$ 23490 M<sup>-1</sup> cm<sup>-1</sup>), respectively. These are ascribed to charge transfer, Ru<sup>II</sup>(d $\pi$ ) $\rightarrow \pi^*$ (phenazine) (MLCT). The bimetallic compound **4a** displayed two intense transitions at 690 nm ( $\varepsilon = 36450 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 645 nm ( $\varepsilon = 32300 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively. Notably, the two-phenazine moieties in the bridging ligand  $[L^2]^-$  are not identical and hence the two major transitions in the visible region are believed to be due to the presence of two acceptor chromophores in the bridging ligand. Interestingly, the intensities of MLCT transitions in 4 are significantly higher than those of the mononuclear compounds 2 and 3. This spectral behavior of the polynuclear complexes with repeating acceptor chromophores has been reported<sup>[6b]</sup> in the literature. The complexes also showed multiple UV-range transitions, which are assigned to inter- or intra-ligand transitions.

The redox behavior of the complexes **2**–**4** was studied in dichloromethane {maintaining  $10^{-3}$  M concentration of the complex and  $10^{-1}$  M concentration of the supporting electrolyte,  $[nBu_4N](ClO_4)$ } in the potential range 2.0 to -1.5 V by using platinum or glassy carbon working electrodes. The reported potentials (Table 2, Figure 5) are referenced to the saturated calomel electrode (SCE). The value for the ferrocene/ferrocenium couple under our experimental conditions was 0.39 V.

The mononuclear complex  $[Ru(bpy)_2L^1]ClO_4$  (2a) showed an electrochemically reversible  $Ru^{III}/Ru^{II}$  response at 0.15 V. Associated with it is an irreversible response, which appeared at a potential of 1.05 V. The redox behavior of the closely related system,  $[Ru(phen)_2L^1]ClO_4$  2b, is similar to that of 2a. Constant potential coulometry at 0.40 V of both 2a and 2b resulted in rapid transformations to 3a and 3b, respectively. The voltammetric behavior of the com-

# FULL PAPER



Scheme 3.



plexes, **3a** and **3b** was similar. These showed a reversible reductive response near -0.35 V. Exhaustive electrolysis of **3a** at -0.60 V produced a blue solution, which reverted to

the parent bivalent complex, **3a** under our experimental conditions. However, we managed to record an EPR spectrum of the reduced complex, by performing the controlled potential bulk electrolysis of **3a** at 260 K and quickly freezing the electrolyzed solution at 77 K. The EPR spectrum showed (Figure S3) an intense signal at g = 2.001 without any *g*-anisotropy, indicating large free radical<sup>[16]</sup> (ligand) contributions to the SOMO. We thus conclude that upon reduction of **3a**, an electron is added to the ketonic function of the phenazine ligand to result in a free radical-containing phenazine ligand [LO]<sup>-</sup> that resembles<sup>[10]</sup> pyocyanine. The main feature of the cyclic voltammogram of the dimetallic complexes **4a** and **4b** consisted of two closely spaced responses at 0.70, 0.85 V and 0.75, 0.90 V, respectively. These are assigned to two successive electron transfers at the two

# FULL PAPER

Table 2. Electronic spectra and cyclic voltammetric data.

Compound	Abs. $[\lambda_{\max} / nm (\epsilon / M^{-1} cm^{-1})]^{[a]}$	Cyclic voltammetry <sup>[c,</sup> Oxidation $E_{1/2}$ [V] $(\Delta E_p$ [mV])	<sup>d]</sup> Reduction $E_{1/2}$ [V] $(\Delta E_p \text{ [mV]})$
2a	585 (16385), 420 (8770), 285 (41555)	0.15 (70), 1.05 <sup>[e]</sup>	-1.33 (90)
3a	565 (23490), 400 <sup>[b]</sup> (12085), 320 <sup>[b]</sup> (18790), 290 (43830)	0.85 (100)	$-0.35$ (100), $-0.91^{[f]}$
4a	690 (36450), 645 (32300), 340 (20480), 295 (36310)	0.70 (80), 0.85 (90)	-0.88 (90)
2b	585 (17390), 415 (8900), 285(44250)	$0.15(75), 1.10^{[e]}$	-1.35 (100)
3b	565(29610), 390 <sup>[b]</sup> (12340), 320 <sup>[b]</sup> (14640), 265 (45770), 225 (61135)	0.90 (100)	$-0.30$ (80), $-1.00^{[f]}$
4b	690 (42155), 645 (36190), 325 (23060), 265 (116680), 225 (129170)	0.75 (70), 0.90 (80)	-0.85 (80)

[a] Solvent: acetonitrile. [b] Shoulder. [c] Solvent: dichloromethane, supporting electrolyte:  $[nBu_4N](ClO_4) \ 10^{-1} \text{ m}$ ; scan rate: 50 mV<sup>-1</sup>s<sup>-1</sup>. [d] Sample concentration ca.  $10^{-3}$  m. [e] Irreversible, the value corresponds to  $E_{pa}$ . [f] Irreversible, the value corresponds to  $E_{pc}$ .



Figure 4. UV/Vis spectra of  $(L^1)^-$ , (-); (2a), (....); (3a), (-----); (4a), (-----) in acetonitrile.

ruthenium centers. The magnitude of  $\Delta E$  signifies moderate electronic interactions between the ruthenium centers.

Our present work has demonstrated that the phenazine ligand [6-p-anisyl-2-(p-anisylamino)-3(4H)-p-anisylimine-9methoxyphenazine], HL<sup>1</sup>, upon coordination to ruthenium is susceptible to fascinating metal-mediated chemical transformations leading to isolation of the three new ruthenium complexes 2–4 of three different ligands (viz.  $[L^1]^-$ , LO and  $[L^2]^{-}$ ) from the reaction of  $[Ru(CH_3OH)_2(N \wedge N)_2]^{2+}$  and HL<sup>1</sup>. The latter two ligands are formed in situ due to oxidative hydroxylation and dimerization reactions of the coordinated ligand,  $[L^1]^-$ . To authenticate these transformations, X-ray structure analyses of a mononuclear ruthenium complex of LO as well as a diruthenium complex of the bridging ligand [L<sup>2</sup>]<sup>-</sup> were analyzed. Presently, we are pursuing our work to understand the effects of ancillary ligands and the metal ions on the chemical transformations of the reference phenazine ligands.



Figure 5. Cyclic voltammograms for the compounds (a) 2a, (b) 3a, and (c) 4a in dichloromethane at a scan rate 50 mV s<sup>-1</sup>.

## **Experimental Section**

**Materials:** The precursor compounds cis-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O and cis-[Ru(phen)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O were prepared according to the reported procedures.<sup>[17]</sup> The ligand HL<sup>1</sup> was synthesized as before.<sup>[7]</sup> Silica gel and aluminum oxide for TLC were obtained from Merck, India and Sisco Research Laboratories Pvt. Ltd., Bombay. RuCl<sub>3</sub>·nH<sub>2</sub>O was purchased from Arora Mathey Ltd., and 2,2'-bipyridine and 1,10-phenanthroline monohydrate were obtained from Qualigens and Merck, India, respectively. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte, for spectroscopic

and electrochemical studies HPLC-grade solvents were used. Other chemicals and reagents were of reagent-grade and used as received.

#### **Physical Measurements**

Microanalytical data (C, H and N) were collected with a Perkin-Elmer 240C elemental analyzer. A Perkin-Elmer 783 spectrophotometer was used for the measurement of IR spectral data. <sup>1</sup>H NMR spectroscopic data was recorded with a Bruker Avance 300 spectrometer using SiMe<sub>4</sub> as an internal standard. Electrochemical measurements were performed at 298 K under a dry nitrogen atmosphere on a PC-controlled PAR Model 273A electrochemistry system with a gas tight single-compartment cell. Voltammetric experiments were carried out in dichloromethane maintaining the sample concentration at ca.  $10^{-3}$  M. The solution was degassed with the flow of dry nitrogen and the working electrode surface was polished before each measurement. A platinum disk working electrode, platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All redox potentials in this work are reported against the saturated calomel electrode. The value for the ferrocenium/ferrocene couple under our experimental conditions was 0.39 V. EPR spectral measurements were carried out with a Varian Model 109C E-line Xband spectrometer as described before,<sup>[18]</sup> fitted with a quartz Dewar for measurements at 77 K, and the spectroscopic data were calibrated against the spectrum of DPPH. Electrospray mass spectra were recorded with a micro mass Q-TOF mass spectrometer (Serial no. YA. 263). Electronic spectroscopic data were recorded with a Perkin-Elmer Lambda 950 UV/Vis spectrophotometer.

**CAUTION!** Although no problems were encountered in this work, transition metal perchlorate complexes with organic ligands are potentially explosive. Heating of dried samples must be avoided; handling of small quantities must proceed with great caution using proper protection.

#### Syntheses

The complexes **2–4** were synthesized following a general procedure. Specific details for representative complexes are given below.

Reactions of [Ru(bpy)<sub>2</sub>(MeOH)<sub>2</sub>]<sup>2+</sup>with HL<sup>1</sup>: A mixture of cis-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (0.065 g, 0.125 mmol) and AgNO<sub>3</sub> (0.042 g, 0.25 mmol) in dry methanol (25 mL) was heated at reflux for 2 h. The initial violet solution changed to orange red. The cooled solution was filtered through Whatman 42 filter paper to remove the precipitated AgCl. The ligand HL1 (0.070 g, 0.125 mmol) along with two drops of NEt<sub>3</sub> was then added to the above filtrate. The resulting mixture was heated at reflux for 6 h. The solution finally became blue and its volume was reduced to ca. 10 mL. The concentrated solution was then poured into diethyl ether (50 mL) to precipitate a dark product. The crude product was then subjected to chromatography on a preparative alumina TLC plate for purification. It was first eluted with CHCl<sub>3</sub>; a small band of unreacted phenazine ligand was first separated, which was followed by a blue (2) band. The unmoved dark band was collected and was again loaded on a fresh TLC plate and chloroform/acetonitrile (3:2) was then used as the eluent. This resulted in the separation of two distinct bands, viz. violet (3) and blue (4). The compounds 2-4 were collected by complete evaporation of the eluates. Recrystallization of these from different solvent mixtures yielded the products in their crystalline states. The yields and characterization data of the complexes are as follows.

 $[Ru(bpy)_2(L^1)](ClO_4)$  (2a): This was crystallized from a dichloromethane/hexane (1:1) solvent mixture. Yield: 0.015 g (10%). C<sub>54</sub>H<sub>45</sub>ClN<sub>8</sub>O<sub>8</sub>Ru (1069.50): calcd. C 60.58, H 4.20, N 10.47; found C 60.56, H 4.25, N 10.45. IR (KBr):  $\tilde{v} = 1615$  s, 1560 s, 1502 s, 1464 m, 1446 m, 1423 m, 1285 w, 1245 s, 1115 vs, 1100 vs, 838 m, 770 s, 625 s cm<sup>-1</sup>. ESI-MS: m/z (%): 971 [M – ClO<sub>4</sub><sup>-</sup>]<sup>+</sup>, where M = molecular mass of the compound.  $\Lambda_{\rm M}$  in acetonitrile at 25 °C: 130 Ω<sup>-1</sup> cm<sup>2</sup>M<sup>-1</sup>.

**[Ru(bpy)<sub>2</sub>(LO)](ClO<sub>4</sub>)<sub>2</sub> (3a):** This was crystallized from an acetonitrile/toluene (1:4) solvent mixture. Yield: 0.069 g (45%). C<sub>54</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>13</sub>Ru (1184.10): calcd. C 54.72, H 3.71, N 9.46; found C 54.73, H 3.74, N 9.41. IR (KBr):  $\tilde{v} = 1670$  s, 1605 s, 1550 s, 1504 s, 1463 m, 1444 m, 1278 w, 1248 s, 1248 s, 1115 s, 1090 s, 836 m, 767 s, 620 s cm<sup>-1</sup>. ESI-MS: *m/z* (%): 493 [M – 2ClO<sub>4</sub><sup>-</sup>]<sup>2+</sup>.  $A_{\rm M}$  in acetonitrile at 25 °C: 250 Ω<sup>-1</sup> cm<sup>2</sup>M<sup>-1</sup>.

**[(bpy)<sub>2</sub>RuL<sup>2</sup>Ru(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (4a):** Evaporation of the third fraction from the TLC plate yielded the dimeric blue **4a**. Yield: 0.054 g (35%). This fraction was recrystallized from acetonitrile/toluene. C<sub>108</sub>H<sub>89</sub>Cl<sub>3</sub>N<sub>16</sub>O<sub>20</sub>Ru<sub>2</sub> (2239.38): calcd. C 57.87, H 3.97, N 10.00; found C 57.95, H 4.00, N 10.01. IR (KBr):  $\tilde{v} = 1605$  s, 1565 w, 1504 s, 1481 m, 1464 w, 1445 m, 1382 vs, 1250 s, 1115 vs, 1030 s, 837 w, 768 s, 625 s cm<sup>-1</sup>. ESI-MS: *m/z* (%): 647 [M – 3ClO<sub>4</sub><sup>-</sup>]<sup>3+</sup>.  $\Lambda_{\rm M}$  in acetonitrile at 25 °C: 370 Ω<sup>-1</sup> cm<sup>2</sup>M<sup>-1</sup>.

**Reactions of**  $[Ru(phen)_2(MeOH)_2]^{2+}$  with HL<sup>1</sup>: This reaction was performed as described above, except that *cis*-Ru(phen)\_2Cl<sub>2</sub> was used in place of *cis*-Ru(bpy)\_2Cl<sub>2</sub>. The yields and characterization data of the complexes are collected below.

**[Ru(phen)<sub>2</sub>(L<sup>1</sup>)](ClO<sub>4</sub>) (2b):** This was recrystallized using a dichloromethane/THF/hexane solvent mixture (1:1:1). Yield: 0.013 g (8%). C<sub>58</sub>H<sub>45</sub>ClN<sub>8</sub>O<sub>8</sub>Ru (1117.50): calcd. C 62.28, H 4.02, N 10.02; found C 62.25, H 4.10, N 9.98. IR (KBr):  $\tilde{v} = 1610$  s, 1548 m, 1504 s, 1427 s, 1384 s, 1245 s, 1175 m, 1100 m, 1027 w, 721 m, 620 s cm<sup>-1</sup>. ESI-MS: *m/z* (%): 1018 [M - ClO<sub>4</sub><sup>-</sup>]<sup>+</sup>. *A*<sub>M</sub> in acetonitrile at 25 °C: 140 Ω<sup>-1</sup> cm<sup>2</sup>M<sup>-1</sup>.

**[Ru(phen)<sub>2</sub>(LO)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (3b):** Crystalline compound of 3b was obtained by slow evaporation of the solution of the compound in a dichloromethane/acetonitrile (1:2) solvent mixture. Yield: 0.075 g (47%). C<sub>60</sub>H<sub>48</sub>F<sub>6</sub>N<sub>8</sub>O<sub>13</sub>RuS<sub>2</sub> (1368.21): calcd. C 52.62, H 3.50, N 8.18; found C 52.55, H 3.60, N 8.10. IR (KBr):  $\tilde{v} = 1670$  s, 1610 s, 1552 s, 1505 m, 1463 w, 1430 w, 1412 w, 1276 vs, 1250 s, 1163 m, 1116 s, 1030 s, 840 m, 721 w, 638 s cm<sup>-1</sup>. ESI-MS: *m/z* (%): 517 [M - 2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>2+</sup>. *A*<sub>M</sub> in acetonitrile at 25 °C: 270 Ω<sup>-1</sup> cm<sup>2</sup>M<sup>-1</sup>.

**[(phen)<sub>2</sub>RuL<sup>2</sup>Ru(phen)<sub>2</sub>](CIO<sub>4</sub>)<sub>3</sub> (4b):** The thin rod-shaped crystalline compound was obtained from an acetonitrile/toluene (1:1) solvent mixture. Yield: 0.040 g (25%). C<sub>116</sub>H<sub>89</sub>Cl<sub>3</sub>N<sub>16</sub>O<sub>20</sub>Ru<sub>2</sub> (2333.64): calcd. C 59.65, H 3.81, N 9.60; found C 59.63, H 3.87, N 9.55. IR (KBr):  $\tilde{v} = 1605$  s, 1564 w, 1502 s, 1481 s, 1427 w, 1408 m, 1383 vs, 1130 s, 1029 m, 842 m, 610 s cm<sup>-1</sup>. ESI-MS: *m/z* (%): 678 [M – 3ClO<sub>4</sub>–]<sup>3+</sup>.  $\Lambda_{\rm M}$  in acetonitrile at 25 °C: 400  $\Omega^{-1}$  cm<sup>2</sup>M<sup>-1</sup>.

Syntheses of Compounds 3 and 4 from 2.  $2a \rightarrow 3a$  Conversion: A solution of the compound [Ru(bpy)<sub>2</sub>(L<sup>1</sup>)](ClO<sub>4</sub>) (2a) [50 mg in 250-mL aqueous methanol (1:9)] was heated at reflux in air for 0.5 h. The blue solution became violet. The mixture was evaporated to dryness and the crude product was purified on an alumina TLC plate using a chloroform/acetonitrile (3:2) solvent mixture as the eluent. A violet band of the compound **3a** was collected. It was finally crystallized from an acetonitrile/toluene solvent mixture, yield 90%.

The compound 3b was similarly obtained from 2b, the yield was 86%.

**2a** $\rightarrow$ **4a Conversion:** A solution of the compound **2a** in dry methanol was heated at reflux under a dry nitrogen atmosphere for 6 h. The resultant blue solution was evaporated to dryness and was loaded on an Al<sub>2</sub>O<sub>3</sub>-TLC plate for purification. A minor violet

# FULL PAPER

band (**3a**, yield 5%) and a major blue band (**4a**, yield 75%) were eluted using a chloroform/acetonitrile (3:2) solvent mixture.

The compound **4b** was similarly obtained from **2b**. The yield of **4b** was 80%.

**X-ray Crystallography:** Single crystals of  $[Ru(phen)_2(LO)](CF_3-SO_3)_2 \cdot 2H_2O$  (**3b**) were grown by slow evaporation of an acetonitrile/ dichloromethane (2:1) solvent mixture and the single crystals of  $[\{(bpy)_2Ru\}_2(L^2)^-](CIO_4)_3$  (**4a**) were grown by slow diffusion of an acetonitrile solution of **4a** into toluene. Crystallographic data are collected in Table 3 and further details are noted below.

Table 3. Crystallographic data and refinement results for 3b and  $4a. \label{eq:abs}$ 

Compound	3b	4a
Empirical formula	C <sub>60</sub> H <sub>48</sub> F <sub>6</sub> N <sub>8</sub> O <sub>13</sub> RuS <sub>2</sub>	C108H89Cl3N16O20Ru2
Molecular mass	1368.25	2239.44
<i>T</i> [K]	293(2)	273(2)
Wavelengths [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	P21/c (no. 14)	P-1 (no. 2)
a [Å]	11.3828(13)	11.6057(18)
b [Å]	22.640(2)	15.236(2)
c [Å]	24.2105(19)	33.086(5)
a [°]	90	79.286(3)
β [°]	109.044(4)	89.143(3)
γ [°]	90	75.031(3)
V [Å <sup>3</sup> ]	5897.7(10)	5550.0(15)
Ζ	4	2
$D_{\text{calcd.}} [\text{mg}\text{m}^{-3}]$	1.541	1.340
Crystal dimensions [mm]	$0.23 \times 0.18 \times 0.16$	$0.03 \times 0.16 \times 0.21$
$\theta$ range for data collection [°]	1.27-28.08	1.3-26.1
Reflections collected	28248	21643
Unique reflections	13468	15050
Largest diff. between		
peak and hole [eÅ <sup>-3</sup> ]	-1.085, 2.731	-0.64, 1.36
Final R indices	$R_1 = 0.0451$	$R_1 = 0.0695$
$[I > 2\sigma(I)]$	$wR_2 = 0.1597$	$wR_2 = 0.1021$

[Ru(phen)<sub>2</sub>(LO)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (3b): X-ray quality crystals of 3b were obtained by slow evaporation of an acetonitrile/dichloromethane (2:1) solvent mixture. A crystal of dimension  $(0.23 \times 0.18 \times 0.16 \text{ mm}^3)$  was mounted, data were collected with a Bruker SMART CCD 1000 diffractometer equipped with a graphite crystal incident beam monochromator having Mo- $K_{\alpha}$  radiation  $(\lambda = 0.71073 \text{ Å})$ , and were processed with SAINT.<sup>[19]</sup> These were corrected for absorption using SADABS<sup>[20]</sup> (transmission factors: 1.000-0.742). A total of 24248 reflections were collected of which 13468 were unique ( $R_{int} = 0.0436$ ) and these were used in subsequent analysis. The structure was solved by direct methods using the program SHELXS-97<sup>[21]</sup> and refined by full-matrix leastsquares techniques against  $F^2$  using SHELXL-97.<sup>[22]</sup> Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained. Crystallographic drawings were prepared using the programs PLATON<sup>[23]</sup> and SCHAKAL.[24]

 $[(bpy)_2RuL^2Ru(bpy)_2](CIO_4)_3$  (4a): X-ray quality crystals of 4a were obtained by slow diffusion of an acetonitrile solution of the compound into toluene. A crystal of dimension  $(0.03 \times 0.16 \times 0.21 \text{ mm}^3)$  was mounted, and the data were collected with a Bruker Smart CCD diffractometer using graphite-monochromated Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å) at 273 K. These were corrected for Lorentz polarization effects and an empirical absorption correction was made with the help of the SAINT<sup>[19]</sup> program. A total of 21643 reflections were measured, of which 15050 reflections were unique ( $R_{int} = 0.060$ ). The data [ $I > 2\sigma(I)$ ] were used for solution and refinement by full-matrix least-squares on  $F^2$  using the SHELXL-97 package.<sup>[22]</sup> The non-hydrogen atoms having full occupancies were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions, but not refined. The refinement was converged at R = 0.0695 and  $wR_2 = 0.1021$  with residual electron density 1.36 eÅ<sup>3</sup> and -0.64 eÅ<sup>3</sup>. The maximum electron densities have no chemical significance as they were located at ca. 0.7 Å from a heavy atom. The calculations were performed using the Bruker Smart 5.63 software for data reduction, all other calculations and graphics were done using the PLATON<sup>[23]</sup> software package and ORTEP.<sup>[25]</sup>

Crystal data and refinement details are listed in Table 3. CCDC-290869 (for **3b**) and -290868 (for **4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see also the footnote on the first page of this article): NMR spectra of a class of representative complexes (Figure S1). Observed ESI-MS spectra for representative complexes (a)  $(2a)^+$ , (b)  $(3a)^{2+}$ , (c)  $(4a)^{3+}$  (Figure S2) and EPR spectrum of a frozen acetonitrile/toluene glass (1:1) of  $(3a)^-$  at 77 K (Figure S3).

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