

# Extended terpyridyl and triazine complexes of d<sup>6</sup>-metal centres

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The reaction of a series of readily available extended terpyridyl and extended triazine ligands with several d<sup>6</sup>-metal centres has been investigated. This has led to the isolation and characterisation of nine new complexes, one of which is the first reported transition metal complex to contain the 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt) ligand. Two of the new complexes have had their molecular structures confirmed *via* X-ray crystallography studies. It has been shown that changes in the electronic properties of the coordinated ligand results in modulation of the electrochemical and photophysical properties of the complex to which it is coordinated. Furthermore, the emission properties of extended terpyridyl complexes incorporating the [Re(CO)<sub>3</sub>(MeCN)]<sup>+</sup> centre suggest that luminescence in these complexes is from an extended terpyridyl based intraligand state.

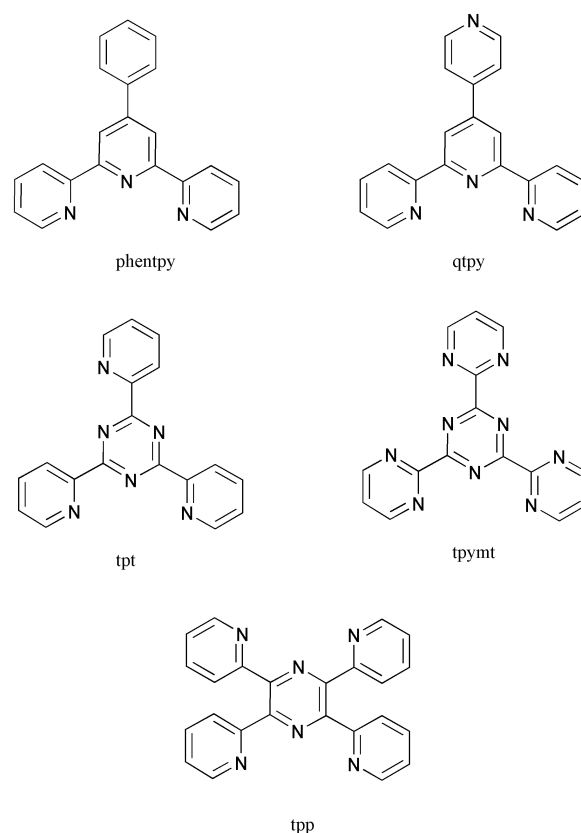
## Introduction

In recent years ruthenium(II) and rhenium(I) complexes containing polypyridyl chelating ligands have been extensively studied. The rich photophysical and redox properties associated with these complexes makes them potentially useful in areas as diverse as light harvesting,<sup>1</sup> electron transfer,<sup>2</sup> non-linear optics,<sup>3</sup> photovoltaics,<sup>4</sup> self-assembly,<sup>5</sup> and probes for biologically relevant molecules such as DNA.<sup>6</sup> Work in this latter area has largely centred on bidentate extended phenanthroline type ligands such as dipyrrodo[3,2-*a*:2',3'-*c*]phenazine<sup>7</sup> (dppz) and 4,7-diphenyl-1,10-phenanthroline (dpphen).<sup>8</sup>

Such work has produced metallo-intercalators with high DNA binding affinities. However, despite the frequent use as ligands for d<sup>8</sup>-metallo-intercalators,<sup>9</sup> tridentate ligands such as terpyridine (tpy) and its analogues are much less studied. Thorp and colleagues have used tpy as an auxiliary ligand in the synthesis of redox active ruthenium systems<sup>10</sup> and also reported that a Ru<sup>IV</sup> complex that incorporates the commercially available extended triazine 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) can redox cleave DNA.<sup>11</sup> These ligands offer other attractive features: they present a planar aromatic system projecting away from the metal centre, can display η<sup>1</sup>, η<sup>2</sup>, or η<sup>3</sup> coordination modes, and are freely available or easily synthesised. By varying the ligands and metal centres used, the charge, chirality, steric demand and electronic properties of this basic architecture may be modulated. Yet, despite recently reported work demonstrating that extended 2,2':6',2''-terpyridine ligands in themselves are highly cytotoxic toward several human tumour cell lines,<sup>12</sup> the DNA binding properties of complexes containing these ligands and related extended triazines have yet to be studied.

As part of a long-term project involving the construction of a library of extended tpy complexes that may function as DNA probes, we report the syntheses of a series of Ru<sup>II</sup> and Re<sup>I</sup> complexes incorporating these ligands, several of which are shown to possess interesting photophysical properties.

The initial study described herein involved five well characterised ligands including two extended triazines: 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt), and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt). Two extended terpyridines; 2,2':4,4'':6,2''-quaterpyridine (qtpy), 4'-phenyl-2,2':6',2''-terpyridine (phentpy) and the structurally related tetra-2-pyridyl-1,4-pyrazine (tpp) were also used—Scheme 1. The coordination of these ligands to three d<sup>6</sup>-metal centres, [Ru(tpy)]<sup>2+</sup>, [(phen)<sub>2</sub>-Ru]<sup>2+</sup>, and [Re(CO)<sub>3</sub>(MeCN)]<sup>+</sup> (tpy = 2,2':6',2''-terpyridine,



Scheme 1 Ligands used in this study.

bpy = 2,2'-bipyridine), was then investigated. Of the 15 possible combinations produced by this matrix only three, [Ru(tpy)-(tpt)]<sup>2+</sup>,<sup>11</sup> [Ru(tpy)(phentpy)]<sup>2+</sup>,<sup>13</sup> and [Ru(tpy)(tpp)]<sup>2+</sup>,<sup>14</sup> have previously been reported. Consequently, we investigated the syntheses of the other 12 members of this series.

## Experimental

### Materials and procedures

The ligands tpymt,<sup>15</sup> qtpy,<sup>16</sup> phentpy,<sup>17</sup> and tpp<sup>18</sup> and complexes [Ru(tpy)Cl<sub>3</sub>]<sup>19</sup> and [Ru(phen)<sub>2</sub>Cl<sub>2</sub>]<sup>20</sup> were all synthesised *via* literature methods. All other chemicals were purchased from

commercial sources and were used as supplied unless otherwise stated. Solvents were obtained from commercial sources and were dried and purified using standard literature methods. Unless otherwise stated all reactions were carried out under an oxygen free nitrogen atmosphere.

### Physical measurements

Unless otherwise stated,  $^1\text{H}$  NMR spectra were recorded on a Bruker AM250 machine working in Fourier transform mode. Mass spectral data was collected on a Micromass Prospec spectrometer operating in positive ion fast atom bombardment mode (FAB+) with a NOBA matrix. UV/Vis spectra were recorded on a Unicam UV2 or Varian-Carey bio-3 UV-Visible spectrometer in twin beam mode. Spectra were recorded in matched quartz cells (Helmer) and were baseline corrected. Emission spectra were recorded on a Hitachi F4500 spectrophotometer operating in luminescence wavelength scan mode. Elemental analyses were obtained using a Perkin-Elmer 2400 analyser working at 975 °C. Cyclic voltammetry were recorded using an EG&G model 362 potentiostat using the EG&G 270 Electrochemical Research Software or Electrochemistry Power-suite software package. A three-electrode cell was used with an  $\text{Ag}^+/\text{AgCl}$  reference electrode separated from a Pt disk working electrode and Pt wire auxiliary electrode. 0.1 mol  $\text{dm}^{-3}$  tetra-*n*-butylammonium hexafluorophosphate in acetonitrile, doubly recrystallised from ethyl acetate/diethyl ether, was used as supporting electrolyte. A scan rate of 200 mV  $\text{s}^{-1}$  was employed.

### Syntheses

**[Ru(tpy)(qtpy)][(PF<sub>6</sub>)<sub>2</sub>], 1[(PF<sub>6</sub>)<sub>2</sub>].** [Ru(tpy)Cl<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O (220 mg, 0.50 mmol), and qtpy (2 eq., 310 mg, 1.0 mmol) were heated to 180 °C with stirring in freshly distilled ethylene glycol (15 cm<sup>3</sup>) for 2 hours. The cooled purple solution was diluted with water (20 ml) and filtered to remove a fine black precipitate. The solution was treated with NH<sub>4</sub>PF<sub>6</sub> (3 eq.), which resulted in the precipitation of a purple solid, that was collected on a sinter, washed with water (2  $\times$  20 cm<sup>3</sup>) and diethyl ether (2  $\times$  20 cm<sup>3</sup>) and air dried. The crude product was dissolved in acetonitrile (2 cm<sup>3</sup>) and chromatographed on silica eluted with 7 : 1 : 1, acetonitrile–water–KNO<sub>3</sub> (sat.). The main purple band containing the product was reduced in volume to 5 cm<sup>3</sup>, and treated with NH<sub>4</sub>PF<sub>6</sub> to precipitate the product. The precipitate was filtered, washed with water (2  $\times$  20 cm<sup>3</sup>), diethyl ether (2  $\times$  20 cm<sup>3</sup>) and dried *in vacuo*. Yield = 240 mg (51.3%), purple solid.  $^1\text{H}$  NMR (d<sup>3</sup>-MeCN):  $\delta_{\text{H}}$  7.10–7.25 (m, 4H), 7.38 (dd, 2H), 7.43 (dd, 2H), 7.88–8.03 (m, 4H), 8.41 (dd, 2H), 8.51 (dm, 2H), 8.67 (m, 2H), 8.75 (dd 2H), 9.02 (m, 3H), 9.08 (d, 2H). FAB-MS; *m/z* (%): 791 (80) [ $\text{M}^+ - [\text{PF}_6]$ ], 646 (100) [ $\text{M}^+ - 2[\text{PF}_6]$ ]. Anal. calc. for C<sub>35</sub>H<sub>25</sub>N<sub>7</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 790.0858. Found: 790.0792. Elemental analysis: Calc. for C<sub>35</sub>H<sub>25</sub>N<sub>7</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 44.97; H, 2.69; N, 10.49. Found: C, 44.99; H, 2.74; N, 10.44%.

**[Ru(tpy)(tpymt)][(PF<sub>6</sub>)<sub>2</sub>], 2[(PF<sub>6</sub>)<sub>2</sub>].** [Ru(tpy)Cl<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O (200 mg, 0.45 mmol) and tpymt (3 eq., 429 mg, 1.362 mmol) were heated to 180 °C in freshly distilled ethylene glycol (20 cm<sup>3</sup>) for 1 hour. The purple solution was diluted with water (20 cm<sup>3</sup>) and filtered to remove unreacted ligand. NH<sub>4</sub>PF<sub>6</sub> was added in excess until precipitation of a purple solid was complete, which was collected by filtration and washed with ice-cold water (2  $\times$  20 cm<sup>3</sup>) and air-dried. The crude product was taken up in the minimum amount of 5 : 3 water–acetone and loaded onto a Sephadex CM-C25 ion exchange chromatography column. Elution with 0.05 M NaCl in 5 : 3 water–acetone removed a brown impurity that was discarded. The desired product was eluted as a purple band with a 0.1 M NaCl solution, and recovered by reducing the volume of eluent, precipitation with NH<sub>4</sub>PF<sub>6</sub> and filtration. The product was washed with ice-cold water (2  $\times$  20 cm<sup>3</sup>) and dried *in vacuo*. Yield = 209 mg (49.46%),

purple solid.  $^1\text{H}$  NMR (d<sup>3</sup>-MeNO<sub>2</sub>):  $\delta_{\text{H}}$  7.15 (td, 2H), 7.42 (dd, 2H), 7.54 (dd, 2H), 7.88 (t, 1H), 8.00 (td, 2H), 8.17 (dd, 2H), 8.60 (d, 2H), 8.64 (t, 1H), 8.91 (d, 2H), 9.14 (dd, 2H), 9.31 (d, 2H). FAB-MS; *m/z* (%): 795 (30) [ $\text{M}^+ - [\text{PF}_6]$ ], 325 (100) [ $\text{M}^{2+} - 2[\text{PF}_6]$ ]. Anal. calc. for C<sub>30</sub>H<sub>20</sub>N<sub>12</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 795.0619. Found: 795.0590. Elemental analysis: Calc. for C<sub>30</sub>H<sub>20</sub>N<sub>12</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 38.35; H, 2.15; N, 17.89. Found: C, 38.75; H, 2.34; N, 18.24%.

**[Ru(phen)<sub>2</sub>(phentpy)][(PF<sub>6</sub>)<sub>2</sub>], 3[(PF<sub>6</sub>)<sub>2</sub>].** [Ru(phen)<sub>2</sub>Cl<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (300 mg, 0.53 mmol) and phentpy (163 mg, 0.53 mmol) were suspended in MeOH (40 cm<sup>3</sup>) and purged with nitrogen for 10 minutes. The suspension was then brought to reflux for 10 hours. After cooling to room temperature the solution was reduced *in vacuo* and then loaded onto a silica chromatography column. The product was eluted with 7 : 1 : 0.5 acetonitrile–water–KNO<sub>3</sub>(sat.), with the desired product being collected as the first main red band. The fractions containing the product were concentrated and addition of NH<sub>4</sub>PF<sub>6</sub> afforded precipitation of the product as its hexafluorophosphate salt, which was collected, washed with iced water (2.25 ml) and dried *in vacuo*. Yield = 210 mg (37.4%), orange solid.  $^1\text{H}$  NMR (d<sup>3</sup>-MeCN):  $\delta_{\text{H}}$  6.79 (td, 1H), 6.80 (m, 2H), 6.99 (dd, 1H), 7.21 (td, 1H), 7.32 (m, 2H), 7.46 (dd, 1H), 7.57 (m, 2H), 7.76 (dd, 1H), 7.80 (dd, 1H), 7.94 (m, 3H), 8.01–8.34 (m, 8H), 8.41 (dd, 1H), 8.58 (dd, 1H), 8.71 (dd, 1H), 8.74 (dd, 1H), 8.79 (d, 1H), 8.87 (d, 2H). FAB-MS; *m/z* (%): 771 (15) [ $\text{M}^{2+} - 2[\text{PF}_6]$ ], 591 (30) [ $\text{M}^+ - \text{phen} - 2[\text{PF}_6]$ ]. Anal. calc. for C<sub>45</sub>H<sub>31</sub>N<sub>7</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 916.1326. Found: 916.1348. Elemental analysis: Calc. for C<sub>45</sub>H<sub>31</sub>N<sub>7</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 50.95; H, 2.95; N, 9.24. Found: C, 50.63; H, 2.74; N, 9.47%.

**[Ru(phen)<sub>2</sub>(qtpy)][(PF<sub>6</sub>)<sub>2</sub>], 4[(PF<sub>6</sub>)<sub>2</sub>].** This complex was prepared in an analogous way to 3, Yield = 31.4%, red solid.  $^1\text{H}$  NMR (d<sup>6</sup>-acetone):  $\delta_{\text{H}}$  7.27 (td, 1H), 7.44 (dd, 1H), 7.74 (dd, 1H), 7.81 (dd, 1H), 7.92–8.06 (m, 4H), 8.23 (m, 4H), 7.36–8.55 (m, 7H), 8.22 (dd, 1H), 8.29 (dd, 1H), 8.32 (dd, 2H), 8.36 (m, 4H), 9.02 (dd, 1H), 9.23 (s, 2H), 9.39 (dd, 1H). FAB-MS; *m/z* (%): 916 (25) [ $\text{M}^+ - [\text{PF}_6]$ ], 772 (40) [ $\text{M}^{2+} - 2[\text{PF}_6]$ ]. Anal. calc. for C<sub>44</sub>H<sub>32</sub>N<sub>8</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 919.1435. Found: 919.1478. Elemental analysis: Calc. for C<sub>44</sub>H<sub>32</sub>N<sub>8</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 49.68; H, 3.03; N, 10.53. Found: C, 50.12; H, 2.95; N, 10.11%.

**[Ru(phen)<sub>2</sub>(tpt)][(PF<sub>6</sub>)<sub>2</sub>], 5[(PF<sub>6</sub>)<sub>2</sub>].** This complex was prepared in an analogous way to 3, Yield = 19.35%, red solid.  $^1\text{H}$  NMR (d<sup>6</sup>-acetone):  $\delta_{\text{H}}$  6.94 (dd, 1H), 7.18 (m, 2H), 7.37 (td, 1H), 7.50 (dd, 1H), 7.59 (dd, 1H), 7.66 (td, 1H), 7.73 (td, 1H), 7.85 (dd, 1H), 7.96 (m, 2H), 8.06–8.25 (m, 4H), 8.33–8.51 (m, 6H), 8.69 (dd, 1H), 8.77 (dd, 1H), 8.84 (dd, 1H), 8.91 (dd, 1H), 8.96 (dd, 1H), 9.42 (dd, 1H), 9.94 (dd, 1H). FAB-MS; *m/z* (%): 919 (40) [ $\text{M}^+ - [\text{PF}_6]$ ], 774 (40) [ $\text{M}^{2+} - 2[\text{PF}_6]$ ]. Anal. calc. for C<sub>42</sub>H<sub>28</sub>N<sub>10</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 919.1184. Found: 919.1129. Elemental analysis: Calc. for C<sub>42</sub>H<sub>28</sub>N<sub>10</sub>RuP<sub>2</sub>F<sub>12</sub>: MeCN: C, 47.84; H, 2.83; N, 13.95. Found: C, 48.18; H, 2.85; N, 13.56%.

**[Ru(phen)<sub>2</sub>(tpp)][(PF<sub>6</sub>)<sub>2</sub>], 6[(PF<sub>6</sub>)<sub>2</sub>].** This complex was prepared in an analogous way to 3, Yield = 18.3%, orange solid.  $^1\text{H}$  NMR (d<sup>6</sup>-acetone):  $\delta_{\text{H}}$  6.73 (br, 1H), 6.92 (br, 1H), 7.17 (m, 1H), 7.22 (td, 1H), 7.51 (dd, 1H), 7.57–7.91 (m, 9H), 8.04 (dd, 1H), 8.12 (m, 2H), 8.18–8.48 (m, 10H), 8.64 (dd, 1H), 8.75–8.84 (m, 2H), 8.98 (dd, 1H), 9.16 (br, 1H). FAB-MS; *m/z* (%): 850 (60) [ $\text{M}^{2+} - 2[\text{PF}_6]$ ], 670 (80) [ $\text{M}^+ - \text{phen} - 2[\text{PF}_6]$ ]. Calc. for C<sub>48</sub>H<sub>32</sub>N<sub>10</sub>RuPF<sub>6</sub> ( $\text{M}^+ - [\text{PF}_6]$ ): 995.1497. Found: 995.1511. Elemental analysis: Calc. for C<sub>48</sub>H<sub>32</sub>N<sub>10</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 50.58; H, 2.83; N, 12.29. Found: C, 50.44; H, 2.95; N, 12.52%.

**[Re(CO)<sub>3</sub>(MeCN)(phentpy)](CF<sub>3</sub>SO<sub>3</sub>), 7(CF<sub>3</sub>SO<sub>3</sub>).** tpt (256 mg, 0.83 mmol) was added to a refluxing solution of (CO)<sub>3</sub>ReCl (300 mg, 0.83 mmol) in toluene (100 cm<sup>3</sup>). The mixture was

**Table 1** Summary of crystallographic data for **3** and **6**

	<b>3</b> <sup>a</sup>	<b>6</b>
Empirical formula	C <sub>48</sub> H <sub>40</sub> F <sub>12</sub> N <sub>8</sub> O <sub>3</sub> P <sub>2</sub> Ru	C <sub>50</sub> H <sub>40</sub> F <sub>12</sub> N <sub>12</sub> O <sub>3</sub> P <sub>2</sub> Ru
<i>M</i>	1166.88	1279.95
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ ( <i>C</i> <sub>1</sub> <sup>i</sup> , no. 2)	<i>P</i> $\bar{1}$ ( <i>C</i> <sub>1</sub> <sup>i</sup> , no. 2)
Crystal dimensions/mm	0.40 × 0.12 × 0.10	0.34 × 0.24 × 0.08
<i>T</i> /K	150(2)	150(2)
<i>a</i> /Å	10.5019(13)	12.420(2)
<i>b</i> /Å	13.6177(17)	12.765(3)
<i>c</i> /Å	17.423(2)	17.803(3)
<i>α</i> /°	87.481(2)	86.927(4)
<i>β</i> /°	72.803(2)	76.677(4)
<i>γ</i> /°	86.833(3)	87.185(4)
<i>U</i> /Å <sup>3</sup>	2375.6(5)	2740.7(9)
<i>Z</i>	2	2
<i>D</i> <sub>c</sub> /Mg m <sup>-3</sup>	1.631	1.551
<i>F</i> (000)	1178	1292
<i>μ</i> (Mo-Kα)/mm <sup>-1</sup>	497	0.443
Final <i>RI</i> (on <i>F</i> ) <sup>a</sup>	0.0599	0.0797
Final <i>wR2</i> (on <i>F</i> ) <sup>a</sup>	0.1577	0.2508

<sup>a</sup> A weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0740P)^2 + 0.00P]$  where  $P = (F_o^2 + 2F_c^2)/3$  was used in the latter stages of refinement. <sup>b</sup> A weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.1756P)^2 + 1.32P]$  where  $P = (F_o^2 + 2F_c^2)/3$  was used in the latter stages of refinement.

refluxed under N<sub>2</sub> for 4 hours and then cooled. The resulting precipitate was collected by filtration and was stirred in DCM (50 cm<sup>3</sup>) for 10 min to remove any unreacted ligand. The orange solid was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 cm<sup>3</sup>) and Et<sub>2</sub>O (2 × 20 cm<sup>3</sup>) and dried *in vacuo* (quantitative yield).

150 mg (0.242 mmol) of the resultant solid and AgCF<sub>3</sub>SO<sub>3</sub> (63 mg, 0.242 mmol) were refluxed for 10 hours in freshly distilled acetonitrile, after which the solvent was removed *in vacuo*. The yellow solid was taken up into CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and filtered through Celite to remove the insoluble AgCl. The mother liquor was reduced to 1 cm<sup>3</sup>, then added to cold pentane (100 cm<sup>3</sup>), resulting in precipitation of the product, which was filtered and dried *in vacuo*. Mass = 135 mg (72%), pale yellow solid. <sup>1</sup>H NMR (d<sup>6</sup>-acetone): δ<sub>H</sub> 2.09 (s, 3H), 7.32 (dd, 1H), 7.63 (m, 3H), 7.76 (td, 1H), 7.96 (t, 1H), 8.11–8.24 (m, 3H), 8.42 (dd, 1H), 8.51 (td, 1H), 8.91 (dd, 1H), 9.1–9.35 (m, 3H). FAB-MS; *m/z* (%): 702 (30) [M<sup>+</sup> – MeCN – CO], 674 (100) [M<sup>+</sup> – MeCN – CO], 552 (80) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN – 2CO]. Anal. calc. for C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>Re (M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>): 621.0937. Found: 621.0947. Elemental analysis: Calc. for C<sub>27</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>ReSF<sub>3</sub>: C, 42.13; H, 2.36; N, 7.28. Found: C, 42.13; H, 2.78; N, 7.01%.

**[Re(CO)<sub>3</sub>(MeCN)(qtpy)][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>, 8[CF<sub>3</sub>SO<sub>3</sub>]**. This complex was prepared in an analogous way to **7**. Yield = 72%, pale yellow solid. <sup>1</sup>H NMR (d<sup>6</sup>-acetone): δ<sub>H</sub> 2.09 (s, 3H), 7.64 (m, 3H), 7.78 (td, 1H), 7.89 (td, 1H), 8.05–8.28 (m, 3H), 8.41 (t, 1H), 8.52 (td, 1H), 8.90 (d, 1H), 9.11–9.34 (m, 3H). FAB-MS; *m/z* (%): 582 (40) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN], 554 (50) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN – CO], 525 (30) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN – 2CO]. Anal. calc. for C<sub>25</sub>H<sub>19</sub>N<sub>5</sub>O<sub>3</sub>Re (M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>): 624.1046. Found: 624.1051. Elemental analysis: Calc. for C<sub>26</sub>H<sub>19</sub>N<sub>5</sub>O<sub>6</sub>ReSF<sub>3</sub>: C, 40.43; H, 2.48; N, 9.06. Found: C, 39.95; H, 2.50; N, 9.16%.

**[Re(CO)<sub>3</sub>(MeCN)(tpt)][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>, 9[CF<sub>3</sub>SO<sub>3</sub>]**. This complex was prepared in an analogous way to **7**. Yield = 67%, green solid. <sup>1</sup>H NMR (d<sup>3</sup>-MeNO<sub>2</sub>): δ<sub>H</sub> 2.14 (s, 3H), 7.8 (m, 2H), 8.06 (td, 1H), 8.19 (m, 1H), 8.30 (d, 1H), 8.98 (m, 4H), 9.25 (m, 2H). FAB-MS; *m/z* (%): 624 (10) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>], 583 (60) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN], 555 (30) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN – CO], 532 (10) [M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub> – MeCN – 2CO]. Anal. calc. for C<sub>23</sub>H<sub>15</sub>N<sub>7</sub>O<sub>3</sub>Re (M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>): 624.0794. Found: 624.0810. Elemental analysis: Calc. for C<sub>24</sub>H<sub>15</sub>N<sub>7</sub>O<sub>6</sub>ReSF<sub>3</sub>: C, 37.31; H, 1.96; N, 12.69. Found: C, 37.70; H, 1.69; N, 13.11%.

### Crystal structure determination

Crystallographic data for **3** and **6** are summarised in Table 1. For both complexes studied, data collected were measured on a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system and complex scattering factors were taken from the program package SHELXTL<sup>21</sup> as implemented on the Viglen Pentium computer. Hydrogen atoms were placed geometrically and refined with a riding model and with *U*<sub>iso</sub> constrained to be 1.2 times *U*<sub>eq</sub> of the carrier atom.

CCDC reference numbers 192147 and 192148.

See <http://www.rsc.org/suppdata/dt/b2/b208211j> for crystallographic data in CIF or other electronic format.

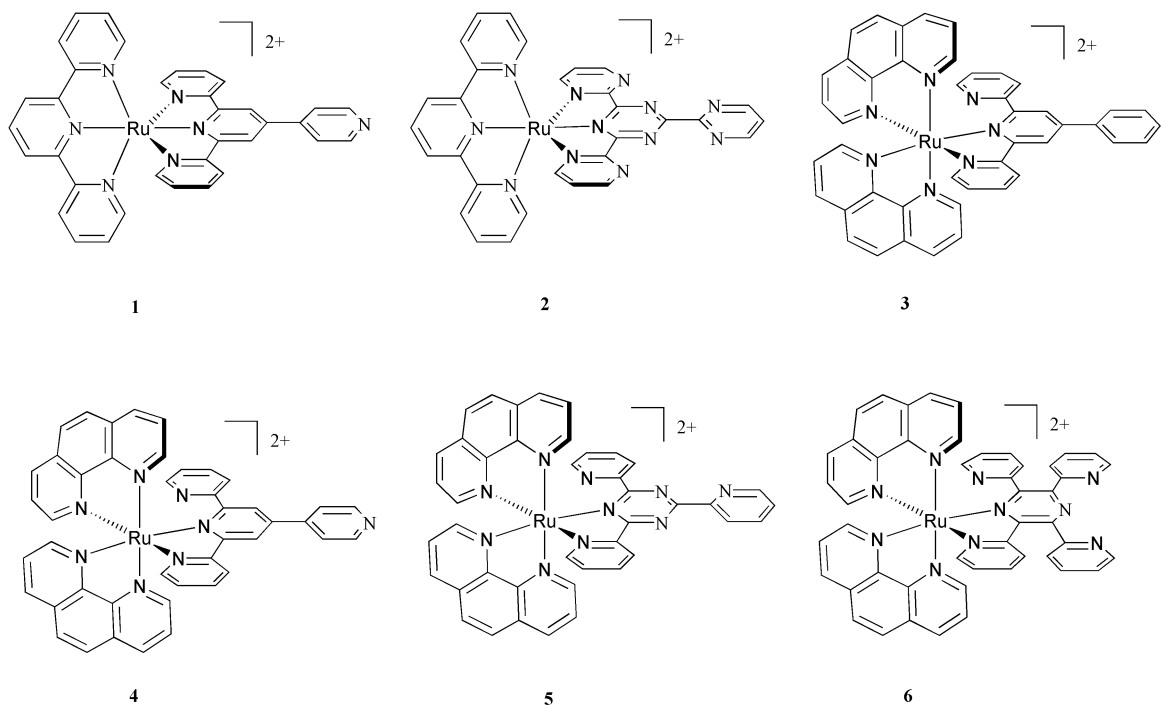
## Results and discussion

### Synthetic studies

**Synthesis of complexes containing the Ru<sup>II</sup>(tpy) domain.** The reaction of qtpy and tpymt with [Ru(tpy)Cl<sub>3</sub>] was first investigated. It was found that the use of low boiling point solvents, such as methanol, ethanol or water, resulted in low yields (<15%) of the required product [Ru(tpy)(qtpy)]<sup>2+</sup>, **1**—Scheme 2. However, at an elevated temperature of 180 °C using freshly distilled ethylene glycol as the solvent the yield of **1**, isolated as a hexafluorophosphate salt, was increased to 50%. The low yield at low temperatures is presumably due to other unisolated kinetically favoured species, formed from the coordination of the 4'-pyridyl moiety. The reaction of tpymt with [Ru(tpy)Cl<sub>3</sub>] proved to be more problematical.

The synthesis of tpymt was first reported alongside tpt.<sup>15</sup> This ligand would appear to be an attractive building block for coordination chemistry as it possesses three terpyridyl-like coordination sites. Yet, despite this, its coordination chemistry is virtually undeveloped. Lippard and Lerner reported that the reaction of tpymt with Pb<sup>II</sup> results in polymetallic products containing intact tpymt. In contrast to this, Cu<sup>II</sup> centres cause hydrolysis of tpymt producing coordinated bis(2-pyrimidyl-carbonyl)amide anion.<sup>22</sup> Since this work in the 1970s, the only literature report involving non-hydrolyzed tpymt comes from the Lehn lab, where it has been used in Pb<sup>II</sup> templated self-assembly.<sup>23</sup> So, surprisingly, although tpymt has been known for over 40 years, no transition metal complexes of this ligand have been reported.

tpymt was synthesised *via* adapted literature procedures.<sup>15,22</sup> The reaction of tpymt with [Ru(tpy)Cl<sub>3</sub>] was then investigated.



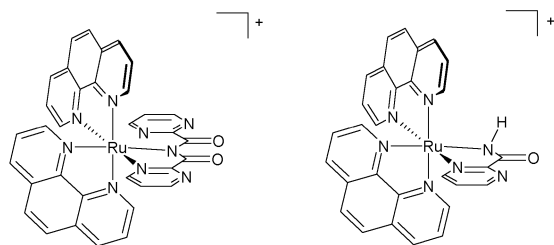
**Scheme 2** New complexes synthesised containing Ru<sup>II</sup>(tpy) and Ru<sup>II</sup>(phen)<sub>2</sub> domains.

We initially used preparative conditions analogous to those reported for tpt, but spectroscopic studies revealed evidence of hydrolysis. A synthesis involving short reaction time and dry degassed solvents was then investigated. Several solvent systems, such as methanol, ethanol, and nitromethane, were tried. However, even when [Ru(tpy)Cl<sub>3</sub>] was first treated with Ag<sup>+</sup>, no reaction occurred. Further studies revealed that a single product could be obtained using anhydrous, N<sub>2</sub> saturated, ethylene glycol as a solvent and a large excess of tpymt. Heating this mixture to 180 °C for 30 minutes resulted in a deep purple solution from which the complex [Ru(tpy)(tpymt)]<sup>2+</sup>, **2**, was isolated in good yields. As far as we are aware this is the first reported transition metal complex of intact tpymt. Indeed, once synthesised **2** is relatively robust. Even after a period of days, aqueous solutions of **1** show no detectable signs of hydrolysis.

**Synthesis of complexes containing the Ru<sup>II</sup>(phen)<sub>2</sub> domain.** [Ru(phen)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O] was refluxed in methanol with two equivalents of the appropriate ligand, the resulting crude product was purified by silica chromatography, leading to the isolation of products **3** to **6** in ca. 20–40% yield—Scheme 2.

All attempts to synthesise the analogous tpymt complex in this series failed due to the hydrolysis of the ligand resulting in both bis(2-pyrimidyl)carboximidato and pyridine-2-carboxylic acid amide species (Scheme 3).

Although the products were not separated they were easily identified through FAB-MS and <sup>1</sup>H-NMR studies. It seems clear from these results that complexes containing coordinated tpymt are appreciably more sensitive towards hydrolysis than



**Scheme 3** Products identified from the reaction of [Ru(phen)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O] with tpymt.

tpt analogues and this may well restrict its use as an oligotopic ligand.

#### Synthesis of complexes containing the Re<sup>I</sup>(CO)<sub>3</sub>(L) domain.

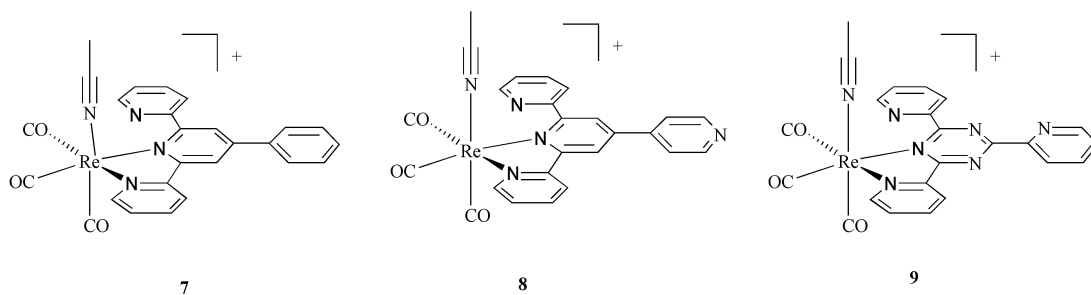
Building on methodology developed by various groups in the 1980s and 1990s for polypyridyl complexes of rhenium(I), we used a two step procedure to obtain water soluble complexes containing the [Re(CO)<sub>3</sub>(MeCN)]<sup>+</sup> metal centre.

Reaction of Re(CO)<sub>3</sub>Cl with the relevant extended terpyridine in refluxing toluene results in the precipitation of the brightly coloured product complex in 90–95% yield. These intermediates, two of which, [Re(CO)<sub>3</sub>Cl(phenpy)]<sup>24</sup> and ([Re(CO)<sub>3</sub>Cl(tpt)]),<sup>25</sup> have been reported previously, are only soluble in relatively nonpolar organic solvents, thus to enhance solubilities in polar and protic solvents the complexes were then treated with AgCF<sub>3</sub>SO<sub>3</sub> in refluxing distilled acetonitrile, resulting in the isolation of charged products **7–9**—Scheme 4. All three of the new complexes display good solubilities in a wide range of solvents. Attempts to carry out analogous reactions with both tpymt and tpp again proved to be problematical, producing low yields of intractable materials. We are currently investigating alternative procedures to obtain such species.

#### Spectral studies

All new complexes were characterised by 1-D and 2-D <sup>1</sup>H-NMR, FAB-, ES- and accurate mass spectroscopy. In several cases, using a combination of 1-D and 2-D techniques such as COSY, it was possible to fully assign spectra. For example, the 400 MHz <sup>1</sup>H NMR spectrum of **1** in d<sup>3</sup>-nitromethane showed only the signals associated with the complex and no impurities—Fig. 1.

The spectrum is well defined and integrates to the required 20 protons. Although the complex shows two-fold symmetry the exact assignments of the protons are still not obvious, but were made with the help of COSY experiments. The four doublets residing at 9.15, 8.91, 8.60 and 8.16 ppm all have large coupling constants of around 9 Hz, indicating they are adjacent to ring nitrogens. In the 2-D experiment the doublet at 8.91 ppm is cross-coupled to the triplet at 8.64 ppm, which integrates to one proton, therefore these signals are assigned as protons j and k respectively. As protons g and i are inequivalent due to



Scheme 4 Complexes synthesised containing the  $\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})$  domain.

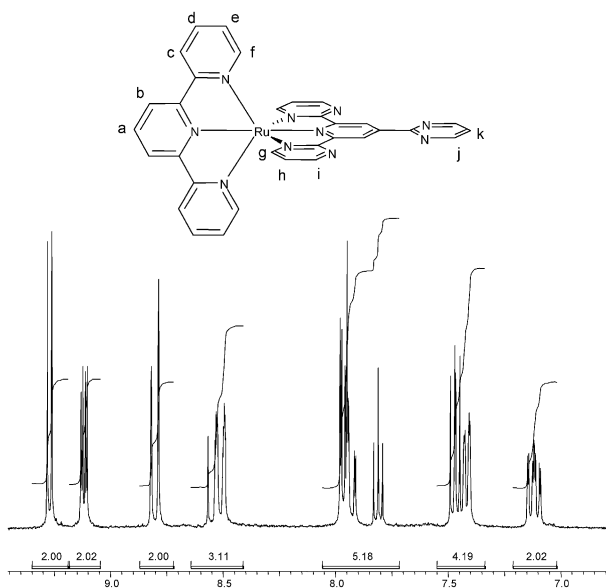


Fig. 1 The 400 MHz  $^1\text{H}$  NMR spectrum of **1** in  $d^3$ -nitromethane.

coordination to ruthenium, they can be assigned to the double doublets at 9.15 and 8.16 ppm. Again in COSY experiments, both of these protons cross couple to the triplet at 7.54 ppm, which is therefore assigned to proton h. The triplet at 7.88 ppm, which integrates to only one proton, is assigned as the central proton, a, on the tpy ligand, with the doublet at 9.30 ppm ( $J = 5$  Hz) being protons b. The remaining doublet at 8.60 ppm with 9 Hz splitting can be assigned to proton f. Analysis of cross coupling allowed the protons at 7.41 (doublet), 7.15 (triplet) and 8.00 ppm (triplet) to be assigned to protons c, d and e respectively. The spectra of complexes incorporating  $(\text{phen})_2\text{-Ru}^{\text{II}}$  and  $\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})$  moieties are more complicated. Although each of the spectra integrates to the expected number of protons, due to the asymmetric coordination mode of the extended terpyridine ligands all aromatic protons are inequivalent. In each  $\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})$  complex the coordinated acetonitrile ligand appears as a singlet, integrating to three protons, at around 2.2 ppm. This shows a downfield shift of around 0.5–1 ppm relative to free acetonitrile and is comparable to values reported elsewhere.<sup>26</sup>

The mass spectra of all the complexes were determined using either FAB or positive ion ES techniques. Typically the spectra show the sequential loss of any counter ions followed by loss of any other monodentate ligands such as pyridine or carbonyl.

### X-Ray crystallography studies

Crystallographic quality crystals of  $[\mathbf{3}][(\text{PF}_6)_2]$  were obtained by vapour diffusion—Fig. 2. Relevant bond lengths and angles are shown in Table 2.

As expected, the phenpty ligand is coordinated in a bidentate  $\eta^2$  mode, with the ruthenium centre taking up a distorted octahedral coordination geometry. *trans*-angles at the  $\text{Ru}^{\text{II}}$  site range from 171.85(14)–173.33(15)°. Ru–N bonds involving the

Table 2 Selected bond lengths (Å) and angles (°) for  $[\mathbf{3}][(\text{PF}_6)_2]$

Ru–N(1)	2.114(4)	Ru–N(5)	2.065(4)
Ru–N(2)	2.052(4)	Ru–N(6)	2.077(4)
Ru–N(4)	2.064(4)	Ru–N(7)	2.062(4)
N(2)–Ru(1)–N(7)	94.37(14)	N(4)–Ru(1)–N(6)	95.88(15)
N(2)–Ru(1)–N(4)	90.01(14)	N(5)–Ru(1)–N(6)	83.63(14)
N(7)–Ru(1)–N(4)	173.68(15)	N(2)–Ru(1)–N(1)	78.51(14)
N(2)–Ru(1)–N(5)	96.86(14)	N(7)–Ru(1)–N(1)	86.38(14)
N(7)–Ru(1)–N(5)	95.08(15)	N(4)–Ru(1)–N(1)	98.97(14)
N(4)–Ru(1)–N(5)	79.86(15)	N(5)–Ru(1)–N(1)	175.25(14)
N(2)–Ru(1)–N(6)	174.08(14)	N(6)–Ru(1)–N(1)	101.09(14)
N(7)–Ru(1)–N(6)	79.71(14)		

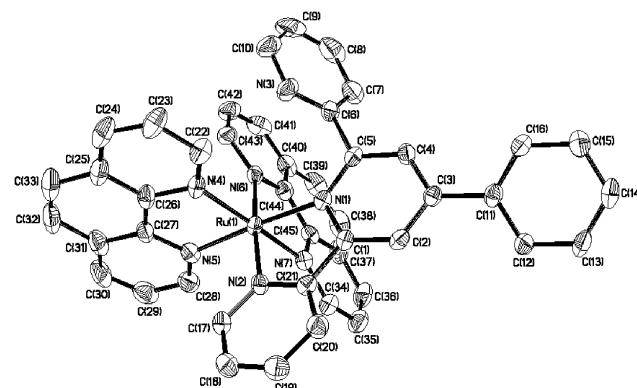


Fig. 2 ORTEP<sup>35</sup> plot of the cation in  $[\mathbf{3}][(\text{PF}_6)_2]$ . Hydrogens and lone pairs are removed for clarity.

phen ligands vary from 2.062(4)–2.077(4) Å. The two coordinated pyridyl rings are distorted away from planarity by a twist angle of 16.1°, while the phenyl ring projects away from the metal centre and displays a 33.8° twist relative to the attached coordinated pyridyl ring. As has been observed in related systems,<sup>27</sup> the uncoordinated pyridyl ring tends to coplanarity with one of the phenanthroline ligands. This stacking leads to a twist of 54.3° relative to the adjacent coordinated pyridyl ring.

Recent studies<sup>28,29</sup> on the coordination chemistry of tpp have demonstrated that it has two possible modes for bidentate coordination. In mode A,  $\eta^2$ -coordination involves nitrogens on pyridine and pyrazine rings, while the other more symmetrical coordination mode, B, involves nitrogens on adjacent pyridyl rings—Fig. 3.

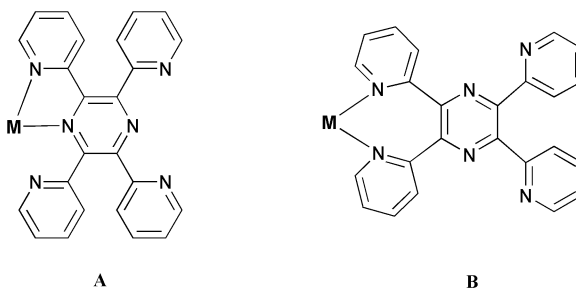
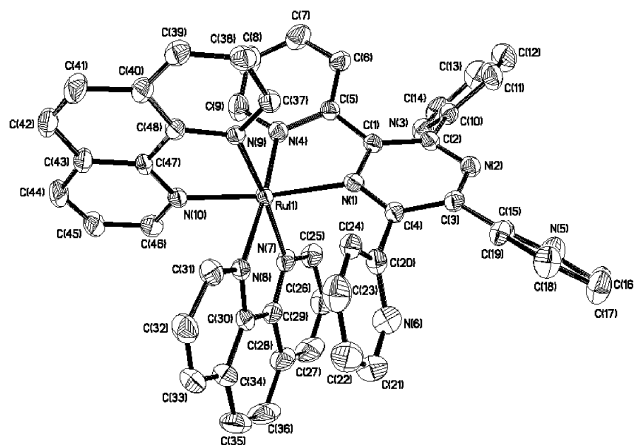


Fig. 3 Possible  $\eta^2$ -coordination modes of tpp.

**Table 3** Selected bond lengths (Å) and angles (°) for [6]((PF<sub>6</sub>)<sub>2</sub>)

Ru–N(1)	2.118(4)	Ru–N(8)	2.088(4)
Ru–N(4)	2.053(4)	Ru–N(9)	2.062(4)
Ru–N(7)	2.076(4)	Ru–N(10)	2.076(4)
N(4)–Ru(1)–N(9)	88.49(16)	N(10)–Ru(1)–N(8)	80.25(15)
N(4)–Ru(1)–N(10)	93.84(16)	N(7)–Ru(1)–N(8)	79.44(16)
N(9)–Ru(1)–N(10)	79.60(15)	N(4)–Ru(1)–N(1)	78.60(15)
N(4)–Ru(1)–N(7)	98.43(16)	N(9)–Ru(1)–N(1)	97.00(14)
N(9)–Ru(1)–N(7)	172.75(15)	N(10)–Ru(1)–N(1)	171.85(14)
N(10)–Ru(1)–N(7)	97.70(15)	N(7)–Ru(1)–N(1)	86.53(15)
N(4)–Ru(1)–N(8)	173.33(15)	N(8)–Ru(1)–N(1)	107.46(15)
N(9)–Ru(1)–N(8)	93.44(15)		

An analysis of the <sup>1</sup>H-NMR data for **6** suggested that for the Ru<sup>II</sup>(phen)<sub>2</sub> centres coordination of tpp was *via* the less symmetric A mode. This hypothesis was confirmed *via* X-ray crystallography studies on the hexafluorophosphate salt of **6**, obtained *via* vapour diffusion of diethyl ether into a nitromethane solution of this complex—Fig. 4. Relevant bond lengths and angles are printed in Table 3.

**Fig. 4** ORTEP plot of the cation in [6]((PF<sub>6</sub>)<sub>2</sub>). Hydrogens and lone pairs are removed for clarity.

The coordination geometry at the Ru atom is distorted octahedral with *trans*-angles at the Ru<sup>II</sup> site ranging from 171.85(14)–173.33(15)°. Ru–N bonds involving the phen ligands vary from 2.062(4)–2.076(4) Å. As observed in related structures,<sup>29</sup> while the Ru–N bond length for the coordinated pyridyl ligand of tpp is comparable to that seen for the phen ligands (2.053(4) Å), the Ru–N distance for the coordinated pyrazine is slightly longer at 2.118(4) Å. There is significant twisting between the pyrazine and coordinated pyridyl rings (21.3°). However, dihedral angles between the pyrazine and uncoordinated pyridyl rings are much higher, ranging between 44.1 and 70.4°. As observed in **3**, this latter value is due to stacking between the uncoordinated pyridyl ring and one of the phenanthroline ligands—the distance between the two rings being 3.354 Å.

Small crystals of **2** were also obtained by diethyl ether vapour diffusion into acetonitrile solutions of its hexafluorophosphate salt. However, due to a poor quality data set and a high degree of counter-ion disorder, consequent X-ray crystallography studies produced a solution that is not of publishable quality. Nevertheless, these studies did confirm the cationic connectivities obtained from NMR studies.

### Electrochemical studies

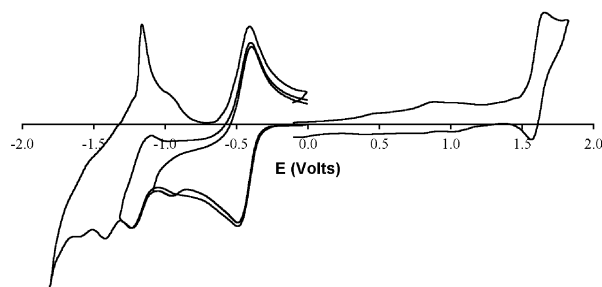
Using cyclic voltammetry the electrochemical properties of the new complexes were studied. All of the ruthenium complexes show characteristic reversible Ru<sup>III/II</sup> oxidation couples. For example, **2** shows a reversible Ru<sup>III/II</sup> oxidation couple at 1.62 V (*vs.* Ag/AgCl) which is anodically shifted by around 300 mV

**Table 4** Electrochemistry data (in volts) for the complexes in acetonitrile solution *vs.* an Ag/AgCl reference electrode

Compound	Oxidations <sup>a</sup>	Reductions
<b>1</b>	1.37	–1.10, –1.41, –1.78 <sup>b</sup>
<b>2</b>	1.62	–0.45, –1.25, <sup>b</sup> –1.45, <sup>b</sup> –1.62 <sup>b</sup>
<b>3</b>	1.28	–1.25, –1.37, –1.45 <sup>b</sup>
<b>4</b>	1.34	–1.13, –1.39, –1.67 <sup>b</sup>
<b>5</b>	1.49	–0.96, –1.41, –1.72 <sup>b</sup>
<b>6</b>	1.43	–0.87, –1.37, –1.59, <sup>b</sup> –1.71 <sup>b</sup>
<b>7</b>	1.36 <sup>b</sup>	–1.15, –1.36, <sup>b</sup> –1.55 <sup>b</sup>
<b>8</b>	1.41 <sup>b</sup>	–1.11, –1.28, <sup>b</sup> –1.60 <sup>b</sup>
<b>9</b>	1.66 <sup>b</sup>	–0.57, –1.02, <sup>b</sup> –1.28 <sup>b</sup>

<sup>a</sup> Unless otherwise stated couples are reversible with  $|I_{pc}/I_{pa}| = 1$  and  $\Delta E_p < 100$  mV. <sup>b</sup> Chemically irreversible couple, therefore only  $E_p$  value quoted.

relative to [(tpy)<sub>2</sub>Ru]<sup>2+</sup>.<sup>30</sup> The first ligand-based reduction, which is reversible, is observed at 0.44 V. Further irreversible ligand-based reductions are seen at more cathodic potentials. While, for reductions above –1.46 V, a stripping peak at 1.15 V is observed on the return sweep—Fig. 5.

**Fig. 5** CV of [6]((PF<sub>6</sub>)<sub>2</sub>) in acetonitrile/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

The other Ru<sup>II</sup> complexes all display similar Ru<sup>III/II</sup> oxidation couples, with potentials being dependant upon the nature of the extended terpyridine ligand. For both the tpyRu<sup>2+</sup> and (phen)<sub>2</sub>Ru<sup>2+</sup> series, coordinated ligands with a higher number of nitrogen atoms result in more anodic oxidation couples—Table 4.

This is consistent with previous studies showing that as ligands become more electron deficient there is concomitant lowering of the ligand LUMO, resulting in enhanced  $\pi$  acceptor properties and more anodic Ru<sup>III/II</sup> oxidation couples.<sup>31</sup> The first ligand-based reduction also reflects the relative electron deficiency within the series, with couples becoming more facile as the number of nitrogens in a ligand increases. As expected, for the corresponding rhenium complexes, the Re<sup>III/II</sup> couple is characteristically irreversible, but nevertheless the same trend in redox potentials are observed.

### Photophysical studies

**Electronic absorption spectra.** The UV-visible absorption spectra of all the complexes were recorded in acetonitrile solution at room temperature. These data are summarised in Table 5.

The low energy bands (350–550 nm) present in all of the Ru<sup>II</sup> complexes are characteristic of Ru(d)  $\rightarrow$  L( $\pi^*$ ) MLCT transitions involving the various pyridyl components of the coordinated ligands. These low energy transitions are similar in both energy and intensity (5000–20000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) to those observed in the numerous tris-phenanthroline and bis-terpyridine type complexes present in the literature, giving rise to their intense red through to purple colours. The intense higher energy bands, typically <300 nm, can be assigned to ligand centred  $\pi \rightarrow \pi^*$  and n  $\rightarrow \pi^*$  transitions.

**Table 5** Photophysical data for complexes **1–9** recorded in acetonitrile solution

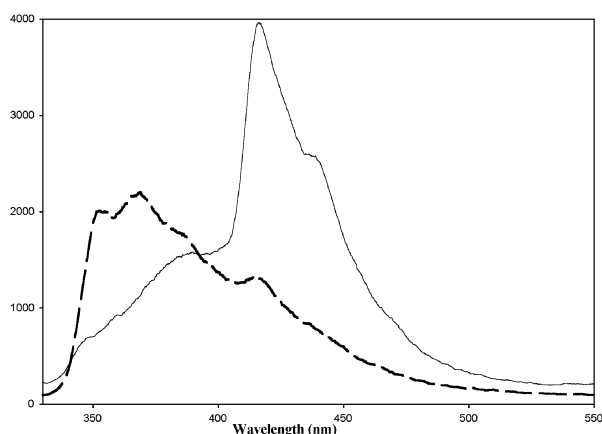
Compound	Absorption $\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )	Emission $\lambda_{\text{em}}/\text{nm}$ ( $\lambda_{\text{ex}}/\text{nm}$ )
<b>1</b>	229 (sh), 238 (25584), 273 (36438), 309 (35498), 324 (sh), 485 (15204)	—
<b>2</b>	269 (35121), 296 (20531), 316 (14572), 330 (18346), 474 (13796)	—
<b>3</b>	220 (60272), 264 (72782), 310 (sh), 385 (7134), 450 (9775)	595 (450)
<b>4</b>	244 (31138), 287 (45977), 450 (10428)	674 (450)
<b>5</b>	264 (62239), 284 (sh), 402 (sh), 432 (9912), 470 (7519)	725 (450)
<b>6</b>	264 (75751), 344 (21820), 427 (11308), 488 (7306)	715 (430)
<b>7</b>	251 (26207), 277 (26735), 328 (17372)	370 (310)
<b>8</b>	253 (28110), 279 (sh), 330 (12727)	417 (310)
<b>9</b>	251 (26604), 295 (27103), 302 (25108), 377 (5171)	—

The rhenium(I) complexes show much simpler absorption spectra, typically consisting of a sharp  $\text{Re(d)} \rightarrow \text{L}(\pi^*)$  transition appearing around 300–320 nm with a tail extending to around 450 nm in the visible region. The ligand centred  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions appear as either two bands or one broad band in the 230–300 nm region of the spectrum. Again these values are typical of other  $\text{Re}^{\text{I}}$  polypyridyl complexes found in the literature.

**Electronic emission spectra.** **1** and **2** are not luminescent at room temperature. This behaviour is consistent with reports on analogous compounds. The lowest lying excited  $^3\text{MLCT}$ , normally centered on the ligand  $\pi^*$  LUMO, is very low lying in complexes related to  $[(\text{tpy})_2\text{Ru}]^{2+}$ , undergoing fast non-radiative deactivation.<sup>32</sup>

**3–6** show characteristic emission spectra for complexes containing  $\text{Ru}^{\text{II}}(\text{phen})_2$  domains.<sup>30</sup> Excitation at 450 nm results in broad unstructured emissions occurring between 595 and 725 nm—Table 5, that are typical of emission from a  $d\pi(\text{Ru}) \rightarrow \pi^*(\text{diimine})$  MLCT. The energy of this emission again correlates with the nature of the ligand incorporated into the complex. The more nitrogen atoms present in the extended terpyridyl ligand, the lower the energy of the emission. These observations are consistent with the trends observed in the electrochemical data, indicating that as the ligand  $\pi^*$  orbital, which is the LUMO complex, becomes lower in energy, there is a corresponding shift to longer wavelength emission. Corresponding studies on the analogous  $\text{Re}^{\text{I}}$  complexes reveal contrasting properties.

It has been pointed out that the photophysical properties of  $[\text{Re}(\text{CO})_3(\text{L})(\text{diimine})]$  complexes are often more easy to interpret than corresponding  $\text{Ru}^{\text{II}}$  systems as they usually only possess one chromophoric diimine ligand.<sup>33</sup> However, it is also known that, in several cases,  $[\text{Re}(\text{CO})_3(\text{L})(\text{diimine})]$  complex emission is actually from intraligand  $\pi\pi^*$  states.<sup>33,34</sup> Within this context, the results of the excitation of the rhenium complexes **7** and **8** are revealing—Fig. 6.



**Fig. 6** Emission spectra of **[7][CF<sub>3</sub>SO<sub>3</sub>]** (broken line) and **[8][CF<sub>3</sub>SO<sub>3</sub>]** (full line) in acetonitrile.

Luminescence in these complexes is only observed on excitation at 310 nm, resulting in high energy structured emissions, suggesting that luminescence in these complexes is not from the  $d\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})$  MLCT manifold. It is known that luminescence from intraligand  $\pi\pi^*$  states results in well-resolved vibronic structure. Thus it seems likely that emission from **7** and **8** is from phenpty and qtpy based states respectively, which is consistent with the energy of the observed luminescence.

Complex **8** possesses the relatively electron deficient qtpy ligand. This will result in a lower  $\pi\pi^*$  energy gap than that of phenpty, and as would be expected from this argument, emission from **8** is at appreciably longer wavelength than that of **7**. At present more detailed photophysical studies are underway to confirm this hypothesis. Complex **9** showed no emission even when excited at a range of different wavelengths. To our knowledge, this is first time the emission properties of  $\text{Re}^{\text{I}}(\text{CO})_3$ - (triazine) systems have been studied and this may or may not be a general phenomenon.

## Conclusions

Nine new complexes containing extended tpy ligands and three different  $d^6$  metal centres have been synthesised. It has been found that the electrochemical and photophysical properties of the complexes are highly dependent on the nature of the incorporated extended terpyridyl ligand. All the complexes show good solubility in a variety of organic solvents. By counterion metathesis such systems are easily rendered water-soluble. Future work will focus on the interaction of this matrix of compounds with biologically significant molecules.

## Acknowledgements

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