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Red Phosphorescence in Ru^{II} Complexes of a Tridentate N-Heterocyclic Carbene Ligand Incorporating Tetrahydropyrimidine

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A new N-heterocyclic carbene ligand *N*,*N*′-bis(2-pyridyl)-tetrahydropyrimidinium hexafluorophosphate (**1**) has been synthesized and characterized. Its homoleptic Ru^{II} complex **2** exhibits a more facile oxidation (+1.17 V vs. SCE) relative to the prototypical $[Ru(tpy)_2]^{2+}$ (+1.32 V vs. SCE) complex (tpy = 2,2′:6′,2′′-terpyridine). The heteroleptic Ru^{II} complex **3**, incorporating **1** and 4′-*p*-tolyl-tpy, also displays a more positive oxidising potential (+1.28 V vs. SCE) than $[Ru(tpy)_2]^{2+}$. The X-ray crystal structures of complexes **2** and **3** confirm the meridional tridentate coordination of ligand **1** to Ru^{II}. The Ru–C bond length is shorter in heteroleptic complex **3** [1.901(7) Å] than in homoleptic complex **2** [1.969(2) Å and 1.972(3) Å]. The complexes display broad metal-to-ligand charge-transfer absorption bands in the visible region (**2**: λ_{max} = 440 and 470 nm; **3**: λ_{max} = 440 and 473 nm), and their solid-state emission is redshifted (**2**: λ_{max} = 753 nm; **3**: λ_{max} = 735 nm) considerably relative to that of $[Ru(tpy)_2]^{2+}$ (λ_{max} = 620 nm).

Introduction

The ruthenium(II) polypyridyl complex $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and its derivatives have widely been used as the photoactive component in molecular assemblies because of its long-lived excited-state lifetime at room temperature (1100 ns).[1–4] An advantage of these complexes is that the Ru–N bonds of metal-chelating bpy ligands are inert enough to afford electrochemically and photochemically stable complexes. One disadvantage, however, is that in polynuclear systems based on $[Ru(bpy)_3]^{2+}$, the stereogenic metal centres also generate diastereomers, and further substitution on the bpy ligands may lead to *facial* and *meridional* isomers.[5–9] Tridentate ligands, such as 2,2′:6′,2′′-terpyridine (tpy) are, therefore, much more attractive because of the inherent linearity and isomeric purity obtained in multinuclear assemblies.[4,10] Although the $[Ru(tpy)_2]^{2+}$ prototype has distinct structural advantages over $[Ru(bpy)_3]^{2+}$, its short excited-state lifetime of 0.25 ns at room temperature[11,12] limits its use in photosensitizer applications. The short lifetime may be attributed to the weaker ligand field generated by the tpy ligand, relative to that of bpy, which leads to a decrease in the energy gap between the emissive triplet metal-to-ligand charge transfer (^{3}MLCT) and the non-emissive metal-centred triplet (^{3}MC) states.[13] The latter, therefore, becomes thermally accessible from the ^{3}MLCT state.

Much attention has therefore been directed on the synthesis and design of new tridentate ruthenium(II) complexes with prolonged excited-state lifetimes.[14–21] The most popular approach has focused on manipulating the energy difference between the ^{3}MLCT and the ^{3}MC states. Stabilization of the ^{3}MLCT state relative to the ^{3}MC state leads to a greater energy gap between the two states.[11,22–27] However, lowering of the ^{3}MLCT state renders the complex less useful for photosensitizer applications, owing to the usual deactivation pathway for low-energy emitting ruthenium(II) complexes according to the energy gap law.[1,10,28,29] Recently, Hammarström and Johansson[30–32] demonstrated that design of tridentate ligands with larger bite angles than tpy can produce octahedral complexes that lead to a greater ^{3}MLCT–^{3}MC gap and hence longer excited-state lifetimes. Further studies by Ruben[33] and Heinze[34] show a similar effect. Cyclometallating tridentate ligands[35] and alternative N-heterocycles behave as strong σ donors[36–38] and have also been used to increase the energy gap between the ^{3}MLCT and the ^{3}MC states. Earlier, we reported an *N*,*N*′-dipyridyl-imidazolyl ligand with a view to increase the σ-donating ability of the tridentate ligand. However, Ru^{II} preferred a bidentate coordination mode rather than a tridentate one because of the unfavourable bite angles generated by the central five-membered imidazolium ring.[39]

Herein we report the synthesis, solid-state structure and electrochemical properties of two ruthenium(II) complexes of a readily synthesized tridentate ligand in which the central pyridine ring of tpy is replaced by a six-membered N-

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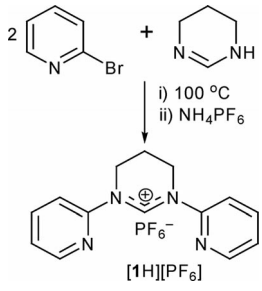
heterocyclic carbene (NHC). The basis of such a ligand design is to equip the tridentate ligand with a stronger σ-donating ability than tpy in order to destabilize the ^{3}MC state of its Ru^{II} complex, and, thus, allow room-temperature red emission from its Ru^{II} complexes.

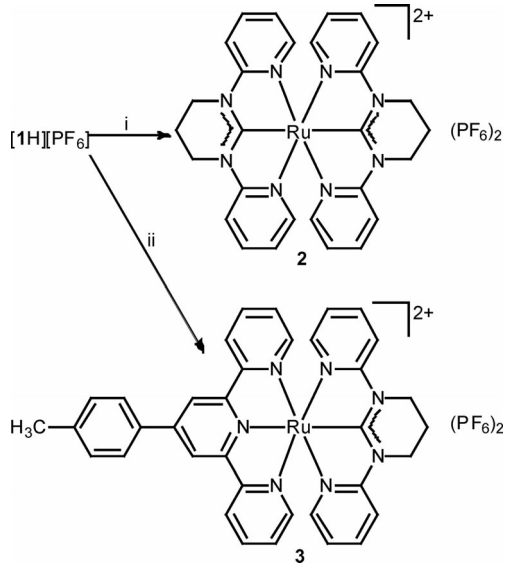
Results and Discussion

The carbene ligand precursor, *N*,*N*′-bis(2-pyridyl)-tetrahydropyrimidinium hexafluorophosphate ([**1**H][PF_6]), was synthesized following a protocol analogous to that of Chen and Lin.[40] A mixture of 1,4,5,6-tetrahydropyrimidine and 2-bromopyridine in a molar ratio of 1:4 was heated at 100 °C without solvent under a N_2 atmosphere (Scheme 1). Addition of methanolic NH_4PF_6 solution to this reaction mixture precipitated [**1**H][PF_6] as a beige crystalline powder. Reaction of [**1**H][PF_6] with ruthenium trichloride in 2:1 proportions in refluxing ethylene glycol in the presence of triethylamine and subsequent addition of an aqueous solution of NH_4PF_6 resulted in the precipitation of a yellow compound (Scheme 2). Recrystallization of the product from acetonitrile/ethyl ether afforded yellow crystals of the homoleptic carbene complex, [(**1**)$_2$Ru(PF_6)$_2$] (**2**), an unusual colour for Ru^{II} complexes of tridentate ligands.



Scheme 1. Synthesis of the carbene precursor ligand.

Complex **2** crystallizes as a highly symmetrical complex (Figure 1), and, in the margin of accuracy, the immediate coordination geometry around Ru has a D_{2d} symmetry. The conformation of the saturated ring thus does not seem to have any noticeable influence on the structure, as found in other coordination complexes incorporating $(CH_2)_3$-bridged donor atoms.[46,47] Ru–C_{NHC} distances (1.97 Å) in **2** are significantly shorter than those observed in other complexes with bi- or tridentate pyridyl-carbene ligands [1.99–2.07 Å, av. 2.05(2) Å][39,41–45] and are at the short end of the distances observed in Ru carbene complexes, in general (1.91–2.20 Å, av. 2.06(5) Å].[48] The average N–C14/C28 distance [1.349(3) Å], however, is comparable to the average observed in other Ru carbene complexes [1.36(2) Å].[48] The short Ru–C_{NHC} bond is thus most likely a consequence of the tridentate coordination of **1**[49] and does not indicate an increase in bond order. In previous studies, we concluded that the bidentate instead of tridentate coordination of the five-membered, unsaturated *N*,*N*′-dipyridyl-dihydroimidazolyl carbene ligand arises as a result of the unfavourable coordination geometry caused by the five-membered



Scheme 2. Syntheses of the carbene complexes of ruthenium (i) $RuCl_3$, ethylene glycol (reflux), aqueous NH_4PF_6. (ii) [4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine]$RuCl_3$, ethylene glycol (170–180 °C), aqueous NH_4PF_6.

ring.[39] Ring extension reduces the C_{Py}–N–C_{NHC} angle from 118.7(2)° in *N*,*N*′-dipyridyl-dihydroimidazolyl[39] to 113.7(2)–113.9(2)° in **1**, which enables the tridentate coordination of **1** to Ru with a comparable coordination geometry around Ru (C_{NHC}–Ru–N angles: **2**, 76.6(1)–77.0(1)°; *N*,*N*′-dipyridyl-dihydroimidazolyl,[39] 78.0(1)°].

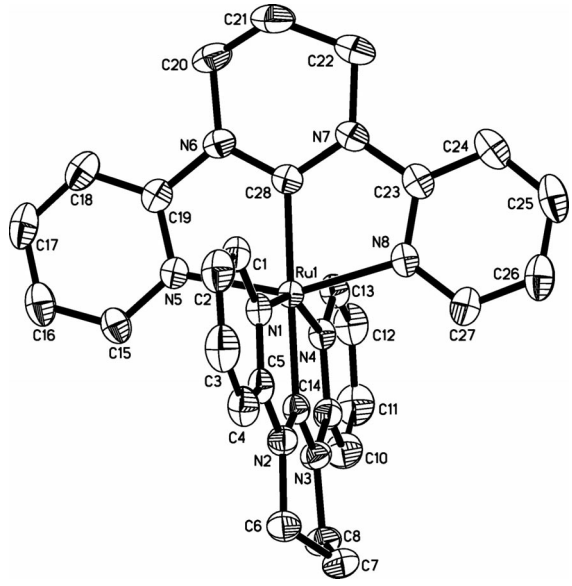


Figure 1. Crystal structure of **2**. Hydrogen atoms, PF_6 anions and co-crystallized solvent are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Ru1–C28, 1.969(2) Å; Ru1–C14, 1.972(3) Å; Ru1–N1, 2.084(2) Å; Ru1–N4, 2.093(2) Å; Ru1–N5, 2.091(2) Å; Ru1–N8, 2.088(2) Å; N2–C14, 1.345(3) Å; N3–C14, 1.349(3) Å; N6–C28, 1.351(3) Å; N7–C28, 1.350(3) Å; C14–Ru1–N1, 76.98(9)°; C14–Ru1–N4, 76.60(9)°; C28–Ru1–N5, 76.82(9)°; C28–Ru1–N8, 76.91(9)°.

In order to have further insight into the binding properties of the new tridentate carbene ligand, we synthesized the heteroleptic carbene complex [(**1**)Ru(ttpy)]$(PF_6)_2$ (**3**) {ttpy = 4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine} by reaction of [**1**H][PF_6] with (ttpy)$RuCl_3$ in ethylene glycol and subsequent metathesis to its PF_6^- salt (Scheme 2). The product was purified by column chromatography, and recrystallization from an acetonitrile/toluene mixture afforded orange crystals.

Heteroleptic complex **3** (Figure 2) again displays a very symmetrical coordination of the two ligands. There are no significant differences between the Ru–N distances and C/N–Ru–N angles of the carbene ligand and those of the terpyridine ligand. The Ru–C_{NHC} bond in **3** [1.901(7) Å] is significantly shorter than that in **2**, and one of the shortest bonds yet observed in Ru carbene complexes (1.91–2.20 Å, av. 2.06(5) Å].[48] The average N–C_{NHC} bond length in **3** [1.36(2) Å], however, does not change significantly. The short Ru–C_{NHC} distance is thus most likely caused by a combination of the tridentate coordination of the carbene ligand[49] and an increase in the σ bonding of the carbene to Ru, which becomes more Lewis acidic when bipyridylcarbene in **2** is replaced by terpyridine in **3**.

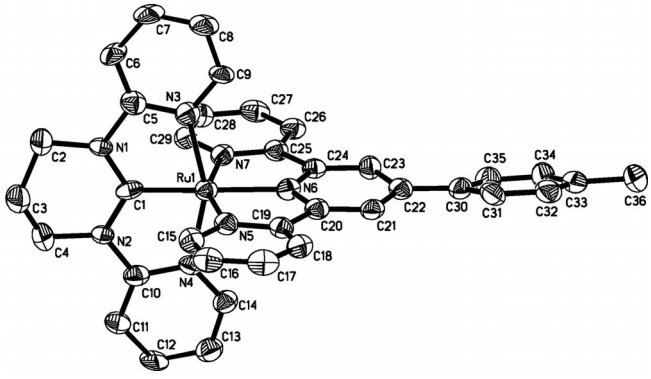


Figure 2. Crystal structure of **3**. Hydrogen atoms and PF_6 anions are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Ru1–C1, 1.901(7) Å; Ru1–N3, 2.088(6) Å; Ru1–N4, 2.082(6) Å; Ru1–N5, 2.082(5) Å; Ru1–N6, 2.037(5) Å; Ru1–N7, 2.076(5) Å; N1–C1, 1.339(9) Å; N2–C1, 1.374(9) Å; C1–Ru1–N3, 77.6(3)°; C1–Ru11–N4, 79.0(3)°, N6–Ru1–N5, 77.0(2)°; N6–Ru1–N7, 78.2(2)°.

The precursor ligand and the two complexes were also characterized by ^1H and ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum, the resonance for the 6′ (N*C*N) carbon atom shows expected changes while going from [**1**H][PF_6] to **3** and to **2**.[50] While the NCN carbon in [**1**H][PF_6] resonates at δ = 152 ppm, the same carbon atom in the homoleptic complex **2** shows a signal that experiences a large downfield shift to 235 ppm. This is expected for deprotonation and subsequent coordination of a NCN carbon atom to ruthenium in **2**. The replacement of one carbene ligand in **2** by a more π-accepting terpyridine ligand in **3** induces a further downfield shift of 2 ppm. This is also in accordance with a shorter Ru–C bond in **3** than that in **2** by ca. 0.07 Å.

The electrochemical behaviour of complexes **2** and **3** has been examined by cyclic voltammetry at a platinum electrode in purified acetonitrile under a dry argon atmosphere (Table 1). On the positive side of the saturated calomel electrode (SCE), the homoleptic carbene complex **2** shows a quasireversible Ru(III/II) couple at 1.17 V vs. SCE with a difference of 80 mV between the cathodic and anodic peak potentials. For comparison, it may be noted that the same Ru(III/II) couple for $[Ru(tpy)_2]^{2+}$ appears at 1.32 V vs. SCE,[51] i.e. **2** is more easily oxidised than $[Ru(tpy)_2]^{2+}$, which indicates that ligand **1** is a stronger donor ligand than tpy. Complex **3** also shows a quasireversible Ru(III/II) couple at 1.28 V vs. SCE, at slightly more positive potential relative to **1** as only one NHC ligand is coordinated to Ru^{II}. At negative potentials vs. SCE, both complexes display irreversible ligand-based reduction peaks. Complex **3** shows two such reduction peaks, at –1.34 and –1.88 V vs. SCE. The first reduction peak is designated as a ttpy-based reduction, which is in the range observed for homo- and heteroleptic terpyridine complexes.[4] The second peak is due to the reduction of the carbene ligand **1**. Complex **2** on the other hand shows only one irreversible reduction peak at –1.90 V vs. SCE. The observation of reduction peaks at such negative potentials in both complexes may be attributed to the loss of delocalization between the two peripheral pyridine rings in carbene ligand **1**. The complex [Ru(tpy)(4-Et-py)$_3$]$(PF_6)_2$ (where 4-Et-py = 4-ethylpyridine), a complex with three independent pyridine ligands, also shows a second irreversible reduction at –2.0 V vs.

Table 1. Spectroscopic, photophysical and electrochemical data for the ligand [**1**H][PF_6] and Ru^{II} complexes **2** and **3** in deaerated CH_3CN solutions.

	Absorption λ_{max} [nm] (ε [$\times 10^{-3}$ M^{-1}cm^{-1}])	Emission[a] λ_{em} [nm]	Electrochemistry[b] $E_{1/2}$(oxid.)	$E_{1/2}$(red.)	
[**1**H][PF_6]	290 (1.67), 244 (39.2)	–		–1.20 (50)	
2	470 (2.2), 440 (2.45), 384 (2.98), 357 (4.63), 302 (57.4), 248 (35.9), 207 (19.4)	753 (293 K)	1.17 (80)	–1.90 (irr)[c]	
3	473 (5.51), 440 (6.40), 296 (42.5), 245 (20.1)	735 (293 K)	1.28 (70)	–1.34 (irr)[c]	–1.88 (irr)[c]
$Ru(tpy)_2^{2+}$[d]	476 (17.7), 309 (70.2), 271 (55.9)[d]	620 (77 K)[e]	1.32[f]	–1.27[f]	–1.52[f]
$Ru(tpy)(4\text{-Et-py})_3^{2+}$[g]	504 (5.40), 450 (4.50), 318 (35.8), 274 (21.5), 238 (26.7), 210 (32.7)	–	1.24	–1.25	–2.0

[a] In the solid state. [b] Potentials are in V vs. SCE for acetonitrile solutions, 0.1 M in Bu_4NPF_6, recorded at 25 ± 1 °C at a sweep rate of 100 mV/s. The difference between cathodic and anodic peak potentials (mV) is given in parentheses. [c] Irreversible; potential is given for the cathodic wave. [d] From ref.[53] [e] From ref.[54] [f] From ref.[51] [g] 4-Et-py = 4-ethylpyridine, from ref.[52]

SCE.[52] The electrochemical studies clearly indicate that **1** has stronger σ-donating ability than tpy, which is essential in order to increase the energy gap between the ^{3}MLCT and ^{3}MC states by destabilizing the ^{3}MC state.

The UV/Vis spectra of both **2** and **3** in acetonitrile solution display the expected ^{1}MLCT bands in the 400–500 nm region. The UV part of the spectra is dominated by π→π* transitions in the ligand moieties, centred around 302 nm for **2** and 296 nm for **3**. Though the extinction coefficient for the MLCT band is lower for **2** than for **3**, the π→π* transition has a higher molar absorptivity in **2** than in **3**. Table 1 reveals that replacement of a tpy ligand by three pyridine ligands has a considerable impact on the extinction coefficient of the lowest energy MLCT band. Whereas bis-(terpyridine)-type complexes have ε values for the above-mentioned band in the range of ca. 20000 $M^{-1}cm^{-1}$, those for the tris(pyridine)-terpyridine complexes are ca. 5000 $M^{-1}cm^{-1}$. A similar change in the extinction coefficient for the lowest energy MLCT band is also observed in the heteroleptic complex **3** and, even further, in **2**. These observations further reinforce our deduction from the electrochemical data that the pyridine groups in **1** behave more independently than those in a fully delocalized ligand like tpy.

Complexes **2** and **3** were not emissive in fluid solution at room temperature. The emission data for **2** (753 nm) and **3** (735 nm) from powder samples demonstrate a large redshift with respect to those for the solid samples of $[Ru(tpy)_2]^{2+}$ (620 nm, see Table 1). Such a redshift has previously been noted for the Ru^{II} complexes of π-donating tridentate ligands based on tertiary *N*,*N*′-dimethyl-*N*,*N*′-dipyrid-2-yl-pyridine-2,6-diamine[34] and 4′-(pyrrol-2-yl)-2,2′:6′,2′′-terpyridine.[55] Similarly, the large redshift in emission wavelengths in our complexes arise from both the increased σ donation of the carbon and the π-donation of the nitrogen atoms in the tetrahydropyridimine portion of **1** relative to that in tpy. The red emission of these complexes compares favourably to the solid-state phosphorescence of Ru^{II} complexes made with tridentate pyrazolyl bis(pyridine) ligands (666–810 nm),[56] which are also used in phosphorescent organic light-emitting diodes.[57,58]

Conclusions

Herein we have successfully designed and synthesized a dipyridyl NHC ligand that acts as a stronger σ donor than terpyridine while maintaining a tridentate chelating binding mode around the metal ion. The crystal structures of the two Ru^{II} complexes confirm the tridentate *meridional* binding mode of the new dipyridyl carbene ligand. The Ru(II/III) couple for complexes **2** and **3** clearly indicates that carbene ligand **1** involved in this present work is a better σ donor than terpyridines, which lead to a emission in the red (735 and 753 nm) in the solid-state at room temperature. Further investigations of new red-emitting Ru^{II} complexes of **1** are underway.

Experimental Section

Syntheses of the Compounds

***N*,*N*′-Bis(2-pyridyl)-tetrahydropyrimidinium Hexafluorophosphate ([1H][PF$_6$]):** 1,4,5,6-Tetrahydropyrimidine (1.25 mL, 15 mmol) and 2-bromopyridine (5.0 mL, 52 mmol) were mixed in a round-bottomed flask under an N_2 atmosphere. The mixture was stirred with heating at 100 °C for 48 h, during which the initial colourless reaction mixture turned dark brown. The mixture was cooled and poured into a saturated methanolic solution of NH_4PF_6 (50 mL). A beige precipitate appeared. The suspension was cooled to 0 °C for 2 h, filtered and dried. Yield = 1.0 g. (18%). ^{1}H NMR (CD_3CN, 700 MHz): δ = 10.36 (s, 1 H, 6′), 8.55 (m, 2 H, 6,6′′), 8.04 (td, J^t = 8, J^d = 1 Hz, 2 H, 4, 4′′), 7.51 (d, J^d = 8 Hz, 2 H, 3, 3′′), 7.47 (m, 2 H, 5, 5′′), 4.10 (t, J^t = 6 Hz, 4 H, 2′,4′), 2.45 (quint., J^t = 6 Hz, 2 H, 3′) ppm. ^{13}C NMR (CD_3CN, 175 MHz): δ = 152.0, 150.2, 149.8, 141.3, 124.7, 113.9 44.3, 19.2 ppm. HRMS (ESI): *m*/*z* = 239.1293 [M – PF_6]$^+$ ($C_{14}H_{15}N_4$ requires 239.1296). $C_{14}H_{15}N_4PF_6$ (384.13): calcd. C 43.76, H 3.93, N 14.58; found C 43.60, H 3.86, N 14.40.

[Ru(1)$_2$](PF$_6$)$_2$ (2): To a solution of $RuCl_3 \cdot 3H_2O$ (26 mg, 0.1 mmol) in ethylene glycol (5 mL) was added [**1**H][PF_6] (80 mg, 0.21 mmol) and triethylamine (2 drops). The resulting mixture was then heated at reflux for 8 h, cooled and added dropwise to an aqueous solution of NH_4PF_6 (5 mL containing 500 mg). The resulting yellow precipitate was collected by filtration, dried, dissolved in acetonitrile and purified by column chromotography (SiO_2, acetonitrile:aq. KNO_3, 7:1). The nitrate salt was metathesized to the PF_6 salt by addition of solid NH_4PF_6 followed by extraction by dichloromethane. The solvent was removed under reduced pressure. Recrystallization from acetonitrile/diethyl ether afforded a yellow crystalline product. Yield = 30 mg (34%). ^{1}H NMR (CD_3CN, 700 MHz): δ = 7.74 (td, J^t = 8, J^d = 1 Hz, 2 H, 4,4′′), 7.56 (dd, J^d = 6, J^d = 1 Hz, 2 H, 6,6′′), 7 (d, J^d = 9.0 Hz, 2 H, 3,3′′), 6.79 (td, J^t = 6, J^d = 1 Hz, 2 H, 5,5′′), 4.26 (t, J^t = 6 Hz, 4 H, 2′,4′), 2.81 (q, J^t = 6 Hz, 2 H, 3′) ppm. ^{13}C NMR (CD_3CN, 175 MHz): δ = 235.2 (N*C*N), 163.6, 156.3, 140.1, 121.5, 112.2, 42.1, 21.4 ppm. HRMS (ESI): *m*/*z* = 723.1119 [M – PF_6]$^+$ ($C_{28}H_{28}N_8PF_6Ru$ requires 723.1116), 289.0740 [M – 2PF_6]$^{2+}$ ($C_{28}H_{28}N_8Ru$ requires 289.0734). $C_{28}H_{28}N_8RuP_2F_{12}$ (868.12): calcd. C 38.76, H 3.25, N 12.92; found C 38.67, H 3.36, N 12.29.

[Ru{4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine}(1)](PF$_6$)$_2$·2H$_2$O (3): To a suspension of [4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine] $RuCl_3$ (53 mg, 0.1 mmol) in ethylene glycol (5 mL) was added [**1**H][PF_6] (40 mg, 0.11 mmol) and triethylamine (2 drops). The resulting mixture was then stirred at 170 °C for 6 h, cooled and added dropwise to an aqueous solution of NH_4PF_6 (5 mL containing 500 mg). The resulting brown precipitate was collected by filtration, dried, dissolved in acetontrile and purified by column chromotography (SiO_2, acetonitrile:aq. KNO_3, 7:1). The second orange band contained the product. The nitrate salt was metathesized to the PF_6 salt by addition of solid NH_4PF_6 followed by extraction by dichloromethane. The solvent was removed under reduced pressure. Recrystallization from acetonitrile/toluene afforded an orange crystalline product. Yield = 25 mg (26%). ^{1}H NMR (CD_3CN, 700 MHz, CD_2HCN): δ = 8.96 (s, 2 H, tpy$^{3',5'}$), 8.59 (d, J^d = 8 Hz, 2 H, tpy$^{3,3''}$), 8.08 (d, J^d = 8 Hz, 2 H, tpy$^{2''',6'''}$), 7.94 (d, J^d = 6 Hz, 2 H, carbene$^{6,\ 6''}$), 7.92 (td, J^t = 7, J^d = 1 Hz, 2 H, tpy$^{4,4''}$), 7.75 (td, J^t = 8, J^d = 2 Hz, 2 H, carbene$^{4,4''}$), 7.57 (d, J^d = 8 Hz, 2 H, tpy$^{3''',5'''}$), 7.43 (d, J^d = 8 Hz, 2 H, tpy$^{6,6''}$), 7.19 (td, J^t = 8, J^d = 1 Hz, 2 H, tpy$^{5,5''}$), 7.06 (dd, J^d = 6, J^d = 1 Hz, 2 H, carbene$^{3,3''}$), 6.76 (td, J^t = 6, J^d = 1 Hz, 2 H, carbene$^{5,5''}$), 4.35 (t, J^t = 6 Hz, 4 H, carbene$^{2',4'}$), 2.87 (q, J^t = 6 Hz, 2 H, carbene$^{3'}$), 2.53 (s, 3 H,

tpy^{CH3}) ppm. ^{13}C NMR (CD_3CN, 175 MHz, CD_2HCN): δ = 237.1 (*N*C*N*), 163.4, 159.0, 157.3, 154.0, 152.0, 150.7, 142.1, 140.3, 138.9, 135.0, 131.3, 128.7, 128.1, 125.5, 121.9, 121.6,112.2, 42.7, 21.7, 21.5 ppm. HRMS (ESI): *m*/*z* = 808.1323 [M – $2H_2O$ – PF_6]$^+$ ($C_{36}H_{31}N_7PF_6Ru$ requires 808.1320), 331.5847 [M – $2H_2O$ – $2PF_6$]$^{2+}$ ($C_{36}H_{31}N_7Ru$ requires 331.5836). $C_{36}H_{31}N_7RuP_2F_{12}\cdot 2H_2O$ (989.14): calcd. C 43.73, H 3.57, N 9.92; found C 44.12, H 3.76, N 9.23.

CCDC-800801 (2) and -800802 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Materials, instrumentation and general information on the X-ray crystallography are presented.

Acknowledgments

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