Ru(II) complexes of polyarylated terpyridines: unexpected side-chain C-metallation and photosensitization of electron transfer

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Abstract

The new ligands 4,4′-diphenyl-6,6′-di(4-ethoxycarbonylphenyl)-2,2′:6′,2′-terpyridine (H4), its non-carboxylated 4,6,4′,6′-tetraphenyl analogue (H5) and the 4,4′-diphenyl-6,6′-di(4-methoxyphenyl) analogue were prepared in high yields via double Krohnke reactions. Reactions with activated (ttpy)RuCl3 (ttpy is 4′-p-tolyl-2,2′:6′,2′-terpyridine) provided the symmetrical N6-coordinated complexes, [Ru(H4)(ttpy)](PF6)2 and [Ru(H5)(ttpy)](PF6)2, along with the novel, unsymmetrical C-metallated analogues [Ru(H4)(ttpy)]PF6 and [Ru(H5)(ttpy)]PF6, in which an unprecedented side-chain metallation occurred in lieu of incomplete substitution. A crystallographic analysis of [Ru(H5)(ttpy)]NO3 confirmed the N5C donor set in these products and revealed a distorted binding of 5− as well as ‘n-stacking’ between its uncoordinated pyridine and the ttpy ligand. The diester [Ru(H4)(ttpy)]PF6 was hydrolyzed to the diacid complex [Ru(H3)3(ttpy)](PF6)2 (H3 is 4,4′-diphenyl-6,6′-di(4-carboxyphenyl)-2,2′:6′,2′-terpyridine). Measurements of the photogeneration of methyl viologen cation radical with [Ru(H5)(ttpy)](PF6)2 and [Ru(H3)3(ttpy)](PF6)2 as sensitizers showed that the presence of carboxyl groups in the latter provided a distinct benefit, owing to the formation of the neutral form [Ru(3)(ttpy)]0 but this was insufficient to overcome the detrimental effect of inter-ligand repulsions. © 2001 Published by Elsevier Science B.V.

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1. Introduction

A large number of Ru(II) complexes have been explored as photosensitizers which undergo photoinduced electron transfer (PET) reactions with electron accepting quencher molecules. PET generates charge-separated states that can initiate useful redox chemistry, such as the generation of H2 from H2O [1]. With cationic electron acceptors such as methyl viologen (MV2+), 1,1′-dimethyl-4,4′-bipyridinium, it has been found that neutral or anionic Ru(II) complexes of ionizable ligands, such as carboxylated or sulfonated bipyridines, undergo faster PET than do their cationic analogues, owing in part to electrostatic assistance [2]. PET to semiconductor particles can proceed from even extremely short-lived excited states with the help of attractive interactions between carboxylated sensitizers and semiconductor surface [3], and ionizable complexes are now routinely used for anchoring to such surfaces [4].

There have been no analogous examples with ionizable tridentate ligands, such as 2,2′:6′,2′-terpyridine (tpy). While tpy complexes generally suffer from comparatively short excited-state lifetimes, analogues bearing electron-withdrawing groups [5,6] and cyclometallated analogues [7–9] have displayed enhanced triplet and luminescence lifetimes, and would further benefit from electrostatic assistance. However, the few known [10] examples of terpyridine carboxylic acids required arduous methods for their preparation and/or cannot be readily applied to our purposes.

We describe here the facile Krohnke synthesis [11] of such a ligand, its transformation to a Ru(II) complex, the characterization of an unusual C-metallated side-product, and the ability of the complex to undergo PET to MV2+. 
2. Experimental

2.1. Preparation of 4,4′-diphenyl-6,6′-di(4-ethoxy-carbonylphenyl)-2,2′:6′,2′-terpyridine (H4)

2,6-Di[2-(1-pyridyl)-1-oxo-ethyl]pyridine diiodide [12] (2) (0.30 g) and 3-(4-carboxyphenyl)-1-(2-pyridyl)-propenone [13] (1a) (0.25 g, 2 equiv.) were added to excess NH4OAc in glacial AcOH, with heating to reflux for 3 h. After cooling, the precipitate was collected, washed with CH2OH, 3 × 50 ml) and dried. The crude diacid H3, was a tan powder (1.45 g, 95% yield). This was taken up in SOCl2 (100 ml) and heated to reflux under argon for 2 h. After removal of volatiles in vacuo, absolute EtOH (100 ml) was added, and the mixture again heated to reflux under argon for 2 h. Once rid of solvent, the crude diester was dissolved in warm CHCl3 and purified on a short column (alumina-N, 2.98 CH2OH–CHCl3), then recrystallized (EtOH) to give a white powder (1.58 g, 80% yield). M.p.: 277–280 °C. 1H NMR (CDCl3, δ ppm): 3.90 (s, 2H, H3), 7.85 (d, 2H, H2A), 8.33 (d, 4H, H-Ph), 8.22 (d, 4H, H-Ph), 8.09 (t, 1H, H7), 8.07 (s, 2H, H5), 7.88 (d, 4H, 4-PhH), 7.54 (m, 6H, 4-PhH6A), 4.37 (q, 4H, CH2), 1.47 (t, 6H, CH3). 13C NMR (CDCl3, δ ppm): 166.5, 156.6, 155.9, 155.3, 150.3, 143.5, 138.8, 137.9, 130.8, 129.2, 127.2, 127.0, 121.6, 119.0, 118.4, 80.1, 29.6. FAB MS; m/z (%): 682 (100) [M + H] 654 (5) [M – C2H5], 636 (15) [M – OC2H5]. Anal. Found: C, 79.24; H, 5.11; N, 6.09. Calc. for C45H32N6O4: C, 79.28; H, 5.17; N, 6.16%.

2.2. Preparation of 3-(4-methylphenyl)-1-(2-pyridyl)-2-propenone (1b)

2-Acetylpyridine (3.43 g, 28 mmol) and 4-tolualdehyde (3.38 g, 28 mmol) were dissolved in 1:1 CH2O−5aqueous KOH (100 ml) and the solution was stirred for 2 h in an ice bath. The precipitate was collected, washed with H2O and dried, giving pale yellow flakes (5.50 g, 88%). A portion of the product was recrystallized (CH2OH) as pale yellow flakes for characterization. M.p.: 79–82 °C. 1H NMR (CDCl3, δ ppm): 8.73 (d, 1H, py–H6), 8.26 (d, 1H, vinyl H); 8.19 (d, 1H, py–H6); 7.91 (d, 1H, vinyl H); 7.88 (dd, 1H, py–H45), 7.62 (d, 2H, ArH), 7.48 (dd, 1H, py–H45), 7.21 (d, 2H, ArH), 2.42 (s, 3H, CH3). 13C NMR (CDCl3, δ ppm): 189.5, 154.4, 148.8, 144.9, 141.1, 137.0, 132.5, 129.6, 128.9, 126.8, 122.9, 119.9, 21.6. FAB MS; m/z (%): 224 (100) [M + H], 136 (44) [M – py]. Anal. Found: C, 80.89; H, 5.57; N, 6.22. Calc. for C16H13NO: C, 80.69; H, 5.87; N, 6.27%.

2H NMR assignments use the standard tpy numbering for H4, H5 and 6, and the ring labels of Scheme 1 for the Ru complexes.

2.3. Preparation of 4,6,4′,6′-tetraphenyl-2,2′:6′,2′-terpyridine (H5)

In the same manner as for crude H3, 0.60 g of 3-phenyl-1-(2-pyridyl)propenone (1b) and 2 (1.00 g, 0.5 equiv.) were converted to H5, obtained as a white powder (0.89 g, 98% yield). M.p.: 277–280 °C. 1H NMR (CDCl3, δ ppm): 7.87 (s, 2H, H3), 7.75 (d, 2H, H5), 7.56 (s, 2H, H3), 7.08 (d, 2H, 6-PhH2), 7.04 (d, 2H, 4-PhH2), 6.87 (t, 1H, H3), 6.76 (m, 6H, 4, 6-PhH6A). 13C NMR (TFA-d, δ ppm): 151.2, 151.0, 147.4, 145.4, 139.0, 138.8, 130.7, 129.1, 122.0, 121.4, 120.7, 116.5, 115.1, 114.9, 114.6, 110.4. FAB MS; m/z (%): 538 [M + H]. Anal. Found: C, 87.14; H, 5.01; N, 7.99. Calc. for C39H27N3: C, 87.12; H, 5.06; N, 7.82%.

2.4. Preparation of [Ru(tppy)(H4)][PF6]2 and [Ru(tppy)(N,N,C-4)]PF6

Ru(tppy)Cl4 (0.030 g) was added to a solution of AgBF4 (0.035 g, 3 equiv.) in acetone (10 ml) and the mixture was heated to reflux under argon for 30 min. The AgCl precipitate was filtered off, DMF (5 ml) was added to the dark purple filtrate, and the acetone was removed in vacuo. This was added to a warmed solution of H4 (0.045 g, 1.18 equiv.) in DMF (5 ml) and the mixture was heated to reflux in the dark under argon for 48 h, then freed of solvent in vacuo. The residue was redissolved in minimal CH2OHN and sufficient aqueous NH4PF6 was added to cause precipitation of a dark red powder. Some pure [Ru(H4)(tppy)][PF6]2 was isolated after trituration of this crude product with CH2OH, filtration and evaporation of the filtrate to provide a red powder. A further amount was obtained by chromatography (silica, 14:2 CH2CN–satd. KNO3–H2O) of the CH2OH-insoluble residue. The less polar fraction was washed with H2O, reprecipitated with NH4PF6 as before, then precipitated from CH2CN with EtO to provide [Ru(t4)]PF6, a purple powder (0.010 g, 15% yield). 1H NMR (CD2CN, δ ppm): 8.93 (s, 1H), 8.87 (d, 1H), 8.52 (s, 1H), 8.18 (d, 2H), 8.17 (s, 1H), 8.14 (d, 1H), 8.11 (s, 1H), 8.08 (d, 2H), 7.92 (d, 1H, H4A), 7.78 (m, 18H), 7.49 (d, 1H), 7.47 (d, 2H), 7.43 (s, 1H), 7.42 (d, 1H), 7.30 (d, 1H, H6A), 7.23 (dd, 1H), 7.07 (dd, 1H), 7.20 (dd, 1H), 6.31 (s, 1H, H6), 5.78 (s, 1H, H6A), 4.48 (q, 4H, OCH2CH2), 3.89 (q, 4H, OCH2CH2), 2.60 (s, 3H, ArCH3), 1.46 (t, 6H, OCH2CH3), 0.90 (t, 6H, OCH2CH3). FAB MS; m/z (%): 1104 (100) [M – H – PF6], 1031 (15) [M – H – PF6 – COOEt]. The more polar material [Ru(H4)(tppy)][PF6]2 was similarly treated and isolated as a red powder (total 0.048 g, 61% total yield). 1H NMR (CD2CN, 330 K, δ ppm): 9.05 (d, 2H, H4sc), 8.80 (s, 2H, H5B), 8.60 (t, 1H, H8), 8.35 (d, 2H, H6D), 8.04 (dd, 2H, H4A), 7.84 (s, 2H, H5), 7.80 (d, 4H, H2D), 7.80 (d, 2H, H5), 7.56 (d, 2H, H6D), 7.51
was collected by vacuum filtration, washed with H₂O, and dried. A second crop was isolated by adding an additional 50 ml of H₂O to the filtrate and cooling the solution overnight. The combined crops recrystallized (CH₃OH) as white needles (1.08 g, 68%). M.p.: 104–105 °C. ¹H NMR (CDCl₃, δ ppm): 8.08 (d, 2H, Ar–H), 7.82 (d, 1H, vinyl–H), 7.69 (d, 2H, Ar–H), 7.58 (d, 2H, vinyl–H), 7.43 (m, 3H, Ar–H), 7.05 (d, 2H, Ar–H), 3.95 (s, 3H, OCH₃). ¹³C NMR (CDCl₃, δ ppm): 188.7, 163.7, 143.9, 135.1, 131.1, 130.8, 130.3, 128.9, 128.4, 121.9, 113.9, 55.5. EI MS; m/z (%): 238 (100) [M] 135 (50) [M – PhCH=CH]. Anal. Found: C, 79.98; H, 5.94. Calc. for C₁₆H₁₄O₂: C, 80.65; H, 5.92%.

2.7. Preparation of 4,4''-diphenyl-6,6''-di(4-methoxyphenyl)-2,2'':6',2''-terpyridine (6)

2,6-Di[2-(N-pyridyl)-1-oxo-ethyl]pyridine diiodide (2) [12] (0.30 g, 0.500 mmol) and 4'-methoxychalcone (1c) (0.25 g, 1.00 mmol) were added to a solution of excess NH₄OAc (2.0 g) in glacial AcOH (5 ml), and the resulting solution was heated to reflux for 5 h. The precipitate, which formed upon cooling overnight, was collected, washed with CH₃OH (3 x 50 ml) and dried, yielding a white powder which recrystallized (CHCl₃ – CH₃OH) as white needles (0.54 g, 90%). M.p.: 293–296 °C. ¹H NMR (TFA-d, δ ppm): 7.85 (s, 2H, H₂C=CH), 7.74 (d, 2H, H₂C=CH), 6.07 (s, 2H, H₂C=CH), 5.15 (d, 1H, H₃N), 2.57 (s, 2H, ArCH₂). FAB MS; m/z (%): 961 (100) [M – H₂PF₆]. A crystallographic sample of [Ru(tttpy)(N,N,C-5)PF₆] was obtained by omitting the second NF₆ treatment and diffusion of Et₂O into an acetone solution. The more polar fraction provided red [Ru(H₅(tttpy))(PF₆)₂] (0.055 g, 68% yield).

2.8. Crystal structure determination of [Ru(tttpy)(N,N,C-5)NO₃]

Diffraction intensities were collected on a Nonius Kappa CCD instrument using a fine-focus sealed tube Mo Kα source and graphite monochromator (λ = 0.71073 Å). C₆₆H₅₃N₅O₇Ru·0.25H₂O, M = 1027.60, purple needle (0.20 x 0.15 x 0.12 mm); monochromatic, a = 12.6538(12), b = 17.077(2), c = 22.5488(18) Å, β = 104.524(6)°, V = 4717.0(8) Å³, Dcalc = 1.447 g cm⁻³, space group P2₁/n, Z = 4, μ (Mo Kα) = 0.391 mm⁻¹; T = 150.0(1) K, 37 511 reflections collected (θ = 4.09–23.26°, completeness to θ = 23.26° 99.8%, 0 ≤ h ≤ 14, 0 ≤ k ≤ 18, −25 ≤ l ≤ 24), 6698 unique (Rint = 0.271), corrected for absorption (Denzo-SMN) and used in all calculations. Heavy atom positions were determined by direct methods (SHELXS-97). The remaining non-hydrogen atoms were located by difference Fourier maps, while the hydrogen atoms were assigned idealized positions. Structure refinement used full-matrix least-square refinement using SHELXL-97.
squares on $F^2$ (SHELXL-97). Rings D and L were constrained to fit regular hexagons (C–C 1.39 Å). Ring F/G was disordered over two equally populated rotational orientations. All but the hydrogen atoms and the solvent oxygen atoms were refined anisotropically. With 665 refined parameters, the final $wR(F^2)_3$ was 0.2055 (all data), goodness-of-fit $^2 = 1.047$, with $R(F)$ = 0.0826 for the 3458 reflections where $I > 2\sigma(I)$; largest difference peak and hole 0.555 and $-0.540$ e Å$^{-3}$. Table 1 presents selected bond lengths and angles.

2.9. Preparation of [Ru(H_3)(ttipy)](PF_6)_2

A sample of [Ru(H_4)(ttipy)](PF_6)_2 (0.1001 g, 71.7 μmol) in 5 ml of DMF was heated to reflux with NaOH (10 ml 0.10 N) while stirring for 4 h. After cooling and quenching with HPF_6 (60% in H_2O), the precipitates were collected and washed with H_2O. The solid was redissolved in CH_3CN and washed with hexanes, followed by a removal of volatiles in vacuo to yield 0.0854 g (89%) of [Ru(H_3)(ttipy)](PF_6)_2. $^1$H NMR (CD_3CN, 330 K, δ ppm): 8.05 (d, 2H, H_3^4E), 8.10 (t, 1H, H_2^4C), 7.39 (m, 4H, H_3^3A), 7.30 (dd, 2H, H_5^5E), 7.29 (d, 2H, H_6^4D), 7.27 (s, 2H, H_5^5B), 7.25–7.27 (m, 6H, H_3^3B, H_4^4D, H_6^6E), 7.39 (m, 4H, H_3^3A), 7.30 (dd, 2H, H_5^5B), 7.14 s, 2H, H_3^3B), 6.21 (d, 4H, H_2^2A), 2.57 (s, 3H, ArCH_3). ES MS; $m/z$: 525 [M – 2PF_6]^+. The product was ≥95% pure but attempts at recrystallization of an analytical sample resulted in the partial loss of the elements of HPF_6, producing insoluble material.

2.10. Electron transfer measurements

Sample solutions (2.5 ml) containing [Ru(H_5)(ttipy)](PF_6)_2 (4.03 × 10$^{-5}$ M), [Ru(H_3)(ttipy)](PF_6)_2 (3.97 × 10$^{-5}$ M) or [Ru(ttipy)](PF_6)_2 (3.99 × 10$^{-5}$ M), MV(PF_6)_2 (9.45 × 10$^{-5}$ M) and triethanolamine (5 × 10$^{-2}$ M) in CH_3CN were prepared in 3 ml cuvettes for measurements and data treatment as detailed elsewhere [15]. The absorbance due to MV$^+$ ($\lambda_{\text{max}}$ 600 nm, $\epsilon_{\text{max}}$ 10060 cm$^{-1}$) [16] was monitored over time first under irradiation, then in the dark, and this cycle was repeated twice more with each sample. After converting the absorbance data to MV$^{2+}$, the average maximum MV$^{2+}$ yields and the average initial growth rates were assessed. The pseudo-first-order rate constants for the formation ($k_i$) and quenching ($k_q$) of MV$^{2+}$ were obtained from application of the kinetic model [15]

$$\frac{d[MV^{2+}]}{dt} = k_i[MV^0]_0 - (k_i + k_q + k_{d1})[MV^+]_0 - k_{d2}[MV^{2+}]_0$$

using $k_d$ parameter values measured from a prior analysis of the subsequent aerobic decays in the dark (where $k_i = k_q = 0$).

3. Results and discussion

3.1. Synthesis

The chalcone derivative 1a [13] and the dipyridinium salt 2 [12] were condensed in the presence of NH_4$^+$ to give the new terpyridinediacid H_3, Scheme 1). The full characterization of H_3 and its use in complexation were precluded by its low solubility, but its identity was determined by NMR spectroscopy in CF_3COOD. Esterification provided the soluble and fully characterized H_4 in 76% isolated yield from 1a. Unfortunately, reactions of H_4 with RuCl_3 or Ru(DMSO)_2Cl_2 were not clean and incomplete. But, after activation with Ag$^+$, reaction of the known [14] (ttipy)RuCl_3 (ttipy is 4′-p-tolyl-2,2′:6′,2″-terpyridine) with H_4, followed by an anion exchange, provided a mixture of two PF_6$^-$ salts. One was a red complex, the expected [Ru(H_4)(ttipy)](PF_6)_2 (61% isolated yield), and the other was a purple salt later assigned the C-metallated structure [Ru(4′-ttipy)]PF_6 (15% isolated yield). Complex [Ru(H_4)(ttipy)](PF_6)_2 was hydrolyzed with NaOH, then treated
Scheme 1. Reagents and conditions: (i) excess NH₄OAc, HOAc, reflux, 2 h; (ii) SOCl₂, reflux, then EtOH, reflux; (iii) Ru(ttpy)Cl₃, AgBF₄, acetone, reflux, 0.5 h, then H₄ or H₅, DMF, reflux, 8 h; (iv) excess NH₄PF₆ in H₂O, CH₃CN; (v) NaOH, DMF, reflux, 4 h, then HPF₆. 

with HPF₆ to provide an 89% isolated yield of the diacid [Ru(H₅)(ttpy)](PF₆)₂, the first carboxylated terpyridine complex of Ru(II).

In an entirely analogous manner, the new chalcone 1b was transformed to the 4,6,4,6-tetraphenyl ligand H₅ (86% overall isolated yield from commercially available materials), then to a mixture of its complexes (Scheme 1). The major product was again the red, N₅-ligated product [Ru(H₅)(ttpy)](PF₆)₂ in 68% yield, and the minor, purple product (7% yield) was assigned the N₅C-coordinated structure [Ru(N₅C-5)(ttpy)]PF₆, on the basis of spectral similarities with [Ru(N₄)(ttpy)]PF₆, whose crystallography confirmed its structure (vide infra).

As an illustration of the generality of the ligand synthesis, we also prepared the 6,6-di(4-methoxyphenyl)-4,4-diphenyl analogue 6 from the new chalcone 1c (61% overall isolated yield from commercially available materials) as an example bearing an electron-releasing substituent, though it was not transformed to a Ru(II) complex.

The identification of the C-metallated products [Ru(4)(ttpy)]PF₆ and [Ru(5)(ttpy)]PF₆ involved a number of techniques. The lack of symmetry was immediately evident from the ¹H NMR spectra and was confirmed by a dtd splitting pattern for the central pyridine ring signals revealed by the COSY spectra. Not all resonances were assignable but a strongly upfield-shifted singlet (5.8 ppm) undergoing long-range coupling to one of the pair of doublets was assigned to the hydrogen next to the site of metallation (H-3) on a p-phenylene ring (ring A). Such a shift has been found in other instances of C-metallation [8,9]. The shielding is analogous to that seen at the 6 positions of N₅-coordinated terpyridines and is also attributable to the ring current of the orthogonal ligand (ttpy, in this instance). Another example is provided by our new N₅-coordinated terpyridine complexes [Ru(H₄)(ttpy)](PF₆)₂, [Ru(H₅)(ttpy)](PF₆)₂ and [Ru(H₃)(ttpy)](PF₆)₂, all of which have 6/6'-phenyl ortho H (ring A) lying above the terminal pyridines of the ttpy ligand (ring E), and all three show a doublet near 6.2 ppm. Analogously, [Ru(4)(ttpy)]PF₆ and [Ru(5)(ttpy)]PF₆ showed singlets near 6.3 ppm that were assigned to the uncoordinated pyridine H (ring E), and the strong upfield shift was again ascribed to the same ring current effect.

The electronic spectrum of [Ru(4)(ttpy)]PF₆ revealed two bands, at 530 nm (ε 17 200 M⁻¹ cm⁻¹) and 380 nm (ε 10 000 M⁻¹ cm⁻¹) in accordance with similar MLCT bands observed with other C-metallated species [8,9]. The latter is assigned to metal-to-ligand charge transfer [9] to 4-. The main product, [Ru(H₄)(ttpy)](PF₆)₂, absorbed at a position (488 nm, 22 600 M⁻¹ cm⁻¹) more typical of terpyridine complexes. The new C-metallated complexes are distinctive in several respects. They are, to our knowledge, the first instances of optional C-metallation by ligands otherwise able to bind exclusively through pyridine nitrogens. Previous instances of C-metallation with tridentates have been intentional in that the ligands bore fewer than three nitrogens. Optional C-metallation may have occurred previously but has not been reported: for instance, a purple side-product was noted during the complexation of 6,6'-diphenylterpyridine [17], but it was not isolated nor characterized. Secondly, side-chain metallation occurs here in lieu of an incomplete substitution. When the N₃ donor set along the meridional
plane is misaligned, the usual result is a ‘hypo-chelated’ \( N_5 Cl \)-coordinated species [18]. Here, the availability of \( C \)-metallation sites on the 6 and 6’ side-chains in either misaligned orientation precludes ‘hypo-chelation’. Although there are many examples of terpyridines acting as bidentates with pendant, non-coordinated pyridines [9,18,19], H4 and H5 provide the first examples of \( C \)-metallated varieties, acting moreover as tridentates. Thus, the pendant pyridine groups constitute protonation, alkylation or perhaps metal coordination sites not previously available in \( C \)-metallated complexes.

The solvent may have an effect on the distribution of \( N_6 \) and \( N_5 C \)-coordinated products [9], as can the occurrence of ‘\( \pi \)-stacking’ [19], but we note that the observed preference for \( N_6 \)-coordination is consistent with an initial coordination by a distal pyridine at one of two axial metal sites, as opposed to the one equatorial site, whereas an excess of the \( N_5 C \)-metallated complexes.

Fig. 1. ORTEP diagram of \([\text{Ru}(\text{ttpy})]\text{NO}_3\) showing 50% probability ellipsoids and disorder in a phenyl ring. H atoms and the counteranions have been omitted for clarity.

3.2. Molecular structure of \([\text{Ru}(\text{5} \text{ttpy})]\text{NO}_3\)

Although attempts were made to obtain high quality crystals of all complexes, useable crystals were instead obtained with the \( \text{NO}_3^- \) salt of \([\text{Ru}(\text{5} \text{ttpy})]^+\). In addition to supporting the \( N_5 C \) binding assigned by NMR, the structure (Fig. 1) confirmed the ‘\( \pi \)-stacking’ of the ttpy ligand with the uncoordinated pyridine of \( 5^- \). Indeed, the centroid-to-centroid separation between rings D and F is 3.39 Å and they lie virtually parallel to one another (8° interplanar angle). Perhaps to accommodate this, ring C is pulled away from the metal, resulting in a long Ru–N(51) bond (2.22 Å), but there is no detectable distortion of the ring C–ring E junction (N(51)–C(52)–C(91) 121 ± 1°). Nevertheless, the coordination to ring B (Ru–N(61) 2.02 Å) is weaker than is usual (viz. Ru–N(21) 1.94 Å), while the bond to the carbanionic ring A is shorter (Ru–C(71) 1.99Å). It would appear that the strong Ru–C bond to ring A forces a weaker coordination of ring B and especially ring C, and allows the uncoordinated ring E to tilt away from the ttpy central pyridine ring J, thereby avoiding inter-ligand steric congestion.

It is also noteworthy that those phenyl and tolyl rings attached to the metal-coordinated pyridine rings D and L are essentially coplanar (interplanar angles of 16.3 and 10.0°, respectively) to permit conjugation, as we have observed before [21], but the rings F/G attached to the uncoordinated pyridine are tilted out of plane (30.6–38.7° interplanar angles) to avoid steric congestion at the ortho positions.

3.3. Photoinduced electron transfer

The homoleptic \( 6,6^-\text{diphenyl-2,2’:6’,2”-terpyridine} \) (dptpy) complex of Ru(II) was non-luminescent even at 77 K, with an immeasurably short excited-state lifetime (\( \tau \)) [22]. In this and other instances of steric congestion in the vicinity of the metal [23], inter-ligand steric interactions were deemed responsible for weakening the ligand fields and thereby rendering a metal-centred, triplet d–d state (\(^3MC\)) more accessible from the lig-
and-centred, charge-transfer state (3CT) that is involved in the photoinduced electron transfer. The 3MC state provides an efficient route of non-radiative energy loss and a shortened $\tau$. This steric effect was expected to be milder in the heteroleptic complexes [Ru(H5)(tppy)]-(PF6)$_2$ and [Ru(H5,3)(tppy)](PF6)$_2$, where only one ligand bears substituents at the 6-positions. Indeed, [Ru(dptpy)$_2$]$^{2+}$ was photoactive in the presence of SCN$^-$ due to the congestion [22], but no such sensitivity was noted in [Ru(H4)(tppy)](PF6)$_2$ or [Ru(H5)-(tppy)](PF6)$_2$. The 4,4’,4’-tri phenyl-2,2’,6’,2”-terpyridine analogue was much a better emitter ($\tau$ ca. 0.2 μs in 4:1 EtOH–MeOH) than was [Ru(dptpy)$_2$]$^{2+}$ or even the unsubstituted tpy complex [24], presumably because of conjugation by the phenyl groups stabilizing the 3CT state relative to the 3MC state. We anticipated that the 4- and 4’-phenyl groups in [Ru(H5)(tppy)](PF6)$_2$ and [Ru(H5,3)(tppy)](PF6)$_2$ would serve the same purpose, with conjugation exemplified by rings D and L in the crystal structure of [Ru(5)(tppy)]NO$_3$ and elsewhere [21]. We also expected that 4,4”-diphenyl substitution would help to rigidify the complex, thereby increasing the barrier to the structural reorganization that accompanies the 3CT→3MC transition, and hinder solvent-induced quenching. These factors, combining to mitigate a reduced congestion, constitute improvements over the dptpy case [22].

Methodology developed earlier [15] was used to comparatively assess the ability of [Ru(H5)(tppy)](PF6)$_2$ or [Ru(H5,3)(tppy)](PF6)$_2$ to sensitize the production of methyl viologen cation radical (MV$^+$) from methyl viologen as an electron acceptor by oxidative quenching, under continuous irradiation in CH$_3$CN and with triethanolamine as a sacrificial reductant. Table 2 reports the steady-state yields of MV$^+$ and the pseudo-first-order rate constants for its formation ($k_i$) and quenching ($k_q$). We found that [Ru(H5,3)(tppy)](PF6)$_2$ led to a concentration of MV$^+$ about double that with [Ru(H5)(tppy)](PF6)$_2$. Kinetic analysis suggested that this improvement arose from a faster electron transfer (larger $k_i$) tempered by a concomitant increase in MV$^+$ quenching (larger $k_q$). With much larger $k_i$ and $k_q$ values, [Ru(tppy)$_2$]$^{2+}$ produced only about 1.4 times higher steady-state concentrations of MV$^+$ than did [Ru(H3,5)(tppy)](PF6)$_2$ under identical conditions.

With just one 6,6”-diarylated ligand, complex [Ru(H5)(tppy)](PF6)$_2$ was still a much weaker sensitizer than [Ru(tppy)$_2$]$^{2+}$ (τ 0.95 ns) [25], presumably because of a very low $\tau$ value despite the opportunity for added conjugation. The presence of carboxylate groups in [Ru(H3,5)(tppy)](PF6)$_2$ was evidently beneficial, leading to faster MV$^+$ formation and quenching than with [Ru(H5)(tppy)](PF6)$_2$, and this can be ascribed to favourable intermolecular interactions involving the deprotonated form [Ru(3)(tppy)]$^+$. Nevertheless, this benefit was insufficient to overcome the deficit in $\tau$ of [Ru(H5)(tppy)](PF6)$_2$, relative to [Ru(tppy)$_2$]$^{2+}$. We are currently exploring new sensitizer designs that incorporate carboxylate substituents on a less-congested framework.

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### References


