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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 (H**4**), its non-carboxylated 4,6,4″,6″-tetraphenyl analogue (H**5**) and the 4,4″-diphenyl-6,6″-di(4-methoxyphenyl) analogue were prepared in high yields via double Kröhnke reactions. Reactions with activated (ttpy)$RuCl_3$ (ttpy is 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) provided the symmetrical N_6-coordinated complexes, [Ru(H**4**)(ttpy)]$(PF_6)_2$ and [Ru(H**5**)(ttpy)]$(PF_6)_2$, along with the novel, unsymmetrical *C*-metallated analogues [Ru(**4**)(ttpy)]PF_6 and [Ru(**5**)(ttpy)]PF_6, in which an unprecedented side-chain metallation occurred in lieu of incomplete substitution. A crystallographic analysis of [Ru(**5**)(ttpy)]NO_3 confirmed the N_5C donor set in these products and revealed a distorted binding of $\mathbf{5}^-$ as well as 'π-stacking' between its uncoordinated pyridine and the ttpy ligand. The diester [Ru(H**4**)(ttpy)]$(PF_6)_2$ was hydrolyzed to the diacid complex [Ru(H_2**3**)(ttpy)]$(PF_6)_2$ (H_2**3** 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(H**5**)(ttpy)]$(PF_6)_2$ and [Ru(H_2**3**)(ttpy)]$(PF_6)_2$ 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.

Keywords: X-ray crystallography; *C*-Metallation; Photoinduced electron transfer; Ruthenium(II) complexes; Aryl-substituted terpyridines

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 H_2 from H_2O [1]. With cationic electron acceptors such as methyl viologen (MV^{2+}, 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 Kröhnke 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 MV^{2+}.

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2. Experimental

2.1. Preparation of 4,4″-diphenyl-6,6″-di(4-ethoxycarbonylphenyl)-2,2′:6′,2″-terpyridine (H**4**)

2,6-Di[2-(1-pyridyl)-1-oxo-ethyl]pyridine diiodide [12] (**2**) (0.30 g) and 3-(4-carboxy phenyl)-1-(2-pyridyl)-propenone [13] (**1a**) (0.25 g, 2 equiv.) were added to excess NH_4OAc in glacial AcOH, with heating to reflux for 3 h. After cooling, the precipitate was collected, washed (CH_3OH, 3×50 ml) and dried. The crude diacid H_2**3** was a tan powder (1.45 g, 95% yield). This was taken up in $SOCl_2$ (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 $CHCl_3$ and purified on a short column (alumina-N, 2:98 CH_3OH–$CHCl_3$), then recrystallized (EtOH) to give a white powder (1.58 g, 80% yield). M.p.: 270 °C. ^{1}H NMR ($CDCl_3$, δ ppm):[2] 8.94 (s, 2H, $H^{3/5}$), 8.75 (d, 2H, $H^{3'\&5'}$), 8.33 (d, 4H, 6-Ph), 8.22 (d, 4H, 6-Ph), 8.09 (t, 1H, $H^{4'}$), 8.07 (s, 2H, $H^{5/3}$), 7.88 (d, 4H, 4-PhH^2), 7.54 (m, 6H, 4-PhH$^{3\&4}$), 4.37 (q, 4H, CH_2), 1.47 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 166.5, 156.6, 155.9, 155.3, 150.3, 143.5, 138.8, 137.9, 130.8, 130.0, 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) $[M-C_2H_5]$, 636 (15) $[M-OC_2H_5]$. *Anal.* Found: C, 79.24; H, 5.11; N, 6.09. Calc. for $C_{45}H_{35}N_3O_4$: 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 CH_3OH–5% aqueous KOH (100 ml) and the solution was stirred for 2 h in an ice bath. The precipitate was collected, washed with H_2O and dried, giving pale yellow flakes (5.50 g, 88%). A portion of the product was recrystallized (CH_3OH) as pale yellow flakes for characterization. M.p.: 79–82 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 8.73 (d, 1H, py–H^6), 8.26 (d, 1H, vinyl H), 8.19 (d, 1H, py–H^3), 7.91 (d, 1H, vinyl H), 7.88 (dd, 1H, py–$H^{4/5}$), 7.62 (d, 2H, ArH), 7.48 (dd, 1H, py–$H^{5/4}$), 7.21 (d, 2H, ArH), 2.42 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 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 $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%.

[2] H NMR assignments use the standard tpy numbering for H**4**, H**5** 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 (H**5**)

In the same manner as for crude H_2**3**, 0.60 g of 3-phenyl-1-(2-pyridyl)propenone (**1b**) and **2** (1.00 g, 0.5 equiv.) were converted to H**5**, obtained as a white powder (0.89 g, 98% yield). M.p.: 277–280 °C. ^{1}H NMR ($CDCl_3$, δ ppm):[1] 7.87 (s, 2H, $H^{3/5}$), 7.75 (d, 2H, $H^{3'\&5'}$), 7.56 (s, 2H, $H^{5/3}$), 7.08 (d, 2H, 6-PhH^2), 7.04 (d, 2H, 4-PhH^2), 6.87 (t, 1H, $H^{4'}$), 6.76 (m, 6H, 4,6-PhH$^{3\&4}$). ^{13}C 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 $C_{39}H_{27}N_3$: C, 87.12; H, 5.06; N, 7.82%.

2.4. Preparation of [Ru(ttpy)(H**4**)]$(PF_6)_2$ and [Ru(ttpy)(N,N,C-4)]PF_6

Ru(ttpy)Cl_3[14] (0.030 g) was added to a solution of $AgBF_4$ (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 H**4** (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 CH_3CN and sufficient aqueous NH_4PF_6 was added to cause precipitation of a dark red powder. Some pure [Ru(H**4**)(ttpy)]$(PF_6)_2$ was isolated after trituration of this crude product with CH_3OH, filtration and evaporation of the filtrate to provide a red powder. A further amount was obtained by chromatography (silica, 14:2:1 CH_3CN–satd. KNO_3–H_2O) of the CH_3OH-insoluble residue. The less polar fraction was washed with H_2O, reprecipitated with NH_4PF_6 as before, then precipitated from CH_3CN with Et_2O to provide [Ru(**4**)(ttpy)]PF_6 as a purple powder (0.010 g, 15% yield). ^{1}H NMR (CD_3CN, δ ppm):[1] 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, $H^{4/3A}$), 7.78 (m, 18H), 7.49 (d, 1H), 7.47 (d, 2H), 7.43 (s, 1H), 7.42 (d, 1H), 7.30 (d, 1H, $H^{3/4A}$), 7.23 (dd, 1H), 7.07 (dd, 1H), 7.20 (dd, 1H), 6.31 (s, 1H, H^E), 5.78 (s, 1H, H^{6A}), 4.48 (q, 4H, OCH_2CH_3), 3.89 (q, 4H, OCH_2CH_3), 2.60 (s, 3H, $ArCH_3$), 1.46 (t, 6H, OCH_2CH_3), 0.90 (t, 6H, OCH_2CH_3). FAB MS; m/z (%): 1104 (100) $[M-H-PF_6]$, 1031 (15) $[M-H-PF_6-COOEt]$. The more polar material [Ru(H**4**)(ttpy)]$(PF_6)_2$ was similarly treated and isolated as a red powder (total 0.048 g, 61% total yield). ^{1}H NMR (CD_3CN, 330 K, δ ppm):[1] 9.05 (d, 2H, $H^{3\&5C}$), 8.80 (s, 2H, $H^{3/5B}$), 8.60 (t, 1H, H^{4C}), 8.35 (d, 2H, $H^{3/6E}$), 8.04 (dd, 2H, $H^{4/5E}$), 7.84 (s, 2H, H^F), 7.80 (d, 4H, $H^{2/3D}$), 7.80 (d, 2H, H^G), 7.56 (d, 2H, $H^{6/3E}$), 7.51

(m, 4H, $H^{3/2D}$), 7.51 (m, 2H, H^{4D}), 7.51 (d, 2H, H^{G}), 7.40 (m, 4H, H^{3A}), 7.31 (dd, 2H, $H^{5/4E}$), 7.14 (s, 2H, $H^{5/3B}$), 6.20 (d, 4H, H^{2A}), 3.92 (q, 4H, OCH_2), 2.54 (s, 3H, $ArCH_3$), 1.15 (t, 6H, OCH_2CH_3). ^{13}C NMR (CD_3CN, δ ppm): 167.0, 165.9, 160.1, 157.3, 153.5, 150.2, 148.2, 141.8, 139.4, 137.2, 135.5, 133.7, 131.8, 131.5, 130.8, 130.3, 130.0, 128.4, 128.3, 128.2, 127.9, 125.5, 124.4, 121.5, 120.8, 61.9, 21.2, 14.0. FAB MS; m/z (%): 1250 (100) [$M-2PF_6$], 1105 [$M-PF_6$]. *Anal.* Found: C, 54.43; H, 3.55; N, 6.26. Calc. for $C_{67}H_{52}F_{12}N_6O_4P_2Ru\cdot 1/2NH_4PF_6$: C, 54.46; H, 3.68; N, 6.16%.

2.5. Preparation of [Ru(ttpy)(H5)](PF_6)$_2$ and [Ru(ttpy)(N,N,C-5)]PF_6

The reaction of Ru(ttpy)Cl_3 (0.035 g) with H**5** (0.035 g, 1.0 equiv.) and work-up were carried out in the same manner as with H**4**. The less polar material was isolated as the PF_6^-, salt, [Ru(**5**)(ttpy)]PF_6, a purple powder (0.005 g, 7% yield). ^1H NMR (CD_3CN, δ ppm):[1] 8.89 (s, 1H, H^{B}), 8.87 (d, 1H, $H^{3/5C}$), 8.48 (s, 1H, H^{B}), 8.21 (d, 2H), 8.16 (s, 1H, H^{J}), 8.13 (t, 1H, H^{4C}), 8.07 (s, 1H, H^{J}), 7.88 (d, 1H, $H^{3/6A}$), 7.77–7.48 (m, 22H), 7.43 (d, 2H), 7.29 (d, 1H, $H^{5/3C}$), 7.09 (dd, 1H), 7.08 (dd, 1H), 6.66 (t, 1H, $H^{4/5A}$), 6.40 (t, 1H, $H^{5/4A}$), 6.26 (s, 1H, H^{E}), 5.15 (d, 1H, $H^{6/3A}$), 2.47 (s, 3H, $ArCH_3$). FAB MS; m/z (%): 961 (100) [$M-H-PF_6$]. A crystallographic sample of [Ru(ttpy)(*N,N,C*-**5**)]NO_3 was obtained by omitting the second NH_4PF_6 treatment and diffusion of Et_2O into an acetone solution. The more polar fraction provided red [Ru(H**5**)(ttpy)](PF_6)$_2$ (0.055 g, 68% yield). ^1H NMR (CD_3CN, 330 K, δ ppm):[1] 9.05 (d, 2H, $H^{3\&5C}$), 8.77 (s, 2H, H^{B}), 8.60 (t, 1H, H^{4C}), 8.23 (d, 2H, $H^{3/6E}$), 8.00 (dd, 2H, $H^{4/5E}$), 7.88 (d, 2H, $H^{2/3G}$), 7.85 (s, 2H, H^{F}), 7.80 (d, 4H, $H^{2A/D}$), 7.68 (d, 2H, $H^{6/3E}$), 7.57 (m, 4H, $H^{3A/D}$), 7.57 (m, 2H, $H^{4A/D}$), 7.57 (d, 2H, H^{G}), 7.29 (dd, 2H, $H^{5/4E}$), 7.10 (s, 2H, H^{B}), 7.09 (t, 2H, $H^{4D/A}$), 6.80 (dd, 4H, $H^{3D/A}$), 6.10 (d, 4H, $H^{2D/A}$), 2.62 (s, 3H, $ArCH_3$). ^{13}C NMR (CD_3CN, δ ppm):[1] 168.1, 160.4, 159.9, 156.8, 156.6, 153.1, 149.9, 148.1, 141.4, 138.9, 138.3, 137.0, 135.6, 135.0, 131.5, 131.0, 130.2, 129.4, 129.3, 128.5, 128.2, 127.9, 127.8, 128.6, 125.3, 125.2, 121.7, 121.1, 21.3. FAB MS; m/z (%): 1107 (100) [$M-PF_6$], 962 (35) [$M-2PF_6$]. *Anal.* Found: C, 57.61; H, 3.70; N, 6.80. Calc. for $C_{61}H_{44}F_{12}N_6P_2Ru\cdot H_2O$: C, 57.69; H, 3.65; N, 6.62%.

2.6. Preparation of 3-(4-methoxyphenyl)-1-(2-pyridyl)-2-propenone (1c)

4-Methoxyacetophenone (1.00 g, 6.67 mmol) was added to a cooled solution of 4-tolualdehyde (0.71 g, 6.67 mmol) in 70:30 CH_3OH–5% KOH (100 ml) and the resulting solution was stirred at ~50 °C for 5 h. The precipitate, which formed upon cooling overnight, was collected by vacuum filtration, washed with H_2O, and dried. A second crop was isolated by adding an additional 50 ml of H_2O to the filtrate and cooling the solution overnight. The combined crops recrystallized (CH_3OH) as white needles (1.08 g, 68%). M.p.: 104–105 °C. ^1H NMR ($CDCl_3$, 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, OCH_3). ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{14}O_2$: 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 NH_4OAc (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 CH_3OH (3 × 50 ml) and dried, yielding a white powder which recrystallized ($CHCl_3$–CH_3OH) as white needles (0.54 g, 90%). M.p.: 293–296 °C. ^1H NMR (TFA-d, δ ppm): 8.78 (s, 2H, $H^{3/5}$), 8.72 (d, 2H, $H^{3'\&5'}$), 8.55 (t, 1H, $H^{4'}$), 8.50 (s, 2H, $H^{5/3}$), 8.06 (d, 4H, 4-PhH^2), 8.02 (d, 4H, 6-PhH^2), 7.75 (m, 6H, 4-$PhH^{3\&4}$), 7.29 (d, 4H, 6-PhH^3). ^{13}C NMR (TFA-d, δ ppm): 156.6, 154.0, 147.0, 140.1, 139.0, 134.3, 126.7, 125.6, 122.5, 122.3, 120.2, 118.3, 115.7, 115.4, 112.3, 108.5, 47.7. FAB MS; m/z (%): 597 (100) [M]. *Anal.* Found: C, 81.29; H, 5.25; N, 6.91. Calc. for $C_{41}H_{31}N_3O_2$: C, 82.39; H, 5.23; N, 7.03%.

2.8. Crystal structure determination of [Ru(ttpy)(N,N,C-5)]NO_3

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). $C_{61}H_{43}N_7O_3Ru\cdot 0.25H_2O$, $M = 1027.60$, purple needle (0.20 × 0.15 × 0.12 mm); monoclinic, a = 12.6538(12), $b = 17.077(2)$, $c = 22.5488(18)$ Å, β = 104.524(6)°, $V = 4717.0(8)$ Å^3, $D_{calc} = 1.447$ g cm^{-3}, space group $P2_1/n$, $Z = 4$, 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° 98.9%, $0 \le h \le 14$, $0 \le k \le 18$, $-25 \le l \le 24$), 6698 unique ($R_{int} = 0.271$), 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-

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_2**3**)(ttpy)](PF_6)$_2$

A sample of [Ru(H**4**)(ttpy)](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_2**3**)(ttpy)](PF_6)$_2$. ^{1}H NMR (CD_3CN, 330 K, δ ppm):[1] 9.05 (d, 2H, $H^{3\&5C}$), 8.79 (s, 2H, $H^{3/5B}$), 8.60 (t, 1H, H^{4C}), 8.34 (d, 2H, $H^{3/6E}$), 8.01 (dd, 2H, $H^{4/5E}$), 7.88 (s, 2H, H^F), 7.78 (d, 2H, H^G), 7.75 (d, 4H, $H^{2/3D}$), 7.65 (d, 2H, $H^{6/3E}$), 7.52–7.47 (m, 6H, $H^{3/2D}$, H^{4D}, H^G), 7.39 (m, 4H, H^{3A}), 7.30 (dd, 2H, $H^{5/4E}$), 7.14 (s, 2H, $H^{5/3B}$), 6.21 (d, 4H, H^{2A}), 2.57 (s, 3H, $ArCH_3$). ES MS; m/z: 525 $[M-2PF_6]^{2+}$. 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.

Table 1
Selected bond lengths (Å) and bond angles (°) for [Ru(ttpy)(**5**)]NO_3

Bond lengths	
Ru(1)–C(71)	1.992(11)
Ru(1)–N(21)	1.944(7)
Ru(1)–N(11)	2.016(8)
Ru(1)–N(61)	2.024(7)
Ru(1)–N(31)	2.047(9)
Ru(1)–N(51)	2.216(8)
Bond angles	
N(21)–Ru(1)–C(71)	95.0(4)
N(21)–Ru(1)–N(11)	79.7(3)
C(71)–Ru(1)–N(11)	92.1(4)
N(21)–Ru(1)–N(61)	174.6(3)
C(71)–Ru(1)–N(61)	79.6(3)
N(11)–Ru(1)–N(61)	101.0(3)
N(21)–Ru(1)–N(31)	79.0(3)
C(71)–Ru(1)–N(31)	89.1(4)
N(11)–Ru(1)–N(31)	158.7(3)
N(61)–Ru(1)–N(31)	100.2(3)
N(21)–Ru(1)–N(51)	109.1(3)
C(71)–Ru(1)–N(51)	155.8(3)
N(11)–Ru(1)–N(51)	90.5(3)
N(61)–Ru(1)–N(51)	76.3(3)
N(31)–Ru(1)–N(51)	97.1(3)
C(72)–C(71)–Ru(1)	130.9(7)
C(76)–C(71)–Ru(1)	114.4(7)
N(51)–C(52)–C(91)	120.8(10)

[3] $w = [\sigma^2(F_o^2) + (0.0550P)^2 + 16.1243P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$; goodness-of-fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{rflns} - N_{params})\}^{1/2}$.

2.10. Electron transfer measurements

Sample solutions (2.5 ml) containing [Ru(H**5**)(ttpy)](PF_6)$_2$ (4.03×10^{-5} M), [Ru(H_2**3**)(ttpy)](PF_6)$_2$ (3.97×10^{-5} M) or [Ru(ttpy)$_2$](PF_6)$_2$ (3.99×10^{-5} M), MV(PF_6)$_2$ (9.45×10^{-3} 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^+ (λ_{max} 600 nm, ε_{max} 10 060 M^{-1} 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 $MV^{\bullet+}$ concentrations, the average maximum $MV^{\bullet+}$ yields and the average initial growth rates were assessed. The pseudo-first-order rate constants for the formation (k_f) and quenching (k_q) of $MV^{\bullet+}$ were obtained from application of the kinetic model [15]

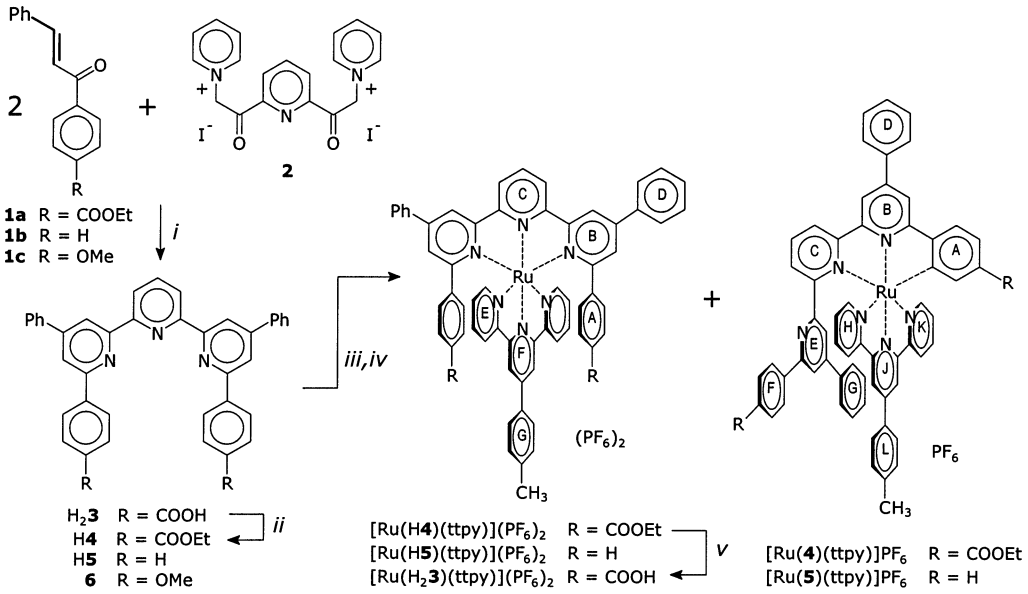
$$\frac{d[MV^{\bullet+}]}{dt} = k_f[MV^{2+}]_0 - (k_f + k_q + k_{d1})[MV^{\bullet+}]_t - k_{d2}[MV^{\bullet+}]_t^2 \quad (1)$$

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

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_2**3** (Scheme 1). The full characterization of H_2**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)$_4$Cl$_2$ were not clean and incomplete. But, after activation with Ag^+, reaction of the known [14] (ttpy)$RuCl_3$ (ttpy 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**)(ttpy)](PF_6)$_2$ (61% isolated yield), and the other was a purple salt later assigned the *C*-metallated structure [Ru(**4**)(ttpy)]PF_6 (15% isolated yield). Complex [Ru(H**4**)(ttpy)](PF_6)$_2$ was hydrolyzed with NaOH, then treated



Scheme 1. Reagents and conditions: (i) excess NH_4OAc, HOAc, reflux, 2 h; (ii) $SOCl_2$, reflux, then EtOH, reflux; (iii) Ru(ttpy)Cl_3, $AgBF_4$, acetone, reflux, 0.5 h, then H**4** or H**5**, DMF, reflux, 8 h; (iv) excess NH_4PF_6 in H_2O, CH_3CN; (v) NaOH, DMF, reflux, 4 h, then HPF_6.

with HPF_6 to provide an 89% isolated yield of the diacid [Ru(H**5**)(ttpy)]$(PF_6)_2$, 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 H**5** (86% overall isolated yield from commercially available materials), then to a mixture of its complexes (Scheme 1). The major product was again the red, N_6-ligated product [Ru(H**5**)(ttpy)]$(PF_6)_2$ in 68% yield, and the minor, purple product (7% yield) was assigned the N_5C-coordinated structure [Ru(N_2C-**5**)(ttpy)]PF_6, on the basis of spectral similarities with [Ru(**4**)(ttpy)]-PF_6, 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)]PF_6 and [Ru(**5**)(ttpy)]PF_6 involved a number of techniques. The lack of symmetry was immediately evident from the ^{1}H 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 N_3-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 N_3-coordinated terpyridine complexes [Ru(H**4**)(ttpy)]$(PF_6)_2$, [Ru(H**5**)(ttpy)]$(PF_6)_2$ and [Ru(H_2**3**)(ttpy)]$(PF_6)_2$, 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)]PF_6 and [Ru(**5**)(ttpy)]PF_6 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)]PF_6 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 $\mathbf{4}^-$. The main product, [Ru(H**4**)(ttpy)]-$(PF_6)_2$, 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 N_3 donor set along the meridional

plane is misaligned, the usual result is a 'hypo-chelated' N_5Cl-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], H**4** and H**5** 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_5C-coordinated products [9], as can the occurrence of 'π-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_5C-coordinated product would have been expected from an initial binding of the central pyridine. This preference may be a result of the steric hindrance to an approach of the central pyridine nitrogens by the 4- and 4″-phenyl groups when H**4** or H**5** are in their free-ligand (*anti*, *anti*) conformations [20]. We note that C-metallation at terminal pyridines would have provided no steric advantage. Thus, the highly congested ligands H**4** and H**5** behaved much like less-congested terpyridines, differing only in the nature of the product of misalignment.

3.2. Molecular structure of [Ru(5)(ttpy)]NO_3

Although attempts were made to obtain high quality crystals of all complexes, useable crystals were instead obtained with the NO_3^- salt of [Ru(**5**)(ttpy)]$^+$. In addition to supporting the N_5C binding assigned by NMR, the structure (Fig. 1) confirmed the 'π-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′-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 (τ) [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 (^{3}MC) more accessible from the lig-

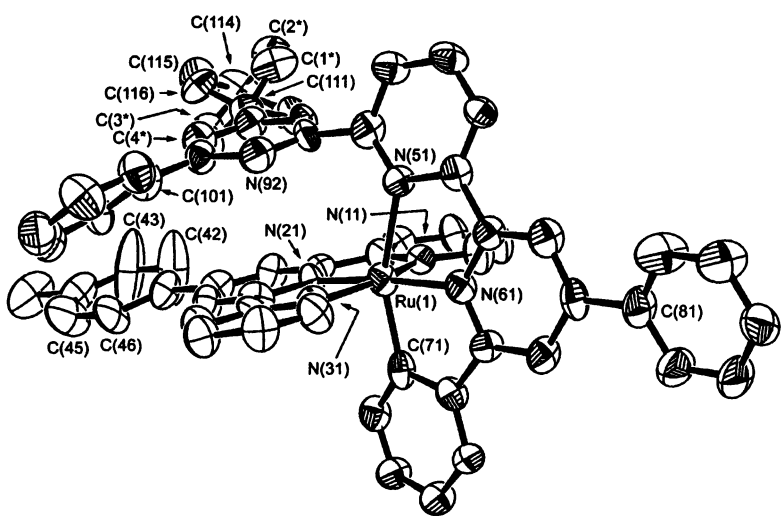


Fig. 1. ORTEP diagram of [Ru(**5**)(ttpy)]NO_3 showing 50% probability ellipsoids and disorder in a phenyl ring. H atoms and the counteranions have been omitted for clarity.

Table 2
Kinetic parameters (uncertainties in least-significant digits in brackets) for the photogeneration of $MV^{\bullet+}$

Complex	$[MV^{\bullet+}]_{max}$ (μM)	$k_f \times 10^5$ (s^{-1})	$k_q \times 10^3$ (s^{-1})
$[Ru(H\mathbf{5})(ttpy)](PF_6)_2$	1.9	0.072(1)	0.5(1)
$[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$	4.0(3)	0.17(2)	2.4(6)
$[Ru(ttpy)_2](PF_6)_2$	5.5(5)	1.12(1)	8.8(6)

and-centred, charge-transfer state (^{3}CT) that is involved in the photoinduced electron transfer. The ^{3}MC state provides an efficient route of non-radiative energy loss and a shortened τ. This steric effect was expected to be milder in the heteroleptic complexes $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$ and $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$, where only one ligand bears substituents at the 6-positions. Indeed, $[Ru(dptpy)_2]^{2+}$ was photoreactive in the presence of SCN^- due to the congestion [22], but no such sensitivity was noted in $[Ru(H\mathbf{4})(ttpy)](PF_6)_2$ or $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$. The 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine analogue was a much better emitter (τ 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 ^{3}CT state relative to the ^{3}MC state. We anticipated that the 4- and 4″-phenyl groups in $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$ and $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$ would serve the same purpose, with conjugation exemplified by rings D and L in the crystal structure of $[Ru(\mathbf{5})(ttpy)]NO_3$ 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 $^3CT \rightarrow {}^3MC$ 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 $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$ or $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$ to sensitize the production of methyl viologen cation radical ($MV^{\bullet+}$) from methyl viologen as an electron acceptor by oxidative quenching, under continuous irradiation in CH_3CN and with triethanolamine as a sacrificial reductant. Table 2 reports the steady-state yields of $MV^{\bullet+}$ and the pseudo-first-order rate constants for its formation (k_f) and quenching (k_q). We found that $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$ led to a concentration of $MV^{\bullet+}$ about double that with $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$. Kinetic analysis suggested that this improvement arose from a faster electron transfer (larger k_f) tempered by a concomitant increase in $MV^{\bullet+}$ quenching (larger k_q). With much larger k_f and k_q values, $[Ru(ttpy)_2]^{2+}$ produced only about 1.4 times higher steady-state concentrations of $MV^{\bullet+}$ than did $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$ under identical conditions.

With just one 6,6″-diarylated ligand, complex $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$ was still a much weaker sensitizer than $[Ru(ttpy)_2]^{2+}$ (τ 0.95 ns) [25], presumably because of a very low τ value despite the opportunity for added conjugation. The presence of carboxyl groups in $[Ru(H_2\mathbf{3})(ttpy)](PF_6)_2$ was evidently beneficial, leading to faster $MV^{\bullet+}$ formation and quenching than with $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$, and this can be ascribed to favourable intermolecular interactions involving the deprotonated form $[Ru(\mathbf{3})(ttpy)]^0$. Nevertheless, this benefit was insufficient to overcome the deficit in τ of $[Ru(H\mathbf{5})(ttpy)](PF_6)_2$, relative to $[Ru(ttpy)_2]^{2+}$. We are currently exploring new sensitizer designs that incorporate carboxylate substituents on a less-congested framework.

Acknowledgements

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