Synthesis and structural characterization of some polypyridyl and tris(1H-pyrazol-1-yl)methane ruthenium(II) complexes

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Dedicated to Professor Jim Coxon, teacher and colleague, on the occasion of his 65th birthday

Abstract
Ruthenium(II) complexes of the ligands tris(1H-pyrazol-1-yl)methane (tpm) and 4’-(4-toluyl)-2,2’:6’,2”-terpyridine (ttp) have been prepared and studied as part of a model study for work with a more complicated ditopic ligand. In [Ru(tpm)₂Cl]⁺, one tpm ligand is found to coordinate in a facial tridentate manner, while the second tpm ligand acts as a bidentate ligand. The pendant pyrazolyl group of this second tpm ligand could not be induced to coordinate, even when the chloride ligand is removed by reaction with silver(I) ions. X-ray crystallographic studies are reported for four compounds: [Ru(tpm)(bpy)Cl](PF₆), [Ru(tpm)(bpy)(OH₂)](ClO₄)₂, [Ru(ttp)(bpy)Cl](PF₆), and [Ru(ttp)(bpy)(bpe)](PF₆)₂ (bpe = trans-1,2-bis(4-pyridyl)ethylene).

Keywords: Ruthenium(II); facial coordination; pendant donor; X-ray crystallography

Introduction
The initial motivation for this work was to establish the conditions under which a tpm derivative could be induced to coordinate to a ruthenium centre that already had a tpm ligand attached to it. The intention was to conduct a model study to guide our work with a more complicated and less readily available ditopic terpyridine-tpm ligand, 4’-(4-(2,2,2-tris(1H-pyrazol-1-yl)ethoxymethyl)phenyl)-2,2’:6’,2”-terpyridine (pzt) (Figure 1).
In particular, we hoped that we would be able to achieve regioselective coordination to the ditopic ligand through the use of metal complexes that already had either facial tridentate or meridional tridentate ligands attached to the metal centre. If a facial tridentate ligand is attached to a metal centre, the remaining three coordination sites on an octahedral metal centre must also be disposed in a facial manner. In principle, therefore, the known compound \([\text{Ru(tpm)Cl}_3]^{2-3}\) should be restricted to the tpm binding site of the ditopic ligand, if it is to replace all three chloride ligands with heterocyclic donors. On the other hand, a ttp complex, \([\text{Ru(ttp)Cl}_3]^4\), might be expected to bind to the terpyridyl binding site. In these kinds of reaction, reduction of the ruthenium centre usually occurs during the ligand exchange reaction. The chemistry of the terpyridine type systems is well established, but much less work has been done on tpm based systems. This paper describes the synthesis and structural characterization of some tpm complexes, and also the results of some structural studies on closely related ttp systems.

### Results and Discussion

The coordination chemistry of the ruthenium(II)-tpm system that we have explored is shown in Scheme 1. The reaction of \(\text{Ru(tpm)Cl}_3\), 2, with tpm ligand, 1, afforded a green powder which was collected from a dark blue reaction mixture. \(^1\)H NMR studies on solutions of the green powder sample showed immediately that the green complex was not the bis-tpm complex, 8, that might have been expected if all six pyrazolyl groups of two tpm ligands were coordinated to the ruthenium centre. The \(^1\)H NMR spectrum, shown in Figure 2, contained 14 resonances: twelve in the aromatic region that can be assigned to four sets of pyrazolyl ring protons, and two singlets at around 10.3 and 10.6 ppm assigned to the CH groups of two tpm ligands. Two of the sets of pyrazolyl ring proton signals had integrations twice the size of the other two sets. The \(^{13}\)C NMR data were entirely consistent with these results.

At least two tpm ligands are clearly coordinated to the metal centre, based on the number of NMR signals that are observed, and an ES-MS isotope pattern for a singly charged ion at around

![Figure 1. Ligand pzt](image_url)
565 units is consistent with a formulation of \([\text{Ru(tpm)}_2\text{Cl}]^+\) for the complex ion. The symmetry of the complex that is implied by the NMR data would result if one of the pyrazolyl groups of the second tpm ligand remained uncoordinated and that coordination site were occupied by a chloride ligand. The isotope pattern for a 2+ species at around 265 units is consistent with that complex having lost a chloride ligand in the spectrometer.

Overall, these data are consistent with the product being either structure 3 or the isomer where the methine proton of the bidentate tpm ligand is anti to the chloride ligand. We believe that 3 is the more likely structure for the complex, based on the results of a poorly refined X-ray crystal structure of compound 4 obtained during the synthesis of compounds 4 and 5, and the large change in the chemical shift of one methine proton that was observed on exchanging the chloride ligand for a water ligand. In addition, if the complex were the other isomer there would seem to be no reason why the third pyrazolyl group of the second tpm ligand should not coordinate during the ligand exchange chemistry described below. The same complex, 3, was isolated when either RuCl\(_3\cdot3\text{H}_2\text{O}\) or [Ru(phCN)\(_4\text{Cl}_2\)] were treated with two equivalents of the tpm ligand (Scheme 1).

Reaction of the green complex, 3, with AgClO\(_4\cdot\text{H}_2\text{O}\) in aqueous acetone yielded a blue product which was isolated as the PF\(_6^-\) salt after AgCl was filtered off. Only the starting chloro complex is recovered if the reaction is conducted in dry acetone. \(^1\text{H}\) NMR spectra of the blue complex, 6, contain 15 resonances: twelve resonances in the aromatic region for the four sets of pyrazolyl rings protons, two singlets at around 8.9 and 10 ppm for the CH methine groups hydrogens, and a two proton peak at 6.5 ppm that can be assigned to a coordinated water molecule. ES-MS studies of the blue powder in CH\(_3\text{CN}\) solution show isotope patterns at m/z 693 and 274, that can be assigned to \{[\text{Ru(tpm)}_2(\text{OH})_2]\text{PF}_6^+\}\(^{2+}\), respectively, and these results are entirely consistent with removal of the chloride ligand and its replacement with a water ligand during the reaction. Similar chemistry can be conducted in acetonitrile solution and, under these conditions, the sixth coordination site is occupied by acetonitrile. The \(^1\text{H}\) NMR spectrum of the complex 7 in dms-o-\(_6\), ES-MS in CH\(_3\text{CN}\), and IR of the solid material are all consistent with the presence of the acetonitrile ligand and an uncoordinated pyrazole group.

These results clearly show that while it is possible to remove the chloride ligand, this only occurs if there is a suitable ligand to replace it. The pendant pyrazolyl group does not coordinate. In principle, this ligand substitution reaction could occur for both possible isomers of the isolated bis(tpm) complex, but the reaction will be more difficult for the isomer shown, 3, because coordination of the pendant group can only occur if there is a rearrangement reaction within the coordination sphere.
Scheme 1. Reagents and Conditions: (i) RuCl$_3$.3H$_2$O, EtOH, reflux, 4h; (ii) RuCl$_3$.3H$_2$O or [Ru(ph-CN)$_4$Cl$_2$] (2: 1), EtOH, reflux, 15 min.; (iii) tpm (1 equimolar), EtOH: water (3: 1), reflux, 10 min; (iv) AgClO$_4$, acetone: water (3: 1), reflux, 2 h; (v) NH$_4$PF$_6$; (vi) AgClO$_4$, dry CH$_3$CN, under Ar, reflux, 2 h; (vii) NH$_4$PF$_6$; (viii) CH$_3$CN, acetone: water (3: 1), reflux, 24 h; (ix) AgClO$_4$, acetone, under Ar, reflux, 2 h.
Complexes [Ru(tpm)(bpy)Cl](PF₆), 9, [Ru(tpm)(bpy)(OH₂)][ClO₄]₂, 10, and [Ru(tpm)(bpy)(bpe)](PF₆)₂, 11, provide a good basis with which to compare the properties of the series of bis(tpm) complexes, and were synthesized using literature procedures. All complexes were characterized by NMR and ES-MS techniques. The NMR data for the aqua complex are similar to the reported values for this complex, the chloro complex data are what might be expected, and ES-MS data were also consistent with the proposed structures. The very small change in the NMR data on replacement of the chloride ligand with water in this pair of complexes shows that the nature of the monodentate ligand has very little effect on the chemical shift of the methine proton of a tridentate, facially coordinated tpm ligand. This provides supporting evidence for the isomer assignment made for the bis(tpm) complex above. The large chemical shift change that is observed for one methine proton on exchanging a water ligand for a chloride ligand led us to assign those signals to the bidentate tpm ligand. Further, we conclude that the methine proton must have been in close proximity to the monodentate ligand for such large changes to be observed.

We were more fortunate with this series of complexes in that crystalline material was much more readily obtained. Single crystals of complexes 9 and 10 that were suitable for X-ray structure determination were grown by vapour diffusion of diethyl ether into MeOH solutions of the complexes. Structures of complexes 9 and 10 are shown in Figures 3 and 4, respectively. A further pair of 4′-(4-toluyl)-2,2′:6′,2″-terpyridine (ttp) based complexes, 13 and 14, have also been prepared and crystallographically characterised.
Scheme 2. Reagents and Conditions: (i) bpy, EtOH: water (3: 1), reflux, 5 min; (ii) LiCl, NEt₃, reflux, 10 min; (iii) NH₄PF₆; (iv) AgClO₄, acetone: water (3: 1), reflux, 2 h; (v) bpe, EtOH: water (1: 1), reflux, under Ar, 6 h; (vi) NH₄PF₆.

In both structures 9 and 10, the Ru(II) ions adopt an approximately octahedral geometry with three N atoms (N1, N2, and N5) from tpm ligands coordinated in a facial fashion. Planar bidentate bpy ligands occupy two other positions (N7 and N8), and the sixth coordination site is occupied by a chloride anion in 9 or a water molecule in 10. Bond lengths and bond angles (Table 1) are within the range found for similar structures previously described in the literature.³⁴⁷,⁴⁸ The bond length to the pyrazolyl donor that is trans to the monodentate ligand is shorter than those to the other two donors in both complexes. This may be due to the relative trans influences of the non-tpm ligands in these complexes. However, the bond angle between the pyrazole donors trans to the bpy ligand is marginally smaller than the other angles subtended at ruthenium by the facial tpm ligand. This may be due to steric clashes with the bpy ligand, and provides an alternative explanation for the different bond lengths to the pyrazole donors.
Figure 3. Structure of complex 9 with numbering scheme adopted. One hexafluorophosphate anion is omitted for clarity.

The Ru-Cl bond length in 9 is 2.4114(7) Å, and very similar to that in the ttp complex, 13, at 2.4103(9) Å, while the Ru-OH$_2$ distance in 10 is 2.151(3) Å. In similar pairs of structures described in the literature, the Ru-Cl bond distances (2.395, 2.431, 2.387, and 2.408 Å) of the chloro complexes are also longer than Ru-OH$_2$ distances (2.127, 2.126, 2.119, and 2.139 Å) in the aqua complexes.
Figure 4. Structure of complex 10 with numbering scheme adopted. Two perchlorate anions and one solvated methanol molecule are omitted for clarity.

Both structures 9 and 10 are stabilized by π-π stacking interactions between the plane of bpy ligands of the complexes. The separations between the plane of the bpy ligand of one molecule and the bpy ligand of the adjacent molecule in structures 9 and 10 are 3.4 and 3.5 Å, respectively (Figure 5 and Figure 6). The water ligand in structure 10 is involved in a hydrogen bonding network that involves the methanol solvent molecules and perchlorate anions in the lattice.
Figure 5. π-π stacking interactions between two adjacent molecules in structure 9. The distance between the planes of bpy ligands in the adjacent cations is 3.4 Å.

Figure 6. π-π stacking interactions between two adjacent molecules in structure 10. The distance between the planes of bpy ligands in the adjacent cations is 3.5 Å.
Table 1. Selected bond lengths [Å] and angles [°] for the Ru(II) complexes.

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<th>Ru Complex 9</th>
<th>Ru Complex 10</th>
<th>Ru Complex 13</th>
<th>Ru Complex 14</th>
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<td>2.064(3)</td>
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<td>2.079(3)</td>
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<td>2.151(3)</td>
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Table 2. Crystallographic data

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<th>[Ru(tpm)(bpy)Cl] (PF$_6$), 9</th>
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<th>[Ru(ttp)(bpy)Cl] (PF$_6$), 13</th>
<th>[Ru(ttp)(bpy)(bpe)] (PF$_6$)$_2$·MeOH, 14</th>
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<td>$\text{C}<em>{32}\text{H}</em>{25}\text{ClF}_6\text{N}_5\text{PRu}$</td>
<td>$\text{C}<em>{45}\text{H}</em>{39}\text{F}_{12}\text{N}_7\text{OP}_2\text{Ru}$</td>
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<tr>
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Scheme 3. Reagents and Conditions: (i) EtOH: water (1: 4), reflux, 5 h; (ii) LiCl, reflux, 30 min; (iii) NH₄PF₆; (iv) EtOH: water (1: 1), reflux, 5 h; (v) NH₄PF₆.

The ttp complexes were prepared as shown in Scheme 3. These complexes are new compounds, but they were prepared using reaction conditions that are very similar to those used for the closely related terpyridine complexes. Reaction of ruthenium complex 12 with bpy in boiling aqueous EtOH in presence of LiCl afforded the crude complex 13. After purification on silica gel, the product was collected as its PF₆⁻ salt. ES-MS of the red powder in CH₃CN solution reveals a signal at m/z 616.29 that can be assigned to the [Ru(ttp)(bpy)Cl]+ ion. The observed isotope patterns are a close match to the calculated isotopic distribution patterns for this species.

Single crystals suitable for X-ray were grown by vapour diffusion of diethyl ether into CH₃CN solution of the complex. The structure of the cation is shown in Figure 6. Bond lengths and bond angles are given in Table 1. The bond lengths and angles are within the range found for similar structures described in the literature. In structures 13 and 14, the shortest Ru-N bond length is the Ru-N bond to the central pyridine ring in ttp ligand. The Ru-N bond distances in bpy ligands which are trans to the monodentate ligands (Cl or bpe) are shorter than those in
the other pyridine rings in bpy ligands. These observations are also entirely consistent with the literature values.48-51,55-63

As also shown in Figure 7, the structure is stabilized by π-π stacking interactions between the ttp planes. There are two types of π-π stacking interactions by which the lattice is stabilized. The distance between the planes of the flanking pyridine rings of the adjacent cations is 3.7 Å (centroid-centroid) and the separation of the central pyridine plane in one cation to the flanking pyridine plane in the adjacent cation is approximately 3.6 Å (centroid-centroid).

Figure 6. The molecular structure of complex 13, with a PF$_6^-$ anion omitted for clarity.
Reaction of complex 13 with excess bpe ligand in aqueous EtOH gave complex 14 in good yield (70%). Purification of the crude material was again achieved on silica. The last major fraction was isolated as its PF$_6^-$ salt, a red-orange powder. Again, the complex was characterized by NMR (see Scheme 3 for NMR numbering) and ES-MS techniques. ES-MS isotope patterns at $m/z$ 908.43 and 381.63, can be assigned to $\{[\text{Ru}(\text{ttp})(\text{bpy})(\text{bpe})](\text{PF}_6)\}^+$ and $[\text{Ru}(\text{ttp})(\text{bpy})(\text{bpe})]^2+$, respectively. The observed isotope patterns are also a close match to the calculated isotopic distribution patterns. Single crystals for X-ray crystallography were grown by vapour diffusion of diethyl ether into a mixed CH$_3$CN/MeOH (1:1) solution of the complex and the resulting structure is shown in Figure 8.

The structure of 14 reveals the bpe ligand to be disordered over two orientations in the solid state. The bond angles and distances are consistent with those of similar structures.$^{48,54}$ There are $\pi-\pi$ stacking interactions between the bpe ligands of the adjacent complexes in the lattice of 14.
The separation between the plane of the coordinated pyridine ring of bpe in one cation to the plane of the uncoordinated pyridine ring in the adjacent cation is 3.7 Å (centroid-centroid). (Figure 9).

Figure 8. Molecular structure of complex 14, with two hexafluorophosphate anions and a methanol molecule omitted for clarity. The coordinated bpe ligand exhibits pseudo 2-fold rotational disorder. One of the hexafluorophosphate ions is also disordered.
Figure 9. The π-π stacking interactions in the X-ray structure of complex 14. The distances between the planes of the coordinated pyridine ring of bpe in one complex and uncoordinated pyridine ring in the adjacent cation is 3.7 Å (centroid-centroid).

Experimental Section

General Procedures. All solvents were dried and distilled according to the standard methods prior to use. ¹H NMR and ¹³C NMR spectra were recorded on Varian UNITY-300 or Varian INOVA-500 spectrometers. ¹H NMR and ¹³C NMR chemical shifts are referenced to residual solvent resonances or using TMS as an internal reference. ¹H NMR spectra were assigned using 2D COSY and NOESY techniques. Infrared spectra (400-4000 cm⁻¹) were obtained using a Shimadzu 8201PC Series FTIR interfaced with an Intel 486 PC operating Shimadzu’s HyperIR software. Spectra were obtained using diffuse reflectance method in solid KBr. UV-vis spectra were recorded on a Varian CARY Probe 50 UV-vis Spectrophotometer. Microanalyses were performed at the University of Otago. Solutions (10 µg/mL) for electrospray ionization mass spectrometry (ESI-MS) were recorded using HPLC grade CH₃CN or MeOH or reagent grade...
dmso and MeOH in Micromass LCT Waters 2795 Mass Spectrometer. Mass spectra were measured in positive mode and purified samples have been used.

Pyrazole was obtained from Aldrich and used without further purification. 1,2-Bis-(4-pyridyl)-ethylene (bpe) was used as received from Aldrich. The ligands tris(1H-pyrazol-1-yl)methane (tpm)\(^{64}\) and 4’-(4-toluyl)-2,2’:6’,2”-terpyridine (ttp)\(^{30,65,66}\) were prepared by following literature methods. Complexes [Ru(tpm)Cl\(^3\)], 2,\(^2\) [Ru(tpm)(bpy)Cl]Cl, 9,\(^{2,53}\) [Ru(tpm)(bpy)(OH\(^2\))]ClO\(^4\)\(_2\), 10,\(^2\) [Ru(tpm)(bpy)(bpe)][(PF\(_6\))\(_2\)], 11,\(^{47}\) and [Ru(ttp)Cl\(^3\)], 12,\(^4\) were synthesized according to the literature methods. All other starting materials were obtained commercially and used without further purification.

**Syntheses**

[Ru(tpm)\(^2\)Cl]Cl (3). To [Ru(tpm)Cl\(^3\)], 2, (0.300 g, 0.712 mmol) and LiCl (0.300 g) in water: EtOH (1:3) (40 mL) was added tpm ligand, 1, (0.152 g, 0.712 mmol). The reaction mixture was heated at reflux for 5 min. To the dark green-brown solution was added Et\(_3\)N (12 drops) before it was refluxed for further 10 min to give blue-green solution. The volume of the mixture was reduced to ca. 20 mL on vacuum after it was cooled at r.t. The mixture was kept in the fridge overnight. A green precipitate which was formed was separated from a blue solution by filtration, washed with cold water, then air-dried to afford a green powder. Yield 0.3 g, 57%. \(^1\)H NMR (500 MHz; solvent dmso-\(d_6\)) \(\delta\) 10.58 (1H, s), 10.28 (1H, s), 8.78 (2H, d), 8.74 (1H, d), 8.71 (1H, d), 8.34 (1H, d), 8.04 (2H, d), 7.67 (2H, d), 7.25 (2H, d), 6.94 (1H, dd), 6.83 (2H, dd), 6.66 (2H, dd), 6.62 (1H, d), 6.56 (1H, dd). \(^1\)C NMR (75 MHz; solvent dmso-\(d_6\)) \(\delta\) 147.09 (2C), 146.14 (2C), 145.96 (1C), 144.91 (1C), 135.32 (1C), 133.37 (1C), 130.04 (1C), 109.05 (1C), 108.95 (2C), 108.63 (2C), 108.16 (1C), 80.59 (1C), 75.37 (1C). IR (KBr, cm\(^{-1}\)): 3094 m, 1514 w, 1474 m, 1407 s, 1394 m, 1254 m, 1229 w, 1088 s, 1061 m, 1022 w, 989 w, 910 w, 858 m, 833 m, 787 m, 762 s, 610 w, 588 w. ESI-MS: \(m/z\) 565.2 ([M-Cl]+), 265.03 ([M-Cl]+). UV-vis (CH\(_3\)CN): \(\lambda_{\text{max}} (\varepsilon) = 230.0 (9300), 280.0 (4900), 290.0 (4900), 335.0 (7300)\) nm (L mol\(^{-1}\) cm\(^{-1}\)).


[Ru(tpm)\(^2\)(H\(_2\)O)][ClO\(^4\)]\(_2\) (5). [Ru(tpm)Cl\(^2\)Cl], 3, (0.15 g, 0.25 mmol) and AgClO\(_4\).H\(_2\)O (0.112 g, 0.5 mmol) in 30 mL of acetone were heated at reflux for 4 h. AgCl precipitate was filtered off and the blue solution was taken to dryness in a rotary evaporator. Slow evaporation of acetonitrile solution of the mixture afforded some pale green crystals with poor quality. X-ray diffraction revealed that compound 4 was formed as a side product. The bulk blue solution was separated from the pale crystals through filtration. The product was recrystallized form acetonitrile, washed with diethyl ether, and air-dried to afford a blue powder. Yield 0.17 g, 85%. \(^1\)H NMR (300 MHz; solvent dmso-\(d_6\)) \(\delta\) 10.03 (1H, s), 8.89 (1H, s), 8.78 (3H, m), 8.66 (1H, d), 8.38 (1H, d), 8.15 (2H, d), 7.70 (2H, d), 7.37 (2H, d), 6.99 (1H, t), 6.94 (2H, t), 6.74 (2H, dd), 6.68 (1H, dd), 6.56 (1H, d), 6.42 (2H, b s). IR (KBr, cm\(^{-1}\)): 3140 b, 3042 w, 1628 w, 1520 w, 1441 m, 1355 m, 1310 m, 1285 m, 1252 m, 1231 w, 1094 ss, 1061 m, 991 w, 962 w, 845 s,
756 s, 606 m, 559 ssh. ESI-MS: m/z 629.09 ([M-Cl]+), 565.11 ([M-ClO₄]+), 265.06 ([M-Cl-ClO₄]²⁺).

[Ru(tpm)₂(H₂O)][PF₆]₂ (6). [Ru(tpm)₂Cl]Cl, 3, (0.15 g, 0.25 mmol) and AgClO₄·H₂O (0.112 g, 0.5 mmol) in 30 mL of acetone: water (3: 1) were heated at reflux for 2 h. The pot content was chilled in a refrigerator for 2 h, after AgCl precipitate was filtered off. To the cold solution was added excess NH₄PF₆. The blue precipitate was collected by filtration through Celite, dissolved in CH₃CN and was purified by column chromatography (silica gel eluting with CH₃CN/saturated aqueous KNO₃/water (17:0.5:1)). An excess of NH₄PF₆ was added to the major blue fraction and the solution reduced in volume. The precipitate was collected by filtration through Celite, dissolved in CH₃CN and evaporated to dryness to give [Ru(tpm)₂(H₂O)][PF₆]₂ as a blue powder. Further purification was achieved by recrystallisation from CH₃CN-H₂O solution of the complex. Yield 0.25 g, 90%.

1H NMR (500 MHz; solvent dmso-d₆) δ 10.03 (1H, s), 8.89 (1H, s), 8.77 (2H, d), 8.75 (1H, d), 8.63 (1H, d), 8.36 (1H, d), 8.14 (2H, d), 7.68 (2H, d), 7.36 (2H, d), 6.97 (1H, d), 6.92 (2H, t), 6.71 (2H, t), 6.65 (1H, dd), 6.54 (1H, t), 6.45 (2H(coordinated water molecule), b s).

13C NMR (75 MHz; solvent dmso-d₆) δ 147.72 (1C), 147.55 (2C), 147.40 (2C), 145.53 (1C), 136.62 (1C), 136.07 (2C), 135.97 (1C), 110.39 (1C), 109.83 (1C), 109.64 (2C), 109.63 (2C), 109.39 (1C), 81.85 (1C), 76.49 (1C). IR (KBr, cm⁻¹): 3140 b, 3042 w, 1628 w, 1520 w, 1441 m, 1414 m, 1377 m, 1285 m, 1252 w, 1231 w, 1094 s, 1061 w, 962 w, 845 ssh, 756 s, 606 w, 559 s. ESI-MS: m/z 693.07 ([M-PF₆]⁺), 274.05 ([M-2PF₆]²⁺). UV-vis (CH₃CN): λmax 305.0, 590.0 nm.

Method 1. [Ru(tpm)₂Cl]Cl, 3, (0.15 g, 0.25 mmol) and AgClO₄·H₂O (0.112 g, 0.5 mmol) in 30 mL of dry acetonitrile were heated at reflux for 4 h. AgCl was filtered off and the yellowish solution was taken to dryness on vacuum. The crude material was recrystallised by vapour diffusion of diethyl ether into the acetonitrile solution of the complex. Yield 0.11 g, 58%.

1H NMR (300 MHz; solvent dmso-d₆) δ 10.06 (1H, s), 8.96 (1H, s), 8.77 (2H, d), 8.75 (1H, d), 8.69 (1H, d), 8.37 (1H, d), 8.16 (2H, d), 7.68 (2H, d), 7.34 (2H, d), 6.91-6.94 (3H, m), 6.70-6.71 (3H, m), 6.61 (1H, dd), 6.45 (2H(coordinated water molecule), b s).

13C NMR (75 MHz; solvent dmso-d₆) δ 149.86, 147.11, 146.65, 145.79, 145.14, 141.20, 136.76, 135.90, 134.68, 130.42, 130.20, 124.27, 118.21, 120.39, 109.58, 109.24, 108.84, 108.14, 107.06, 80.75, 75.79, 1.26. IR (KBr, cm⁻¹): 3123 msh, 2995 msh, 1518 m, 1472 w, 1441 m, 1412 ssh, 1379 w, 1286 m, 1250 m, 1090 ssh, 991 w, 955 w, 862 m, 837 m, 818 m, 758 s, 625 ssh, 608 m, 446 w. ESI-MS: m/z 670.13 ([M-ClO₄]⁺), 285.59 ([M-2ClO₄]²⁺). UV-vis (CH₃CN): λmax 265.1, 290.0, 305.0 nm.

Method 2. [Ru(tpm)₂(H₂O)][Cl][PF₆]₂, 6, and acetonitrile (2 mL) in 20 mL acetone: water (3: 1) were heated at reflux for 24 h. The yellow-orange solution was taken to dryness after it was cooled at r.t. The crude material was recrystallised by vapour diffusion of diethyl ether into the acetonitrile solution of the complex. The precipitate was separated by filtration, washed with ether, then air-dried to give a yellow-orange powder. Yield 0.14 g, 74%.

[Ru(tpm)(bpy)Cl][PF₆] (9). Crystals suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into MeOH solution of the complex within a week. 1H NMR (300 MHz; solvent dmso-d₆) δ
MHz; solvent dmso-$d_6$ δ 10.24 (s, 1H), 8.87 (d, 2H), 8.76-8.75 (m, 4H), 8.62 (d, 1H), 8.38 (d, 2H), 8.19 (dd, 2H), 6.75 (dd, 2H), 6.89 (m, 2H), 6.81 (d, 1H), 6.45 (m, 1H). $^{13}$C NMR (75 MHz; solvent dmso-$d_6$) δ 158.88, 152.29, 147.45, 144.62, 136.07, 135.58, 134.49, 125.76, 123.52, 109.16, 108.71, 75.30.

[Ru(tpm)(bpy)(OH$_2$)](ClO$_4$)$_2$ (10). Crystals suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into MeOH solution of the complex within two days. $^1$H NMR (300 MHz; solvent dmso-$d_6$) δ 9.26 (s, 1H), 8.95 (d, 2H), 8.77-8.76 (m, 4H), 8.56 (d, 1H), 8.49 (d, 2H), 8.30 (dd, 2H), 7.75 (dd, 2H), 6.98 (m, 2H), 6.88 (d, 1H), 6.45 (m, 1H), 5.76 (s, 2H, coordinated H$_2$O molecule). $^{13}$C NMR (75 MHz; solvent dmso-$d_6$) δ 158.90, 153.15, 147.43, 146.02, 137.32, 136.89, 135.68, 126.32, 123.95, 109.44, 108.19, 75.63.

[Co(ttp)(bpy)(bpe)]Cl$_2$$_6$ (11). Crystals suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into CH$_3$CN solution of the complex within two days.

$^1$H NMR (500 MHz; solvent dmso-$d_6$, see Scheme 3 for numbering) δ 10.23 (d, 1H, H$_6^B$), 9.24 (s, 2H, H$_3^{'},$ H$_5^{'},$), 9.02 (m, 3H, H$_3,$ H$_3^{'},$ H$_3^B$), 8.74 (d, 1H, H$_3^A)$, 8.46 (t, 1H, H$_4^B$), 8.34 (d, 2H, H$_2^{'},$ H$_6^{'},$), 8.18 (t, 1H, H$_5^B$), 8.10 (m, 2H, H$_4,$ H$_4^{'},$), 7.87 (t, 1H, H$_4^A$), 7.74 (d, 2H, H$_6,$ H$_6^{'},$), 7.61 (d, 2H, H$_3^{'},$ H$_5^{'},$), 7.53 (d, 1H, H$_6^A$), 7.48 (t, 2H, H$_5,$ H$_5^{'},$), 7.18 (t, 1H, H$_3^A$), 2.57 (s, 3H, H$_7$). $^{13}$C NMR (75 MHz; solvent dmsod-$d_6$) δ 158.74, 158.44, 157.81, 155.83, 152.10, 151.95, 151.82, 145.19, 139.95, 137.04, 136.66, 135.63, 133.48, 130.00, 127.53, 127.48, 127.01, 126.56, 124.15, 123.84, 123.57, 119.67, 21.05. IR (KBr, cm$^{-1}$): 3070 m, 1605 m, 1520 w, 1462 m, 1427 m, 1405 m, 1395 m, 1366 m, 1356 m, 1348 m, 1300 m, 127.53, 127.48, 127.01, 126.56, 124.15, 123.57, 119.67, 21.05. ESI-MS: $m/z$ 616.29 ([M-PF$_6$]$^+$.) UV-vis (CH$_3$CN): $\lambda_{max}$ ($\varepsilon$) = 285.0 (55880), 295.0 (55561), 295.0 (55561), 504.9 (10025) nm (L mol$^{-1}$ cm$^{-1}$).
washed with water, ether, then dissolved in CH$_3$CN and evaporated to dryness to give the pure product as a dark red powder. Yield 0.048 g, 70%. Red block of crystals suitable for X-ray crystallography were grown by vapour diffusion of diethyl ether into CH$_3$CN/MeOH (1:1) solution of the complex over a week. $^1$H NMR (500 MHz; solvent acetone-$d_6$, see Scheme 3 for numbering) $\delta$ 9.36 (s, 2H, H$_3^t$, H$_5^t$), 9.20 (d, 1H, H$_6^b$), 9.12 (d, 3H, H$_3$, H$_3^b$), 8.86 (d, 1H, H$_5^a$), 8.60-8.57 (m, 1H, H$_{4b}$), 8.35-8.32 (dd, 2H, H$_4$), 8.29 (d, 2H, H$_6$), 8.27-8.25 (m, 4H), 8.25-8.24 (d, 2H, H$_2^a$, H$_6^a$), 8.16-8.08 (m, 2H, H$_{5b}$, H$_{4b}$), 7.92 (d, 1H, H$_E$), 7.89 (d, 1H, H$_{6a}$), 7.82 (d, 1H, H$_E$), 7.74-7.73 (m, 2H, H$_4$), 7.73-7.72 (m, 2H), 7.63 (d, 2H, H$_{3^a}$, H$_{5^a}$), 7.39-7.36 (m, 1H, H$_{5a}$), 2.60 (s, 3H, CH$_3$). $^{13}$C NMR (75 MHz; solvent acetone-$d_6$) $\delta$ 158.79, 158.05, 157.80, 156.68, 153.50, 153.07, 152.19, 151.57, 148.91, 144.83, 144.57, 141.22, 139.00, 138.15, 137.83, 134.39, 133.60, 131.36, 130.36, 129.12, 128.21, 127.77, 127.22, 125.48, 124.86, 124.27, 124.07, 121.52, 20.65. IR (KBr, cm$^{-1}$): 3674 m, 3626 w, 3304 w, 3107 w, 1630 m, 1607 m, 1539 m, 1506 m, 1470 m, 1447 w, 1427 m, 1406 m, 1352 w, 1315 w, 1290 w, 1205 w, 1163 w, 1022 w, 978 m, 839 s sh, 789 s, 764 s, 739 m, 718 w, 656 w, 619 w, 559 s sh, 509 w, 494 w, 486 w, 474 w, 418 w. ESI-MS: $m/z$ 908.43 ([M-PF$_6$]$^+$), 381.63 ([M-2PF$_6$]$_2^{2+}$). UV-vis (CH$_3$CN): $\lambda_{max}$ ($\varepsilon$) = 290.0 (157928), 385.0 (10060), 429.9 (14261) nm (L mol$^{-1}$ cm$^{-1}$).

**Crystal structure determinations**

Single crystals of 9 and 10 were grown by vapour diffusion of diethyl ether into the MeOH solutions of the complexes at r.t. Single crystals of 13 and 14 were also obtained by vapour diffusion of diethyl ether into CH$_3$CN and CH$_3$CN/MeOH solutions of the complexes at r.t., respectively. Single crystals of each compound were used for structure determination. The X-ray data were collected on a Siemens P4 four circle diffractometer, using a Siemens SMART 1K CCD area detector and irradiating the sample with graphite monochromated MoK$_\alpha$ ($\lambda$ 0.71073 Å) radiation. The crystals were mounted 5.5 cm from the detector. The data were collected by the SMART$^{67}$ program and processed with the help of SAINT$^{68}$ to apply Lorentz and polarization corrections to the diffraction spots (three-dimensional integration). SADABS$^{69}$ was used to scale the diffractions if required. The structures were solved by direct methods and refined using the SHELXTL$^{70}$ program. Hydrogen atoms were placed at calculated ideal positions and refined using a riding model. Crystallographic data are shown in Table 2. Details of the structures have been deposited with the Cambridge Crystal Database, deposition numbers 277148 – 277151.

X-ray Crystallography data in the form of Crystallographic information files (CIF).
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