Synthesis and structural characterization of some polypyridyl and tris(1*H*-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(1*H*-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: $[Ru(tpm)(bpy)Cl](PF_6)$, $[Ru(tpm)(bpy)(OH_2)](ClO_4)_2$, $[Ru(ttp)(bpy)Cl](PF_6)$, and $[Ru(ttp)(bpy)(bpe)](PF_6)_2$ (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(1*H*-pyrazol-1-yl)ethoxymethyl)phenyl)-2,2':6',2"-terpyridine (pzt)[1] (Figure 1).

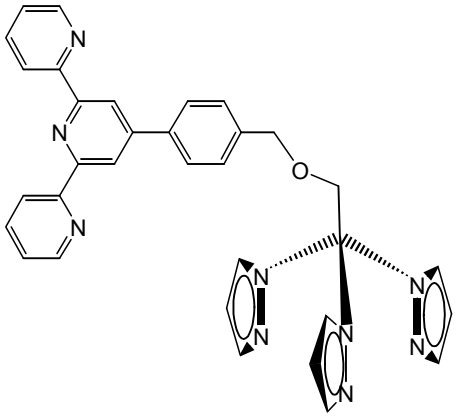


Figure 1. Ligand pzt[1].

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 $[Ru(tpm)Cl_3]$[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, $[Ru(ttp)Cl_3]$[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,[5-46] 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 $Ru(tpm)Cl_3$, **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.

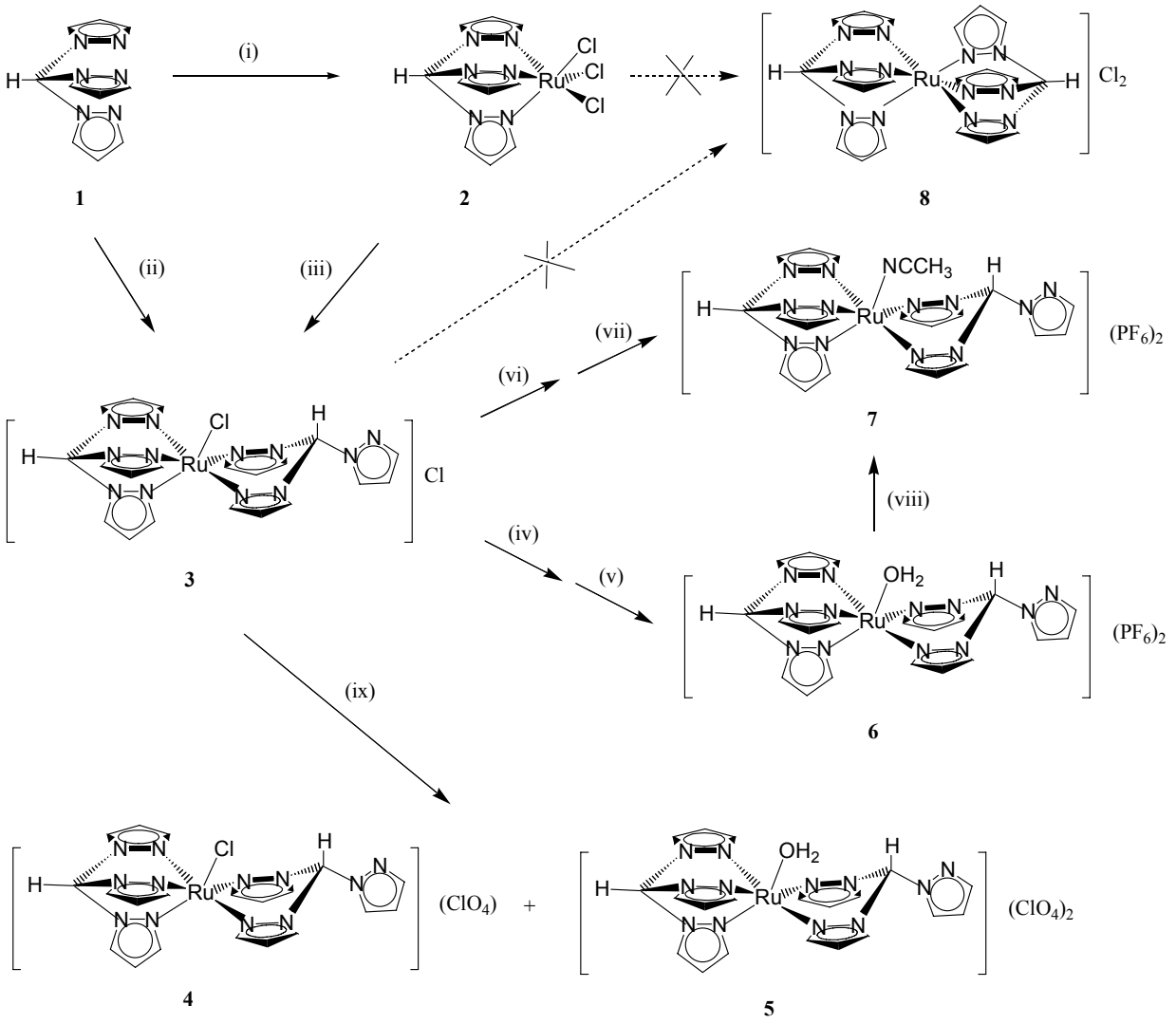
At least two tpm ligands are clearly coordinated to the metal centre, based on the number of NMR signals that are observed, and an ES-MS isotope pattern for a singly charged ion at around

565 units is consistent with a formulation of $[Ru(tpm)_2Cl]^+$ 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 $RuCl_3.3H_2O$ or $[Ru(phCN)_4Cl_2]$ were treated with two equivalents of the tpm ligand (Scheme 1).

Reaction of the green complex, **3**, with $AgClO_4.H_2O$ 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}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_3CN solution show isotope patterns at *m/z* 693 and 274, that can be assigned to $\{[Ru(tpm)_2(OH_2)]PF_6\}^+$ and $[Ru(tpm)_2(OH_2)]^{2+}$, 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}H NMR spectrum of the complex **7** in dmso-d_6, ES-MS in CH_3CN, 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) $RuCl_3.3H_2O$, EtOH, reflux, 4h; (ii) $RuCl_3.3H_2O$ or $[Ru(ph\text{-}CN)_4Cl_2]$ (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_4PF_6; (vi) $AgClO_4$, dry CH_3CN, under Ar, reflux, 2 h; (vii) NH_4PF_6; (viii) CH_3CN, acetone: water (3: 1), reflux, 24 h; (ix) $AgClO_4$, acetone, under Ar, reflux, 2 h.

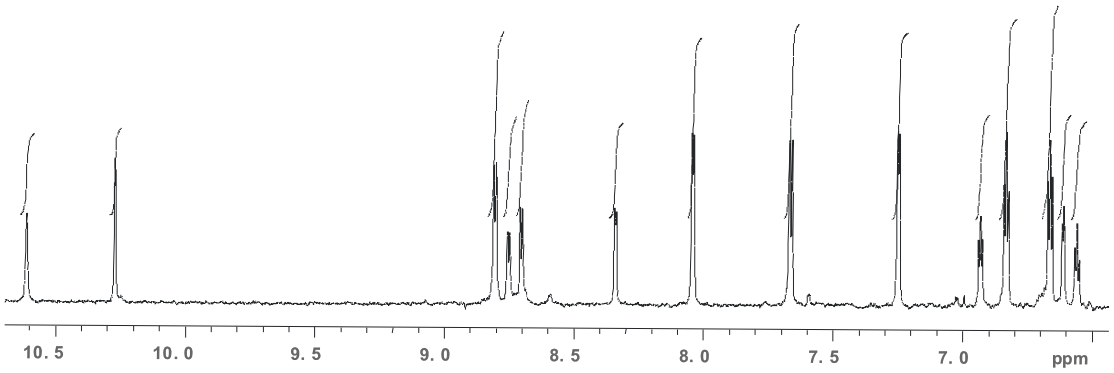
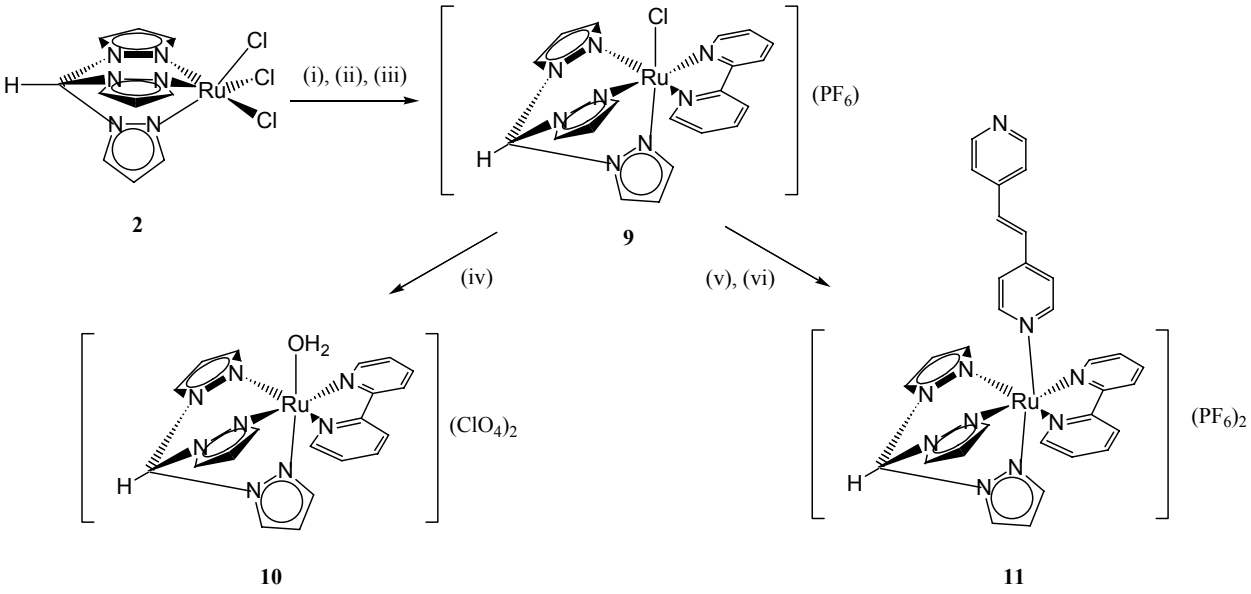


Figure 2. ^{1}H NMR spectra of [Ru(tpm)$_2$Cl] Cl, **3**, in dmso-d_6 solution.

Complexes [Ru(tpm)(bpy)Cl](PF_6), **9**, [Ru(tpm)(bpy)(OH_2)](ClO_4)$_2$, **10**, and [Ru(tpm)(bpy)(bpe)](PF_6)$_2$, **11**, provide a good basis with which to compare the properties of the series of bis(tpm) complexes, and were synthesized using literature procedures.[2,47] 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, NEt_3, reflux, 10 min; (iii) NH_4PF_6; (iv) $AgClO_4$, acetone: water (3: 1), reflux, 2 h; (v) bpe, EtOH: water (1: 1), reflux, under Ar, 6 h; (vi) NH_4PF_6.

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.[3,47,48] 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.

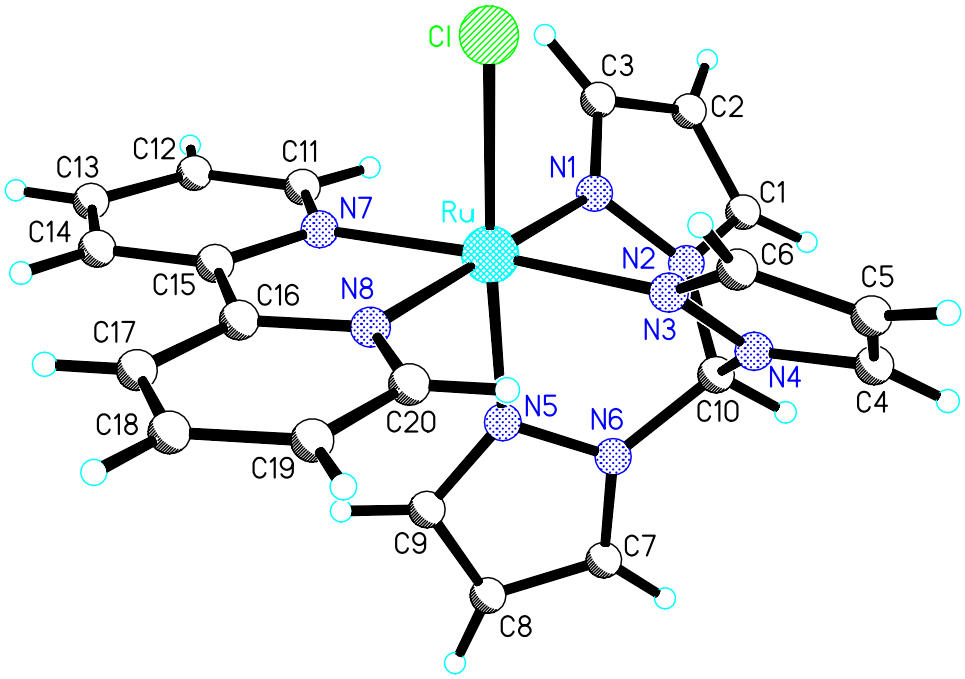


Figure 3. Structure of complex **9** with numbering scheme adopted. One hexafluorophosphate anion is omitted for clarity.

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,[49] 2.431,[50] 2.387,[48] and 2.408 Å[51]) of the chloro complexes are also longer than Ru-OH_2 distances (2.127,[52] 2.126,[50] 2.119,[48] and 2.139 Å[51]) in the aqua complexes.

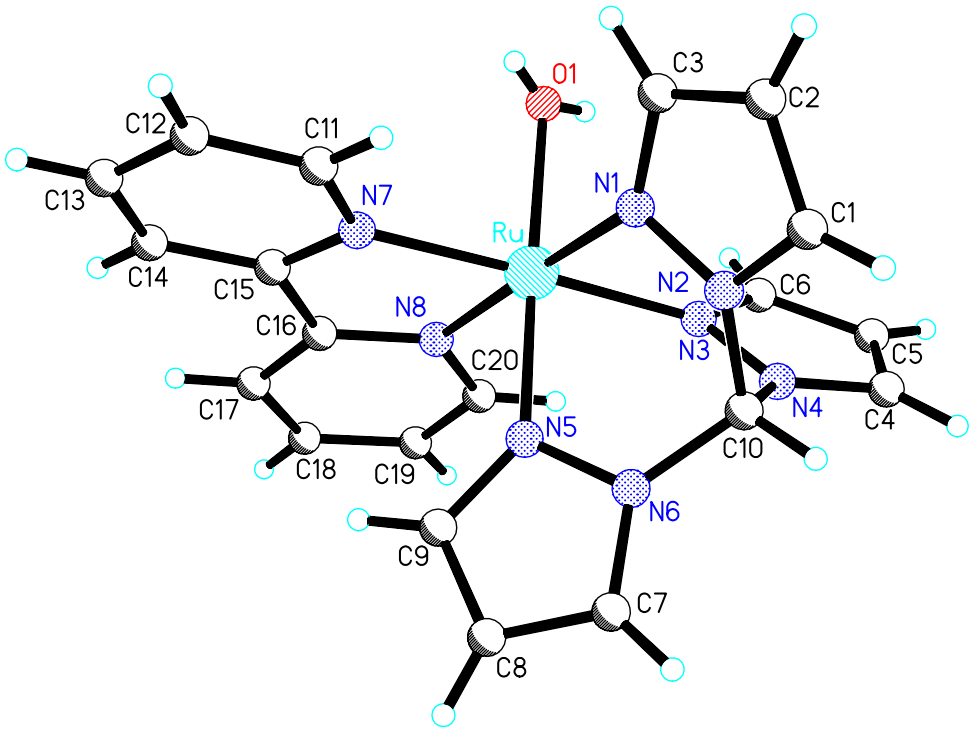


Figure 4. Structure of complex **10** with numbering scheme adopted. Two perchlorate anions and one solvated methanol molecule are omitted for clarity.

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.

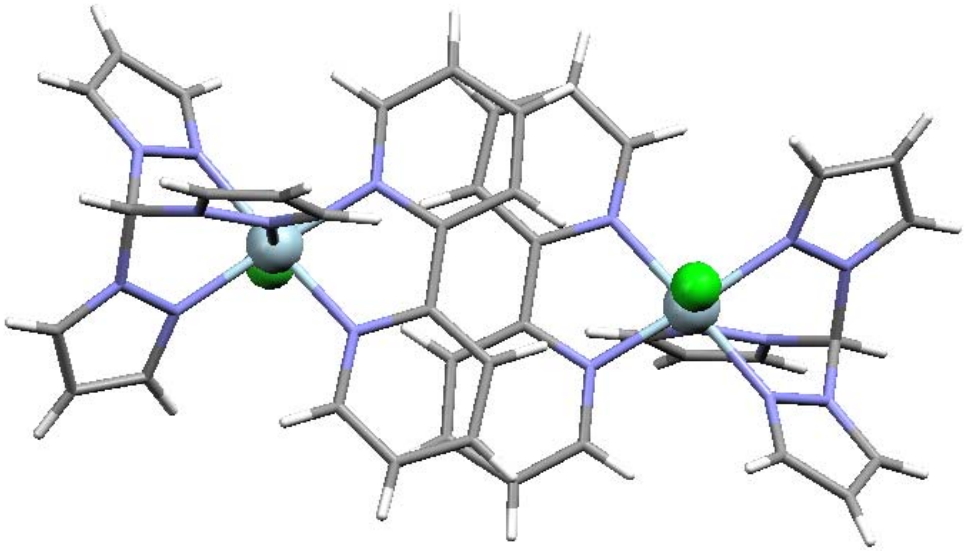


Figure 5. π-π stacking interactions between two adjacent molecule in structure **9**. The distance between the planes of bpy ligands in the adjacent cations is 3.4 Å.

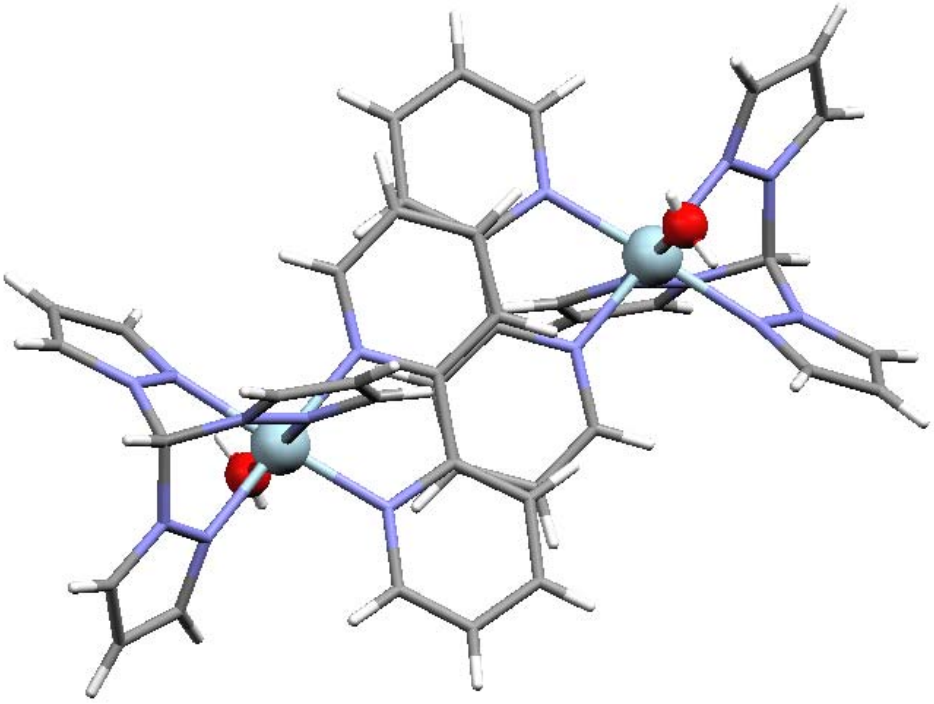


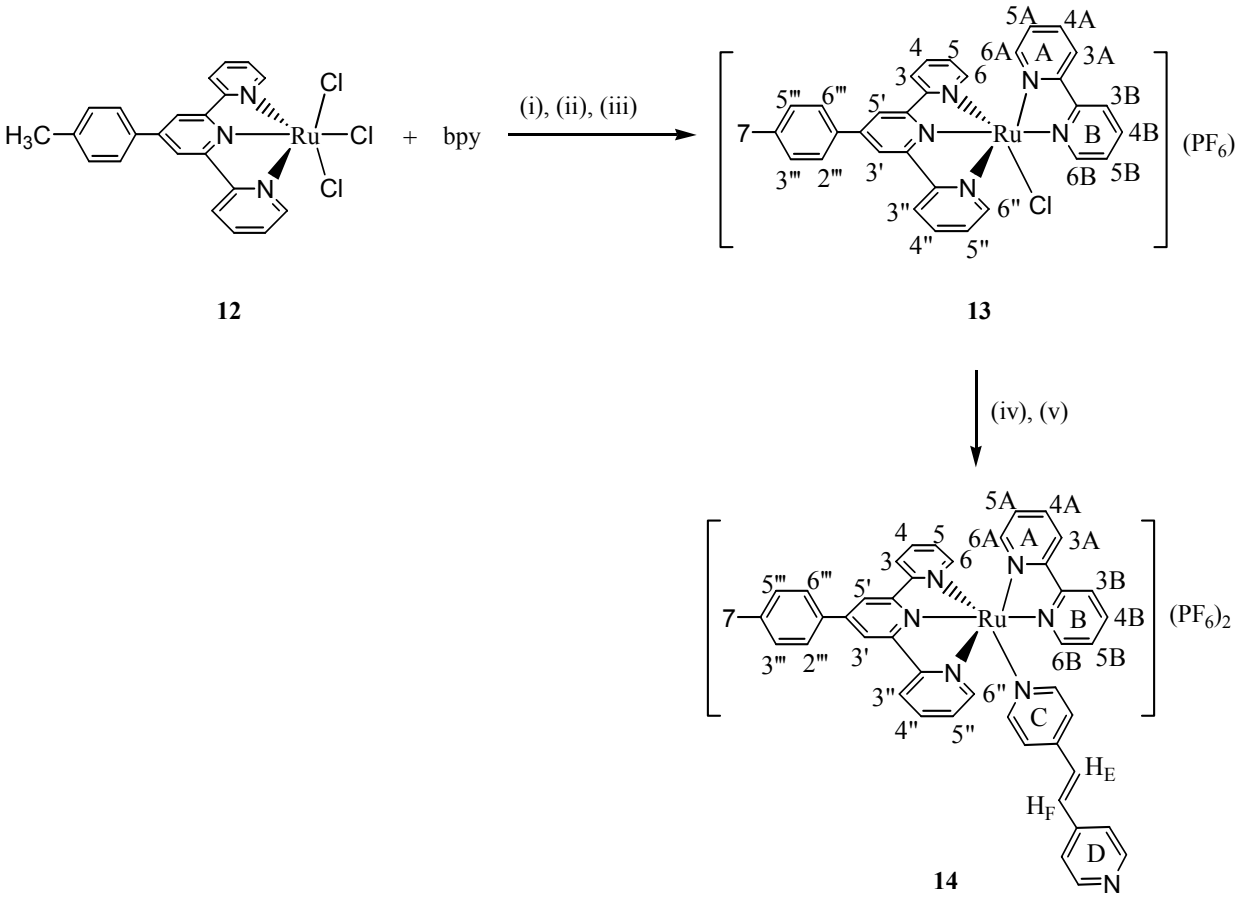
Figure 6. π-π stacking interactions between two adjacent molecule in structure **10**. The distance between the planes of bpy ligands in the adjacent cations is 3.5 Å.

Table 1. Selected bond lengths [Å] and angles [°] for the Ru(II) complexes.

Ru Complex **9**		Ru Complex **10**		Ru Complex **13**		Ru Complex **14**	
Ru-N(5)	2.022(2)	Ru-N(5)	2.011(3)	Ru-N(2)	1.949(3)	Ru-N(2)	1.955(5)
Ru-N(7)	2.035(2)	Ru-N(7)	2.051(4)	Ru-N(4)	2.033(3)	Ru-N(4)	2.056(5)
Ru-N(8)	2.044(2)	Ru-N(8)	2.053(3)	Ru-N(1)	2.064(3)	Ru-N(1)	2.068(5)
Ru-N(3)	2.065(2)	Ru-N(3)	2.076(4)	Ru-N(3)	2.065(3)	Ru-N(3)	2.067(5)
Ru-N(1)	2.063(2)	Ru-N(1)	2.077(4)	Ru-N(5)	2.079(3)	Ru-N(5)	2.078(5)
Ru-Cl	2.4114(7)	Ru-O(1)	2.151(3)	Ru-Cl	2.4103(9)	Ru-N(6)	2.10(4)
N(5)-Ru-N(7)	90.49(9)	N(5)-Ru-N(7)	91.63(14)	N(2)-Ru-N(4)	95.56(11)	N(2)-Ru-N(4)	97.2(2)
N(5)-Ru-N(8)	92.12(9)	N(5)-Ru-N(8)	88.69(13)	N(2)-Ru-N(1)	79.24(10)	N(2)-Ru-N(1)	79.6(2)
N(7)-Ru-N(8)	79.05(9)	N(7)-Ru-N(8)	79.06(14)	N(4)-Ru-N(1)	88.47(10)	N(4)-Ru-N(1)	91.7(2)
N(5)-Ru-N(1)	85.88(9)	N(5)-Ru-N(1)	87.51(14)	N(2)-Ru-N(3)	80.05(11)	N(2)-Ru-N(3)	79.6(2)
N(7)-Ru-N(1)	99.01(9)	N(7)-Ru-N(1)	99.63(14)	N(4)-Ru-N(3)	95.71(11)	N(4)-Ru-N(3)	88.3(2)
N(8)-Ru-N(1)	177.22(9)	N(8)-Ru-N(1)	175.94(14)	N(1)-Ru-N(3)	159.17(11)	N(1)-Ru-N(3)	159.0(2)
N(5)-Ru-N(3)	87.64(9)	N(5)-Ru-N(3)	87.49(13)	N(2)-Ru-N(5)	172.73(11)	N(2)-Ru-N(5)	175.7(2)
N(7)-Ru-N(3)	176.24(9)	N(7)-Ru-N(3)	177.87(14)	N(4)-Ru-N(5)	78.44(11)	N(4)-Ru-N(5)	78.5(2)
N(8)-Ru-N(3)	97.74(9)	N(8)-Ru-N(3)	98.97(14)	N(1)-Ru-N(5)	104.48(11)	N(1)-Ru-N(5)	100.1(2)
N(1)-Ru-N(3)	84.12(9)	N(3)-Ru-N(1)	82.28(13)	N(3)-Ru-N(5)	96.35(11)	N(3)-Ru-N(5)	100.4(2)
N(5)-Ru-Cl	175.26(6)	N(5)-Ru-O(1)	178.29(13)	N(2)-Ru-Cl	91.63(8)	N(2)-Ru-N(6)	89.1(18)
N(7)-Ru-Cl	91.49(7)	N(7)-Ru-O(1)	89.22(13)	N(4)-Ru-Cl	171.24(8)	N(4)-Ru-N(6)	172.5(15)
N(8)-Ru-Cl	92.48(7)	N(8)-Ru-O(1)	92.93(13)	N(1)-Ru-Cl	87.96(7)	N(1)-Ru-N(6)	93.3(13)
N(1)-Ru-Cl	89.56(7)	N(1)-Ru-O(1)	90.89(13)	N(3)-Ru-Cl	90.45(8)	N(3)-Ru-N(6)	88.9(15)
N(3)-Ru-Cl	90.62(7)	N(3)-Ru-O(1)	91.70(13)	N(5)-Ru-Cl	94.73(8)	N(5)-Ru-N(6)	95.2(18)

Table 2. Crystallographic data

Compound	[Ru(tpm)(bpy)Cl] (PF_6), **9**	[Ru(tpm)(bpy)(H_2O)] $(ClO_4)_2$.MeOH, **10**	[Ru(ttp)(bpy)Cl] (PF_6), **13**	[Ru(ttp)(bpy)(bpe)] $(PF_6)_2$.MeOH, **14**
Formula	$C_{20}H_{18}ClF_6N_8PRu$	$C_{21}H_{24}Cl_2N_8O_{10}Ru$	$C_{32}H_{25}ClF_6N_5PRu$	$C_{45}H_{39}F_{12}N_7OP_2Ru$
M	651.91	720.45	761.06	1084.84
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	10.8239(9)	14.9764(17)	13.0766(15)	10.7421(10)
b/Å	15.0829(13)	14.4923(18)	19.140(3)	21.633(2)
c/Å	14.3141(12)	14.3878(16)	12.2565(16)	19.3655(14)
α°	90	90	90	90
β°	97.314(2)	116.902(2)	100.049(2)	99.463(2)
γ°	90	90	90	90
V/Å^3	2317.8(3)	2784.8(6)	3020.6(7)	4438.9(7)
Z	4	4	4	4
T/K	88(2)	113(2)	93(2)	93(2)
μ/mm^{-1}	0.938	0.824	0.731	0.522
Reflections collected	18093	16052	21587	38264
Independent reflections	4720	5653	5207	9001
Observed	3805	4140	3790	7398
Parameters refined	334	382	481	807
R [I > 2σ(I)]	0.0274	0.0445	0.0356	0.0397
Rw [I > 2σ(I)]	0.0650	0.1078	0.0692	0.0933



Scheme 3. *Reagents and Conditions:* (i) EtOH: water (1: 4), reflux, 5 h; (ii) LiCl, reflux, 30 min; (iii) NH_4PF_6; (iv) EtOH: water (1: 1), reflux, 5 h; (v) NH_4PF_6.

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.[48,53,54] 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 PF_6^- salt. ES-MS of the red powder in CH_3CN 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 CH_3CN 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.[48-51,55-63] 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).

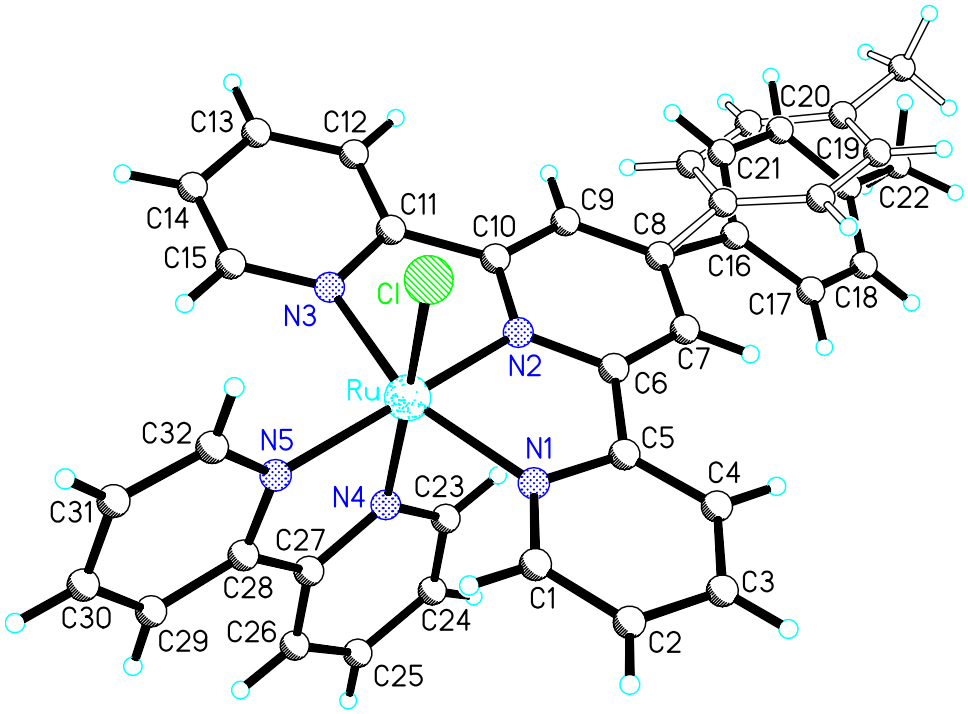


Figure 6. The molecular structure of complex **13**, with a PF_6^- anion omitted for clarity.

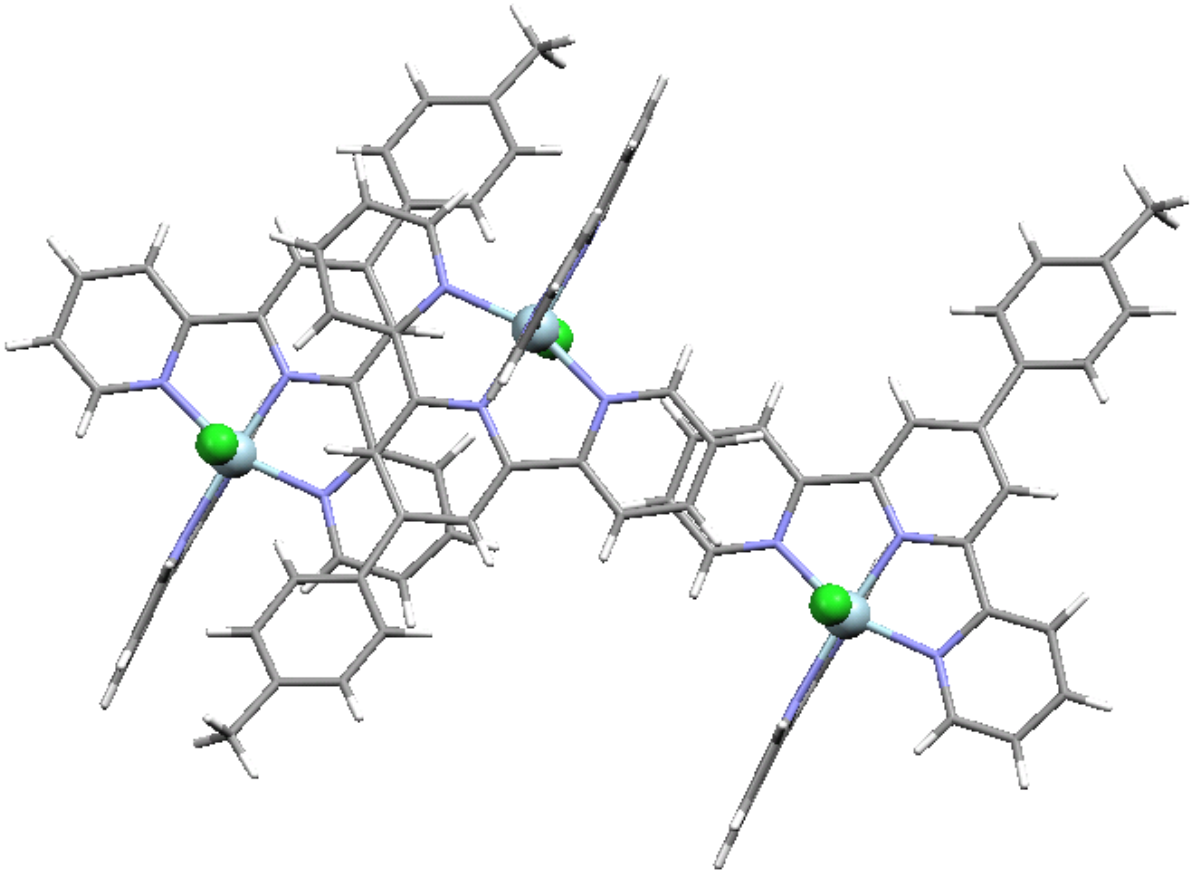


Figure 7. π-π stacking interactions (face-face) between the planes of the ttp groups in crystal structure of complex **13**. The distance between the planes of the flanking pyridine rings of the adjacent cations is 3.7 Å (centroid-centroid) and the separation of the central pyridine plane in one cation to the flanking pyridine plane in the adjacent cation is approximately 3.6 Å (centroid-centroid).

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 $\{[Ru(ttp)(bpy)(bpe)](PF_6)\}^+$ and $[Ru(ttp)(bpy)(bpe)]^{2+}$, 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_3CN/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 π-π 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).

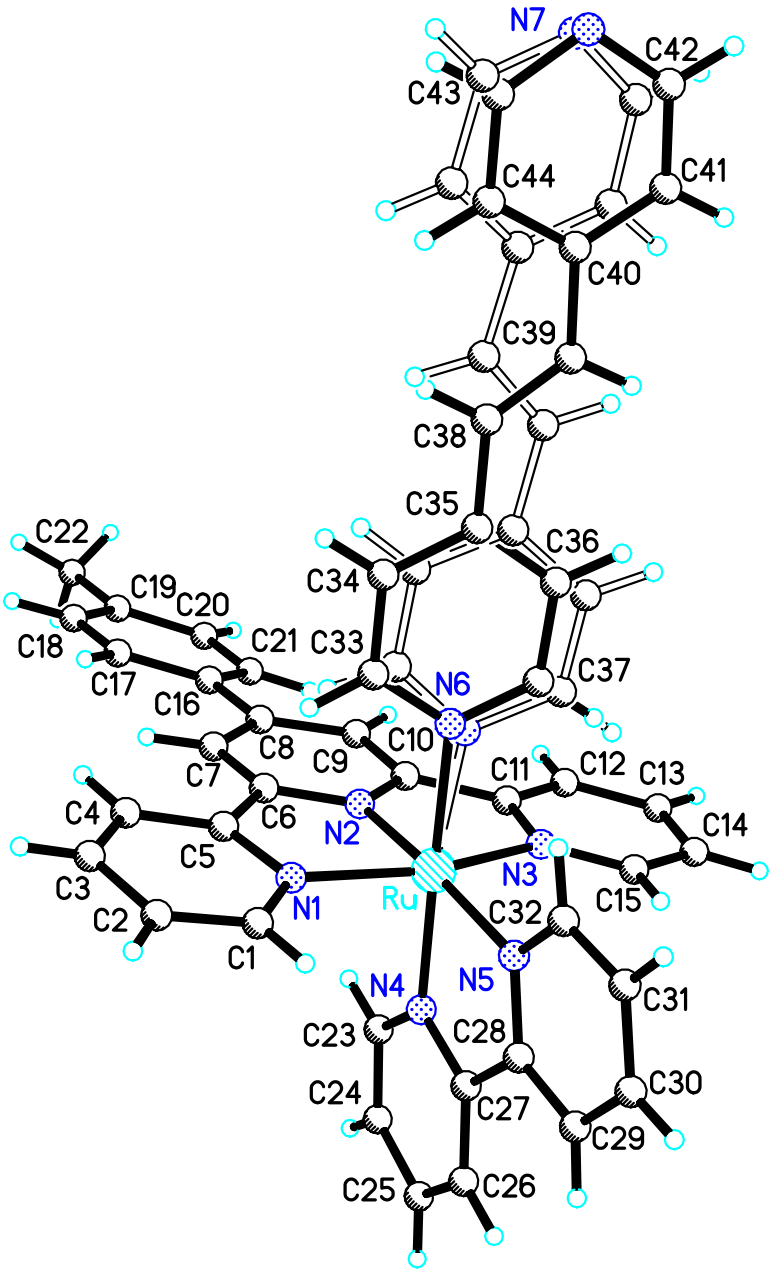


Figure 8. Molecular structure of complex **14**, with two hexafluorophosphate anions and a methanol molecule omitted for clarity. The coordinated bpe ligand exhibits pseudo 2-fold rotational disorder. One of the hexafluorophosphate ions is also disordered.

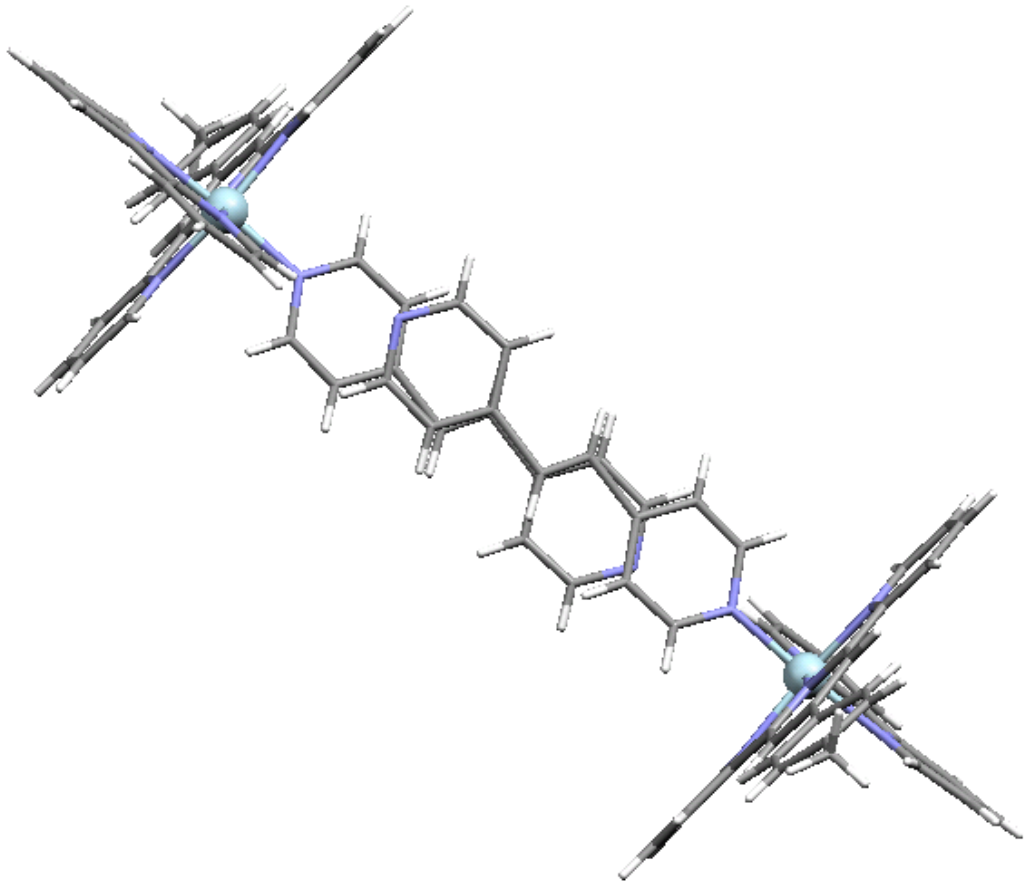


Figure 9. The π-π stacking interactions in the X-ray structure of complex **14**. The distances between the planes of the coordinated pyridine ring of bpe in one complex and uncoordinated pyridine ring in the adjacent cation is 3.7 Å (centroid-centroid).

Experimental Section

General Procedures. All solvents were dried and distilled according to the standard methods prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian UNITY-300 or Varian INOVA-500 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced to residual solvent resonances or using TMS as an internal reference. ^{1}H 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 CH_3CN 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(1*H*-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

$[Ru(tpm)_2Cl]Cl$ (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_3N (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) δ 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). ^{13}C NMR (75 MHz; solvent dmso-d_6) δ 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 ($[M\text{-}Cl]^+$), 265.03 ($[M\text{-}Cl]^{2+}$). UV-vis (CH_3CN): λ_{max} (ε) = 230.0 (9300), 280.0 (4900), 290.0 (4900), 335.0 (7300) nm (L mol^{-1} cm^{-1}). Anal. Calc. for $C_{20}H_{20}Cl_2N_{12}Ru.1.5H_2O$ (627.46): C 38.28, H 3.69, N 26.79%; found: C 38.24, H 3.43, N 26.45.

$[Ru(tpm)_2(H_2O)](ClO_4)_2$ (5). $[Ru(tpm)_2Cl]Cl$, **3**, (0.15 g, 0.25 mmol) and $AgClO_4.H_2O$ (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 acetone-benzene 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 acetone-benzene, 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) δ 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, 1414 m, 1377 w, 1310 m, 1285 msh, 1252 m, 1231 w, 1094 ssh, 1061 m, 991 w, 962 w, 845 s,

756 s, 606 m, 559 ssh. ESI-MS: *m/z* 629.09 ($[M\text{-}Cl]^+$), 565.11 ($[M\text{-}ClO_4]^+$), 265.06 ($[M\text{-}Cl\text{-}ClO_4]^{2+}$).

$[Ru(tpm)_2(H_2O)](PF_6)_2$ (6). $[Ru(tpm)_2Cl]Cl$, **3**, (0.15 g, 0.25 mmol) and $AgClO_4.H_2O$ (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 NH_4PF_4. The blue precipitate was collected by filtration through Celite, dissolved in CH_3CN and was purified by column chromatography (silica gel eluting with CH_3CN/saturated aqueous KNO_3/water (17:0.5:1)). An excess of NH_4PF_6 was added to the major blue fraction and the solution reduced in volume. The precipitate was collected by filtration through Celite, dissolved in CH_3CN and evaporated to dryness to give $[Ru(tpm)_2(H_2O)](PF_6)_2$ as a blue powder. Further purification was achieved by recrystallisation from CH_3CN-H_2O solution of the complex. Yield 0.25 g, 90 %. ^{1}H NMR (500 MHz; solvent dmso-d_6) 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). ^{13}C NMR (75 MHz; solvent dmso-d_6) 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), 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 m, 991 w, 962 w, 845 ssh, 756 s, 606 w, 559 s. ESI-MS: *m/z* 693.07 ($[M\text{-}PF_6]^+$), 274.05 ($[M\text{-}2PF_6]^{2+}$). UV-vis (CH_3CN): λ_{max} 305.0, 590.0 nm.

$[Ru(tpm)_2(CH_3CN)](ClO_4)_2$ (7). Method 1. $[Ru(tpm)_2Cl]Cl$, **3**, (0.15 g, 0.25 mmol) and $AgClO_4.H_2O$ (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 recrystallized by vapour diffusion of diethyl ether into the acetonitrile solution of the complex. Yield 0.11 g, 58%. ^{1}H NMR (300 MHz; solvent dmso-d_6) 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), 661 (1H, dd), 2.7 (3H (coordinated CH_3CN), s). ^{13}C NMR (75 MHz; solvent dmso-d_6) 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, 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 ($[M\text{-}ClO_4]^+$), 285.59 ($[M\text{-}2ClO_4]^{2+}$). UV-vis (CH_3CN): λ_{max} 265.1, 290.0, 305.0 nm.

Method 2. $[Ru(tpm)_2(H_2O)](PF_6)_2$, **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%.

$[Ru(tpm)(bpy)Cl](PF_6)$ (9). Crystals suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into MeOH solution of the complex within a week. ^{1}H NMR (300

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), 7.65 (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_2O 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.

[Ru(ttp)(bpy)Cl](PF$_6$) (13). To [Ru(ttp)Cl$_3$], **12**, (0.237 g, 0.539 mmol) in 80 mL EtOH:water (4:1), was added bpy (0.094 g, 0.6 mmol). The mixture was allowed to reflux for 5 h, excess solid LiCl was added, and the mixture was heated for an additional 45 min. To the cold reaction micture was added excess aqueous NH_4PF_6 solution, then the volume of the mixture was reduced on vacuum to about 40 mL. The brown precipitate was collected by filtration through Celite, recrystallized from acetone and diethyl ether (1:5) to afford a brown powder. Further purification was achieved by column chromatography (silica gel eluting with CH_3CN/toluene (2:1)). An excess of NH_4PF_6 was added to the major red-purple fraction and the solution reduced in volume. The precipitate was collected by filtration through Celite, dissolved in CH_3CN and evaporated to dryness to give [Ru(ttp)(bpy)Cl](PF$_6$) as a dark red powder. Yield 0.187 g, 55%. Red blocks of crystals suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into CH_3CN 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_{6B}), 9.24 (s, 2H, $H_{3'}$, $H_{5'}$), 9.02 (m, 3H, H_3, $H_{3''}$, H_{3B}), 8.74 (d, 1H, H_{3A}), 8.46 (t, 1H, H_{4B}), 8.34 (d, 2H, $H_{2'''}$, $H_{6'''}$), 8.18 (t, 1H. H_{5B}), 8.10 (m, 2H, H_4, $H_{4''}$), 7.87 (t, 1H, H_{4A}), 7.74 (d, 2H, H_6, $H_{6''}$), 7.61 (d, 2H, $H_{3'''}$, $H_{5'''}$), 7.53 (d, 1H, H_{6A}), 7.48 (t, 2H, H_5, $H_{5''}$), 7.18 (t, 1H, H_{5A}), 2.57 (s, 3H, H_7). ^{13}C NMR (75 MHz; solvent dmso-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, 1404 m, 1354 w, 1312 w, 1292 w, 1250 m, 1196 m, 1161 w, 1018 m sh, 968 w, 841 s sh, 791 s, 760 s, 729 m, 656 m, 559 s, 494 w, 459 w, 424 w. ESI-MS: *m/z* 616.29 ([M-PF$_6$]$^+$). UV-vis (CH_3CN): λ_{max} (ε) = 285.0 (55880), 295.0 (55561), 504.9 (10025) nm (L mol^{-1} cm^{-1}).

[Ru(ttp)(bpy)(bpe)](PF$_6$)$_2$ (14). To [Ru(ttp)(bpy)Cl], **13**, (0.050 g, 0.074 mmol) in 25 mL EtOH: water (1: 1), was added excess bpe (0.128 g, 0.7 mmol). The mixture was refluxed for 5 h. The volume of the cold solution was reduced to half by rotary evaporation. To the resulting yellow-red solution was added excess NH_4PF_6. A dark red microcrystalline material was precipitated immediately. The precipitate was collected by filtration through Celite, after it was kept in the refrigerator for 2 h. The product was then purified by column chromatography (silica gel eluting with CH_3CN/saturated solution KNO_3/water (10:2:1). An excess of NH_4PF_6 was added to the last major red band. The precipitate was collected by filtration through Celite,

washed with water, ether, then dissolved in CH_3CN 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_3CN/MeOH (1:1) solution of the complex over a week. ^{1}H NMR (500 MHz; solvent acetone-d_6, see Scheme 3 for numbering) δ 9.36 (s, 2H, H_3', H_5'), 9.20 (d, 1H, H_{6B}), 9.12 (d, 3H, H_3, H_{3B}), 8.86 (d, 1H, H_{3A}), 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, $H_{2'''}$, $H_{6'''}$), 8.16-8.08 (m, 2H, H_{5B}, H_{4B}), 7.92 (d, 1H, H_F), 7.89 (d, 1H, H_{6A}), 7.82 (d, 1H, H_E), 7.74-7.73 (m, 2H, H_5), 7.73-7.72 (m, 2H), 7.63 (d, 2H, $H_{3'''}$, $H_{5'''}$), 7.39-7.36 (m, 1H, H_{5A}), 2.60 (s, 3H, CH_3). ^{13}C NMR (75 MHz; solvent acetone-d_6) δ 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 ($[M-2PF_6]^{2+}$). UV-vis (CH_3CN): λ_{max} (ε) = 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_3CN and CH_3CN/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 $Mo_{K\alpha}$ (λ 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).

Acknowledgements

The authors would like to thank Professor W. T. Robinson and Dr. J. Wikaira for their help with X-ray structural investigations associated with this project. A University of Canterbury Doctoral Scholarship (R.Z.) is gratefully acknowledged.

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