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Solvent effects in the reactions of 6-phenyl-2,2′-bipyridine with ruthenium(II)

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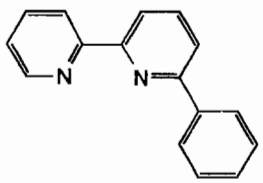
Abstract

The reaction of $[Ru(tpy)Cl_3]$ with the potentially cyclometallating ligand 6-phenyl-2,2′-bipyridine (HL) has been examined in a variety of solvents. In glacial acetic acid the ligand acts as a substituted 2,2′-bipyridine and reacts to give the complex cation $[Ru(tpy)(HL)Cl]^+$, containing a bidentate N,N′-bonded HL ligand. The structure of this complex has been unambiguously established from its ^1H NMR spectrum. In contrast, the use of water as a solvent gives the cyclometallated complex cation $[Ru(tpy)(L)]^+$. In methanol and butan-1-ol, mixtures of these two products are formed. The work has been extended to 2,2′:6′,2″-terpyridines with aromatic substituents in the 4′ position and the complexes have been characterised by ^1H NMR, electronic and FAB mass spectroscopic techniques and also by cyclic voltammetry.

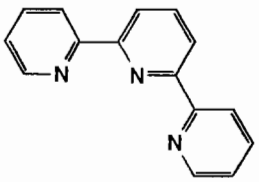
Introduction

Ruthenium oligopyridine complexes have attracted much recent interest [1]. Analogs in which a carbon donor atom replaces one or more of the nitrogen donor set have been shown to possess useful photophysical and photoelectrochemical properties [2]. We have been interested in the development of systematic synthetic methodologies for the preparation of such chelation-stabilised metal-aryls [3–5].

We have previously shown that 2-phenylpyridine may act as a C,N analog of bpy [4] (bpy = 2,2′-bipyridine) and that 6-phenyl-2,2′-bipyridine (HL) may act either as a C,N,N analog of tpy (tpy = 2,2′:6′,2″-terpyridine) or as an N,N analog of bipyridine with a non-coordinated phenyl residue [5]. Recently, Sauvage and co-workers have reported the synthesis and weak luminescence of the cyclometallated species $[Ru(toltpy)(L)][PF_6]$ (toltpy = 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine) [6].



HL



tpy

We now wish to report the systematic syntheses of both cyclometallated and non-metallated products from the reaction of $[Ru(tpy)Cl_3]$ with 6-phenyl-2,2′-bipyridine, and the effect of the solvent on the course of these reactions.

Experimental

^1H NMR spectra were recorded on Brüker WM250 and AM400 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix. Electrochemical measurements were performed using an AMEL model 553 potentiostat, model 567 function generator and model 721 integrator connected to an X-Y recorder via an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum bead working and auxiliary electrodes

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and an Ag–AgCl reference. Acetonitrile, freshly distilled from CaH_2 and then P_4O_{10}, was used as solvent in all cases. The base electrolyte was 0.1 M $[Bu_4^nN][BF_4]$, recrystallised from ethanol/water and rigorously dried. Potentials are quoted versus the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.0$ V), and all potentials were referenced to internal ferrocene added at the end of each experiment. The complexes $[Ru(tpy)Cl_3]$ [7], $[Ru(Phtpy)Cl_3]$ [7], $[Ru(toltpy)Cl_3]$ [7] and $[Ru(tpy)(bpy)Cl][PF_6]$ [8] were prepared according to the published procedures.

Syntheses

6-Phenyl-2,2'-bipyridine (HL)

The ligand was prepared by the general method of Kröhnke [9] as previously described [5]. We have, however, found methanol to be a more reliable solvent than glacial acetic acid for this reaction. ^1H NMR (MeCN): δ 8.68 (1H, d, $H_{6'}$), 8.63 (1H, d, $H_{3'}$), 8.39 (1H, d, H_3), 8.22 (2H, d, H_o), 7.97 (2H, t, $H_{4,4'}$), 7.92 (1H, d, H_5), 7.54 (1H, t, H_p), 7.52 (2H, t, H_m), 7.43 (1H, td, $H_{5'}$).

[Ru(tpy)(HL)Cl][PF6]

$[Ru(tpy)Cl_3]$ (0.029 g, 0.065 mmol) and HL (0.015 g, 0.065 mmol) were heated to reflux in glacial acetic acid (5 cm^3) with 3 drops of *N*-ethylmorpholine for 2 h. The solvent was removed *in vacuo*, and the red solid redissolved in methanol. The red solution was filtered, to remove any traces of unreacted $[Ru(tpy)Cl_3]$, and the filtrate treated with methanolic $[NH_4][PF_6]$ to yield $[Ru(tpy)(HL)Cl][PF_6]$ (0.035 g, 73%). Mass spectrum (+ve FAB): *m/z* 602 $\{Ru(tpy)(HL)Cl\}^+$, 567 $\{Ru(tpy)(HL)\}^+$, 370 $\{Ru(tpy)Cl\}^+$, 334 $\{Ru(tpy)\}^+$. *Anal.* Found: C, 49.6; H, 3.3; N, 9.4. Calc. for $[Ru(tpy)(HL)Cl][PF_6]$: C, 49.8; H, 3.1; N, 9.4%.

[Ru(Phtpy)(HL)Cl][PF6]

The complex was synthesised in an analogous way to $[Ru(tpy)(HL)Cl][PF_6]$ using $[Ru(Phtpy)Cl_3]$ (0.022 g, 0.043 mmol) and HL (0.010 g, 0.043 mmol). The red complex $[Ru(Phtpy)(HL)Cl][PF_6]$ (0.020 g) was obtained in 56% yield. Mass spectrum (FAB): *m/z* 678 $\{Ru(Phtpy)(HL)Cl\}^+$, 642 $\{Ru(Phtpy)(HL)\}^+$, 446 $\{Ru(Phtpy)Cl\}^+$, 410 $\{Ru(Phtpy)\}^+$.

[Ru(toltpy)(HL)Cl][PF6]

The complex was synthesised in an analogous way to $[Ru(tpy)(HL)Cl][PF_6]$ using $[Ru(toltpy)Cl_3]$ (0.023 g, 0.043 mmol) and HL (0.010 g, 0.043 mmol). The red complex $[Ru(Phtpy)(HL)Cl][PF_6]$ (0.021 g, 58%) was obtained. Mass spectrum (FAB): *m/z* 692 $\{Ru(toltpy)(HL)Cl\}^+$, 655 $\{Ru(toltpy)(HL)\}^+$, 460 $\{Ru(toltpy)Cl\}^+$, 424 $\{Ru(toltpy)\}^+$.

[Ru(tpy)(L)][PF6]

$[Ru(tpy)Cl_3]$ (0.029 g, 0.065 mmol) and HL (0.015 g, 0.065 mmol) were heated to reflux in aqueous methanol (5:1 MeOH:H_2O, 10 cm^3) with 3 drops of *N*-ethylmorpholine for 2 h. The purple solution was filtered, to remove any traces of unreacted $[Ru(tpy)Cl_3]$, and the filtrate treated with methanolic $[NH_4][PF_6]$ to yield a purple solid. This solid was purified by column chromatography (silica; acetonitrile:sat. aq. KNO_3:H_2O 28:2:1) followed by anion metathesis, to yield the purple complex $[Ru(tpy)(L)][PF_6]$ (0.017 g, 37%). Mass spectrum (FAB): *m/z* 566 $\{Ru(tpy)(L)\}^+$. *Anal.* Found: C, 52.2; H, 3.3; N, 9.6. Calc. for $[Ru(tpy)(L)][PF_6]$: C, 52.4; H, 3.1; N, 9.8%.

[Ru(Phtpy)(L)][PF6]

$[Ru(Phtpy)Cl_3]$ (0.034 g, 0.065 mmol) and HL (0.015 g, 0.065 mmol) were heated to reflux in aqueous butanol (1:1, 10 cm^3) with 3 drops of *N*-ethylmorpholine for 2 h. The purple solution was filtered, to remove any traces of unreacted $[Ru(tpy)Cl_3]$, and the filtrate treated with silver acetate (0.1 g, excess). The mixture was heated to reflux for 10 min and then filtered through celite. The purple solution was taken to dryness, redissolved in the minimum of hot methanol and loaded directly onto a silica column. The column was eluted with H_2O/MeCN/KNO_3 (acetonitrile:sat. aq. KNO_3:H_2O 28:2:1). The purple complex $[Ru(Phtpy)(L)][PF_6]$ (0.015 g) was obtained (after anion metathesis) from the fast running purple band in 29% yield. Mass spectrum (FAB): *m/z* 642 $\{Ru(Phtpy)(L)\}^+$.

[Ru(toltpy)(L)][PF6]

The complex was synthesised in an analogous way to $[Ru(Phtpy)(L)][PF_6]$ using $[Ru(toltpy)Cl_3]$ (0.034 g, 0.065 mmol) and HL (0.015 g, 0.065 mmol) in methanol/water (5:1, 10 cm^3). After chromatography and anion metathesis, the purple complex $[Ru(toltpy)(L)][PF_6]$ (0.021 g, 41%) was obtained. The complex was identical to that previously reported by Sauvage and co-workers [6]. Mass spectrum (FAB): *m/z* 656 $\{Ru(toltpy)(L)\}^+$.

General method for experiments examining the effect of solvents on the reaction

$[Ru(Ytpy)Cl_3]$ (0.022 mmol, Y = H, Ph or tol) and HL (0.005 g, 0.022 mmol) were heated to reflux in the desired solvent (10 cm^3) with 3 drops of *N*-ethylmorpholine. The reaction was monitored by TLC and heating continued until no starting material remained. In the case of aqueous or methanolic solvents, methanolic $[NH_4][PF_6]$ was then added directly. For other solvent systems, the solvent was removed *in vacuo* and the solid redissolved in methanol before the addition of methanolic $[NH_4][PF_6]$. The solution was cooled and

the resulting solid analysed by ^1H NMR spectroscopy in CD_3CN solution.

Results and discussion

The reaction of one equivalent of the brown, paramagnetic, ruthenium(III) complex $[Ru(tpy)Cl_3]$ with one equivalent of 6-phenyl-2,2′-bipyridine in glacial acetic acid under reflux in the presence of the reducing agent *N*-ethylmorpholine gave a deep red solution. A similar red solution containing the same product was eventually obtained in the absence of the *N*-ethylmorpholine reducing reagent. The reaction was monitored by thin layer chromatography (TLC, silica plate; acetonitrile:sat. aq. KNO_3:H_2O 28:2:1) which showed the major product to be a fast-running red product ($R_F \approx 0.7$; consistent with a unipositive complex). A small impurity of an $[Ru(tpy)_2]^{2+}$ salt ($R_F \approx 0.35$) was also observed. The reaction was complete within 1 h. Prolonged reaction times (48 h) did not lead to the formation of any additional species. The solvent was removed *in vacuo*, and the solid residue was redissolved in methanol. The product was isolated as the hexafluorophosphate salt by the addition of methanolic $[NH_4][PF_6]$. The ^1H NMR spectrum of a solution of the product in CD_3CN indicated that one major product had been obtained with a high degree of purity (>95%). The product is highly soluble in acetonitrile, acetone and methanol and may be recrystallised from any of these solvents to give a red product in about 70% yield. Alternatively, the product of the reaction may be purified by column chromatography (silica; acetonitrile:sat. aq. KNO_3:H_2O 28:2:1) followed by anion metathesis to the hexafluorophosphate salt (giving the complex in about 40% yield). Analytical, mass spectroscopic, ^1H NMR spectroscopic, and electrochemical data are discussed below and confirm that this species is $[Ru(tpy)(HL)Cl][PF_6]$.

In contrast, heating one equivalent of $[Ru(tpy)Cl_3]$ with one equivalent of HL under reflux in butan-1-ol (which has a very similar boiling point to glacial acetic acid) in the presence of *N*-ethylmorpholine led to the formation of a red–purple coloured solution. Again, only short reaction times were required (2 h). TLC showed the formation of the same red product as before and a new, purple, product which ran very slightly faster. Chromatographic analysis indicated that the two products were formed in about a 1:1 ratio. This ratio was confirmed by ^1H NMR spectroscopy. Again, small amounts of $[Ru(tpy)_2]^{2+}$ salts were observed to be formed.

The use of methanol as the solvent for the reaction of $[Ru(tpy)Cl_3]$ with HL had little effect on the reaction time or on the nature of products formed, but significantly altered the product ratio. The ratio of purple:red product was about 10:1 (confirmed by TLC and ^1H NMR spectroscopy). Using 1:1 mixtures of methanol:acetic acid and butan-1-ol:acetic acid gave similar product ratios to those in methanol and butan-1-ol, respectively.

When the reaction was performed in water, it led almost exclusively to the formation of the purple product. Due to the poor solubility of both $[Ru(tpy)Cl_3]$ and HL in water, the reaction proceeded only slowly. It proved to be preferable to conduct the reaction in water with a little added methanol. In this solvent mixture, the purple product was again favoured and reaction times were comparable to those in pure methanol. The purple compound may be purified by column chromatography (to remove trace impurities of the red product and $[Ru(tpy)_2]^{2+}$ salts) followed by anion metathesis to give the complex in 37% yield. The purple complex has been confirmed to be the cyclometallated product $[Ru(tpy)(L)][PF_6]$ and is discussed further below.

No reaction occurred when $[Ru(tpy)Cl_3]$ and HL were heated together in acetonitrile or acetone, presumably due to the complete insolubility of $[Ru(tpy)Cl_3]$ in these solvents.

Heating the red product in water or in alcoholic solvents did not lead to the formation of any of the purple product. Similarly, heating the purple product in glacial acetic acid did not lead to the formation of any of the red product.

To investigate the applicability of this solvent effect, the reactions were repeated using 4′-substituted terpyridines. The reactions of $[Ru(Phtpy)Cl_3]$ (Phtpy = 4′-phenyl-2,2′:6′,2″-terpyridine) or $[Ru(toltpy)Cl_3]$ with HL in glacial acetic acid gave rise to single red products. The reactions went to completion within about 2 h. The red products were shown to be salts of the substituted analogs of $[Ru(tpy)(HL)Cl]^+$.

The low solubility of $[Ru(Phtpy)Cl_3]$ in water and in methanol was such that no products were formed even after prolonged periods of heating under reflux. In butan-1-ol a 1:1 mixture of purple:red products was obtained. The complex $[Ru(toltpy)Cl_3]$ is more soluble, and prolonged heating under reflux in methanol led to the predominant formation of a purple product.

The +ve FAB mass spectrum of the red complex obtained from $[Ru(tpy)Cl_3]$ shows main peaks centred at *m/z* 602 corresponding to $[Ru(tpy)(HL)Cl]^+$ with the correct isotopomer distribution. A smaller peak corresponding to the loss of a chloride (*m/z* 567 $[Ru(tpy)(HL)]^+$) is also observed, as are much smaller fragmentation peaks corresponding to $[Ru(tpy)Cl]^+$ (*m/z* 370) and $[Ru(tpy)]^+$ (*m/z* 334). The ^1H NMR spectrum is sharp and well-resolved (confirming that the ruthenium is in the diamagnetic 2+ oxidation state).

A formulation $[Ru(tpy)(HL)Cl][PF_6]$ is suggested by the mass spectral data, and this is supported by partial microanalysis. The complexes $[Ru(Ytpy)(HL)Cl][PF_6]$ (Ytpy = Phtpy or toltpy) show the same fragmentation patterns in their +ve FAB mass spectra, as does the related complex $[Ru(tpy)(bpy)Cl][PF_6]$.

The ^1H NMR spectrum of the complex $[Ru(tpy)(HL)Cl][PF_6]$ in CD_3CN is shown in Fig. 1 and has been assigned with the aid of a double-quantum filtered COSY spectrum in the region δ 5.8–9.0 ppm (Fig. 2). The connectivity of the doublet at δ 10.15 was determined in a separate decoupling experiment. The spectra of the related complexes with the phenyl and tolyl substituted terpyridines are readily assigned by comparison. These results are presented in Table 1 along with the ^1H NMR spectroscopic data for $[Ru(tpy)(bpy)Cl][PF_6]$.

There are two possible conformers for the cation $[Ru(tpy)(HL)Cl]^+$ and these are shown in Fig. 3. In both of the conformers, the tpy ligand acts as a planar meridional terdentate ligand, but in **1** the chloride ligand is *trans* to the central pyridine ring of the HL ligand, whereas in the second isomer, **2**, it is *trans* to the terminal pyridine ring.

There are insufficient peaks in the ^1H NMR spectrum in CD_3CN for the presence of both conformers in solution. The doublet at δ 10.15 (corresponding to H_6 on the terminal pyridine ring of HL) is typical for an H_6 proton lying adjacent to a coordinated chloride [10]. This unequivocally confirms the conformation of the complex. If the phenyl group were adjacent to the chloride group, as in conformer **2**, then such a peak would be absent. The phenyl group must be therefore be attached to the pyridine ring *trans* to the chloride, i.e. only conformer **1** is formed.

It is instructive to compare the ^1H NMR spectroscopic data for $[Ru(tpy)(bpy)Cl][PF_6]$ and $[Ru(tpy)(HL)Cl][PF_6]$ (identical but for a phenyl ring in the 6 position of the bpy ligand). The environments and the chemical shifts corresponding to the protons of ring A of the bpy fragment and the terminal tpy ring, D, are very similar in the two complexes. Ring B of the bpy fragment shows slight differences which are to be expected since HL bears a phenyl substituent in the 6 position. The major differences are in the shifts of the central tpy ring, E. Compared to the chemical shifts in the unsubstituted complex $[Ru(tpy)(bpy)Cl][PF_6]$, the proton H_{3E} shows an upfield shift of 0.54 ppm while the proton H_{4E} moves upfield by 0.45 ppm in $[Ru(tpy)(HL)Cl][PF_6]$. This upfield shift is a result of the increased shielding by the phenyl ring, C, which must be stacked with the central tpy ring, E. We have observed a similar upfield shift in the related complex [Ru(tpy)-

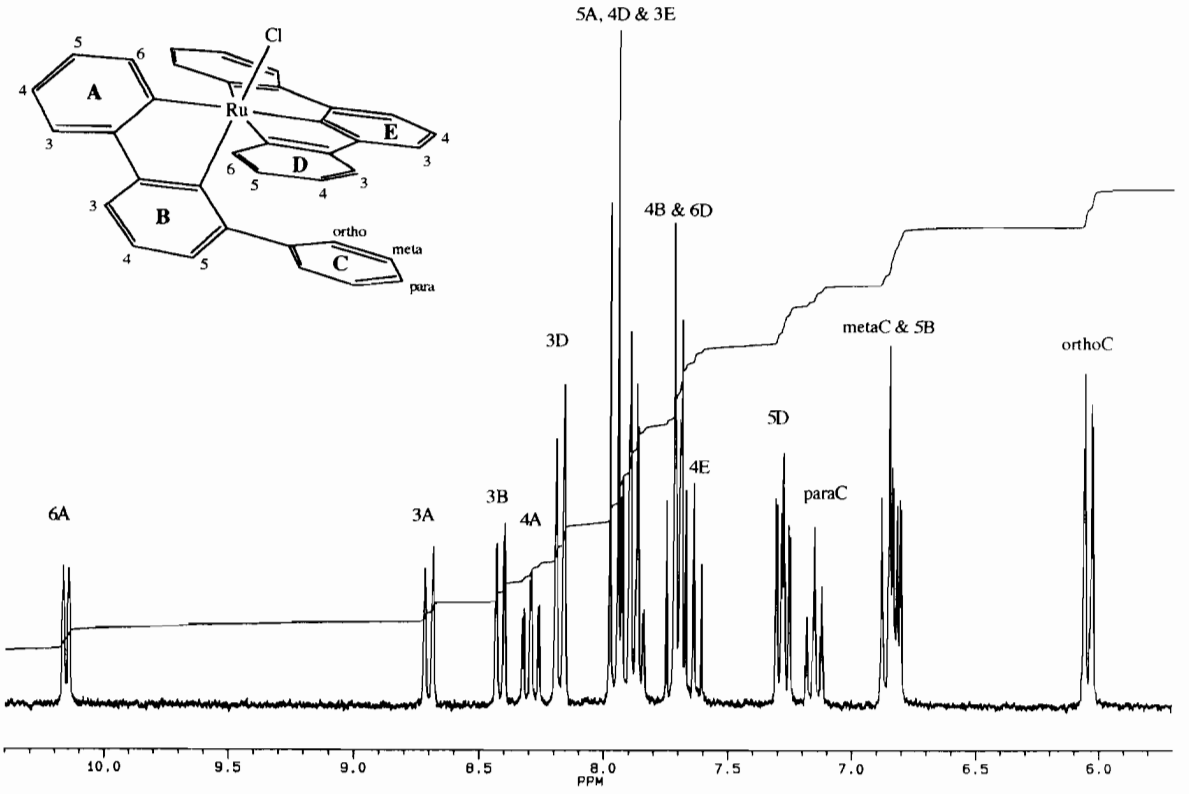


Fig. 1. 250 MHz ^1H NMR spectrum of $[Ru(tpy)(HL)Cl][PF_6]$ in CD_3CN.

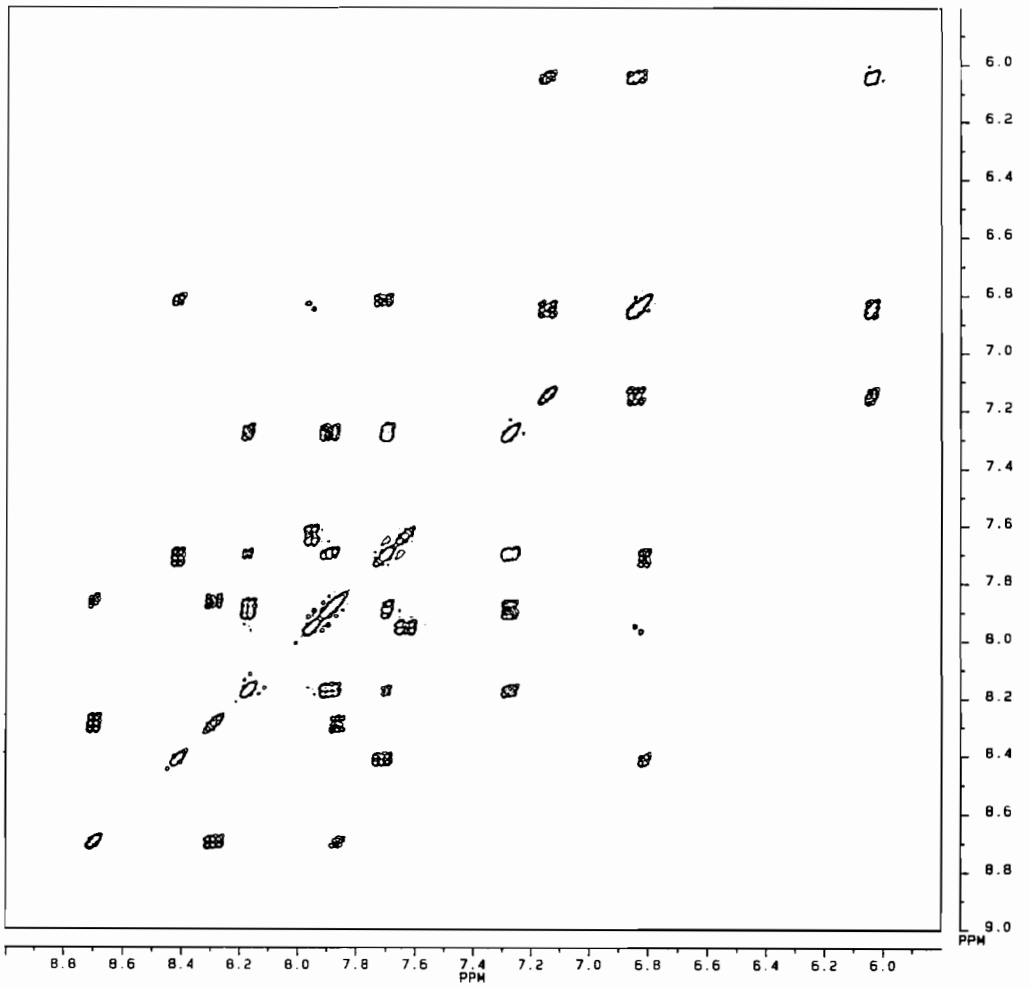


Fig. 2. 400 MHz ^{1}H NMR COSY spectrum of [Ru(tpy)(HL)Cl][PF_6] in CD_3CN (δ 5.8–9.0 ppm). (The peak at δ 10.15 ppm, was assigned by a separate decoupling experiment.)

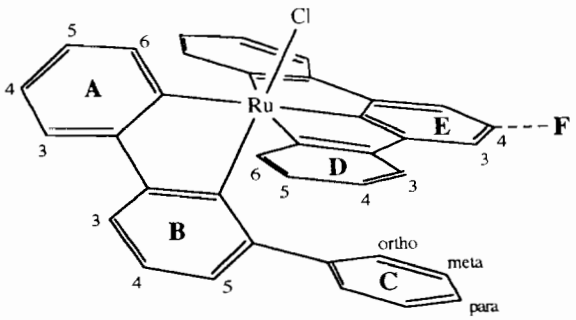
(qtpy)][PF_6]$_2$ (qtpy = 2,2′:6′,2″:6″,2‴-quaterpyridine) where it is a pyridyl ring that is stacked with the central ring (E) of the terpyridine) [11]. This is further proof that it is conformer **1** that is produced. A stacking interaction between the phenyl ring and the central tpy ring would not be possible in conformer **2**.

The symmetry of the tpy ligand and the stacked phenyl ring, C, indicate either that the two rings, C and E, must be directly stacked (and not offset as is often favourable for stacked aromatics [12]) or that the phenyl ring, C, must slide back and forth across the tpy ring, E, rapidly on the ^{1}H NMR spectroscopic timescale. Modelling suggests that an edge-on (T-type) interaction of the two rings is prevented on steric grounds.

The protons on the uncoordinated phenyl ring, C, show a considerable upfield shift from the position of their resonances observed in the spectrum of the free ligand in acetonitrile solution. This effect is greatest for the *ortho* proton ($\Delta\delta$ +2.16 ppm) and falls off rapidly with increasing distance from the interannular C–C bond (*meta* $\Delta\delta$ +0.67 ppm, *para* $\Delta\delta$ +0.37 ppm). It is not possible to say how much of this coordination shift is a result of the stacking with the central tpy ring and how much is due to the coordination of the adjacent bpy fragment.

The cyclic voltammetric behaviour of these redox-active chloro complexes in acetonitrile solution has also been investigated. These data are presented in Table 2 along with those for [Ru(tpy)(bpy)Cl][PF_6]. The complexes all exhibit a reversible oxidation process close to +0.4 V (versus Fc/Fc$^+$) corresponding to the ruthenium(II)/(III) couple. A small and variable oxidation wave at about +1 V (versus Fc/Fc$^+$) is sometimes observed, corresponding to formation of the solvent cation [Ru(tpy)(bpy)(MeCN)]$^+$ in the electrochemical cell, as we have previously noted for the complex [(tpy)Ru(μ-qpy)Ru(tpy)Cl][PF_6]$_3$ (qpy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine) [10]. An irreversible reductive process occurs at about −2.0 V (versus

TABLE 1. ^{1}H NMR spectroscopic data for [Ru(Ytpy)(Xbpy)Cl][PF_6] complexes in CD_3CN



	[Ru(tpy)(bpy)Cl]$^+$ {X=H} {Y=H}	[Ru(tpy)(HL)Cl]$^+$ {X=Ph} {Y=H}	[Ru(Phtpy)(HL)Cl]$^+$ {X=Ph} {Y=Ph}	[Ru(toltpy)(HL)Cl]$^+$ {X=Ph} {Y=Tolyl}
6A	10.20	10.15	10.18	10.18
5A	7.95	7.89	7.9	7.92
4A	8.25	8.29	8.31	8.31
3A	8.58	8.70	8.72	8.71
3B	8.30	8.41	8.42	8.43
4B	7.66	7.71	7.7	7.71
5B	6.94	6.83	6.83	6.83
6B	7.31			
ortho C		6.04	6.07	6.07
meta C		6.85	6.85	6.83
para C		7.15	7.14	7.12
6D	7.66	7.70	7.74	7.72
5D	7.26	7.28	7.30	7.29
4D	7.88	7.86	7.9	7.87
3D	8.37	8.17	8.33	8.30
3E	8.49	7.96	8.21	8.16
4E	8.09	7.64		
ortho F			7.6/7.9	7.48/7.89
meta F			7.6/7.9	7.48/7.89
para F			7.6	
Me (tolyl)				2.50

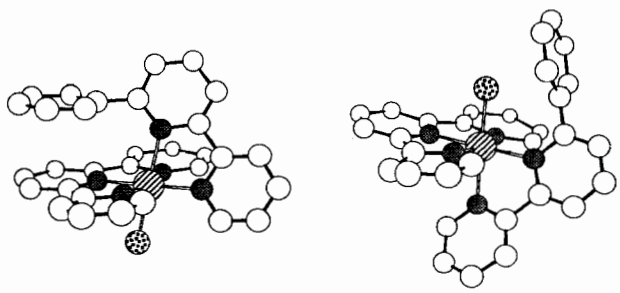


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Fig. 3. The possible conformers of the complex cation, [Ru(tpy)(HL)Cl]$^+$.

Fc/Fc$^+$). The phenyl and tolyl substituents have only a small effect on the redox potentials of these complexes [7]. The ruthenium(II)/(III) oxidation potential for [Ru(tpy)(HL)Cl]$^+$ is slightly, cathodically, shifted with respect to [Ru(tpy)(bpy)Cl]$^+$. This is in accord with our findings for other complexes with a stacked non-coordinated pyridyl residue [11].

The principal features of the electronic spectra of these complexes are presented in Table 3. The broad MLCT band at ~500 nm is unaffected by the introduction of the phenyl group at the 6 position of bpy. A significant shift is observed when the phenyl and tolyl groups are introduced onto the 4′ position of the tpy fragment. This is consistent with this transition being from the metal to the tpy ligand, as expected since the π^*-orbitals of the tpy ligand will be of lower energy than those of the bpy ligand. The small shift to lower energy on the addition of aromatic substituents is consistent with that found in bis(terpyridine) ruthenium(II) systems [7].

TABLE 2. Electrochemical data for [Ru(Ytpy)(Xbpy)Cl][PF_6] complexes in acetonitrile[a]

	X	Y	$[Ru(Ytpy)(Xbpy)Cl]^+$	$[Ru(Ytpy)(Xbpy)MeCN]^+$
$[Ru(tpy)(HL)Cl]^+$	Ph	H	0.45	0.98
$[Ru(Phtpy)(HL)Cl]^+$	Ph	Ph	0.44	0.95
$[Ru(toltpy)(HL)Cl]^+$	Ph	Tol	0.40	1.00
$[Ru(tpy)(bpy)Cl]^+$	H	H	0.42	0.96

[a]All potentials (in V) quoted vs. Fc/Fc^+; $[^nBu_4N][PF_6]$ supporting electrolyte.

TABLE 3. Electronic spectroscopic data for solutions of [Ru(Ytpy)(Xbpy)Cl][PF_6] in acetonitrile

[Ru(tpy)(bpy)Cl][PF_6]					
λ (nm)	502	315	292	280	238
($\epsilon \times 10^{-3}$)	(11.1)	(33.5)	(39.1)	(34.4)	(36.7)
[Ru(tpy)(HL)Cl][PF_6]					
λ (nm)	502	316sh[a]	305	278	237
($\epsilon \times 10^{-3}$)	(10.7)	(35.9)	(38.1)	(27.1)	(33.5)
[Ru(Phtpy)(HL)Cl][PF_6]					
λ (nm)	508	300sh	285		230sh
($\epsilon \times 10^{-3}$)	(10.1)	(39.4)	(44.5)		(35.4)
[Ru(toltpy)(HL)Cl][PF_6]					
λ (nm)	510	300	288		230
($\epsilon \times 10^{-3}$)	(11.9)	(44.2)	(43.3)		(33.5)

[a]sh = shoulder.

The +ve FAB mass spectrum of the purple complex obtained from the reaction of [$Ru(tpy)Cl_3$] with HL shows a main cluster of peaks centred at *m/z* 566, with the correct isotopic distribution, corresponding to $[Ru(tpy)(L)]^+$. No fragmentation peaks are observed. The ^1H NMR spectrum is sharp and well-resolved confirming that the complex is diamagnetic (i.e. that the ruthenium is in the +2 oxidation state). The mass spectrum is thus consistent with a formulation [Ru(tpy)(L)][PF_6] and this is supported by partial microanalytical data. The purple complexes obtained from [$Ru(Phtpy)Cl_3$] and [$Ru(toltpy)Cl_3$] show analogous parent ion peaks in their +ve FAB mass spectra (*m/z* 642 and 656, respectively). The complex $[Ru(toltpy)(L)]^+$ has been previously described by Sauvage and co-workers [6], and the compound reported here is identical in all respects.

The ^1H NMR spectrum of the purple complex [Ru(tpy)(L)][PF_6] in acetonitrile solution (Fig. 4) has been assigned with the aid of a double-quantum filtered COSY experiment (Fig. 5). The presence of the upfield proton at δ 5.7 is indicative of cyclometallation, and corresponds to a proton adjacent to the site of metallation (H_{6C}). The protons 5C and 4C on the metallated ring also experience upfield shifts, both with respect to the free ligand and to the non-metallated complex [Ru(tpy)(HL)Cl][PF_6]. We have observed similar upfield-shifted resonances corresponding to the protons on the metallated ring in the related complex $[Ru(bpy)_2(L')][PF_6]$ (HL' = 2-phenylpyridine) [4]. The symmetry of the tpy ligand about the central ring suggests that the phenyl ring binds in a similar fashion to a pyridyl ring and that the overall structure of the complex cation must be similar to that observed for $[Ru(Ytpy)_2]^{2+}$ [7].

The chemical shifts of the resonances corresponding to the protons on ring A of the metallated HL ligand in [Ru(tpy)(L)][PF_6] are very similar to those for the corresponding protons on rings D. This is slightly surprising as ring A is *trans* to the site of metallation whilst rings D are *cis* to it. The chemical shifts of the protons on these rings are shifted slightly (±0.15 ppm) but not uniformly, with respect to the corresponding protons in $[Ru(tpy)_2][PF_6]_2$ [13]. In the COSY spectrum, a small cross peak is observed between the resonances assigned as 3E and 6C. This peak may reflect a through-space NOE interaction. No similar cross peak is observed between the resonances 3E and 6A. This may indicate that the Ru–C bond is shorter than the Ru–N bond or that there is a slight distortion of the tpy ligand towards the metallated phenyl ring. Unfortunately we have been unable to obtain crystals suitable for X-ray analysis for any of the purple complexes.

The ^1H NMR spectra of solutions of [Ru(Phtpy)(L)]-[PF_6] or [Ru(toltpy)(L)][PF_6] in acetonitrile are assigned by comparison with that of [Ru(tpy)(L)][PF_6] and these data are presented in Table 4.

These complexes are also redox active, and the cyclic voltammogram of [Ru(tpy)(L)][PF_6] in acetonitrile solution exhibits a reversible oxidation at +0.12 V (versus Fc/Fc^+) and a reversible reduction at −2.04 V (versus Fc/Fc^+). The ruthenium(II)/(III) potential is comparable with that of $[Ru(bpy)_2(L')][PF_6]$ (−0.05 V versus Fc/Fc^+) which also possesses an N_5C donor set [4]. Both the oxidative and reductive potentials are shifted to significantly lower potential with respect to $[Ru(tpy)_2][PF_6]_2$ (0.92 V, −1.67 V versus Fc/Fc^+) [1]. This is consistent with the increased σ-donation of the ligand upon changing an N donor atom to a C^- donor. The complexes [Ru(Phtpy)(L)][PF_6] (+0.15 V versus Fc/Fc^+) and [Ru(toltpy)(L)][PF_6] (+0.16 V versus Fc/Fc^+) have similar oxidative potentials.

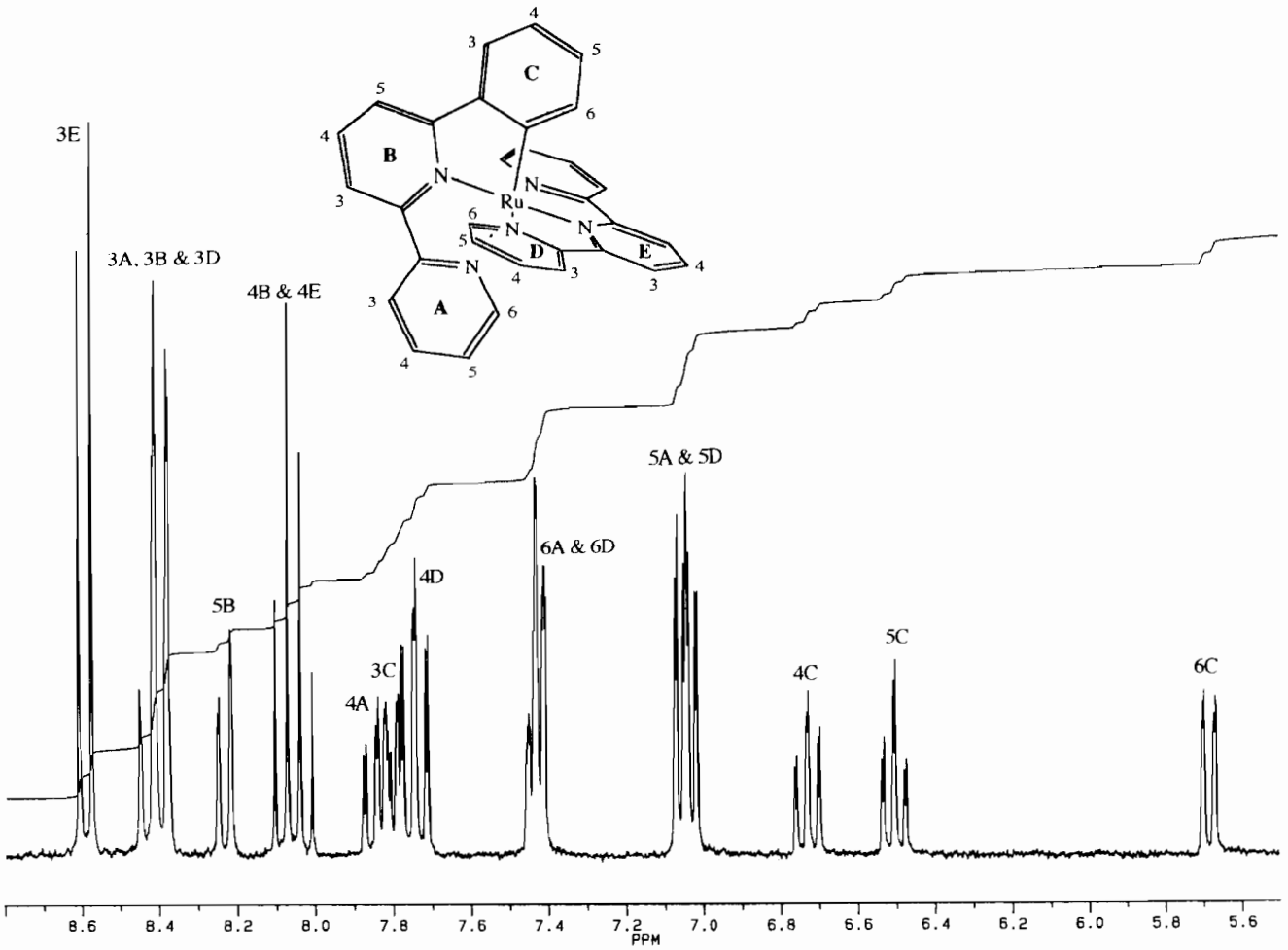


Fig. 4. 250 MHz ^{1}H NMR spectrum of [Ru(tpy)(L)][PF_6] in CD_3CN.

The electronic spectra of the three metallated complexes are similar and are listed in Table 5. The MLCT band (~510 nm) is shifted to higher wavelength with respect to both [Ru(bpy)(tpy)Cl][PF_6] (502 nm) and [$Ru(tpy)_2$][PF_6]$_2$ (475 nm), reflecting the increased σ-donation at the metal centre. The energy of the band is again affected by the presence of substituents on the tpy ligand. The MLCT band at ~380 nm probably corresponds to a transition to the π^* of the metallated ligand (which will be of higher energy than the π^* of tpy) and is relatively unaffected by the substituents on the tpy ligand. Sauvage and co-workers have previously reported the room temperature luminescence of the complex [Ru(toltpy)(L)][PF_6] in alcoholic and nitrilic solvents [6]. The luminescence is weak (of the order of 10^5 times weaker than $[Ru(bpy)_3]^{2+}$) and we have been unable to detect luminescence from any of the three metallated complexes on our less-sensitive fluorescence equipment. It does, however, seem likely that these substituted metallated complexes should exhibit interesting luminescent properties.

The purification (by column chromatography with the acetonitrile/aqueous KNO_3 solvent system) of salts of the metallated complex cations, $[Ru(Phtpy)(L)]^+$ and $[Ru(toltpy)(L)]^+$, is more difficult than that for $[Ru(tpy)(L)]^+$ because the products and the impurities (of $[Ru(Ytpy)(HL)Cl]^+$ salts) run very close together on the column. The addition of an excess of silver(I) acetate to a solution of a mixture of the complexes results in the replacement of the chloride in $[Ru(Ytpy)(HL)Cl]^+$ by a solvent molecule with the precipitation of silver chloride. The metallated product is unaffected by this procedure. The impurity is thus converted to a dipositive ion which is readily separated from the monopositively charged metallated product by chromatography. We have avoided the addition of the silver(I) salt during the preparation of the complexes because of the high affinity of silver(I) for bipyridine units. We anticipated that side reactions between the silver(I) and HL would be detrimental to the yield. However, once the ruthenium(II) complexes have been formed it is unlikely that the chelating ligands, HL or

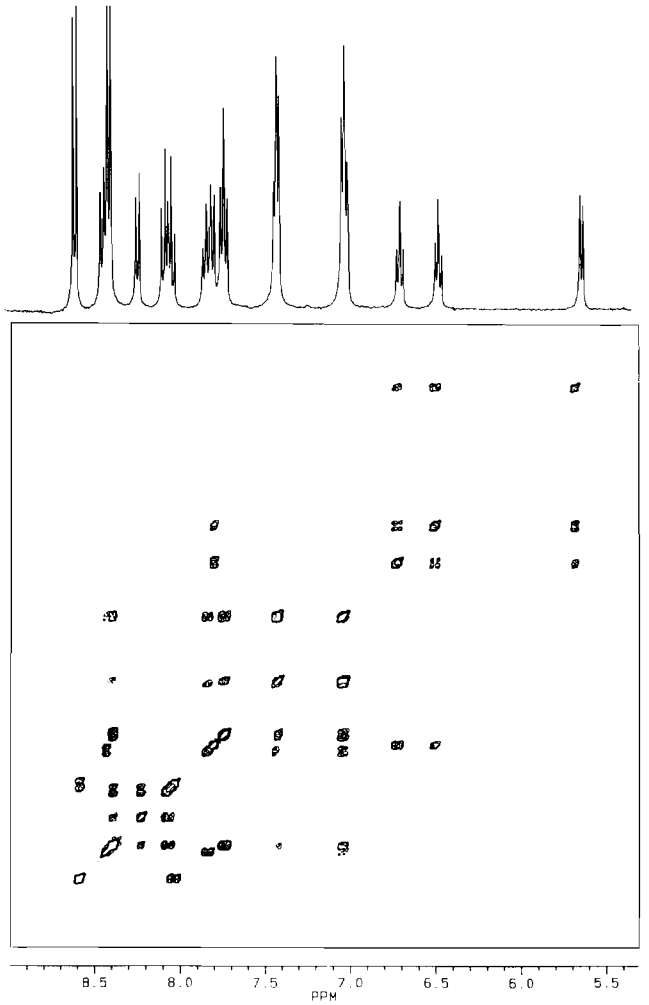


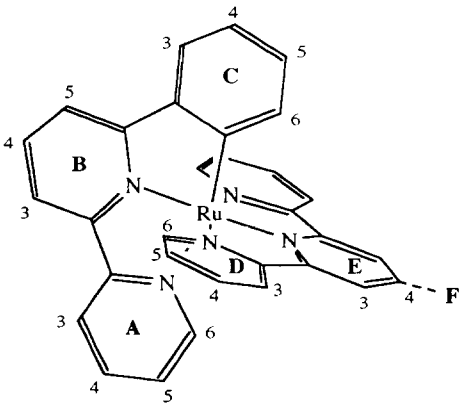
Fig. 5. 400 MHz ^{1}H NMR COSY spectrum of [Ru(tpy)(L)][PF_6] in CD_3CN.

L, will be displaced from the d^6 low spin (kinetically inert) metal centre except under very forcing conditions.

The related complex [Ru(toltpy)(L″)]$^+$ (L″ = bis(2-pyridyl)-1,3-benzene) undergoes an oxidative coupling in the presence of silver(I) [14]. We have not observed any coupling of the metallated complexes containing L during the short periods of heating with silver(I) used in this work, nor have we observed the formation of any ruthenium(III) species by oxidation of the ruthenium(II) complexes with the silver(I) ion.

With a knowledge of the structures of the red and purple products it becomes apparent why the two products are not interconvertible. Heating the red product in aqueous or alcoholic solvents does not result in cyclometallation, as the uncoordinated phenyl group is on the opposite side of the molecule from the chloride which it would have to replace. Metallation would involve a substantial rearrangement of the species and a resultant loss of the stacking interaction (between the phenyl ring and the central ring of the tpy). This

TABLE 4. ^{1}H NMR spectroscopic data for [Ru(Ytpy)(L)][PF_6] in CD_3CN



	[Ru(tpy)L]$^+$ {Y = H}	[Ru(Phtpy)L]$^+$ {Y = Ph}	[Ru(toltpy)L]$^+$ {Y = tolyl}
6A	7.44	7.51	7.45
5A	7.04	7.06	7.05
4A	7.84	7.84	7.80
3A	8.41	8.46	8.42
3B[a]	8.39	8.41	8.40
4B	8.07	8.09	8.07
5B[a]	8.23	8.2	8.25
3C	7.81	7.8	7.80
4C	6.73	6.74	6.73
5C	6.50	6.52	6.52
6C	5.69	5.79	5.78
6D	7.41	7.45	7.45
5D	7.04	7.06	7.05
4D	7.74	7.75	7.80
3D	8.40	8.56	8.55
3E	8.59	8.89	8.87
4E	8.04		
ortho[a] (F)		8.15	8.07
meta[a] (F)		7.7	7.52
para (F)		7.6	
Me (tolyl)			2.50

[a]Ambiguity in the assignment of these resonances.

TABLE 5. Electronic spectroscopic data for solutions of [Ru(Ytpy)(L)][PF_6] in acetonitrile

[Ru(tpy)(L)][PF_6]						
λ (nm)	512	380	317	274[a]	236	
($\epsilon \times 10^{-3}$)	(13.8)	(10.6)	(46.8)	(46.8)	(52.7)	
[Ru(Phtpy)(L)][PF_6]						
λ (nm)	517	383	316	284	275	234
($\epsilon \times 10^{-3}$)	(14.4)	(12.2)	(33.1)	(41.8)	(40.9)	(35.5)
[Ru(toltpy)(L)][PF_6]						
λ (nm)	519	382	316	285[a]	233	
($\epsilon \times 10^{-3}$)	(14.5)	(12.8)	(38.3)	(45.5)	(40.6)	

[a]Broad with a shoulder.

provides a substantial kinetic barrier and the reaction does not occur. Rearrangements involving d^6 low spin metal centres are particularly unfavourable due to the loss of CFSE in the transition state. Heating the purple metallated product in glacial acetic acid cannot lead to the formation of the red product as there is no chloride source. A similar substantial rearrangement would also be required if a chloride source were present.

The presence of only one conformer of the species $[Ru(tpy)(HL)Cl]^+$ in the reaction mixtures obtained from heating $[Ru(tpy)Cl_3]$ with HL is unsurprising. Conformer **1** avoids unfavourable steric interactions between the phenyl group and the chloride and also maximises the favourable stacking interaction between the phenyl ring and the central ring of tpy. This conformer is, therefore, expected to be of lower energy than conformer **2**. Moreover, in conformer **2**, the phenyl ring is in the correct position to displace the chloride and undergo a metallation reaction. It seems probable, therefore, that initial coordination of the ligand HL in the fashion indicated in conformer **2** leads to the formation of the purple metallated product with loss of HCl.

We note that, in this reaction, the solvent effect is such that the higher the dielectric constant of the solvent (and the greater its ability to solvate charged species) the greater the proportion of metallated product formed. A number of explanations are possible – the state of solvation of both starting materials and products will be quite different in glacial acetic acid and water, and the conformation of the ligand HL may also be different. The formation of the metallated and non-metallated products may be dependent on the initial site of coordination by the bipyridine component of HL. The loss of HCl might be more favourable in aqueous solvent than in acetic acid. On the basis of our experimental observations it is not possible to cast further light on the factors controlling the formation of the products. This solvent effect is not applicable to the formation of novel bis(terpyridine)ruthenium(II) complexes; heating $[Ru(tpy)Cl_3]$ with tpy in glacial acetic acid does not lead to the formation of any $[Ru(N,N,N\text{-tpy})(N,N\text{-tpy})Cl]^+$ salts.

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