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Chemistry of a new family of aryl ruthenium species incorporating α-diimine chelation and a pendant imine-phenol function

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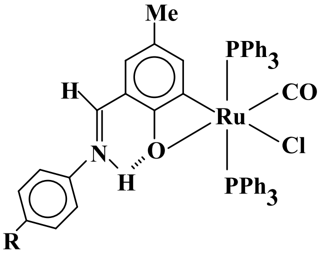
Abstract

The reaction of excess 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) with Ru(η^2-RL)(PPh_3)$_2$(CO)Cl (**1**) has respectively furnished [Ru(η^1-RL)(PPh_3)$_2$(CO)(bpy)](PF_6) (**2**) and [Ru(η^1-RL)(PPh_3)$_2$(CO)(phen)](PF_6) (**3**) in very good yield (η^2-RL is C_6H_2O-2-$CHNHC_6H_4R$(*p*)-3-Me-5, η^1-RL is C_6H_2OH-2-$CHNC_6H_4R$(*p*)-3-Me-5 and R is H, Me, MeO, Cl). The chelation of bpy/phen is attended with the cleavage of Ru–O and Ru–Cl bonds and iminium-phenolato → imine-phenol prototropic shift. The carbon monoxide ligand is located *syn* to the phenolic oxygen in **2** and **3** as opposed *anti* in **1**. The crystal and molecular structures of [Ru(η^1-HL)(PPh_3)$_2$(CO)(bpy)](PF_6)·CH_2Cl_2 (**2**(H)·CH_2Cl_2) and [Ru(η^1-ClL)(PPh_3)$_2$(CO)(phen)](PF_6)·H_2O (**3**(Cl)·H_2O) are reported. In the lattice of **3**(Cl)·H_2O, the water molecules form dimers (O···O, 2.617(8) Å). In the hydrogen bonded imine-phenol function the N···O distance is 2.550(9) Å in **2**(H)·CH_2Cl_2 and 2.581(7) Å in **3**(Cl)·H_2O. The Rubpy fragment in **2**(H)·CH_2Cl_2 along with the CO ligand and the metallated carbon atom define an equitorial plane from which the metallated aldimine fragment (pendant Ph excluded) is rotated by 39.1° due to interligand repulsion and the two Ru–P distances (2.384(3) and 2.456(3) Å) become significantly different. The repulsion also counteracts the *trans* influence of the metallated carbanionic site, the Ru–N bond *trans* to the site being shorter. The behaviour of **3**(Cl)·H_2O is similar. In dichloromethane solution **2** and **3** display a quasireversible Ru^{III}/Ru^{II} cyclic voltammetric response with $E_{1/2}$ in the range 0.75–0.85 V versus SCE. The C≡O stretch in **2** and **3** is 30–40 cm^{-1} higher than that in **1** due to the presence of dπ(Ru)–pπ(bpy/phen) back-bonding. The corresponding MLCT absorption (λ_{max}, ~470 nm) gives rise to fluorescence (λ_{max}, ~540 nm). The reaction of 2-(2-pyridyl)benzthiazole (pbt) with **1** has furnished [Ru(η^1-RL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8**) in which pbt is (N,N) chelated. The properties of **8** are generally similar to those of **2** and **3**.

Keywords: Organoruthenium α-diimine species; Fluorescent ruthenium aryls; Schiff base prototropic shift

1. Introduction

The decarbonylative metallation of 4-methyl-2,6-diformylphenol by Ru(PPh_3)$_3$$Cl_2$ in the presence of primary aromatic amines ($RC_6H_4NH_2$) has been shown to furnish the novel organoruthenium system Ru(η^2-RL)(PPh_3)$_2$(CO)Cl (**1**) incorporating a four-membered chelate ring juxtaposed to a hydrogen bonded iminium-phenolato ring [1]. The reactivity of these compounds is being investigated in this laboratory.



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While alkynes and isonitriles have been found to promote metallacycle expansion [2], bidentate mono-anionic σ-donor reagents such as acetate, nitrate, nitrite, xanthate and pyridine-2-thiolate undergo four-membered chelation [3].

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Herein we explore the possible reaction of **1** with two electroneutral α-diimine ligands viz. 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen), which have both σ-donor and π-acceptor abilities. A facile reaction is indeed observed leading to five-membered α-diimine chelation via displacement of Ru–O and Ru–Cl bonds. The process is attended with a change in the tautomeric state of the Schiff base ligand. The structure and properties of the new organometallics are scrutinized. Organoruthenium compounds incorporating chelated bpy/phen are relatively uncommon [4]. A point of special interest is that such species are potentially luminescent [5]. Preliminary examination has indeed revealed that the present compounds are luminescent in the visible region. Complex **1** also reacts with 2-(2-pyridyl)benzthiazole (pbt) which is found to chelate as an α-diimine.

2. Results and discussion

2.1. Reaction of 1 with bpy/phen: chelation and prototropic shift

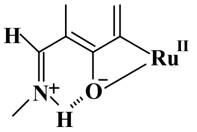
In MeOH–CH_2Cl_2 solution Ru(η^2-RL)$(PPh_3)_2$(CO)Cl (**1**) reacts smoothly with excess bpy in the presence of NH_4PF_6 according to Eq. (1) furnishing the yellow crystalline salt [Ru(η^1-RL)$(PPh_3)_2$(CO)(bpy)](PF_6) (**2**) in excellent yield. The use of phen in place of bpy afforded the salt [Ru(η^1-RL)$(PPh_3)_2$(CO)(phen)](PF_6) (**3**). The R groups

$$\mathbf{1} + \mathrm{bpy} + \mathrm{PF}_6^- \rightarrow \mathbf{2} + \mathrm{Cl}^- \qquad (1)$$

utilized in the present work are H, Me, OMe, Cl. Specific compounds will be identified by putting R in parenthesis: thus **2**(Me) stands for [Ru(η^1-MeL)$(PPh_3)_2$(CO)(bpy)](PF_6).

Both **2** and **3** are diamagnetic (idealized t_{2g}^6) and behave as 1:1 electrolytes in acetone solution (Λ, 115–140 Ω^{-1} cm^2 mol^{-1}). In ^{1}H-NMR the 3-H and 4-Me protons appear as sharp singlets near 6.70 and 1.90 ppm. These protons as well as the 5-H proton are subject to shielding by phosphine phenyl ring [1a,3a,6]. The 5-H signal is observed near 6.8 ppm in **2** but in **3** it merges with the complex aromatic multiplet due to PPh_3 and C_6H_4R protons. The bpy/phen protons resonate in the region 7.7–9.2 ppm.

The conversions **1** → **2** and **1** → **3** are attended with a prototropic shift within the salicylaldimine function. In **1** the metal is coordinated to phenolato oxygen and the schiff base function occurs in the zwitterionic iminium-phenolato tautomeric form **4**. Chelation of bpy/phen is attended with cleavage of the Ru–O bond and the Schiff base fragment becomes an imine-phenol **5**. This is consistent with spectroscopic data. Thus the C=N stretching frequency in **2** and **3** is significantly lower (~1600 cm^{-1}) than that in **1** (~1620 cm^{-1}) as expected [7,8]. Further, the aldimine CH resonance in ^{1}H-NMR in both **2** and **3** occur at significantly lower field (~8.2 ppm) compared to that in **1** (~7.5 ppm). The O–H resonance in both **2** and **3** occurs as a relatively sharp signal (width at half-height 30 Hz) near 13 ppm. On the other hand, the N–H resonance in **1** is broad (width at half-height 150 Hz) due to the quadrupole moment of the nitrogen atom [1a].



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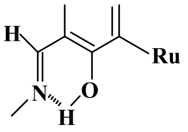

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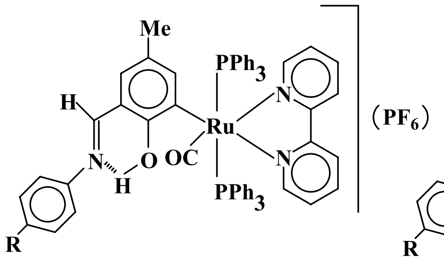
2.2. Structure

Structure determination of [Ru(η^1-HL)$(PPh_3)_2$(CO)(bpy)](PF_6)·CH_2Cl_2 (**2**(H)·CH_2Cl_2) and [Ru(η^1-ClL)$(PPh_3)_2$(CO)(phen)](PF_6)·H_2O (**3**(Cl)·H_2O) has authenticated the binding mode within the cation as in **2** and **3**, respectively. Perspective views are shown in Figs. 1 and 2 and selected bond parameters are listed in Table 1. In the distorted $RuC_2P_2N_2$ coordination spheres the bpy/phen ligand is chelated and the schiff base ligand is



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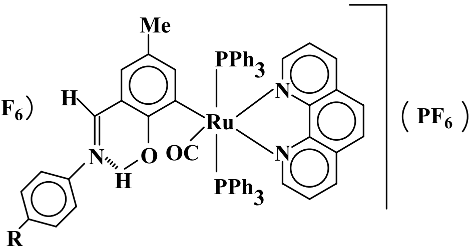

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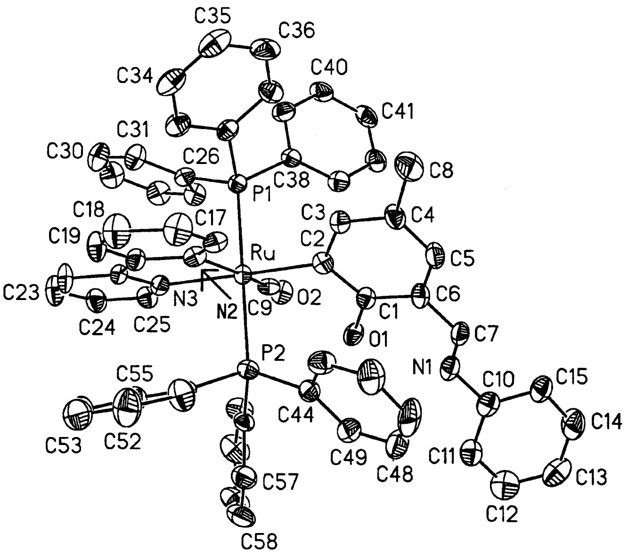


Fig. 1. Perspective view and atom-labeling scheme for the cation of $\mathbf{2}(H)\cdot CH_2Cl_2$.

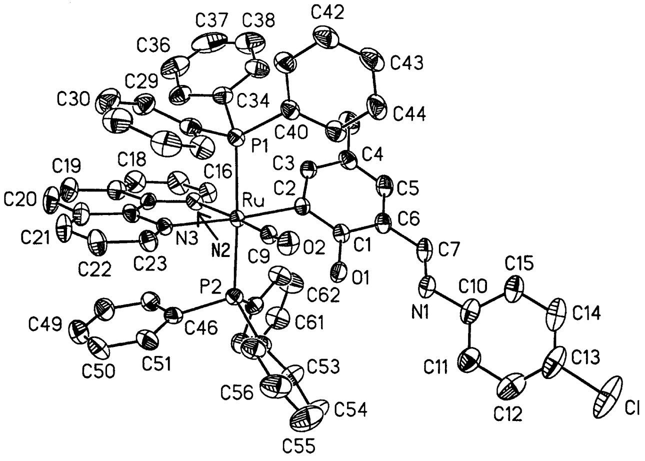


Fig. 2. Perspective view and atom-labeling scheme for the cation of $\mathbf{3}(Cl)\cdot H_2O$.

monodentate, bonded at the C(2) atom only. The phenolic oxygen atom lie too far away (Ru···O(1), 3.220(7) Å in $\mathbf{2}(H)\cdot CH_2Cl_2$ and 3.230(5) Å in $\mathbf{3}(Cl)\cdot H_2O$) for binding.

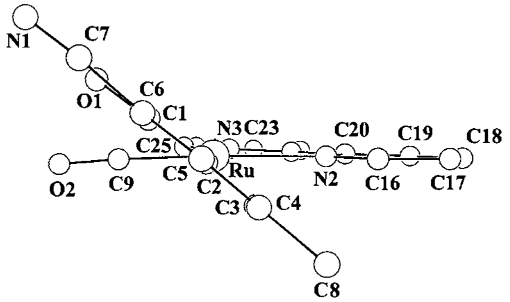
The solvent molecule is $\mathbf{2}(H)\cdot CH_2Cl_2$ is not involved in any significant nonbonded interaction in the lattice. On the other hand in the lattice of $\mathbf{3}(Cl)\cdot H_2O$ water molecules form discrete centrosymmetric dimers (O···O, 2.617(8) Å). The N(1)···O(1) distance in the hydrogen bonded imine-phenol moiety is 2.550(9) Å in $\mathbf{2}(H)\cdot CH_2Cl_2$ and 2.581(7) Å in $\mathbf{3}(Cl)\cdot H_2O$. The corresponding distance in the iminium-phenolato group of **1** is longer, 2.665(12) Å [1]. Thus the cleavage of the Ru–O bond (**1** → **2**/**3**) is attended with prototropic shift as well as a shortening of the N(1)···O(1) length.

The Rubpy fragment in $\mathbf{2}(H)\cdot CH_2Cl_2$ is excellently planar (mean deviation, 0.02 Å). This fragment along

Table 1
Selected bond parameters (bond lengths in Å; bond angles in (°)) for $\mathbf{2}(H)\cdot CH_2Cl_2$ and $\mathbf{3}(Cl)\cdot H_2O$

	$\mathbf{2}(H)\cdot CH_2Cl_2$	$\mathbf{3}(Cl)\cdot H_2O$
Bond lengths		
Ru–P(1)	2.384(3)	2.375(2)
Ru–P(2)	2.456(3)	2.409(2)
Ru–C(2)	2.101(10)	2.090(6)
Ru–C(9)	1.813(9)	1.813(6)
Ru–N(2)	2.172(7)	2.154(5)
Ru–N(3)	2.155(7)	2.133(5)
C(9)–O(2)	1.157(10)	1.134(7)
C(7)–N(1)	1.268(12)	1.257(9)
C(1)–O(1)	1.364(10)	1.350(7)
N(1)···O(1)	2.550(9)	2.581(7)
Bond angles		
P(1)–Ru–P(2)	177.2(1)	177.3(1)
P(1)–Ru–N(2)	91.5(2)	92.5(1)
P(1)–Ru–N(3)	89.5(2)	88.1(1)
P(1)–Ru–C(9)	85.5(3)	86.9(2)
P(1)–Ru–C(2)	91.2(3)	89.6(2)
P(2)–Ru–N(2)	86.1(2)	85.7(1)
P(2)–Ru–N(3)	91.3(2)	89.6(1)
P(2)–Ru–C(9)	97.0(3)	94.7(2)
P(2)–Ru–C(2)	87.7(3)	92.6(2)
Ru–C(9)–O(2)	175.6(8)	175.7(6)
C(2)–Ru–N(2)	98.7(3)	98.2(2)
C(9)–Ru–N(3)	94.8(4)	96.5(2)
C(9)–Ru–N(2)	170.4(4)	173.2(2)
N(2)–Ru–N(3)	76.0(3)	76.7(2)
C(9)–Ru–C(2)	90.5(4)	88.6(2)

with the carbon monoxide ligand and the metallated carbon atom C(2) define an equitorial plane (mean deviation, 0.04 Å; plane A). The metallated aldimine fragment defined by Ru, C(1) to C(8), N(1) and O(1) is also planar (mean deviation of 0.04 Å; plane B). The noncoplanarity of the two planes is highlighted in **6**, the dihedral angle between them being 39.1°. The environment around P(2) is thus more crowded than that around P(1). This is reflected in the unequal bond lengths: Ru–P(1), 2.384(3) Å and Ru–P(2), 2.456(3) Å. The behaviour of $\mathbf{3}(Cl)\cdot H_2O$ complex is qualitatively similar. In the precursor complex **1**, the Schiff base moiety lie on the equitorial plane and the two Ru–P lengths are equal at 2.387(2) Å [1].



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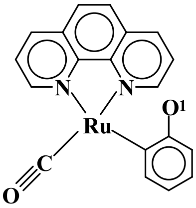
The noncoplanarity of the two planes in **2**(H)·CH_2Cl_2 is believed to originate from repulsive nonbonded interactions between the bpy and Schiff base ligands. In particular the C(16)···C(3) distance, 3.246(6) Å, falls below the sum of van der Waals radii (3.40 Å) of the two carbon atoms [9]. The interaction is thus repulsive, but the repulsion would have been much more if A and B were coplanar. The *trans* influence of the metallated carbanionic site C(2) could be expected to lengthen the Ru–N(3) distance compared to Ru–N(2) distance. In practice the reverse is observed: Ru–N(2), 2.172(7) Å and Ru–N(3) is 2.155(7) Å. The lengthening of Ru–N(2) bond is believed to be due to the C(16)···C(3) repulsion. The behaviour of **3**(Cl)·H_2O is entirely analogous.

In the transformation **1** → **2**/**3** the Schiff base fragment undergoes a large rotation around the metal–carbon bond. As a result the carbon monoxide molecule gets located *syn* to the phenolic C–O function, the torsion angle (O(1)–C(1)···C(9)–O(2)) being 49.9° in **2**(H)·CH_2Cl_2 and 56.3° in **3**(Cl)·H_2O. In **1** the corresponding arrangement is *anti* [1]. The later configuration is disfavoured in **2** and **3** due to steric repulsion between the phenolic and the α-diimine functions as highlighted in the computer generated hypothetical *anti* configuration **7** for the Ru(CO)(phen) fragment. The estimated C(16)···O(1) and N(2)···O(1) distances in **7** are 2.589(7) and 2.885(7) Å, respectively.



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These are much lower than the corresponding van der Waals sums (3.20 and 3.05 Å). The C(16)···O(1) and N(2)···O(1) distances in the observed *syn* configuration are 5.326(7) and 4.904(6) Å respectively. The behaviour of the Ru(CO)(bpy) fragment in **2**(H)·CH_2Cl_2 is analogous.

Table 2
Cyclic voltammetric reduction potentials [a]

Complexes	M(III)–M(II) $E_{1/2}$ [a], V (ΔE_p, mV)
2(H)	0.78(194)
2(Me)	0.77(175)
2(OMe)	0.76(131)
2(Cl)	0.85(203)
3(Me)	0.79(200)
3(OMe)	0.75(115)
3(Cl)	0.84(185)
8(Me)	0.81(178)
8(OMe)	0.77(119)
8(Cl)	0.87(144)

[a] Conditions solvent, dichloromethane; supporting electrolyte, TEAP (0.1(M)); working electrode, platinum; reference electrode, SCE solute concentration, $\sim 10^{-3}$(M); $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, $\Delta E_p = E_{pa} - E_{pc}$.

2.3. Metal redox

In dichloromethane solution both **2** and **3** display a quasireversible (peak-to-peak separation, 100–200 mV) one-electron response assigned to Ru^{III}/Ru^{II} redox. The $E_{1/2}$ values (Table 2) shift marginally to higher potentials as the R-substituent becomes progressively more electron-withdrawing: OMe < Me < H < Cl. The $E_{1/2}$ values are 100–200 mV higher than those in type **1** precursors. The cationic nature of **2** and **3** as well as the presence of back-bonding (vide infra) to bpy/phen are both expected to contribute to this rise of $E_{1/2}$.

2.4. Spectra: back-bonding, charge transfer and fluorescence

The $C\equiv O$ strech in **2** and **3** occurs in the region 1950–1960 cm^{-1}. In the precursor complex **1** as well as in acetate/nitrate/nitrite/xanthate derivatives the stretch systematically lie around 1920 cm^{-1} [3]. The increased frequency in **2** and **3** is believed to be due to the combined effect of cationic charge and significant dπ(Ru)–pπ(bpy/phen) back-bonding.

In dichloromethane solution the complexes display two allowed absorption bands in the region 380–400 and 460–480 nm. Selected UV–vis spectral data are given in Table 3. The solutions are also fluorescent, the peak lying in the region 540–550 nm, Table 3. Excitation spectral studies show that the fluorescence is

Table 3
UV–vis and fluorescence spectral data

Complexes	UV–vis data [a] λ_{max} (nm) (ε [b], $M^{-1}\ cm^{-1}$)	Fluorescence data [a,c] λ_{max} (nm)
2(H)	382(15 760), 466(3860)	541
2(Me)	380(12 140), 477(2230)	543
2(OMe)	386(12 900), 475(2150)	540
2(Cl)	389(14 600), 468(3400)	545
3(Me)	392(12 900), 474(3070)	540
3(OMe)	387(12 760), 475(2540)	531
3(Cl)	394(8040), 472(2000)	560
8(Me)	380(13 000), 500(2600)	586
8(OMe)	386(16 000), 502(2300)	581
8(Cl)	384(14 000), 499(2400)	588

[a] Solvent is dichloromethane.
[b] Extinction coefficient.
[c] Excitation at the higher wavelength absorption peak.

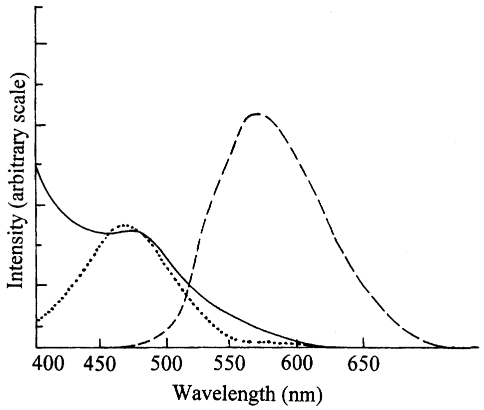


Fig. 3. Absorption (—), fluorescence (---) and excitation (. . .) spectra of **2**(Cl) in dichloromethane solution.

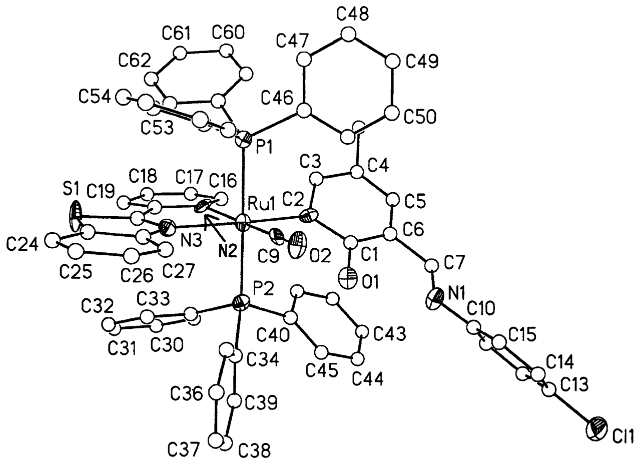
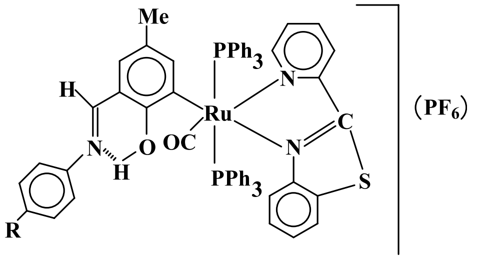


Fig. 4. Perspective view and atom-labelling scheme for molecule 1 (cation only) of **8**(Cl). Selected bond distances are Ru(1)–P(1), 2.414(7); Ru(1)–P(2), 2.464(7); Ru(1)–C(2), 2.10(2); Ru(1)–C(9), 1.86(2); Ru(1)–N(2), 2.20(2); Ru(1)–N(3), 2.19(2). Corresponding distances of molecule 2 are Ru(2)–P(3), 2.427(7); Ru(2)–P(4), 2.474(7); Ru(2)–C(65), 2.13(2); Ru(2)–C(72), 1.83(2); Ru(2)–N(5), 2.18(2); Ru(2)–N(6), 2.18(2).

associated with the absorption band near 470 nm which is assigned to π(Ru)→π*(bpy/phen) MLCT excitation. A representative case is shown in Fig. 3. The fluorescence is believed to originate from the ^{3}MLCT state. We note that the parent organometallics of type **1** do not display any fluorescence in the visible region. Further studies are in progress.

2.5. The case of a pyridylbenzthiazole ligand

The concerned ligand [10] is 2-(2-pyridyl)benzthiazole (pbt) which was found to react with **1** under conditions similar to those used for bpy and phen furnishing the salt [Ru(η^1-RL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8**). Here pbt is chelated in the (N,N) mode like bpy/phen as opposed to the possible alternative (N,S) mode. Structure solution for **8**(Cl) (Fig. 4) confirmed this. The observed bond lengths are grossly similar to those in the



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bpy/phen complexes and the dihedral angle between the Ru(pbt)(CO)C(aryl) plane and the plane of the metallated aldimine fragment is ~42° resulting in unequal Ru–P lengths.

The complexes behave as 1:1 electrolytes and display a quasireversible Ru^{III}/Ru^{II} couple near 0.8 V versus SCE (Table 2). Their spectroscopic behaviour is also similar to those of **2** and **3** (Table 3).

3. Experimental

3.1. Materials

The compounds Ru(PPh_3)$_3$$Cl_2$ [11], Ru(η^2-RL)(PPh_3)$_2$(CO)Cl [1a] and 2-(2-pyridyl)-benzthiazole [10] were prepared by reported methods. The purification of dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as described in previous work [12]. All other chemicals and solvents were of analytical grade and were used as received.

3.2. Physical measurements

Electronic, IR and fluorescence spectra were recorded with Simadzu UV-1601PC spectrophotometer, Perkin–Elmer 783 IR spectrometer and Perkin–Elmer model LS 55 Luminescence spectrometer, respectively. A Bruker 300 MHz FT NMR spectrometer was used to record ^{1}H NMR spectra (Me_4Si internal standard). The numbering scheme used for ^{1}H-NMR is the same as in crystallography. Spin–spin structures are abbreviated as: s, singlet; d, doublet; t, triplet; m, multiplet. Microanalyses (C, H, N) were done using a Perkin–Elmer 240C elemental analyzer. Solution electrical conductivity was measured in a acetone with a Philips PR 9500 bridge using a platinized electrode (cell constant of 1.05). The magnetic behavior of the complexes was examined by PAR 155 vibrating sample magnetometer. All electrochemical measurement were done under a nitrogen atmosphere in dichloromethane solution using a CHI model 620A electrochemical analyzer. The supporting electrolyte was tetraethylammonium perchlorate, and the reported potentials are referenced to the saturated calomel electrode (SCE).

3.3. Synthesis of the complexes, [Ru(η^1-RL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**)

The [Ru(η^1-RL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**) complexes were synthesized in excellent yield (~ 90%) by reacting Ru(η^2-RL)(PPh$_3$)$_2$(CO)Cl (**1**) in MeOH–CH$_2$Cl$_2$ (2:1) at room temperature, with excess bpy in presence of NH$_4$PF$_6$. Details of a representative case are given below. The other compounds were prepared analogously.

3.3.1. [Ru(η^1-HL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**(H))

To a vigorously stirred violet solution of Ru(η^2-HL)(PPh$_3$)$_2$(CO)Cl (50 mg, 0.056 mmol) in a mixture of 30 ml MeOH and 15 ml dichloromethane was added 43 mg (0.275 mmol) of bpy. The mixture was stirred for 3 h when the colour of the solution changed from violet to yellow. Then 14 mg (0.086 mmol) of NH$_4$PF$_6$ was added to the yellow solution which was further stirred for 30 min. The solvent was then removed under reduced pressure, and the yellow solid thus obtained was washed thoroughly with water and finally with a little MeOH followed by drying in vacuo. Yield: 59 mg (91%). Anal. Found: C, 62.83; H, 4.38; N, 3.57. Calc. for C$_{61}$H$_{50}$F$_6$N$_3$O$_2$P$_3$Ru: C, 62.89; H, 4.33; N, 3.61%. IR (KBr, cm^{-1}): 1604 (ν_{CN}), 1956 (ν_{CO}) and 842 ($\nu_{\mathrm{PF_6}}$). ^{1}H-NMR (CDCl$_3$, δ): 8.18 (s, 1H, H(7)), 13.12 (s, 1H, O–H; disappeared on shaking with D$_2$O), 6.72 (s, 1H, H(3)), 6.77–7.41 (m, 38H, 2PPh$_3$, H(5), H(19), H(22), H(11), H(12), H(13), H(14), H(15)), 1.91 (s, 3H, CH$_3$), 8.75 (d, 1H, H(16), J_{HH} 6), 8.19 (t, 1H, H(18), J_{HH} 6.3), 7.73 (t, 1H, H(24), J_{HH} 7.5), 8.41 (d, 1H, H(25), J_{HH} 6.1), 8.06 (m, 2H, H(17), H(23)). $\Lambda_{\mathrm{M}} = 116\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

3.3.2. [Ru(η^1-MeL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**(Me))

Ru(η^2-MeL)(PPh$_3$)$_2$(CO)Cl (50 mg, 0.055 mmol) and bpy (43 mg, 0.275 mmol) were used. Yield: 57 mg (88%). Anal. Found: C, 63.23; H, 4.48; N, 3.49. Calc. for C$_{62}$H$_{52}$F$_6$N$_3$O$_2$P$_3$Ru: C, 63.16; H, 4.45; N, 3.56%. IR (KBr, cm^{-1}): 1604 (ν_{CN}), 1957 (ν_{CO}) and 841 ($\nu_{\mathrm{PF_6}}$). ^{1}H-NMR (CDCl$_3$, δ): 8.18 (s, 1H, H(7)), 13.21 (s, 1H, O–H, disappeared on shaking with D$_2$O), 6.70 (s, 1H, H(3)), 6.79–7.47 (m, 37H, 2PPh$_3$, H(5), H(19), H(22), H(11), H(12), H(14), H(15)), 1.90 and 2.37 (2s, 6H, 2CH$_3$), 8.76 (d, 1H, H(16), J_{HH} 6.3), 8.19 (t, 1H, H(18), J_{HH} 6.3), 7.73 (t, 1H, H(24), J_{HH} 7.6), 8.41 (d, 1H, H(25), J_{HH} 6.0), 8.06 (m, 2H, H(17), H(23)). $\Lambda_{\mathrm{M}} = 122\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

3.3.3. [Ru(η^1-MeOL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**(OMe))

Ru(η^2-MeOL)(PPh$_3$)$_2$(CO)Cl (50 mg, 0.054 mmol) and bpy (42 mg, 0.269 mmol) were employed. Yield: 56 mg (87%). Anal. Found: C, 62.25; H, 4.30; N, 3.58. Calc. for C$_{62}$H$_{52}$F$_6$N$_3$O$_3$P$_3$Ru: C, 62.31; H, 4.39; N, 3.52%. IR (KBr, cm^{-1}): 1609 (ν_{CN}), 1953 (ν_{CO}) and 842 ($\nu_{\mathrm{PF_6}}$). ^{1}H -MR (CDCl$_3$, δ): 8.18 (s, 1H, H(7)), 13.25 (s, 1H, O–H, disappeared on shaking with D$_2$O), 6.69 (s, 1H, H(3)), 6.75–7.34 (m, 37H, 2PPh$_3$, H(5), H(19), H(22), H(11), H(12), H(14), H(15)), 1.91 (s, 3H, CH$_3$), 3.84 (s, 3H, OCH$_3$), 8.76 (d, 1H, H(16), J_{HH} 6.1), 8.19 (t, 1H, H(18), J_{HH} 6.6), 7.72 (t, 1H, H(24), J_{HH} 7.5), 8.41 (d, 1H, H(25), J_{HH} 6.3), 8.05 (m, 2H, H(17), H(23)). $\Lambda_{\mathrm{M}} = 117\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

3.3.4. [Ru(η^1-ClL)(PPh$_3$)$_2$(CO)(bpy)](PF$_6$) (**2**(Cl))

Ru(η^2-ClL)(PPh$_3$)$_2$(CO)Cl (50 mg, 0.054 mmol) and bpy (42 mg, 0.269 mmol) were used. Yield: 58 mg (90%). Anal. Found: C, 61.12; H, 4.07; N, 3.58. Calc. for C$_{61}$H$_{49}$ClF$_6$N$_3$O$_2$P$_3$Ru: C, 61.08; H, 4.12; N, 3.50%. IR (KBr, cm^{-1}): 1605 (ν_{CN}), 1955 (ν_{CO}) and 842 (ν_{PF6}). ^{1}H-NMR (CDCl$_3$, δ): 8.16 (s, 1H, 7(H)), 12.91 (s, 1H, O–H, disappeared on shaking with D$_2$O), 6.73 (s, 1H, H(3)), 6.79–7.35 (m, 37H, 2PPh$_3$, H(5), H(19), H(22), H(11), H(12), H(14), H(15)), 1.91 (s, 3H, CH$_3$), 8.73 (d, 1H, H(16), J_{HH} 6.0), 8.19 (t, 1H, H(18), J_{HH} 6.3), 7.73 (t, 1H, H(24), J_{HH} 7.5), 8.40 (d, 1H, H(25), J_{HH} 6.1), 8.06 (m, 2H, H(17), H(23)). $\Lambda_{\mathrm{M}} = 124\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

3.4. Synthesis of the complexes, [Ru(η^1-RL)(PPh$_3$)$_2$(CO)(phen)](PF$_6$) (**3**)

The [Ru(η^1-RL)(PPh$_3$)$_2$(CO)(phen)](PF$_6$) (**3**) complexes were synthesized in excellent yield (~ 80%) by reacting Ru(η^2-RL)(PPh$_3$)$_2$(CO)Cl (**1**) with excess phen for 4 h when the color of the solution changed from violet to yellow. The general procedure for isolation is similar to what is described for bpy.

3.4.1. [Ru(η^1-MeL)(PPh$_3$)$_2$(CO)(phen)](PF$_6$) (**3**(Me))

Ru(η^2-MeL)(PPh$_3$)$_2$(CO)Cl (50 mg, 0.055 mmol) and phen (87 mg, 0.439 mmol) were employed. Yield: 50 mg (76%). Anal. Found: C, 63.82; H, 4.31; N, 3.44. Calc. for C$_{64}$H$_{52}$F$_6$N$_3$O$_2$P$_3$Ru: C, 63.89; H, 4.36; N, 3.49%. IR (KBr, cm^{-1}): 1593 (ν_{CN}), 1955 (ν_{CO}) and 842 (ν_{PF6}). ^{1}H-NMR (CDCl$_3$, δ): 8.21 (s, 1H, H(7)), 13.27 (s, 1H, O–H, disappeared on shaking with D$_2$O), 6.74 (s, 1H, H(3)), 6.78 (s, 1H, H(5)), 6.62–7.33 (m, 34H, 2PPh$_3$, H(11), H(12), H(14), H(15)), 1.94 and 2.37 (2s, 6H, 2CH$_3$), 9.11 (d, 1H, H(16), J_{HH} 6.0), 8.66 (d, 1H, H(18), J_{HH} 9), 8.05 (d, 1H, H(19), J_{HH} 9.0), 7.94 (d, 1H, H(20), J_{HH} 9.1), 8.25 (d, 1H, H(21), J_{HH} 6.3), 8.84 (d, 1H, H(23), J_{HH} 6.0), 7.78 (m, 2H, H(17), H(22)). $\Lambda_M = 139$ Ω^{-1} cm^2 mol^{-1}.

3.4.2. *[Ru(η^1-MeOL)(PPh_3)$_2$(CO)(phen)](PF_6) (**3** (OMe))*

Ru(η^1-MeOL)(PPh_3)$_2$(CO)Cl (50 mg, 0.054 mmol) and phen (85 mg, 0.429 mmol) were used. Yield: 49 mg (75%). Anal. Found: C, 63.01; H, 4.23; N, 3.49. Calc. for $C_{64}H_{52}F_6N_3O_3P_3Ru$: C, 63.05; H, 4.30; N, 3.45%. IR (KBr, cm^{-1}): 1610 (ν_{CN}), 1952 (ν_{CO}) and 842 (ν_{PF_6}). ^{1}H-NMR ($CDCl_3$, δ): 8.20 (s, 1H, H(7)), 13.29 (s, 1H, O–H, disappeared on shaking with D_2O), 6.73 (s, 1H, H(3)), 6.78 (s, 1H, H(5)), 6.62–7.32 (m, 34H, 2PPh_3, H(11), H(12), H(14), H(15)), 1.94 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 9.12 (d, 1H, H(16), J_{HH} 6.0), 8.65 (d, 1H, H(18), J_{HH} 9.0), 8.04 (d, 1H, H(19), J_{HH} 9.1), 7.94 (d, 1H, H(20), J_{HH} 9.3), 8.25 (d, 1H, H(21), J_{HH} 9.0), 8.84 (d, 1H, H(23), J_{HH} 6.1), 7.77 (m, 2H, H(17), H(22)). $\Lambda_M = 137$ Ω^{-1} cm^2 mol^{-1}.

3.4.3. *[Ru(η^1-ClL)(PPh_3)$_2$(CO)(phen)](PF_6) (**3** (Cl))*

Ru(η^2-ClL)(PPh_3)$_2$(CO)Cl (50 mg, 0.054 mmol) and phen (85 mg, 0.429 mmol) were employed. Yield: 51 mg (78%). Anal. Found: C, 61.79; H, 4.01; N, 3.37. Calc. for $C_{63}H_{49}ClF_6N_3O_2P_3Ru$: C, 61.84; H, 4.04; N, 3.43%. IR (KBr, cm^{-1}): 1604 (ν_{CN}), 1955 (ν_{CO}) and 841 (ν_{PF_6}). ^{1}H-NMR ($CDCl_3$, δ): 8.19 (s, 1H, H(7)), 12.96 (s, 1H, O–H, disappeared on shaking with D_2O), 6.76 (s, 1H, H(3)), 6.79 (s, 1H, H(5)), 6.61–7.40 (m, 34H, 2PPh_3, H(11), H(12), H(14), H(15)), 1.94 (s, 3H, CH_3), 9.09 (d, 1H, H(16), J_{HH} 6.0), 8.65 (d, 1H, H(18), J_{HH} 9.1), 8.04 (d, 1H, H(19), J_{HH} 9.0), 7.93 (d, 1H, H(20), J_{HH} 9.0), 8.28 (d, 1H, H(21), J_{HH} 6.3), 8.85 (d, 1H, H(23), J_{HH} 6.0), 7.79 (m, 2H, H(17), H(22)). $\Lambda_M = 134$ Ω^{-1} cm^2 mol^{-1}.

3.5. *Synthesis of the complexes, [Ru(η^1-RL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8**)*

The [Ru(η^1-RL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8**) complexes were synthesized in excellent yield (~ 80%) by reacting Ru(η^2-RL)(PPh_3)$_2$(CO)Cl (**1**) with excess pbt for 4 h when the colour of the solution changed from violet to orange. The general procedure for isolation is similar to what is described for bpy.

3.5.1. *[Ru(η^1-MeL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8** (Me))*

Ru(η^2-MeL)(PPh_3)$_2$(CO)Cl (50 mg, 0.055 mmol) and pbt (58 mg, 0.273 mmol) were used. Yield: 50 mg (74%). Anal. Found: C, 62.28; H, 4.21; N, 3.36. Calc. for $C_{64}H_{52}F_6N_3O_2P_3RuS$: C, 62.23; H, 4.24; N, 3.40%. IR (KBr, cm^{-1}): 1593 (ν_{CN}), 1949 (ν_{CO}) and 842 (ν_{PF_6}). ^{1}H-NMR ($CDCl_3$, δ): 8.15 (s, 1H, H(7)), 13.33 (s, 1H, O–H, disappeared on shaking with D_2O), 6.59 (s, 1H, H(3)), 6.77–7.20 (m, 35H, 2PPh_3, H(5), H(11), H(12), H(14), H(15)), 1.88 and 2.37 (2s, 6H, 2CH_3), 8.86 (d, 1H, H(16), J_{HH} 6.1), 7.39 (t, 1H, H(17), J_{HH} 7.5), 8.21 (t, 1H, H(18), J_{HH} 7.5), 7.82 (d, 1H, H(19), J_{HH} 9.0), 8.14 (d, 1H, H(24), J_{HH} 7.2), 7.51 (t, 1H, H(25), J_{HH} 7.5), 7.58 (t, 1H, H(26), J_{HH} 7.3), 7.94 (d, 1H, H(27), J_{HH} 9.0). $\Lambda_M =$ 127 Ω^{-1} cm^2 mol^{-1}.

3.5.2. *[Ru(η^1-MeOL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8** (OMe))*

Ru(η^2-MeOL)(PPh_3)$_2$(CO)Cl (50 mg, 0.054 mmol) and pbt (57 mg, 0.268 mmol) were employed. Yield: 52 mg (77%). Anal. Found: C, 61.39; H, 4.23; N, 3.32. Calc. for $C_{64}H_{52}F_6N_3O_3P_3RuS$: C, 61.44; H, 4.19; N, 3.36%. IR (KBr, cm^{-1}): 1610 (ν_{CN}), 1959 (ν_{CO}) and 841 (ν_{PF_6}). ^{1}H-NMR ($CDCl_3$, δ): 8.16 (s, 1H, H(7)), 13.36 (s, 1H, O–H, disappeared on shaking with D_2O), 6.58 (s, 1H, H(3)). 6.77–7.17 (m, 35H, 2PPh_3, H(5), H(11), H(12), H(14), H(15)), 1.87 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 8.85 (d, 1H, H(16), J_{HH} 6.0), 7.39 (t, 1H, H(17), J_{HH} 7.5), 8.22 (t, 1H, H(18), J_{HH} 7.6), 7.80 (d, 1H, H(19), J_{HH} 9.1), 8.15 (d, 1H, H(24), J_{HH} 7.3), 7.50 (t, 1H, H(25), J_{HH} 7.5), 7.55 (t, 1H, H(26), J_{HH} 7.6), 7.96 (d, 1H, H(27), J_{HH} 9.0), $\Lambda_M = 135$ Ω^{-1} cm^2 mol^{-1}.

3.5.3. *[Ru(η^1-ClL)(PPh_3)$_2$(CO)(pbt)](PF_6) (**8** (Cl))*

Ru(η^2-ClL)(PPh_3)$_2$(CO)Cl (50 mg, 0.054 mmol) and pbt (57 mg, 0.268 mmol) were employed. Yield: 53 mg (79%). Anal. Found: C, 60.22; H, 3.96; N, 3.30. Calc. for $C_{63}H_{49}ClF_6N_3O_2P_3RuS$: C, 60.26; H, 3.93; N, 3.35%. IR (KBr, cm^{-1}): 1603 (ν_{CN}), 1965 (ν_{CO}) and 842 (ν_{PF_6}). ^{1}H-NMR ($CDCl_3$, δ): 8.13 (s, 1H, H(7)), 13.02 (s, 1H, O–H, disappeared on shaking with D_2O), 6.62 (s, 1H, H(3)), 6.75–7.18 (m, 35H, 2PPh_3, H(5), H(11), H(12), H(14), H(15)), 1.87 (s, 3H, CH_3), 8.84 (d, 1H, H(16), J_{HH} 6.1), 7.36 (t, 1H, H(17), J_{HH} 9.0), 8.21 (t, 1H, H(18), J_{HH} 7.5), 7.81 (d, 1H, H(19), J_{HH} 9.0), 8.12 (d, 1H, H(24), J_{HH} 7.1), 7.51 (t, 1H, H(25), J_{HH} 7.5), 7.58 (t, 1H, H(26), J_{HH} 7.6), 7.95 (d, 1H, H(27), J_{HH} 9.1). $\Lambda_M = 123$ Ω^{-1} cm^2 mol^{-1}.

3.6. *X-ray structure determination*

Single crystals of [Ru(η^1-HL)(PPh_3)$_2$(CO)(bpy)](PF_6)·CH_2Cl_2 (**2**(H)·CH_2Cl_2) (0.35 × 0.30 × 0.20 mm^3) and [Ru(η^1-ClL)(PPh_3)$_2$(CO)(phen)](PF_6)·H_2O (**3**(Cl)·H_2O) (0.30 × 0.25 × 0.20 mm^3) were grown by slow diffusion of hexane into dichloromethane solutions at room temperature. Cell parameters were determined by a least-squares fit of 30 machine-centred reflections ($2\theta = 14$–$28°$). Data were collected with the ω-scan technique on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Two check reflections measured after every 198 reflections showed no significant intensity reduction in any case. All data were corrected for Lp

Table 4
Crystal data for **2**(Me)·CH_2Cl_2, **3**(Cl)·H_2O and **8**(Cl)

Complexes	**2**(Me)·CH_2Cl_2	**3**(Cl)·H_2O	**8**(Cl)
Empirical formula	$C_{62}H_{52}Cl_2F_6N_3O_2P_3Ru$	$C_{63}H_{51}ClF_6N_3O_3P_3Ru$	$C_{63}H_{49}ClF_6N_3O_2P_3SRu$
Formula weight	1249.95	1241.51	1255.54
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_{1/c}$	$P2_{1/n}$	$P\bar{1}$
a (Å)	19.552(12)	15.137(11)	13.852(10)
b (Å)	16.332(9)	21.549(6)	14.375(8)
c (Å)	17.694(8)	18.076(6)	16.522(8)
α (°)			108.34(4)
β (°)	96.93(4)	103.68(4)	109.94(5)
γ (°)			92.57(5)
V (Å^3)	5609(5)	5729(5)	2893(3)
Z	4	4	2
μ(Mo–K$_\alpha$) (mm^{-1})	0.528	0.473	0.503
D_{calc} (g cm^{-1})	1.480	1.441	1.442
Total reflections	7525	8725	7484
Independent reflections (R_{int})	7173 (0.0621)	8356 (0.0219)	7312 (0.0577)
R_1 [a], wR_2 [b] $[I > 2\sigma(I)]$	0.0733, 0.1672	0.0580, 0.1526	0.0718, 0.1820

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.
[b] $wR_2 = [\Sigma\,w(F_o^2 - F_c^2)^2/\Sigma\,(F_o^2)^2]$.

and an empirical absorption correction [13] was done on the basis of azimuthal scan of six reflections for the crystals.

The metal atom was located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions. Calculations were performed using the SHELXTL, Version 5.03 [14] programme package. Significant crystal data are listed in Table 4.

Single crystals of [Ru(η^1-RL)$(PPh_3)_2$(CO)(pbt)](PF_6) ($0.30 \times 0.25 \times 0.25$ mm^3) grown in the same way as above belonged to the chiral space group $P\bar{1}$ with $Z = 2$ (Table 4). The asymmetric unit generated from Patterson maps and successive Fourier synthesis consisted of a nearly centrosymmetric pair of molecules. This vitiated free least-squares refinement but the gross structure was revealed with certainty. Only the coordination sphere, the metallated ring and the pbt ligand could be refined anisotropically. All the pendant aryl rings (7 per molecule) were affixed as idealized hexagons.

3.7. Computer generation of motif 7

The relative positions of CO and the bpy/phen chelate were retained as in the structures of **2**(H)·CH_2Cl_2 and **3**(Cl)·H_2O but the phenolic oxygen O(1) was shifted so as to correspond to the relative position in **1**(Me) [1], the C–O length being set at 1.35 Å.

4. Conclusion

It is demonstrated that metallacycles of type **1** react smoothly with bpy/phen furnishing the aryl ruthenium salts **2**/**3**. The pbt ligand also binds as an α-diimine yielding **8**. The **1** → **2**/**3**/**8** conversions are attended with cleavage of the Ru–O and Ru–Cl bonds, (N,N) chelation of bpy/phen/pbt, iminium-phenolato → imine-phenol tautomerization and rotameric *anti* → *syn* isomerization of the phenolic C–O function with respect to coordinated carbon monoxide. In **2**/**3**/**8** the metallated aryl ring is turned away from the α-diimine chelate plane due to steric reasons and this results in significantly different Ru–P lengths and an apparent suppression of carbanionic *trans* influence. The Ru^{III}/Ru^{II} reduction potentials of **2**/**3**/**8** are systematically higher than those of **1**. The Ru → α-diimine MLCT absorption in the visible region makes **2**/**3**/**8** fluorescent.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 202253–202255 corresponding to **2**, **3** and **8** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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