Ruthenium complexes of quinone related *N*-aryl-1,2-diimines. Metal mediated synthesis, X-ray structure and chemical reaction†

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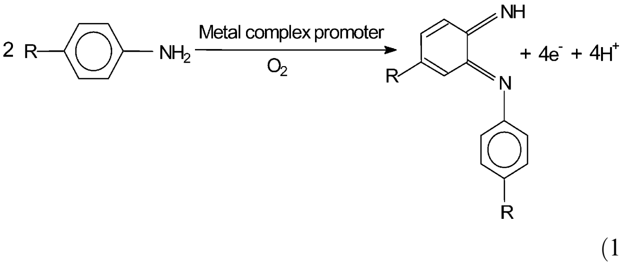
A family of ruthenium *N*-aryl-1,2-diiminoarene chelate complexes, [RuCl$_2$(bpy)(diim)], **1** (bpy = 2,2′-bipyridine, diim = *N*-aryl-1,2-diiminoarene) were isolated from the reaction of [RuCl$_3$(bpy)] and a primary aromatic amine (ArNH$_2$) in the presence of aerial oxygen. The diim ligand was formed *in situ* due to oxidative dimerisation of ArNH$_2$. The metal complex, in this reaction, acts as a mediator. The dichloro complexes were characterized based on their physicochemical data. The X-ray structure of one member of the family was determined and the results used to authenticate the formation of the product from an unusual oxidative fusion of aromatic monoamines. The X-ray structure of **1c** (substituent R on the aromatic ring = Cl) revealed a *cis* geometry with respect to two coordinated chlorides. The bond length trends within the chelate as well as the aromatic rings are consistent with a diimine oxidation state of the ligand bound to ruthenium in its bivalent oxidation state. These complexes showed multiple transitions in the near-IR and visible regions. The highly intense transition at around 540 nm has been assigned to a transition involving two heavily mixed metal–ligand orbitals. The ruthenium(III)/ruthenium(II) couple for the dihalo complexes appeared at a high anodic potential (range 0.50 to 0.90 V), which for differently substituted compounds depend on the Hammett $\sum\sigma_p$ parameters of the substitution on the diim ligand. The syntheses and characterization of a few heteroleptic tris-chelates, [Ru(bpy)(diim)L](ClO$_4$)$_2$·nH$_2$O (L = a bidentate N,N-donor), involving the reaction of **1** with two moles of the silver reagent, [AgL$_2$](ClO$_4$), are reported. The tris-chelates showed intense charge transfer in their electronic spectra and multiple cathodic voltammetric responses, which have been assigned as reductions of coordinated ligands.

Introduction

In recent years, there has been considerable interest[1–6] in the metal complexes of redox non-innocent dioxolene ligand series together with their nitrogen analogues particularly because of their exceptionally rich redox and spectroscopic properties. These complexes feature multiple step redox processes due to changes of oxidation state of both the metal and the ligand themselves. Such metal complexes, in principle, may serve[7] as catalysts in catalytic redox reactions where both the ligands and metals are used as electron reservoirs.

Since the first report[8] of a ruthenium bqdi (bqdi = 1,2-benzoquinone diimine) complex by Warren in 1971, there has been widespread general interest in the ruthenium complexes of 1,2-diimines and their redox partners. Over the past decade quite a large volume of data has been accumulated on the electrochemistry, spectroscopy and electronic structure of ruthenium–diimine systems. However, the previous studies[5] on metal quinone diimines have largely been confined to complexes that are derived from 1,2-diaminobenzene. One major interest in these complexes is the ambiguity in charge distribution, which is shown to be sensitive to the nature of the counter ligands. The oxidation state assignment of such highly delocalized systems can best be assessed[9] by the examination of bond lengths of the coordinated diimine ligands. We note, however, that structurally characterized metal diimines are still scanty[10] in the literature. In this respect, the synthesis and structural characterization of new ruthenium diimine complexes are important.

Herein we wish to report the synthesis and characterization of some new mixed ligand ruthenium-1,2-diimine complexes. A few dichloro complexes of general formula [RuCl$_2$(bpy)(diim)], (diim = *N*-aryl-1,2-benzoquinone diimine) have been synthesized following[6] ruthenium catalyzed oxidative C–N fusion of aromatic monoamines.



(1)

Importantly, the above organic transformation does not occur otherwise in the absence of metal complex mediator. The heteroleptic dichlororuthenium complex thus formed serves as an excellent intermediate for the synthesis of mixed tris-chelates.

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† Electronic supplementary information (ESI) available: partial energy level diagram and molecular orbitals of **1c**. See http://www.rsc.org/suppdata/nj/b2/b203956g/

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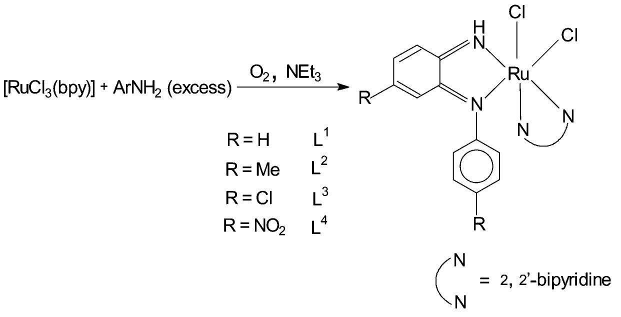
Chloride substitution reactions were achieved, under mild conditions, following the silver assisted *trans*-metallation synthetic strategy, which was developed[11] recently by us.

Results and discussions

Synthesis

The synthesis of [RuCl$_2$(bpy)(diim)] complex (**1**) consists of heating a mixture of [RuCl$_3$(bpy)] and a primary aromatic amine (ArNH$_2$) in large excess (neat) on a steam bath for half an hour. The initial brown coloured paste slowly turned to intense pink within the aforesaid period. Usual work up (Experimental) of the mixture followed by purification on a preparative TLC plate afforded the pink dichloro complex as the major product in *ca.* 50–60% yield. This was isolated as dark crystals, upon crystallization from a 1:1 dichloromethane–hexane solvent mixture. The formation of the diim ligand in this reaction occurs through *ortho*-dimerization of ArNH$_2$ *via* C–N fusion and dehydrogenation. It may be noted that synthesis of the diim ligand from aromatic monoamines otherwise was not achievable.[12] It is believed[6g] that *ortho* fusion of aromatic monoamines follows *cis* coordination of amine residues to the metal centre. The mediator complex holds two amine residues in proximity and also takes part in the redox processes. The organic transformation (eqn. (1)) is a 4e$^-$ oxidation reaction. In comparison, the metal ion undergoes only 1e$^-$ reduction, Ru^{III} + e$^-$ → Ru^{II}, and notably the yields of the products are moderately high, *ca.* 50–60%. The fact that reaction (2) does not proceed at all in the absence of air confirms the participation of aerial O$_2$ in this oxidation reaction. Furthermore, it has been observed that addition of an external base, *e.g.* NEt$_3$, augments the yield of [RuCl$_2$(bpy)(diim)]. Examples of metal catalyzed organic oxidation reactions using aerial O$_2$ are important but scanty in the literature.[6c,13] In order to make a comparison, we also have synthesized a related pink complex, [RuCl$_2$(bpy)(bqdi)] (bqdi = 1,2-benzoquinone diimine) from the reaction of [RuCl$_3$(bpy)] and 1,2-diaminobenzene (reaction (3)). In this reaction 1,2-diaminobenzene is oxidized[6b,14] to bqdi by aerial O$_2$.



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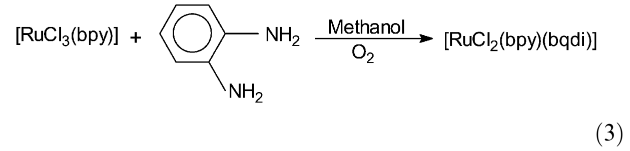

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The ruthenium complex **1** has two dissociable *cis* chlorides (*vide infra*) and hence it appeared to be suitable for the preparation of heteroleptic tris-chelates. We employed a silver assisted *trans*-metallation synthetic strategy (eqn. (4)) for the synthesis of two tris-chelates, *viz.* [Ru(bpy)$_2$(diim)]$^{2+}$ and [Ru(bpy)(diim)(pap)]$^{2+}$ (pap = 2-(phenylazo)pyridine). In this reaction the silver reagent [AgD$_2$]$^+$ acts as a source of Ag$^+$, used for halide abstraction, and also supplies the required quantity of L for chelation. The advantages of this synthesis[11] over the conventional synthesis by substitution reaction have been discussed previously by us. The yields of the tris-chelates are high, > 70%. The hetero ligand complex [Ru(bpy)(diim)(pap)]$^{2+}$ needs special mention since it represents a tris-chelate which contains three different ligands. Such complexes are of interest[15] in the context of tuning redox as well as photophysical properties of the ground and excited states.

$$[\mathrm{RuCl_2(bpy)(diim)}] + 2\,[\mathrm{AgD_2}]^+ \rightarrow [\mathrm{Ru(D)(bpy)(diim)}]^{2+} + 2\,\mathrm{AgCl} + 3\mathrm{D}$$

$$(\mathrm{D = N,N{-}donor})$$

(4)

Structure of [RuCl$_2$(bpy)(diim)] (1c)

The complex of chloro substituted diim, [RuCl$_2$(bpy)(diim)] (**1c**), formed suitable X-ray quality crystals. Fig. 1 shows its molecular structure along with the atomic numbering scheme used. Selected bond distances are listed in Table 1. The physical properties of the other three complexes, *viz.* **1a**, **1b** and **1d**, are similar to those of **1c**, which confirm the structure of these are similar to **1c**.

In complex **1c**, the ruthenium centre is surrounded by a distorted octahedral coordination environment by two *cis* chloride ligands, the bidentate chelating 2,2′-bipyridine ligand and the diimine ligand, which is formed due to fusion of two arylamino residues with the formation of a new C(6)–N(2) bond. The chelate bite angles of the diimine ligand, N(1)–Ru(1)–N(2) (78.49(13)°), and the bpy ligand, N(3)–Ru(1)–N(4) (78.28(13)°), are not distinguishable.

One major interest in the complexes of quinone related ligands is the ambiguity in charge distributions. Crystal structure analysis has now been found to be one of the most powerful tools for the assignment of charge distributions in the complexes. However, we note here that structurally characterized metal–diimine complexes are still only few.[10] In the present complex there are two types of C–N bonds; the C(1)–N(1) and C(6)–N(2) lengths (1.324(4) Å, 1.348(4) Å, respectively) are significantly shorter than the single C(7)–N(2), 1.427(4) Å. The former two C–N lengths fall in the expected range of coordinated imine C–N length. The diimine oxidation state of the ligand under consideration has been further confirmed by examination of the C–C lengths within the quinonoid ring. For example, the two C–C lengths C(2)–C(3) (1.343(5) Å) and C(4)–C(5) (1.353(4) Å) are considerably shorter than the

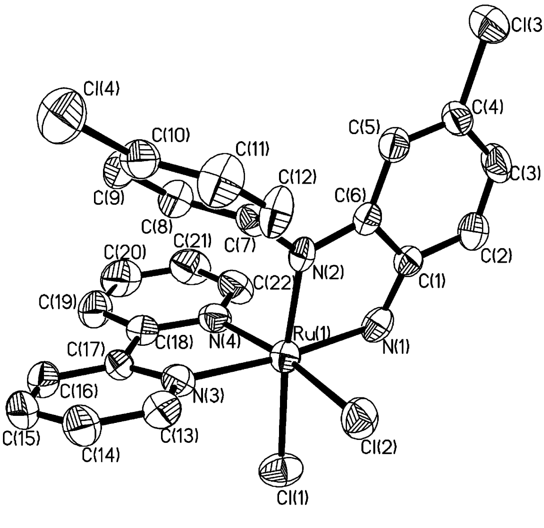

Fig. 1 Molecular structure of [RuCl$_2$(bpy)L^3], (**1c**) showing the atom numbering scheme. Hydrogen atoms are not shown for clarity.

Table 1 Selected bond parameters (distance in Å, angle in °) for $[RuCl_2(bpy)L^3]$, (**1c**)

Ru(1)–N(1)	1.965(3)	N(2)–C(7)	1.427(4)
Ru(1)–N(2)	1.991(3)	C(1)–C(2)	1.422(5)
Ru(1)–N(3)	2.082(3)	C(2)–C(3)	1.343(5)
Ru(1)–N(4)	2.047(3)	C(3)–C(4)	1.417(5)
Ru(1)–Cl(1)	2.3971(12)	C(4)–C(5)	1.353(4)
Ru(1)–Cl(2)	2.3914(10)	C(5)–C(6)	1.406(5)
N(1)–C(1)	1.324(4)	C(1)–C(6)	1.438(5)
N(2)–C(6)	1.348(4)		
N(1)–Ru(1)–N(2)	78.49(13)	N(1)–C(1)–C(6)	114.0(4)
N(3)–Ru(1)–N(4)	78.28(13)	N(2)–C(6)–C(1)	113.0(4)

remaining four C–C lengths in the same ring.[6] This pattern indicates a quinonoid ring and confirms the diimine oxidation state of the ligand. The increment of C–N length compared to –C=N– is attributed to extensive dπ–pπ backbonding in the complexes. The diim ligand is known to participate strongly in dπ–pπ interactions with Ru(II) ($4d^6$).[16] This has been reflected in the M–N and C–N (imine) bond distance data. For example, Ru–N(diim) lengths (average, 1.978(3) Å) are shorter than Ru–N(py) lengths (average, 2.065(3) Å).[17] Clearly, the diimine nitrogens bond Ru(II) more strongly than the pyridine nitrogens. As a result, the C–N(imine) lengths are also elongated. Reported Ru–Cl distances in chloro–Ru^{II} complexes lie[17] in the range 2.389–2.401 Å. The average Ru–Cl length in **1c** is comparable.

Spectral and redox properties

All the compounds gave satisfactory elemental analyses (Experimental). They are soluble in common organic solvents and are diamagnetic. While the solutions of tris-chelates are 1:2 electrolytic,[18] those of the dichloro complexes are non electrolytic. Selected spectral data are collected in Table 2. The N–H stretch[8] occurs as a sharp feature of moderate intensity in the range 3395 to 3420 cm^{-1}. The presence of N–H(imine) was further confirmed by the examination of ^1H NMR spectra of the complexes. Each one of the diim complexes showed a singlet resonance[2c,6] in the range 12.0 to 16.0 δ. The complex $[RuCl_2(bpy)(bqdi)]$ showed two N–H resonances[6a,6b] at 12.0 and 13.4 δ as expected. The aromatic regions of the NMR spectra of the compounds are complex in nature due to overlap of resonances of unique protons. We have not tried to assign them further.

In order to have some insight into the nature of redox and spectroscopically relevant orbitals, a standard extended Hückel MO calculation using the crystallographic parameters was performed on **1c** using the CACAO program by[19] Mealli and Proserpio. We wish to note here that due to obvious limitations, these results are qualitative in nature. A partial energy level diagram and the pictorial presentation of selected MOs are submitted as supporting information (ESI,† Fig. S1 and S2). In this complex, the LUMO and HOMO − 2 are the admixture of the orbitals of metal and diim ligand. In contrast, the HOMO and HOMO − 1 orbitals are almost pure metal d-orbitals with very little contributions of the ligand orbitals.

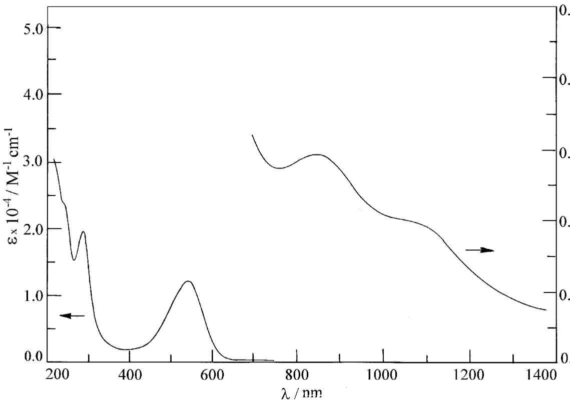

Fig. 2 Electronic spectrum of $[RuCl_2(bpy)L^3]$ (**1c**) in acetonitrile.

The electronic spectral data are collected in Table 2. A representative spectrum of the dichloro complexes is shown in Fig. 2. The two low NIR region transitions in the dichloro complexes may thus be assigned[6f] due to transitions from the non-bonding HOMO and HOMO − 1 to the LUMO. The highly intense transition near 540 nm is assigned to a transition between two heavily mixed metal–ligand orbitals, HOMO − 2 (donor) and LUMO (acceptor). The UV-VIS range electronic spectrum of $[RuCl_2(bpy)(bqdi)]$ **1e** is of similar type in respect of the number of bands and shape.

The general feature of the electronic spectrum of the trischelate, $[Ru(bpy)_2(diim)](ClO_4)_2$ (**2a**), is similar to that of reported[20] $[Ru(bpy)_2(bqdi)](ClO_4)_2$. The low energy part of this spectrum is dominated by a strong absorption at 530 nm. In the quinone oxidation state, the metal–ligand mixing in the donor as well as acceptor orbitals in the mixed ligand complexes, **2**, is expected to be significant. By analogy with the assignments of transitions in $[Ru(bpy)_2(bqdi)](ClO_4)_2$, we assign[20] the transition at 530 nm in **2** is due to $b_2 \rightarrow 2b_2^*$ (HOMO − 2 → LUMO). This transition in the heteroligand tris-chelate, **2b**, red shifts to 550 nm.

The redox behaviour of the complexes was studied in a dinitrogen atmosphere at 298 K using cyclic voltammetry in

Table 2 Spectral data

	IR[a] /cm^{-1}		^1H NMR[b] /ppm			
Compound	$\nu_{N–H}$	$\nu_{C=N}$	δ_{Me}	$\delta_{N=H}$	$\delta_{Aromatic}$	Electronic[c], λ_{max}/nm (ε/M^{-1} cm^{-1})
$[RuCl_2(bpy)L^1]$, (**1a**)	3405	1600	—	15.2	5.4–9.8	1065 (90), 830 (140), 540 (11 690), 290 (19 560), 240[d] (16 950)
$[RuCl_2(bpy)L^2]$, (**1b**)	3400	1605	2.2, 2.1	15.1	5.3–9.4	1070 (125), 820 (205), 545 (13 420), 290 (21 450), 245[d] (23 830)
$[RuCl_2(bpy)L^3]$, (**1c**)	3400	1595	—	15.9	5.6–9.8	1085 (100), 850 (140), 540 (12 090), 290 (19 570), 240[d] (23 670)
$[RuCl_2(bpy)L^4]$, (**1d**)	3420	1595	—	12.7	5.8–9.4	1235 (155), 545 (10 240), 450[d] (7220), 290 (21 850), 247[d] (18 105)
$[RuCl_2(bpy)(bqdi)]$, (**1e**)[e]	3410	1630	—	12.0, 13.4	6.8–8.4	840 (210), 550 (8350), 450[d] (2570), 280 (7380), 235[d] (10 270)
$[Ru(bpy)_2L^3](ClO_4)_2$, (**2a**)	3395	1605	—	14.2	5.6–8.8	980 (90), 770 (170), 530 (19 740), 416[d] (7090), 280 (42 200), 245 (36 000)
$[Ru(bpy)(pap)L^3](ClO_4)_2$, (**2b**)[e]	3400	1605	—	12.4	5.6–8.8	860 (110), 705 (215), 550 (21 580), 460[d] (7810), 355[d] (14 220), 280 (31 740)

[a] In KBr. [b] Unless otherwise stated, the measurements were performed in $CDCl_3$. [c] In acetonitrile. [d] Shoulder. [e] ^1H NMR spectral measurements in CD_3CN.

Table 3 Cyclic voltammetric data[a]

	Anodic responses[b] $E_{\frac{1}{2}}$/V (ΔE_p/mV) E_{pa}/V	Cathodic responses[b] $E_{\frac{1}{2}}$/V (ΔE_p/mV) E_{pc}/V
1a	0.58 (70)	-0.92^d, -1.3^d, -2.4^e
1b	0.54 (80)	-0.87^d, -1.25^d, −1.7 (90), -2.0^e
1c	0.65 (80)	-0.82^d, -1.19^d, −1.8 $(100)^f$
1d	0.89 (80)	−0.36 (60), -0.85^d, -1.95^e
1e	1.01^c	−0.29 (80), −0.85 $(160)^f$, -1.40^d, −1.70 $(100)^f$
2a	1.42^c	−0.33 (90), −1.00 (70), −2.01 $(230)^f$
2b	1.67^c	−0.06 (70), −0.32 (70), −0.55 (90), −1.36 (80), −1.72 (80), −2.2 $(100)^f$

[a] Experiments were carried out in CH_3CN at 298 K using NEt_4ClO_4 as supporting electrolyte. The reported data correspond to a scan rate of 50 mV s^{-1}. [b] $E_{1/2} = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. [c] Irreversible, E_{pa}. [d] The potential corresponds to E_{pc}; reversal scan shows multiple peaks, having small current height, of unclear origin. [e] Irreversible, E_{pc}. [f] Quasi-reversible cathodic response; $i_{pc} > i_{pa}$.

acetonitrile (0.1 M NEt_4ClO_4) using either a platinum (for the potential range 1.5 to −1.0 V) or a glassy-carbon (for the potential range 0.0 to −2.5V) working electrode. The reported potentials are referenced to the saturated calomel electrode (SCE). Voltammetric data are collected in Table 3 and representative voltammograms are shown in Fig. 3.

The dichloro complexes, [$RuCl_2$(bpy)(diim)], displayed a reversible anodic response in the range 0.5 to 0.9 V, which occur at HOMO, a ruthenium(II) orbital. Interestingly, the potential of this response is sensitive to substitution on the diim ligand. The value progressively increases as the substituent R becomes more and more electron withdrawing. The plot of E°_{298} *versus* twice the Hammett substituent constant (σ)[21] is excellently linear (Fig. 3) with a reaction constant (ρ)[22] of 0.188 V. The observed potential, 0.89 V, for the $\mathbf{1d}^+/\mathbf{1d}$ couple is notable high—a value which is much higher than that reported for [$RuCl_2(bpy)_2$] and is close to the reported potential[23] for [$RuCl_2(pap)_2$]. It is now known[22] that pap is a better π-acceptor than bpy. Comparison of the above potentials confirms that the diim ligand is a far better π-acceptor than bpy. These complexes also showed multiple cathodic responses, which are attributed to the ligand reductions. The metal oxidation in the tris-chelates becomes difficult and as a result oxidative responses are shifted anodically. All the ligands of the tris-chelates under consideration are known to undergo multiple reductions and hence a very large number of cathodic responses were observed in the tris-chelates. Notably, all six possible reduction waves in the heterochelate [Ru(pap)(diim)(bpy)]$^{2+}$, **2b**, were observable. It is believed[22] that the first four cathodic responses in **2b** are due to reductions of pap and diim ligands.

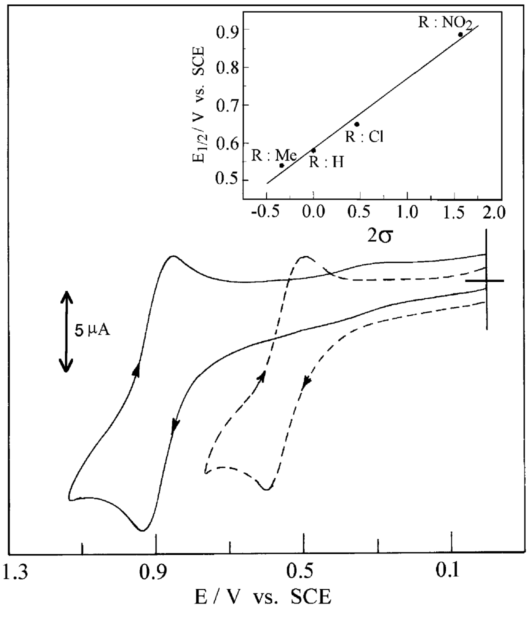

Fig. 3 Segmented cyclic voltammograms of [$RuCl_2(bpy)L^2$], (**1b**) (---) and [$RuCl_2(bpy)L^4$], (**1d**) (——) in acetonitrile solution (0.1 M NEt_4ClO_4) at a scan rate of 50 mV s^{-1}. Inset: A least square plot of $E_{\frac{1}{2}}$ values of the ruthenium(II)–ruthenium(III) couple *versus* 2σ.

Conclusions

The present work further demonstrates that ruthenium(III) metal ion can act as a mediator in bringing about oxidative *ortho*-dimerization of aromatic monoamines to *N*-aryl-1,2-diiminoarenes with the use of aerial oxygen as an oxidant. This organic transformation is otherwise not achievable in the absence of a mediator complex. It has been demonstrated earlier, that iron(III) mediates[6c] oxidation of aromatic monoamines to N-substituted phenazines. In the case of ruthenium(III) mediator, the reduced metal ion (ruthenium(II)) traps the diimine ligand because of strong dπ–pπ interactions by back bonding and the reaction stops at this stage. The resulting metal complexes are fully characterized, and are found to show interesting redox and spectral properties. The present metal promoted reaction has opened up the possibility of designing and synthesizing new metal diimines, which are now under active research.

Experimental

General details

The salt $RuCl_3 . nH_2O$ was obtained from Arora Matthey, Calcutta and was digested thrice with concentrated HCl before use. [$RuCl_3$(bpy)] was prepared from the digested $RuCl_3$ by a reported procedure.[24] Primary aromatic amines, *viz.* aniline, *p*-toluidine, *p*-chloroaniline and *p*-nitroaniline, were obtained from CDH, India. 1,2-Diaminobenzene was obtained from Sigma Chemical Company, USA. $AgNO_3$ and 2,2′-bipyridine were obtained from E-merk (India) Ltd. The silver complexes, [$Ag(bpy)_2$](ClO_4) and [$Ag(pap)_2$](ClO_4), were synthesized as before.[25,26] Solvents and chemicals used for syntheses were of analytical grade and were used as received. Supporting electrolyte (tetraethylammonium perchlorate, TEAP) and solvents for electrochemical work were prepared as described before.[27]

The IR spectra were obtained with a Perkin-Elmer 783 spectrometer, and the ^1H NMR spectra with a Bruker Avance DPX 300 spectrometer using $SiMe_4$ as an internal standard. UV-VIS-NIR spectral measurements were performed in acetonitrile solvent using a JASCO V570 spectrophotometer.

Table 4 Crystallographic data of $[RuCl_2(bpy)L_3]$, (**1c**)

Chemical formula	$C_{22}H_{16}Cl_4N_4Ru$
Formula weight	579.26
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.8575(17)
b/Å	10.3607(17)
c/Å	22.020(4)
β/°	96.544(3)
U/Å^3	2234.3(7)
Z	4
μ/mm^{-1}	1.198
Wavelength/Å	0.71073
GOF	0.978
Coll. reflect.	7791
Unique reflect.	2340
R_{int}	0.0206
R_1 $[I > 2\sigma(I)]$	0.0232
wR_2	0.0335

Electrochemical measurements were made using a PC-controlled EG&G/PAR-273A potentiostat. A conventional three-electrode configuration was used, consisting of platinum/glassy carbon wire working, platinum auxiliary and SCE reference electrodes. Tetraethylammonium perchlorate in excess was used as the supporting electrolyte. The ferrocene–ferrocenium couple was observed at 0.37 V ($\Delta E_p = 70$ mV) under our experimental conditions. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C,H,N).

Synthesis of complexes

[RuCl$_2$(bpy)L^1], (1a). A sample of $[RuCl_3(bpy)]$ (100 mg, 0.27 mmol) was mixed with aniline (1 ml) and the mixture was heated over a steam bath for *ca.* 30 min. Addition of few drops of NEt_3 at the beginning facilitated the reaction. The intense pink crude product was washed thrice with ether to remove excess aniline. The product was then purified on a preparative TLC plate. An intense pink band was eluted with a chloroform–acetonitrile mixture (2:1). On subsequent evaporation of solvent and crystallization from a dichloromethane–hexane mixture, a pure pink crystalline product was obtained. Yield: 55%. Found: C, 51.21; H, 3.72; N, 10.82%. Calc. for $C_{22}H_{18}N_4Cl_2Ru$: C, 51.76; H, 3.53; N, 10.98%.

The other three complexes **1b–1d** were synthesized similarly using the appropriate aromatic amines. Their yields and analytical data are as follows: **[RuCl$_2$(bpy)L^2], (1b).** Yield: 35%. Found: C, 53.03; H, 4.21; N, 10.11%. Calc. for $C_{24}H_{22}N_4Cl_2Ru$: C, 53.53; H, 4.09; N, 10.41%. **[RuCl$_2$(bpy)L^3], (1c).** Yield: 60%. Found: C, 45.52; H, 2.45; N, 9.06%. Calc. for $C_{22}H_{16}N_4Cl_4Ru$: C, 45.59; H, 2.76; N, 9.67%. **[RuCl$_2$(bpy)L^4], (1d).** Yield: 45%. Found: C, 43.61; H, 2.23; N, 13.87%. Calc. for $C_{22}H_{16}N_6O_4Cl_2Ru$: C, 44.00; H, 2.67; N, 14.00%.

[RuCl$_2$(bpy)(bqdi)], (1e). $[RuCl_3(bpy)]$ (100 mg, 0.27 mmol) and benzoquinonediimine (30 mg, 0.27 mmol) were taken in 1:1 ratio in methanol and the mixture was stirred for 2 h at room temperature. The colour of the solution became pink. The solvent was evaporated under vacuum and the pink product was purified on a preparative TLC plate using a chloroform–acetonitrile (1:1) mixture as eluent. Yield: 45%. Found: C, 44.02; H, 2.93; N, 12.11%. Calc. for $C_{16}H_{14}N_4Cl_2Ru$: C, 44.24; H, 3.22; N, 12.90%.

[Ru(bpy)$_2$L^3](ClO$_4$)$_2$, (2a). $[RuCl_2(bpy)L^3]$ (100 mg, 0.17 mmol) and $[Ag(bpy)_2](ClO_4)$ (0.177 mg, 0.34 mmol) were taken in methanol and the mixture was refluxed on a steam bath for 2 h. The solution was then cooled and filtered through a Whatman 41 filter paper to remove precipitated AgCl. The filtrate was then evaporated to dryness. The reddish pink product was purified on a preparative TLC plate using a chloroform–acetonitrile mixture (1:2) as eluent. Yield: 70%. Found: C, 44.76; H, 3.26; N, 9.86%. Calc. for $C_{32}H_{24}N_6O_8Cl_4Ru$: C, 44.49; H, 2.78; N, 9.73%.

[Ru(bpy)(pap)L^3][ClO$_4$]$_2$, (2b). This pink-violet compound was synthesized following the same procedure as described above. In this case $[Ag(pap)_2](ClO_4)$, instead of $[Ag(bpy)_2]$-(ClO_4), was used as the reagent. Yield: 75%. Found: C, 43.60; H, 2.97; N, 10.79%. Calc. for $C_{33}H_{25}N_7O_8Cl_4Ru$: C, 44.50; H, 2.81; N, 11.01%.

Crystallography

An X-ray quality crystal ($0.32 \times 0.13 \times 0.12$ mm^3) of compound **1c** was obtained by slow diffusion of hexane into a dichloromethane solution of the compound. Relevant crystallographic data are collected in Table 4. Intensity data were measured on a Bruker SMART diffractometer equipped with graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å. Data were corrected for Lorentz-polarization effects. A total of 7791 reflections were collected out of which 2340 were unique satisfying the $I > 2\sigma(I)$ criterion and were used in subsequent analysis. The structure was solved by employing SHELXS-97 and refined by using the SHELXL-97 program package.[28] All hydrogen atoms of the ligands were located in calculated positions.

CCDC reference number 178075. See http://www.rsc.org/suppdata/nj/b2/b203956g/ for crystallographic files in CIF or other electronic format.

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