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Structure, photophysics, electrochemistry and DFT calculations of [RuH(CO)(PPh₃)₂(coumarinyl-azo-imidazole)]

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1. Introduction

The coordination complexes of ruthenium with diimine (-N=C-C=N-) ligands like 2,2'-bipyridine,1,10-phenanthroline etc. have been the source of much investigation for a long time [1-4]. The enormous interest in this field originates from the rich redox chemistry [5,6] and excellent photophysical and photochemical activities [7–12]. To further the exploration of newer chemistry of ruthenium compounds, the modification of the diimine function is an interesting method. The replacement of one of the carbons (Cs) in the diimine group by N may design an azoimine -N=N-C=N- group, which can been used to stabilize low valent metal oxidation states [13–17]. This functional group has been incorporated in different aromatic and heterocyclic backbones to monitor the electronic properties of the functional group and the molecule so formed. To implement this idea, the -N=N-C=N- group has been implanted into a coumarine backbone for the synthesis of a photoactive coumarinyl-azoimine motif. Coumarine, a phytochemical, has served as a fluorophore in different molecular platforms for the synthesis of photosensitive materials [18-26], a commercially significant group of organic fluorescent and pharmaceutically important molecules [27-30]. Ruthenium(II)-CO compounds display luminescent behavior, are sufficiently photo stable [31-34] and important catalysts [35]. This has aroused our interest in the synthesis,

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ABSTRACT

2-(Coumarinyl-6-azo)-4-R-imidazole (4-R-LH, 1) and 4-(coumarinyl-6-azo)-5-R-imidazole (5-R-LH, 2) (R = H, Me, Ph) are two classes of -N=N-C=N- ligands used to synthesize [RuH(CO)(PPh₃)₂(4-R-L)] (3) and [RuH(CO)(PPh₃)₂(5-R-LH)Cl] (4). The characterization of the complexes has been done by elemental analysis and spectroscopic methods, and X-ray characterization is reported for one representative complex. The redox properties of the complexes were studied by cyclic voltammetry. They are emissive at room temperature. DFT and time dependent-DFT calculations were performed to explain the electronic structure, spectral and redox properties of the complexes.

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spectral characterization and photophysical studies of azo functionalized coumarine complexes of the ruthenium-hydrido carbonyl system.

2. Experimental

2.1. Materials

Coumarine, methyl iodide and imidazole were available from Sisco Research Lab, Mumbai, India. 4-Phenyl imidazole and 4-methyl imidazole were Sigma–Aldrich reagents. [RuH(CO)Cl-(PPh₃)₃] was prepared by a reported method [36]. 2-(Coumarinyl-6-azo)imidazole and its imidazole substituted derivatives (**1**) were also prepared by a reported method [37]. The purification of dichloromethane and preparation of *n*-tetra-butylammonium perchlorate [*n*Bu₄N][ClO₄] for electrochemical work were done as described previously [38]. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were of reagent grade and were used without further purification. Commercially available SRL silica gel (60–120 mesh) was used for column chromatography.

2.2. Physical measurements

Microanalytical data (C, H, N) were collected on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra, Perkin





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Elmer; model Lambda 25; FTIR spectra (KBr disk, 4000–450 cm⁻¹), Perkin Elmer; model RX-1; ¹H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer. Molar conductance was measured using a Systronics conductivity meter 304 model using ca. 10⁻³ M solutions in acetonitrile. Electrochemical measurements were performed using a computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to the Ag/AgCl electrode in acetonitrile using $[nBu_{4-}]$ $N[ClO_4]$ as the supporting electrolyte. The reported potentials are uncorrected for junction potential. The emission was examined by an LS 55 Perkin Elmer spectrofluorimeter at room temperature (298 K) in acetonitrile solution under degassed conditions. The fluorescence quantum yield of the complexes was determined using Rhodamine 6G as a reference with a known $\phi_{\rm R}$ value of 0.94 [39]. The complex and the reference dve were excited at the same wavelength, maintaining nearly equal absorbance (~ 0.1). and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated according to the following equation:

$$\phi_{\rm S}/\phi_{\rm R} = [A_{\rm S}/A_{\rm R}] \times \left[({\rm Abs})_{\rm R}/({\rm Abs})_{\rm S} \right] \times \left[\eta_{\rm S}^2/\eta_{\rm R}^2 \right]$$

Here ϕ_S and ϕ_R are the fluorescence quantum yield of the sample and reference, respectively, A_S and A_R are the area under the fluorescence spectra of the sample and the reference respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of the refractive index for the respective solvent used for the sample and reference.

2.3. Preparation of compounds

2.3.1. 2-(Coumarinyl-6-azo)-4-phenyl-imidazole, 4-Ph-LH (1c)

The coumarinyl-6-diazonium ion was prepared by adding a NaNO₂ (0.429 g, 6.21 mmol) solution into a 1 N HCl (50 cm³) solution of 6-aminocoumarine (1 gm, 6.21 mmol) at 0–5 °C ice cold conditions. The yellow solution of the coumarinyl-6-diazonium ion was filtered and the filtrate was used for the coupling reaction. To an aqueous solution of 4-phenyl imidazole (0.801 gm, 6.21 mmol) and Na₂CO₃ (2.65 g, 0.025 mmol) at 0–5 °C, the coumarinyl-6-diazonium ion was added in drops with continuous stirring. The orange compound was precipitated, filtered, washed with cold water and extracted with 2 N HCl (50 cm³). The solution was then neutralized with Na₂CO₃ solution, regulating the pH at 7.0. The precipitate of H-2-Cai-4-Ph was filtered, washed and dried. Yield, 1.58 g (81%).

The other coumarine azo compounds 2-(coumarinyl-6azo)imidazole, (4-H-LH) (**1a**) and 2-(coumarinyl-6-azo)-4-methyl imidazole (4-Me-LH) (**1b**) were prepared by identical procedures, in 75–82% yield, using imidazole and 4-methyl imidazole, respectively. The characterization data are reported elsewhere [37].

2.3.2. 4-(Coumarinyl-6-azo)-5-(phenyl)imidazole, 5-Ph-LH (2c)

Following an identical procedure to that for the synthesis of **1c**, a yellow solution of the coumarinyl-6-diazonium ion was coupled with an aqueous solution of 5-phenyl imidazole in sodium carbonate solution, maintained at pH 7 with continuous stirring. The orange compound was precipitated, filtered, washed with cold water and extracted with 2 N HCl (50 cm³). The solution was then neutralized with Na₂CO₃. The precipitate of H-4-Cai-5-Ph was filtered, washed and dried. The isolated yield was 75%.

The other coumarine azo compounds 4-(coumarinyl-6-azo)imidazole,(5-H-LH) (**2a**) and 4-(coumarinyl-6-azo)-5-(methyl)imidazole (5-Me-LH) (**2b**) were prepared by identical

procedures, in 70–80% yield, using imidazole and 4-methyl imidazole, respectively.

Anal. Calc. for 5-H-LH (**2a**), C₁₂H₈N₂O₄: C, 60.00; H, 3.33; N, 23.33. Found: C, 59.95; H, 3.29: N, 23.37%.

Spectral data of **2a**: FAB-MS, m/z: 241, $(M+H)^+$; IR (KBr, cm⁻¹): v_{COO} , 1731; $v_{N=N}$, 1439; $v_{C=N}$, 1566.

Anal. Calc. for 5-Me-LH (**2b**), C₁₃H₁₀N₂O₄: C, 61.42; H, 3.94; N, 22.05. Found: C, 61.44; H, 3.92: N, 22.08%.

Spectral data of **2b**: FAB-MS, m/z: 255, $(M+H)^+$; IR (KBr, cm⁻¹): v_{COO} , 1721; $v_{N=N_*}$ 1438; $v_{C=N_*}$ 1568.

Anal. Calc. for 5-Ph-LH (**2c**), C₁₈H₁₂N₂O₄: C, 68.35; H, 3.80; N, 17.72%. Found: C, 68.39; H, 3.76; N, 17.73%.

Spectral data of **2c**: FAB-MS, m/z: 317, $(M+H)^+$; IR (KBr, cm⁻¹): v_{COO} , 1722; $v_{N=N}$, 1438; $v_{C=N}$, 1569.

2.3.3. Synthesis of [RuH(CO)(PPh₃)₂(4-Ph-L)] (3c)

2-(Coumarinyl-6-azo)-4-(phenyl)imidazole (4-Ph-LH) (50 mg, 0.158 mmol) was dissolved in dry THF (10 ml) followed by addition of Et₃N, and the solution was stirred for 15 min under ambient condition in a nitrogen atmosphere. To the solution [RuH(CO)Cl(PPh₃)₃] (149 mg, 0.158 mmol) in 10 ml THF was added in one portion under stirring conditions. The solution was stirred for another 5 h. The resulting solution turned red. It was kept at room temperature for 1 h and then evaporated under reduced pressure. The crude product was passed down a silica gel column. A red solution was eluted with acetonitrile:benzene (1:10 v/v). Removal of the solvent afforded the analytically pure product **3c** in a yield of 87.33 mg (55%).

Reaction of $[RuH(CO)Cl(PPh_3)_3]$ with 4-H-LH (**1a**) and 4-Me-LH (**1b**) under similar conditions yielded the complexes $[RuH(CO)(PPh_3)_2(4-H-L)]$ (**3a**) (48%) and $[RuH(CO)(PPh_3)_2(4-Me-L)]$ (**3b**) (54%), respectively.

Anal. Calc. for [RuH(CO)(PPh₃)₂(4-H-L)] (**3a**), RuC₄₉H₃₈N₄O₃: C, 65.84; H, 4.25; N, 6.27%. Found: C, 65.88; H, 4.22; N, 6.24%.

FAB-MS, m/z: 894 (M+H)⁺.

Anal. Calc. for $[RuH(CO)(PPh_3)_2(4-Me-L)]$ (**3b**), $RuC_{50}H_{40}N_3O_4$: C, 66.22; H, 4.52; N, 6.18. Found: C, 66.18; H, 4.40; N, 6.14%.

FAB-MS, *m*/*z*: 908 (M+H)⁺.

Microanalytical data are as follows: *Anal.* Calc. for $[RuH(CO)(PPh_3)_2(4-Ph-L)]$ (**3c**), $RuC_{55}H_{42}N_4O_3$: C, 68.10; H, 4.44; N, 5.78. Found: C, 68.14; H, 4.35; N, 5.74%.

FAB-MS, m/z: 969 (M+H)⁺.

2.3.4. Synthesis of [RuH(CO)(PPh₃)₂(5-Ph-LH)]Cl (4c)

A mixture of [RuH(CO)Cl(PPh₃)₃] (149 mg, 0.158 mmol) and the ligand **2c** (50 mg, 0.158 mmol) was stirred in acetonitrile (50 cm³) at 50 °C under a nitrogen atmosphere. After stirring for 7 h, the solution was kept at room temperature for half an hour. Then the resulting solution was evaporated to dryness under reduced pressure and passed down a silica gel column. Again a red solution was eluted with acetonitrile:benzene (1:2 v/v) mixture. The solid red product was recrystallised from a Dichloromethane-hexane mixture.

Reaction of $[RuH(CO)Cl(PPh_3)_3]$ with 5-H-LH (**2a**) and 5-Me-LH (**2b**) under similar conditions yielded the complexes $[RuH(CO)(PPh_3)_2(5-H-LH)]Cl$ (**4a**) and $[RuH(CO)(PPh_3)_2(5-Me-LH)]Cl$ (**4b**).

Anal. Calc. for [RuH(CO)(PPh₃)₂(5-H-LH)]Cl (**4a**), RuC₄₉H₃₉N₄O₃₋ Cl: C, 63.12; H, 3.97; N, 6.01. Found: C, 63.10; H, 3.99; N, 5.98%.

FAB-MS, m/z: 897 (M–Cl)⁺. Anal. Calc. for [RuH(CO)(PPh₃)₂(5-Me-LH)]Cl (**4b**), RuC₅₀H₄₁N₄₋

O₃Cl: C, 64.46; H, 4.12; N, 5.92. Found: C, 64.47; H, 4.09; N, 5.95%. FAB-MS, *m*/*z*: 911 (M−Cl)⁺.

Microanalytical data are as follows: *Anal.* Calc. for [RuH(CO)(PPh₃)₂(5-Ph-LH)]Cl (**4c**), RuC₅₅H₄₃N₄O₃Cl: C, 65.77; H, 4.09; N, 5.58. Found: C, 65.79; H, 4.07; N, 5.60%. FAB-MS, m/z: 968 (M–Cl)⁺.

The crystals were grown by slow diffusion of dichloromethane solution of **4c** $(0.30 \times 0.25 \times 0.24 \text{ mm})$ in hexane. The crystal parameters and refined data are listed in Table 1. The data were collected by a fine focus sealed tube at 293(2) K using a fine focus graphite monochromator Bruker Smart CCD Area Detector (Mo Ka radiation, (λ = 0.71073 Å)). Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range $3.08 \leq 2\theta \leq 50.56^{\circ}$. The *hkl* range was $-15 \leq h \leq 15$; $-16 \leq k \leq 16$; $-17 \leq l \leq 17$. Reflection data were recorded using the ω scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption corrections based on ψ -scans were applied. The quality of the data was found to be 48% above of 2σ level, but the crystal structure was solved unambiguously. Data reduction was carried out by the Bruker SAINT program. The structure was solved by direct methods using SHELXS-97 [40] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima (-0.518, 0.723 e/Å³) were evaluated using SHELXL-97 [41].

2.5. Computational details

All computations were performed using the GAUSSIANO3 (G03) [42] software package. The Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr non-local correlation functional [43] (B3LYP) was used throughout this computation. Elements, except Ru, were assigned to the 6-31G(d) basis set in the calculation. For Ru, the Los Alamos effective core potential plus double zeta (LanL2DZ) [44] basis set was employed. The geometric structures of the complexes in the ground state (S_0) were fully optimized at the B3LYP level. In all cases, vibrational frequencies were calculated and compared with experimental data to ensure that

Table 1

Summarized crystallographic data for $[RuH(CO)(PPh_3)_2(5-Ph-LH)]Cl$ (4c).

Empirical formula	$C_{55}H_{43}N_4O_3P_2CIRu$
Formula weight	1006.39
Crystal system	triclinic
Space group	ΡĪ
a (Å)	13.184(3)
b (Å)	13.721(3)
c (Å)	14.634(3)
α (°)	64.908(4)
β (°)	79.510(5)
γ (°)	76.679(5)
Size (mm ³)	$0.30 \times 0.25 \times 0.24$
V (Å ³)	2322.2(8)
λ (Å)	0.71073
D_{calc} (Mg m ⁻³)	1.439
Ζ	2
T (K)	293(2)
Absorption coefficient (mm ⁻¹)	0.514
Total reflection collected	22117
Unique reflections	8335
Refined parameters	599
hkl range	$-15 \leqslant h \leqslant 15; -16 \leqslant k \leqslant 16;$
	$-17 \leq l \leq 17$
θ Range (°)	1.54-25.28
Largest difference in peak and hole (e Å ⁻³)	0.723 and –0.518
$R^{a}[I > 2\sigma(I)]$	0.0612
wR ^b	0.0966
Goodness-of-fit (GOF) on F^{2c}	0.998

^a $R = \Sigma |F_0 - F_c| / \Sigma F_0.$

^b $wR = [\Sigma w(F_0^2 - F_c^2)/\Sigma w F_0^4]^{1/2}$ where $w = 1/[\sigma^2 (F_0^2) + (0.0290P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$.

^c GOF (Goodness-of-fit) is defined as $[w (F_0^2 - F_c^2)/(n_0 - n_p)]^{1/2}$ where n_0 and n_p denote the number of data and variables, respectively.

the optimized geometries represented local minima. To assign the low lying electronic transitions in the experimental spectra, TDDFT [45] calculations of the complexes were done.

3. Results and discussion

3.1. Coumarinyl-azo-imidazoles and ruthenium-carbonyl complexes

2-(Coumarinyl-6-azo)-4-R-imidazole (4-R-LH, 1) and 4-(coumarinyl-6-azo)-5-R-imidazole (5-R-LH, 2) (R = H(a), Me (b) and Ph (\mathbf{c}) (Scheme 1) were synthesized by coupling of the substituted imidazole with the coumarinyl-6-diazonium ion in neutral (pH 7) medium. In the abbreviation of 1 or 2, H refers to imidazole-N(1)-H and 4-R or 5-R represents H, Me or Ph substitution at the C-4 or C-5 position of the imidazolyl backbone. The N(1)-H of 1 or 2 may dissociate in basic medium to act as a monoanionic bidentate chelating ligand. These two ligands, 1 and 2, differ with reference to the appending –N=N-coumarinyl group at imidazolyl backbone; in 1 the -N=N-coumarinyl is coupled at C-2 and in 2 it is bonded to the C-4 position. Molecule 1, upon N(1)-H dissociation, may act as a bidentate monoanionic chelator, while 2 cannot serve in this manner. The reaction of [RuH(CO)Cl(PPh₃)₃] with **1** in the presence of Et₃N in tetrahydrofuran at room temperature has synthesized $[RuH(CO)(PPh_3)_2(4-R-L)]$ (3) (where $4-R-L^-$ is a monoanionic bidentate chelator). The complexes [RuH(CO)(PPh₃)₂(5-R-LH)]Cl (4) are prepared by the reaction of $[RuH(CO)Cl(PPh_3)_3]$ with 5-R-LH in acetonitrile medium at 50 °C, followed by chromatographic purification using a silica gel column. The structural difference between 3 and 4 has been inherited from the ligands 1 and 2 respectively. The complexes **3** are non-electrolytes and **4** are 1:1 electrolytes in nature in acetonitrile solution (Λ_{M} = 80–105 Ω^{-1} mol⁻¹ cm²). The elemental (C, H, N) analysis and spectroscopic data of the complexes are consistent with the general formula. The diamagnetic nature of the complexes confirms the +2 oxidation state and the low-spin character of the metal center in each complex. Two geometrical isomers are structurally feasible: I, CO trans oriented to N(azo) and II, CO cis to N(azo) (Scheme 1) [17,46]. The X-ray structural characterization of **4c** shows CO *trans* to N(azo). In view of the similar spectroscopic properties, **3a-3c** and 4a-4c are assumed to have a similar structure to isomer I.

3.2. Molecular structure

The single crystal X-ray diffraction study of **4c** was performed at 293 K and the molecular structure of the complex is shown in Fig. 1. The bond parameters are listed in Table 2. The azo N=N distance, 1.277(5) Å (Table 2), is longer than the free ligand distance reported for 1-methyl-2-(phenylazo)imidazole (1.261(2)Å) [47] which indicates electron acceptance of the azoimine group (-N=N-C=N-). The coordination geometry is based on an octahedron defined by a CN₂P₂H coordination set about the central Ru. 5-Ph-LH (2c) is an N(imidazole) and N(azo) chelator; the carbonyl-C and the hydride (H⁻) form a CN₂H square plane around the metal center, and the two PPh₃ molecules occupy two axial positions. The -N=N- group is bonded to the C-2 position of the imidazolyl moiety (N(3)-C(4), 1.375(7) Å). Two Ru-N bond distances are Ru(1)–N(1), 2.123(5) Å and Ru(1)–N(4), 2.144(4) Å; the difference in bond length may be due to the difference in the polarizability of the homocyclic (C=)N(imidazolyl)(N(1)) and exocyclic (-N=)N(4) (N(azo)) donor centers. The Ru-H and N-H bonds are fixed at 1.52 and 1.02 Å [46]. The maximum distortion from the ideal octahedral geometry is manifested in the acute N(1)-Ru(1)-N(4) chelate angle of 74.04(18)°. DFT computations have generated an optimized structure of 4c. The calculated structure is in agreement, in view of its metric parameters, with the experimental



4-R-LH (1); 5-R-LH (2) [RuH(CO)(PPh₃)₂(4-R-L)] (3) [RuH(CO)(PPh₃)₂(4-R-LH)] (4) R = H (a), Me (b), Ph (c)





structure (Table 2). Although we have not crystallized any of the complexes of **3**, we have, however, generated a DFT computed optimized structure of **3c** and the metric parameters are listed in Table 2. A 3D structure of **3c** is given in Fig. 2. Bond parameters in Table 2 are comparable with the structure of **4c**.

The non-covalent interactions, C/N–H··· π and π ··· π , exist to generate a 3D supramolecular structure. The lactone carbonyl (_>=O) forms an intermolecular H-bond with the phenyl proton of 5-Ph-Imz of a neighboring molecule $(C(7)-H(7)\cdots O(2)$: $H(7)\cdots O(2)$, 2.57 Å; $C(7) \cdots O(2)$, 3.493(9) Å; $\angle C(7) - H(7) \cdots O(2)$, 170.00°; symmetry, 2 - x, -y, 1 - z) and constitutes a cyclic dimer (Fig. 3). Two other hydrogen bonds enhance the strength of this interaction and these are $N(2)-H(2)\cdots Cl(1)$ (H(2)···Cl(1), 2.07(9)Å; $N(2)\cdots Cl(1)$, 3.013(6) Å and $\angle N(2)-H(2)\cdots Cl(1)$, 152(6)°; symmetry, 2 – *x*, 1 - y, 2 - z) and $C(6) - H(6) \cdots N(3)$ ($H(6) \cdots N(3)$, 2.57(2) Å; $N(3) \cdots C(6)$, 3.221(9) Å and $\angle C(6) - H(6) \cdots N(3)$, 128(3)°). The existence of C(28)-H(28)···Cg(6) (2.89 Å) and C(42)-H(42)···Cg(10) (2.96 Å) (where Cg(6): C(20)-C(21)-C(22)-C(23)-C(24)-C(25); symmetry, 2 – x, –y, 2 – z. Cg(10): C(44)–C(45)–C(46)–C(47)– C(48)–C(49); symmetry, 1 - x, 1 - y, 1 - z) generate a 1D chain (Fig. 4). The C–H (Ph) functions of PPh₃ are further connected by hydrogen bonding interactions to form a π continuum of a 3D supramolecular structure (Supplementary material, Fig. S1).

3.3. Spectroscopic characterization

Two important infrared spectral bands appear in the region 1920–1935 and 1725–1730 cm⁻¹ (Table 3) and these are ascribed to coordinated v(CO) and v(COO) lactone, respectively [37]. Free CO

is known to appear at 2143 cm⁻¹ [48]. The shifting of v(CO) to lower frequency supports a $d\pi(Ru) \rightarrow \pi^*(CO)$ charge transition. The moderately intense peaks at 1430–1440 and 1565–1575 cm⁻¹, respectively are assigned to the -N=N- and -C=N- stretches of the present series of ligands [49]. The v(N=N) and v(C=N) frequencies in these ligands have been shifted to a higher frequency compared to 1-alkyl-2-(arylazo)imidazoles [49], which may be due to the strong electron withdrawing effect of the lactone ring present in the coumarinyl group. All the complexes display a weak band near the 2110 cm⁻¹ region, which is attributed to v(Ru-H) [47]. The molecular ion peak (M+H)⁺ (in the case of **3**) or (M–Cl)⁺ peak (in the case of **4**) obtained from FAB mass spectra also supports the formation of the complexes.

Solution spectral studies of the complexes have been performed in acetonitrile solution. The UV-Vis spectra are depicted in Fig. 5. The complexes exhibit an intense ligand-localized π - π * transition in the UV region (260-275 nm), accompanied by a moderately intense band at longer wavelength (335–350 nm), which is an $n-\pi^*$ (LC) transition. This is in agreement with free ligand spectra. Two more bands are observed in the visible region, 400-510 nm, and those can plausibly be attributed, by analogy to similar Ru(II) azoimine carbonyl complexes that have been reported in the literature [17,46], to an MLCT transition mixed in part, with XLCT/ILCT (X refers to PPh₃) transition(s). Further support of this assignment will be elaborated in the Theoretical Approaches section (vide infra). In general, the differentiation of XLCT and MLCT can be attributed to a certain extent of mixing between the metal $d\pi$ and phosphorus (PPh₃) $d\pi/p\pi$ orbitals, which results in an increase of the phosphorus character in the HOMO of the metal complexes. Data in



Fig. 1. Single crystal X-ray structure of [RuH(CO)(PPh₃)₂(5-Ph-LH)]Cl (4c).

Fable 2
Selected experimental and theoretical bond parameters of [RuH(CO)(PPh ₃) ₂ (5-Ph-LH)]Cl (4c) and theoretical bond parameters of [RuH(CO)(PPh ₃) ₂ (4-Ph-L)] (3c).

Bond distances (Å)	Experimental	Calculated	Bond angle (°)	Experimental	Calculated
[RuH(CO)(PPh ₃) ₂ (5-Ph-LH)]Cl (4c	:)				
Ru(1)-C(1)	1.873(6)	1.860	C(1)-Ru(1)-N(1)	101.1(2)	102.57
Ru(1)-N(1)	2.123(5)	2.170	C(1)-Ru(1)-N(4)	174.7(2)	177.41
Ru(1)-N(4)	2.144(4)	2.193	N(1)-Ru(1)-N(4)	74.04(18)	74.868
Ru(1) - P(1)	2.3519(16)	2.493	C(1)-Ru(1)-P(1)	88.37(16)	88.556
Ru(1)–P(2)	2.3546(16)	2.497	N(1)-Ru(1)-P(1)	96.29(12)	93.913
Ru(1)–H(1)	1.52(3)	1.610	N(4)-Ru(1)-P(2)	89.69(12)	90.706
O(3)-C(1)	1.120(5)	1.187	P(1)-Ru(1)-P(2)	168.89(6)	172.66
N(3)-N(4)	1.277(5)	1.312			
N(1)-C(2)	1.386(6)	1.409			
N(3)-C(2)	1.362(6)	1.433			
N(4)-C(11)	1.446(6)	1.433			
	Calculated		Bond angle (°)		Calculated
$[RuH(CO)(PPh_3)_2(4-Ph-L)]$ (3c)					
Ru(1)-C(1)	1.864		C(1)-Ru(1)-N(1)		179.40
Ru(1)-N(1)	2.103		C(1)-Ru(1)-N(4)		106.08
Ru(1)-N(4)	2.269		N(1)-Ru(1)-N(4)		74.25
Ru(1) - P(1)	2.485		C(1)-Ru(1)-P(1)		89.58
Ru(1)–P(2)	2.492		N(1)-Ru(1)-P(1)		89.90
Ru(1)–H(1)	1.609		N(4)-Ru(1)-P(2)		95.82
O(3)-C(1)	1.193		P(1)-Ru(1)-P(2)		170.17
N(3)-N(4)	1.321				
N(1)-C(2)	1.402				
N(3)-C(2)	1.358				
N(4)-C(11)	1.433				

Table 3 reveal that in the case of **3c** ([RuH(CO)(PPh₃)₂(4-Ph-L)]) and **4c** ([RuH(CO)(PPh₃)₂(5-Ph-LH)]Cl) the MLCT band is shifted to a longer wavelength and an enhancement of the extinction coefficient has been observed with respect to other complexes. This is likely to be the result of additional π -delocalization provided by the ancillary phenyl substitution on imidazole.

The complexes exhibit a significant fluorescence emission at 570–618 nm (Table 3) at room temperature (Fig. 5) for spectra recorded in deoxygenated acetonitrile solution. In each complex, the entire emission band, originating from a common ground-state species, is ascertained by the same emission excitation spectra throughout the monitored wavelength of 462–510 nm. Furthermore, the excitation spectra, within experimental error, are also effectively identical to the absorption spectrum, which indicates

that the entire emission results from a common Franck–Condon excited state. In all cases, both a large Stokes shift and a structureless peak profile are suggestive of an emission originating from the triplet manifold, possibly possessing the aforementioned MLCT/ XLCT character, which is populated from rapid ISC as a result of spin–orbit coupling. The emission maxima of **3** are red-shifted compared to **4**, demonstrating the influence of the position of the azo bond on photophysical properties. The emission quantum efficiencies of the complexes lie within the range $(1.6–3.0) \times 10^{-4}$ in acetonitrile.

The ¹H NMR spectra of the complexes are recorded in CDCl₃. The proton-numbering pattern is depicted in Scheme 1 and the NMR data of the complexes are listed in Table 4. In each complex a distinct triplet is observed at a δ value of -10.25 to



Fig. 2. Calculated optimized structure of [RuH(CO)(PPh₃)₂(4-Ph-L)] (3c).

-10.75 ppm due to coupling with two *trans* phosphorous nuclei $({}^{2}J_{P-H} = 19-22 \text{ Hz})$. Imidazole protons 5-H for **3** and 2-H for **4** appear as a singlet at 7.45–7.70 ppm. The resonances of phenyl protons of PPh₃ are observed in the 7.05–7.50 ppm region. However, the proton signals for PPh₃ of **3c** and **4c** merge with the resonances of the phenyl protons at the C-4 position. The complexes **4** exhibit a singlet due to the N–H resonance at a δ value of 14.43–15.52 ppm, which is absent in the case of complexes **3**.

3.4. Electrochemistry

The electrochemical properties of the complexes were investigated by cyclic voltammetry in acetonitrile solution at a scan rate of 50 mV S⁻¹ using 0.1 M [n-Bu₄N][ClO₄] as the supporting electrolyte. Data were collected under a nitrogen environment. The potentials are expressed with reference to Ag/AgCl. The results are collected in Table 5. The voltammogram of a representative complex is shown in Fig. 6. The nature of the voltammogram does



Fig. 4. Each discrete unit connected by $C(28)-H(28)\cdots Cg(6)$ and $C(42)-H(42)\cdots Cg(10)$ hydrogen bonding interactions to form a 1D supramolecular chain in **4c**.



Fig. 3. Two neighboring units connected by $C(6)-H(6)\cdots N(3)$, $C(7)-H(7)\cdots O(2)$ hydrogen bonding interactions and also the chloride ions connected to the moiety through $N(2)-H(2)\cdots Cl(1)$ hydrogen bonding interactions in **4c**.

Table 3	
FT IR ^a LIV–Vis ^b and fluorescence ^b spectral of	lata

Comp.	p. IR frequency, $(cm^{-1})^a$					Absorption ^b λ_{max} (nm) (10 ⁻³ ϵ/M^{-1} cm ⁻¹) ^b	$\lambda_{ex}\left(nm ight)$	$\lambda_{em}\left(nm\right)$	Quantum yield ^b (ϕ) $ imes$ 10 ⁴
	vco	VCOO (lactone)	v _{Ru-H}	$v_{N=N}$	$v_{C=N}$				
3a	1925	1728	2101	1430	1925	274 (19.304), 346 (4.33), 374 (7.932), 462 (8.865)	462	580	1.6
3b	1924	1729	2103	1431	1924	270 (20.512), 305 (8.765), 335 (5.58), 447 (7.800)	447	600	1.8
3c	1923	1728	2102	1433	1923	266 (30.725), 355 (8.399), 491 (14.857)	491	618	2.3
4 a	1933	1729	2116	1437	1933	272 (21.876), 345 (4.48), 402 (5.231), 488 (7.890)	488	570	2.4
4b	1931	1729	2115	1436	1931	265 (22.897), 318 (4.578), 400 (5.768), 506 (8.876)	506	596	2.6
4c	1930	1730	2117	1434	1930	265 (28.624), 340 (5.42), 390 (6.302), 510 (11.793)	510	600	3.0

^a In solid KBr discs.

^b In acetonitrile; λ_{ex} = excitation wavelength, λ_{em} = emission wavelength.





Fig. 6. Cyclic voltammogram of [RuH(CO)(PPh₃)₂(4-H-L)] (3a) in acetonitrile.

Fig. 5. UV–Vis spectra of $[RuH(CO)(PPh_3)_2(4\text{-Ph-L})]$ (3c) (–) and $[RuH(CO)(PPh_3)_2(5\text{-Ph-LH})]Cl$ (4c) (–); and fluorescence spectra of 3c (– – –) and **4c** (- - -).

Table 4	
¹ H NMR data [§]	of 2-4 in CDCl ₃

Comp.	δ , ppm (J, Hz)									
	4 or 5-X	5 or 2-H ^d	7-H ^d	8-H ^c	9-H ^c	11-H ^c	12-H ^b	Ru-H ^{e,f}	PPh3 ^c	N-H ^a
2a	7.59 ^a	7.76	8.21	6.49	6.52	8.04	8.22 (7.5)	h	h	13.25
2b	2.54	7.74	8.20	6.46	6.52	8.06	8.21 (7.6)	h	h	13.19
2c	7.35-7.56	7.78	8.24	6.48	6.51	8.07	8.23 (7.5)	h	h	13.28
3a	7.65 ^a	7.59	7.72	6.37	6.39	7.43	7.85 (9.0)	-10.50 (21.0)	7.04-7.28	h
3b	2.05 ^d [4-Me]	7.54	7.81	6.38	6.41	7.68	8.09 (7.5)	-10.67(20.0)	7.11-7.47	h
3c	7.36-7.56 ^c [4-Ph]	7.70	7.99	6.48	6.51	7.67	8.14 (8.0)	-10.27 (21.0)	7.16-7.34	h
4a	7.57 ^a	7.46	7.88	6.35	6.91	7.1	8.00 (9.0)	-10.50 (21.0)	7.10-7.42	14.97
4b	2.07 ^d [5-Me]	7.45	7.93	6.37	6.93	7.72	8.07 (7.9)	-10.67 (22.0)	7.15-7.40	14.43
4c	7.16-7.36 [5-Ph]	7.51	7.96	6.42	6.98	7.71	8.13 (7.0)	-10.74 (19.0)	7.16-7.36	15.82

^a broad singlet; ^b doublet; ^c multiplet; ^d singlet; ^e triplet; ^{f2}J refers to ³¹P-¹H coupling; ^h not applicable. [4-H or 5-H] etc. refer to the signal of the protons in the imidazolyl group. § The ¹H NMR data of **1** are given in Ref [37].

Table 5 Cyclic voltammetric data.^a

Complexes	Cyclic voltammetric data	a		
	Ligand reduction, E (V), ($\Delta E_{\rm p,} {\rm mV})$	Metal oxidation, E (V), ($\Delta E_{\rm p,} \rm mV)$
3a	-1.02 (120)	-1.41 (80)	1.02 (130)	1.44 (70)
3b	-1.00 (115)	-1.35 (90)	1.01 (120)	1.40 (85)
Bc	-1.04 (110)	-1.46 (95)	0.98 (110)	1.35 (90)
l a	-1.12 (110)	-1.50 (100)	1.15 (90)	1.53 (80)
4b	-1.07 (95)	-1.46 (90)	1.10 (85)	1.50 (100)
4c	-1.10 (100)	-1.49 (85)	1.07 (80)	1.48 (95)

^a Solvent dry CH₃CN; Pt-working electrode, Ag/AgCl reference, Pt-auxiliary electrode; [n-Bu₄N](ClO₄) supporting electrolyte, scan rate 50 mV/s; metal oxidation E = 0.5 $(E_{pa} + E_{pc})$, V, $\Delta E_p = |E_{pa} - E_{pc}|$, mV; where E_{pa} is the anodic-peak-potential and E_{pc} is the cathodic-peak-potential.

not change with scan rate (50–200 mV S⁻¹). The cyclic voltammograms of the complexes display two oxidative responses in the potential range 0.98–1.10 and 1.40–1.55 V for the Ru(III)/Ru(II) and Ru(IV)/Ru(III) redox couples respectively. The quasi-irreversible nature is evident from peak-to-peak difference (ΔE_p (E_{pa} – E_{pc}) > 80 mV). The redox assignment has been made on comparing with previously reported results of [RuH(CO)(PPh₃)₂(1-alkyl-2-(naphthyl- α/β -azo)imidazoles)] [17]. Upon scanning cathodically, two quasi-reversible reduction waves are observed in the potential range –1.01 to –1.10 V and –1.40 to –1.50 V for **3** and **4** respectively. It may be regarded as reduction of the coumarinyl-azoimidazole, and the electron is accommodated in the * MO of the chelated azoimine function.

3.5. DFT and TDDFT calculation

DFT calculations were carried out to explain the electronic structures of complexes **3c** and **4c**. The GAUSSIAN 03 program was



Fig. 7. Energy correlation diagram of $[RuH(CO)(PPh_3)_2(4-Ph-L)]$ (**3c**) and $[RuH(CO)(PPh_3)_2(5-Ph-LH)]CI$ (**4c**).

used for this study. The singlet state geometry of all the complexes in the ground state was optimized. The optimized structural data of the two representative complexes are given in Table 2.

The energies and compositions of the complexes are given in the Supplementary material (Table S1, Figs. S2 and S3). An energy correlation diagram between the two types of complexes is shown in Fig. 7. The increase in energy of the MOs in **3c** is in agreement with the higher electron donation of 1c⁻ compare to neutral 2c in the complex 4c. For the complex 3c, the highest occupied molecular orbital (HOMO) is composed of 10-15% Ru and 80-85% coumarinyl-azoimidazole functions. The HOMO of 4c is contributed of metal (\sim 55%) as well as PPh₃ (20–35%) functions. Surface plots of the two types of complexes are shown in *Supplementary* material (Fig. S3). The lowest unoccupied orbital (LUMO) is contributed entirely (~95%) from the coumarinyl-azoimidazole function, although PPh₃ plays the major role for constructing the higher energy unoccupied orbitals (LUMO+2, LUMO+3, LUMO+5 and others). The trend in the difference in energy between the HOMO and LUMO is similar in two types of complexes (3c, 4c).

The Time-Dependent-DFT (TD-DFT) calculations were performed on two representative complexes, **3c** and **4c**, to investigate in detail the characteristics of the electronic transitions (Table 6). The assignments of the calculated transitions to the experimental bands are based on the criteria of the energy and oscillator strength of the calculated transitions. For complex 3c the longest wavelength experimental band, with a maximum at 491 nm, is assigned to the transitions from the HOMO to LUMO orbitals and a mixture of intraligand (ILCT) and metal to ligand charge transfer (MLCT) transitions. The next band, with a maximum at 355 nm, and the band in the UV region are ascribed to multiple charge transfer transitions where ILCT transitions dominate. For complex **4c** the calculated band appears at a longer wavelength than the experimental band. The transition centered at 510 nm is an admixture of MLCT, XLCT (X = PPh₃) and ILCT transitions. The absorption bands in the high-energy spectral region show similar features and are due to multiple charge transfer transitions, being dominated by transitions of mainly ILCT character.

Table 6

Selected list of excitation energies for [RuH(CO)(PPh₃)₂(4-Ph-L)] (3c) and [RuH(CO)(PPh₃)₂(5-Ph-LH)]Cl (4c) obtained from TDDFT calculations in the gas phase.

Excited state	Wavelength (nm)	Oscillator strength	Transitions	Assignment		
[RuH(CO)(PPh ₃) ₂ (4-Ph-L)] (3c)						
1	499	0.3867	(60%) $H \rightarrow L$	ILCT + MLCT		
2	440	0.0145	(68%) $H \rightarrow L+1$	ILCT + MLCT		
4	413	0.0699	(64%) H $-1 \rightarrow L$	MLCT + ILCT + XLCT		
5	382	0.256	$(49\%) \text{ H}-3 \rightarrow \text{L} (24\%) \text{ H}-4 \rightarrow \text{L}$	MLCT + ILCT		
9	343	0.046	$(50\%) \text{ H}-4 \rightarrow \text{L} (36\%) \text{ H}-1 \rightarrow \text{L}+1$	MLCT + ILCT + XLCT		
12	332	0.0474	$(36\%) \text{ H}-1 \rightarrow \text{L+2} (29\%) \text{ H} \rightarrow \text{L+2}$	MXCT + LXCT + MMCT + LMCT		
15	326	0.0196	$(43\%) \text{ H}-2 \rightarrow \text{L+1} (18\%) \text{ H} \rightarrow \text{L+4}$	MLCT + ILCT + LXCT		
19	315	0.0242	$(37\%) \text{ H}-8 \rightarrow \text{L} (32\%) \text{ H}-2 \rightarrow \text{L}+1$	ILCT + XLCT + MLCT		
24	306	0.0217	$(32\%) \text{ H}-2 \rightarrow \text{L+2} (18\%) \text{ H}-1 \rightarrow \text{L+2}$	MXCT + LXCT + MMCT		
31	297	0.03	$(62\%) \text{ H}-4 \rightarrow \text{L+1}$	MLCT + ILCT		
36	291	0.0203	$(50\%) \text{ H}-5 \rightarrow \text{L+1}$	ILCT + XLCT		
37	288	0.0662	$(37\%) \text{ H} \rightarrow \text{L+10} (27\%) \text{ H} \rightarrow \text{L+11}$	ILCT + LXCT		
39	287	0.0721	$(39\%) H-7 \rightarrow L+1$	ILCT + MLCT		
40	285	0.0533	$(37\%) \text{ H}-8 \rightarrow \text{L+1} (27\%) \text{ H} \rightarrow \text{L+11}$	ILCT + XLCT + LXCT		
[RuH(CO)(PPh ₃) ₂ (H	I-4-Cai-5-Ph)]Cl (4c)					
2	597	0.1289	(60%) H-2 \rightarrow LUMO	MLCT + XLCT		
4	564	0.1559	(47%) H-2 \rightarrow LUMO (34%) H-1 \rightarrow LUMO	MLCT + XLCT + ILCT		
5	540	0.0201	(69%) HOMO \rightarrow L+1	MLCT + ILCT		
9	519	0.1211	(62%) $H-2 \rightarrow LUMO$	XLCT + ILCT		
13	495	0.0225	(52%) H $-10 \rightarrow LUMO$	XLCT		
20	440	0.0412	(30%) H $-14 \rightarrow$ LUMO (30%) H $-17 \rightarrow$ LUMO	XLCT + ILCT		
24	407	0.0573	(59%) HOMO \rightarrow L+2	ILCT + MLCT		
36	353	0.0330	(68%) HOMO \rightarrow L+7	ILCT + LXCT		
42	340	0.0418	$(28\%) \text{ H}-13 \rightarrow \text{L}+1$	XLCT		
45	337	0.0256	(37%) HOMO \rightarrow L+9 (15%) H–13 \rightarrow L+1 (16%) H–1 \rightarrow L+3	LXCT + MXCT		

M = metal, L = coumarinyl-azo ligand, X = PPh₃.

The redox properties of the complexes can be explained on the basis of DFT calculations. Oxidation involves electron abstraction from occupied MOs and reduction involves electron addition to unoccupied MOs. Since the HOMO of the complexes has a metal contribution, 10-55%, oxidation can be regarded as oxidation of the metal center, $Ru(II) \rightarrow Ru(III)$ and $Ru(III) \rightarrow Ru(IV)$. Again the observed trend in the oxidation potential for each type of comple $(E_{\text{ox}}: (3\mathbf{a}) > (3\mathbf{b}) > (3\mathbf{c}) \text{ and } (4\mathbf{a}) > (4\mathbf{b}) > (4\mathbf{c})) \text{ correlates well}$ with the energy of the HOMO (E_{HOMO} : (**3a**) < (**3b**) < (**3c**) and (4a) < (4b) < (4c)) (Table 6). Although the ligand orbitals also contribute significantly in the HOMO, the component does not have electrons to be extracted. On the other hand, the ligand contributes 95% to constitute the LUMO and thus the reduction may be referred as electron accommodation in the π^* orbitals of the azoimine group. The HOMO-LUMO energy gap (Fig. 7) has also been well correlated with the difference between the first oxidation (refers to the energy of the HOMO) and first reduction (refers to the energy of the LUMO) potentials.

4. Conclusion

Ruthenium complexes containing two types of coumarinylazoimidazole ligands have been synthesized and characterized by analytical and spectroscopic (Mass, ¹H NMR, IR and UV-Vis) data. The 2-(coumarinyl-6-azo)-4-imidazole ligands bonded to ruthenium in the monoionic bis-chelated [RuH(CO)(PPh₃)₂(4-R-L)] (3) mode and 4-(coumarinyl-6-azo)imidazole ligands in the neutral bis-chelated [RuH(CO)(PPh₃)₂(5-R-LH)]Cl (4) mode. A single crystal X-ray diffraction study of one of the complexes confirms the structure in one case. The complexes are redox active and upon excitation in the MLCT region exhibit emission at room temperature. A TDDFT study shows multiple charge transfer transitions in the visible and UV region.

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Appendix A. Supplementary material

CCDC 855760 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.01.041.

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