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Synthesis and characterisation of some ruthenium(II) complexes of α -N heterocyclic carboxylic acids—X-ray structures of cis-[Ru(PPh_3)₂(L¹)₂]·2CH₃OH and cis-[Ru(PPh_3)₂(L³H)₂] (L¹H = pyridine 2-carboxylic acid and L³H₂ = imidazole 4,5-dicarboxylic acid)

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Abstract

Synthesis and characterisation of ruthenium(II) complexes of several α -*N* heterocyclic carboxylic acids of the general formula [Ru(PPh₃)₂(L)₂] are reported [LH = pyridine 2-carboxylic acid (L¹H), pyrazine 2-carboxylic acid (L²H), imidazole 4,5-dicarboxylic acid (L³H₂) and pyrazine 2,3-dicarboxylic acid (L⁴H₂)]. All the acids behaved as bidentate N–O chelating donors, the second carboxyl group of the dicarboxylic acids remaining free. Electrochemical behaviour of the complexes was explored by cyclic voltammetry. Single-crystal X-ray analysis of the two complexes *cis*-[Ru(PPh₃)₂(L¹)₂]⁻2CH₃OH and *cis*-[Ru(PPh₃)₂(L³H)₂] led to the elucidation of the structures and showed that in both the complexes the two bulky PPh₃ groups were *cis* to each other. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium(II) complexes; α-N heterocyclic carboxylic acid; X-ray structures; Electrochemistry

1. Introduction

 α -N heterocyclic carboxylic acids like pyridine 2-carboxylic acid, pyrazine 2-carboxylic acid, imidazole 4,5dicarboxylic acid and pyrazine 2,3-dicarboxylic acid are recognised as efficient N–O donors exhibiting diverse mode of coordination [1–3]. Pyridine 2-carboxylic acid, generally known as picolinic acid, is an efficient bidentate N–O donor forming five-membered chelates with simple metal ions [1,4–8] as well as with oxometal cations [9–13]. Though the coordination behaviour of picolinic acid towards ruthenium(II) and ruthenium(III) has been reported previously [14–17], there is still room for further exploration, specially after the recognition of the fact that picolinic acid is a tryptophan metabolite [18] and hence has biological implications. It is well known that pyridine and pyrazine rings are, in general, good π -acceptors and can stabilise the ruthenium(II) acceptor centre, which is a well-recognised π -donor species [19–23] whereas imidazole ring is a poorer π -acceptor, a better π -donor and tend to stabilise ruthenium(III) more than ruthenium(II) [2,24]. Hence imidazole carboxylic acids are expected to have less stabilising effect on the ruthenium(II) acceptor centre compared to the corresponding pyridine and pyrazine carboxylic acid ligands. This trend might be reflected in the values of the ruthenium(II)/ruthenium(III) oxidation couples of the complexes reported in the present study.

In continuation of our studies of metal complexes of such α -*N* heterocyclic mono and dicarboxylic acids we report here the synthesis and characterisation of ruthenium(II) complexes of pyridine 2-carboxylic acid (L¹H), pyrazine 2-carboxylic acid (L²H), imidazole 4,5-dicar-

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boxylic acid $(L^{3}H_{2})$ and pyrazine 2,3-dicarboxylic acid $(L^{4}H_{2})$ [25,26] along with the structural characterisation of *cis*-[Ru(PPh₃)₂(L¹)₂]·2CH₃OH and *cis*-[Ru(PPh₃)₂-(L³H)₂].

2. Experimental

2.1. Materials

Commercial ruthenium trichloride, $RuCl_3 xH_2O$, purchased from Arora Matthey (Calcutta, India) was processed by repeated evaporation to dryness with concentrated HCl. $Ru(PPh_3)_3Cl_2$ was prepared using a previously published procedure [27]. All four carboxylic acids (pyridine 2-carboxylic, pyrazine 2-carboxylic, imidazole 4,5-dicarboxylic and pyrazine 2,3-dicarboxylic acids) used as ligands were purchased from Aldrich and AgNO₃ from BDH. All other chemicals were of reagent grade and used without further purification. Tetraethylammonium perchlorate (TEAP) used for electrochemical work was prepared as reported in the literature [28].

2.2. Physical measurements

Elemental analysis was performed with a Perkin-Elmer 240 CHNS/O analyser. IR and electronic spectra were recorded in a Perkin-Elmer 783 spectrophotometer (as KBr pellets) and on Shimadzu UV-Vis recordspectrophotometer, respectively. ing Solution conductance was measured on a Systronics direct reading conductivity meter (Model 304) and magnetic susceptibility was measured with a PAR vibrating sample magnetometer using Hg[Co(SCN)₄] as the calibrant. Electrochemical data were collected with a BAS CV-27 electrochemical analyser and a BAS Model X-Yrecorder at 298 K. Cyclic voltammetry experiments were carried out with a platinum disc working electrode, platinum auxiliary electrode and Ag | AgCl reference electrode.

2.3. Synthesis of complexes

2.3.1. $Ru(PPh_3)_2(L^1)_2 \cdot 2CH_3OH$ (1) $(L^1H = pyridine 2-carboxylic acid)$

2.3.1.1. Preparation of Ag salt of pyridine 2-carboxylic acid. Pyridine 2-carboxylic acid (123 mg, 1 mmol) was dissolved in water and solid NaHCO₃ (84 mg, 1 mmol) was added in small portions when the pH of the solution became \sim 5. Aqueous solution of AgNO₃ (169 mg, 1 mmol) was then added and stirred for about 3 h. Silver picolinate separated out and was filtered and washed with water. It was dried in vacuum over fused CaCl₂.

To the methanolic (60 ml) suspension of the Ag salt of silver picolinate Ru(PPh₃)₃Cl₂ (960 mg, 1 mmol) was added and the reaction mixture was refluxed for 5 h and filtered hot. AgCl residue was rejected. The resultant orange solution deposited shiny orange crystals of **1** on standing. They were filtered, washed with little benzene and cold methanol and dried in vacuum over fused CaCl₂. Yield: 73%. *Anal.* Calc. for RuC₅₀H₄₆-N₂P₂O₆: C, 64.2; H, 4.92; N, 2.99. Found: C, 63.89; H, 4.81; N, 2.90%. IR (KBr pellet, cm⁻¹): 3540^b, 3436^b, 3400, 1670, 1631, 1596, 1483, 1433, 1348, 756, 697, 640, 532, 450 (b = broad).

2.3.2. $Ru(PPh_3)_2(L^2)_2$ (2) $(L^2H = pyrazine 2-carboxylic acid)$

The compound was prepared as a crystalline brown solid by the same procedure as described above through the Ag salt of pyrazine 2-carboxylic acid instead of pyridine 2-carboxylic acid. Yield: 65%. *Anal.* Calc. for RuC₄₆H₃₆N₄P₂O₄: C, 63.3; H, 4.13; N, 6.42. Found: C, 63.23; H, 4.09; N, 6.38%. IR (KBr pellet, cm⁻¹): 3346^b, 3055^b, 1647, 1578, 1482, 1433, 1339, 1320, 790, 702, 647, 521, 453 (b = broad).

2.3.3. $Ru(PPh_3)_2(L^3H)_2$ (3) $(L^3H_2 = imidazole$ 4,5-dicarboxylic acid)

The compound was obtained as yellow crystals using the same procedure as described above taking imidazole 4,5-dicarboxylic acid in place of pyridine 2-carboxylic acid. Yield: 78%. *Anal.* Calc. for $RuC_{46}H_{36}N_4P_2O_8$: C, 59.0; H, 3.84; N, 5.98. Found C, 58.7; H, 3.72; N, 5.89%. IR (KBr pellet, cm⁻¹): 3360^b, 3060, 2620^b, 1720, 1627, 1500, 1481, 1435, 1375, 1315, 750, 698, 629, 530, 425 (b = broad).

2.3.4. $Ru(PPh_3)_2(L^4H)_2$ (4) $(L^4H_2 = pyrazine 2,3-dicarboxylic acid)$

The compound was prepared as reddish-brown crystalline solid by the same procedure as described above replacing pyridine 2-carboxylic acid by pyrazine 2,3-dicarboxylic acid. Yield: 72%. *Anal.* Calc. for RuC₄₈H₃₆N₄P₂O₈: C, 60.0; H, 3.75; N, 5.83. Found: C, 59.3; H, 3.67; N, 5.82%. IR (KBr pellet, cm⁻¹): 3320^b, 3053, 2923^b, 1715, 1627, 1481, 1434, 1333, 744, 695, 635, 524, 445 (b = broad).

2.3.5. $[Ru(L^1)_2(ophen)] \cdot CH_3OH$ (5) and $[Ru(L^1)_2(bipy)] \cdot CH_3OH$ (6)

 $Ru(PPh_3)_2(L^1)_2$ (94 mg, 0.1 mmol) was dissolved in 20 ml methanol and 0.1 mmol of *o*-phenanthroline (18 mg) or 2,2'-bipyridne (16 mg) was added to it. The mixture was refluxed for 4 h and concentrated to a small volume in a rotary evaporator. Orange crystalline compound separated out. It was filtered and washed with ether and finally dried in a CaCl₂ desiccator. Yield: 52%. *Anal.* Calc. for $RuC_{25}H_{20}N_4O_5$ (5): C, 53.85; H, 3.59; N, 10.05. Found: C, 53.5; H, 3.45; N, 9.89%. IR (KBr pellet, cm⁻¹): 3368^b, 1633, 1594, 1425, 1408, 1346, 663, 558, 454 (b = broad). *Anal.* Calc. for RuC₂₃H₂₀N₄O₅ (**6**): C, 51.78; H, 3.75; N, 10.50. Found: C, 51.2; H, 3.70; N, 10.48%. IR (KBr pellet, cm⁻¹): 3339^b, 1635, 1592, 1465, 1446, 1338, 659, 635, 557, 445 (b = broad).

2.4. X-ray crystallography

Single crystals of *cis*-[Ru(PPh₃)₂(L¹)₂]·2CH₃OH (1) and *cis*-[Ru(PPh₃)₂(L³H)₂] (3) were obtained on allowing the hot filtrate (after precipitating out AgCl) to cool slowly to room temperature. An orange crystal of dimension $0.44 \times 0.40 \times 0.32$ mm for 1 and a yellow needle shaped crystal with dimension $0.40 \times 0.25 \times 0.20$ mm for 3 were selected for X-ray diffraction studies. Compound 1 crystallised in the triclinic space group $P\overline{1}$ and 3 in the monoclinic space group P2(1)/n. The

Table 1

Crystal data and structure refinement parameters for cis- $[Ru(PPh_3)_2(L^1)_2]$ ·2CH₃OH (1) and cis- $[Ru(PPh_3)_2(L^3H)_2]$ (3)

	1	3
Empirical formula	C ₅₀ H ₄₆ N ₂ O ₆ P ₂ Ru	C46H43N4O85P2Ru
Formula weight	933.90	950.85
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	P2(1)/n
Unit cell dimensions		
a (Å)	10.355(11)	13.0803(9)
b (Å)	12.152(10)	11.9546(8)
c (Å)	17.255(14)	29.963(2)
α (°)	86.99(5)	90
β (°)	88.29(8)	102.387(1)
γ (°)	89.16(5)	90
V (Å ³)	2167(3)	4576.2(5)
Ζ	2	4
$D_{\rm calc}~({\rm Mg~m^{-3}})$	1.431	1.380
Absorption coefficient (mm^{-1})	0.489	0.469
F(000)	964	1956
Crystal size (mm)	$0.44 \times 0.40 \times 0.32$	$0.40 \times 0.25 \times 0.20$
θ Range for data collection (°)	2.27–25.00	1.60-25.09
Index ranges	$-12 \le h \le 11$,	$-15 \le h \le 15$,
-	$-14 \leq k \leq 14$,	$-13 \leq k \leq 14$,
	$-20 \le l \le 20$	$-35 \le l \le 27$
Reflections collected	7595	23 480
Data/restraints/ parameters	7227/34/490	8122/0/592
Goodness-of-fit on F^2	1.049	1.037
Final R indices	$R_1 = 0.1197$,	$R_1 = 0.0355,$
$[I > 2\sigma(I)]$	$wR_2 = 0.3088$	$wR_2 = 0.0851$
R indices (all data)	$R_1 = 0.2217,$	$R_1 = 0.0451,$
· · · ·	$wR_2 = 0.3516$	$wR_2 = 0.0906$
Largest difference peak and hole ($e \text{ Å}^{-3}$)	5.095 and -0.926	0.657 and -0.496

crystallographic data and refinement parameters for **1** and **3** are summarised in Table 1. Intensity data were collected at 203(2) and 293(2) K, respectively on a Smart CD diffractometer using graphite monochromatised Mo K α radiation ($\lambda = 0.71073$ Å). The intensities were corrected for Lorentz and polarisation effects and for absorption using the ABSCOR program [29]. The structure was solved by the Patterson method. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares, with a riding model for hydrogen atoms, using the SHELXTL PLUS-PC version [30].

3. Results and discussion

3.1. Crystal structures of cis- $[Ru(PPh_3)_2(L^1)_2]$ ·2CH₃OH (1) and cis- $[Ru(PPh_3)_2(L^3H)_2]$ (3)

A complex of the formula $[Ru(PPh_3)_2(L)_2]$ (L = L¹, L², L³H or L⁴H) can exist in the following isomeric forms I–V.



Structure determination of complexes 1 and 3 by single crystal diffraction technique clearly showed that both are the isomer represented by V, with the cis disposition of the two PPh₃ groups. In both the complexes ruthenium(II) acceptor centre is present in a distorted octahedral N₂P₂O₂ geometry, coordinated to a pair of pyridine 2-carboxylic acid or imidazole 4,5-dicarboxylic acid. The two ligands are in two mutually perpendicular planes each of which contains one triphenylphosphine and carboxylate oxygen of the other ligand. The phosphorous and nitrogen atoms as well as the two carboxylate oxygens are situated trans to each other. Figs. 1 and 2 are the ORTEP plots of 1 and 3, respectively, and the relevant bond lengths and bond angles are given in Tables 2 and 3, respectively. In complex 1 the asymmetric unit contains two methanol molecules. For one of them the carbon atom is disordered and only one possible site (C 100, S.O.F = 0.5) could be located even after repeated trials. Quality of the crystals obtained was not ideal and consequently the crystallographic reliability indices R_1 (0.1197) and wR_2 (0.3088) are rather high. However, the basic structure is correct and so important chemical properties of the complex can be accounted for in terms of its structural features but the metric values should not be



Fig. 1. ORTEP plot of cis-[Ru(PPh₃)₂(L¹)₂]·2CH₃OH (1).



Fig. 2. ORTEP plot of cis-[Ru(PPh₃)₂(L³H)₂] (3).

stressed and the data are utilised only to describe the main features. Bite angles [O(89)-Ru(1)-N(81) and O(79)-Ru(1)-N(71)] of the two bidentate chelating N-O donor picolinate ions are practically the same [77.5(3) and 77.4(4)°, respectively] indicating identical binding of the two picolinate ligands which is quite expected. The rather small bite angle is responsible for the appreciable distortion from the octahedral environment. The P(1)-Ru(1)-P(2) angle [96.26(12)°] is greater than 90° and may be attributed to the steric interactions between the two bulky PPh₃ molecules situated cis to each other. The sum of the all four angles contained in the equatorial plane P(1)-O(79)-N(71)-O(89) [O(89)- $Ru(1)-P(1) = 88.9(2)^{\circ}; O(89)-Ru(1)-N(71) = 91.6(3)^{\circ};$ $O(79)-Ru(1)-P(1) = 101.3(3)^{\circ}$ and N(71)-Ru(1)- $O(79) = 77.4(4)^{\circ}$ is 359.2°, which is less than 360° and

Table 2	
Selected	bond

Selected bond lengths (Å) and bond angles (°) for cis-[Ru(PPh₃)₂-(L¹)₂]·2CH₃OH (1)

Bond lengths			
Ru(1)–N(81)	2.060(10)	C(76)–C(77)	1.472(18)
Ru(1)–O(79)	2.065(8)	C(77)–O(79)	1.266(14)
Ru(1)–O(89)	2.097(9)	C(77)–O(78)	1.306(15)
Ru(1)–N(71)	2.113(9)	N(81)-C(86)	1.327(15)
Ru(1) - P(1)	2.319(4)	N(81)-C(82)	1.410(16)
Ru(1)-P(2)	2.321(4)	C(86)-C(87)	1.474(16)
N(71)–C(76)	1.305(17)	C(87)–O(89)	1.227(15)
N(71)-C(72)	1.362(16)	C(87)–O(88)	1.285(16)
Bond angles			
N(81)–Ru(1)–O(79)	92.9(3)	N(81)-Ru(1)-P(2)	175.0(3)
N(81)–Ru(1)–O(89)	77.5(3)	O(79)-Ru(1)-P(2)	86.9(3)
O(79)–Ru(1)–O(89)	165.9(4)	O(89)-Ru(1)-P(2)	101.8(3)
O(79)-Ru(1)-N(71)	77.4(4)	N(71)-Ru(1)-P(2)	88.8(3)
O(89)–Ru(1)–N(71)	91.6(3)	P(1)-Ru(1)-P(2)	96.26(12)
N(81)-Ru(1)-P(1)	88.7(3)	C(76)–N(71)–C(72)	121.6(10)
O(79)-Ru(1)-P(1)	101.3(3)	C(86)-N(81)-C(82)	121.3(10)
O(89) - Ru(1) - P(1)	88.9(2)	C(21)–P(1)–C(31)	97.4(6)
N(71)-Ru(1)-P(1)	174.7(3)	C(51)-P(2)-C(61)	98.7(6)

Table 3									
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for	cis-
[Ru(PPh,	$_{2}(L^{3}H)$	·2] (3)							

Bond lengths			
Ru(1)–N(11)	2.090(2)	C(12)-C(14)	1.481(4)
Ru(1)–N(21)	2.094(2)	O(11)-C(14)	1.212(4)
Ru(1)–O(23)	2.1191(18)	O(12)-C(14)	1.306(4)
Ru(1)–O(13)	2.1485(17)	N(11)-C(13)	1.367(3)
Ru(1)-P(2)	2.3447(7)	N(11)-C(11)	1.322(3)
Ru(1) - P(1)	2.3458(7)	N(12)-C(11)	1.340(3)
N(21)-C(23)	1.370(3)	N(12)-C(12)	1.362(4)
N(21)-C(21)	1.307(3)	C(13)-C(15)	1.468(4)
N(22)-C(22)	1.366(4)	O(14)-C(15)	1.252(3)
N(22)-C(21)	1.341(3)	O(13)-C(15)	1.286(3)
C(23)-C(25)	1.468(4)	C(22)-C(24)	1.474(4)
O(24)-C(25)	1.256(3)	O(21)-C(24)	1.199(4)
O(23)-C(25)	1.279(3)	O(22)-C(24)	1.319(4)
Bond angles			
N(11)-Ru(1)-O(13)	77.82(7)	C(11)–N(11)–C(13)	106.6(2)
O(13)-Ru(1)-P(1)	103.95(5)	C(11)-N(12)-C(12)	108.8(2)
P(1)-Ru(1)-O(23)	87.54(5)	C(21)-N(21)-C(23)	106.6(2)
O(23)–Ru(1)–N(11)	89.07(8)	C(21)-N(22)-C(22)	107.9(2)
P(2)-Ru(1)-P(1)	101.46(2)	N(11)-C(13)-C(15)	117.5(2)
N(21)-Ru(1)-O(13)	91.49(7)	N(21)-C(23)-C(25)	117.9(2)

points to the fact that the ruthenium(II) centre is somewhat displaced from the equatorial plane. Though both of the two Ru–N bonds are situated *trans* to the two phosphorous atoms, their lengths are found to be unequal [Ru(1)–N(81) = 2.060(10) Å and Ru(1)– N(71) = 2.113(9) Å]. Summing up the appropriate bond lengths [P(2)–Ru(1) + Ru(1)–N(81) = 2.321 + 2.060 = 4.381 Å; P(1)–Ru(1) + Ru(1)–N(71) = 2.319 + 2.113 = 4.432 Å; O(79)–Ru(1) + Ru(1)–O(89) = 2.065 + 2.097 = 4.162 Å] it can be clearly seen that the length of the all three axes of the coordination octahedron around the ruthenium(II) acceptor centre are different. This, along with the displacement of the ruthenium(II) centre from the equatorial plane, points to the fact that the complex cis-[Ru(PPh₃)₂(L¹)₂]·2CH₃OH showed distorted octahedral structure which suggests that it might be chemically active to a significant extent. This is substantiated by exploring the reactivity of this compound towards two neutral bidentate ligands, 2,2'bipyridine and *o*-phenanthroline, leading to the isolation of two new compounds, 5 and 6.

In complex 3, each ligand is attached to the ruthenium(II) centre through its tertiary nitrogen of the imidazole moiety and the carboxylate oxygen of the adjacent carboxyl group-the other carboxyl group remaining idle. Sum of all the four angles contained in the equato-[N(11)-O(23)-P(1)-O(13)] plane rial [N(11)-Ru- $O(13) = 77.82(7)^{\circ}; O(13) - Ru - P(1) = 103.95(5)^{\circ}; O(23) - P(1) = 103.95(5) - P(1) = 103$ $Ru-P(1) = 87.54(5)^{\circ}; N(11)-Ru-O(23) = 89.07(8)^{\circ}]$ is 358.38°, which is a little less than 360° and indicates that the ruthenium(II) centre is marginally displaced from the equatorial plane. The Ru-N(21) and Ru–N(11) bonds [2.094(2) and 2.090(2) Å] are slightly longer than usual due to the trans influence of the coordinated PPh₃ groups. The C=O bond of the coordinated carboxylate moiety [1.252(3) Å] is slightly longer than the C=O of the free carboxyl group [1.212(4) Å]. Also the C-O bond length in the coordinated carboxylate moiety [1.286(3) Å] is shorter than the corresponding bond length of the free carboxyl group [1.306(4) Å]. Such difference is indicative of strong coordination of the carboxylate moiety to the ruthenium(II) centre. The large P(1)-Ru-P(2) angle [101.46(2)°] is consistent with the *cis* disposition of the two bulky PPh₃ groups.

3.2. Infrared spectra

The v(C-O) stretch of the -COOH group of the free ligands lies in the 1700–1730 cm⁻¹ range [31,32]. The involvement of the free -COOH group in intramolecular hydrogen bonding in the complexes is reflected in the presence of an irregularly shaped band in the 3400-2500 cm⁻¹ region. Bands at 3540 and 3436 cm⁻¹ in 1 are due to v(O-H) are indicative of the presence of methanol in the crystal lattice. In the IR spectra of the complexes the v(C-O) bands observed in the spectra of the free ligand are found to decrease significantly and appeared in the 1650-1610 and 1390-1350 cm⁻¹ region corresponding to the $v_{as}(C-O)$ and $v_{s}(C-O)$ modes of the coordinated carboxylate moiety. This considerable difference between v_{as} and v_s is indicative of strong coordination of the carboxylate oxygen to the ruthenium(II) acceptor centre [33-35]. The presence of a medium intensity bands in the 1730-1710 cm⁻¹ region in the IR spectra of 3 and 4 suggests that both the carboxyl groups of the dicarboxylic acids are not involved in coordination. Liberation of CO2 gas on

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putting the complexes in a saturated aqueous solution of NaHCO₃ proved the existence of free carboxyl groups. Coordination from the pyridine nitrogen is indicated by the red shift of the pyridine ring in-plane and out-of-plane deformation vibrations (observed near 630-600 and 430-400 cm⁻¹) by 15-20 cm⁻¹ [36,37]. Characteristic band of coordinated PPh₃ is observed in the spectra of 1-4 which is absent in the spectra of complexes 5 and 6.

3.3. Magnetic moment and conductance

All the complexes are diamagnetic and contain ruthenium(II) centre. The complexes behave as non-electrolytes in DMF solution.

3.4. Electronic spectra

As is usual for ruthenium(II) complexes the electronic spectra are dominated by metal to ligand charge trasfer in the visible region. Spectra of these complexes in DMF exhibit two MLCT transitions around 360-400 (Band-I) and 460-480 nm (Band-II) region [38-40] (Table 4).

3.5. Electrochemistry

Electron transfer behaviour of all the complexes was examined in DMF solution by cyclic voltammetry and the results are presented in Table 4. A reversible ruthenium(II)/ruthenium(III) oxidation $(i_{pa}/i_{pc} \approx 1)$ is observed in the 0.50-0.60 V region for all the complexes.

Table 4 Electronic spectra and cyclic voltammetric data (298 K)

Complex	Absorption in DMF maxima, (nm), $(\varepsilon \times 10^{-3}, M^{-1} cm^{-1})$	Oxidation $E_{1/2}$ (V) ^a , ($\Delta E_{\rm p}$, mV) ^b
1	266 (9400), 306 ^s (4034),	+0.67 (60)
2	366 (6530), 467 (721) 211 (55 008), 261 (13 479), 382 (4573), 479 (915)	+0.60 (40)
3	266 (20 192), 277 (15 943), 392 (3359) 467 (3770)	+0.55 (60)
4	268 (19 157), 275 (16 105), 365 (8056), 480 (1230)	+0.61 (60)
5	265 (39 550), 390 ^s (12 750), 442 (7200), 461 (7300)	+0.71 (50)
6	264 (11 571), 392 (21 226), 430 (3602), 481 (2758)	+0.67 (60)

s: shoulder.

^a Conditions: solvent, DMF; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, Ag | AgCl; solute concentration, 10^{-3} M; scan rate, 0.4 V s⁻¹; and temperature, 298 K. $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential.

$$^{\rm b}\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$$

The one-electron nature of the couple is established by comparing its current height with that of the standard ferrocene/ferrocinium couple under exactly identical experimental conditions. ΔE_p values lie around 60 mV and do not vary with the scan rate. The values of the ruthenium(II)/ruthenium(III) oxidation couples are found to follow the expected trend. $E_{1/2}$ values for the complexes containing pyridine 2-, pyrazine 2-carboxylic acid and pyrazine 2,3-dicarboxylic acid are very near to each other and are higher than that containing imidazole 4,5-dicarboxylic acid.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 153386 and 164529 for compounds *cis*-Ru(PPh₃)₂(L¹)₂·2CH₃OH (1) and *cis*-Ru(PPh₃)₂(L³H)₂ (3), 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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