Supporting information for:

Photochemical ligand ejection from non-sterically promoted Ru(II)bis(diimine) 4,4'-bi-1,2,3-triazolyl complexes

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Experimental details.

The complex $[Ru(bpy)_2(btz)][PF_6]_2$ (**1a**) was prepared as previously described and precursors $[RuCl_2(p\text{-cyemene})]_2$ and $[Ru(N\hat{}N)_2Cl_2]$ by literature procedures.[1-3] Other reagents and solvent were purchased from Aldrich Chemicals, Fisher Scientific or Acros Organics and used as supplied. NMR characterisation data were recorded on Bruker 500 Avance or 400 Ascend spectrometers. UV-visible absorption data were recorded on a Agilent Technologies Cary 60 spectrometer whilst mass spectrometry data were collected on a Bruker Micro-Q-TOF instrument.

Synthesis of [RuCl(*p*-cymene)(dmbpy)][PF_6].
$[RuCl_2(p\text{-cymene})]_2$ (100.2 mg, 0.16 mmol) and 4,4'-dimethyl-2,2'-bipyridyl (120.5 mg, 0.65 mmol, 4 eq.) were suspended in 10 mL MeOH and the reaction mixture vigorously stirred at room temperature for 3 hours. After this time, an excess of NH_4PF_6 was added and the volume of the solution reduced by half *in vacuo*. An orange precipitate was observed to form – this was filtered and washed with 10 mL Et_2O. Yield = 153.5 mg (78.2 %) ^{1}H NMR (500 MHz) CD_3CN δ_H 1.02 (s, 3H, CH(CH_3)), 1.04 (s, 3H, CH(CH_3)), 2.20 (s, 3H, *p*-cymene CH_3), 2.59 (s, 6H, dmbpy), 2.64 (sp, $^3J_{HH}$ = 7.2 Hz, 1H, CH(CH$_3$)$_2$), 5.68 (d, $^3J_{HH}$ = 6.2 Hz, 2H, *p*-cymene Ar-CH), 5.89 (d, $^3J_{HH}$ = 6.2 Hz, 2H, *p*-cymene Ar-CH) 7.53 (d, $^3J_{HH}$ = 5.9 Hz, 2H, dmbpy-H_5), 8.17 (s, 2H, dmbpy-H_3), 9.14 (d, $^3J_{HH}$ = 6.0 Hz, 2H, dmbpy-H_6). ^{13}C NMR (125.8 MHz) CD_3CN δ_C 18.5 (*C*H$_3$, *p*-cymene), 20.9 (*C*H$_3$, dmbpy), 21.7 (*C*H$_3$, CH(*C*H$_3$)$_2$), 31.4 (CH, *C*H(CH$_3$)$_2$), 84.5 (*C*H, *p*-cymene Ar), 86.8 (*C*H, *p*-cymene Ar), 103.8 (*C*, *p*-cymene Ar-*C*(CH$_3$)), 105.0 (*C*, *p*-cymene Ar-*C*CH(CH$_3$)$_2$), 124.8 (*C*H, dmbpy-C_3), 128.9 (*C*H, dmbpy-C_5), 153.2 (*C*, 4-Dmbpy-C_4), 154.8 (*C*, dmbpy-C_2), 155.1 (*C*H, dmbpy-C_6). HRMS-ESI calculated for $[RuClN_2C_{22}H_{26}]^+$ m/z = 455.082252, found m/z = 455.082790.

Synthesis of [RuCl(*p*-cymene)(phen)][PF_6].
$[RuCl_2(p\text{-cymene})]_2$ (74.9 mg, 0.12 mmol) and 1,10-phenanthroline (88.1 mg, 0.49 mmol, 4 eq.) were suspended in 7 mL MeOH and the reaction mixture vigorously stirred at room temperature for 3 hours. After this time, an excess of NH_4PF_6 was added and the volume of the solution reduced by half *in vacuo*. An orange precipitate was observed to form – this was filtered and washed with 10 mL Et_2O. Yield = 109.2 mg (74.9 %) ^{1}H NMR (500 MHz) CD_3CN δ_H 1.01 (s, 3H, CH(CH_3)), 1.03 (s, 3H, CH(CH_3)), 2.19 (s, 3H, *p*-cymene CH_3), 2.71 (sp, $^3J_{HH}$ = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 5.86 (d, $^3J_{HH}$ = 6.4 Hz, 2H, *p*-cymene Ar-CH), 6.05 (d, $^3J_{HH}$ = 6.4 Hz, 2H, *p*-cymene Ar-CH), 8.06 (dd, $^3J_{HH}$ = 5.3 Hz, 8.2 Hz, 2H, phen), 8.18 (s, 2H, phen), 8.78 (dd, $^4J_{HH}$ = 0.9 Hz, $^3J_{HH}$ = 8.3 Hz, 2H, phen), 9.69 (dd, $^4J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, phen). ^{13}C NMR (125.8 MHz) CD_3CN δ_C 18.4 (*C*H$_3$, *p*-cymene), 21.7 (*C*H$_3$, CH(*C*H$_3$)$_2$), 31.4 (CH, *C*H(CH$_3$)$_2$), 84.8 (*C*H, *p*-cymene Ar), 86.3 (*C*H, *p*-cymene Ar), 103.0 (*C*, *p*-cymene Ar-*C*(CH$_3$)), 106.0 (*C*, *p*-cymene Ar-*C*CH(CH$_3$)$_2$), 126.9 (*C*H, phen), 128.1 (*C*H, phen), 131.2 (*C*, phen), 139.4 (*C*H, phen), 146.3 (*C*, phen), 155.9 (*C*H, phen). HRMS-ESI calculated for $[RuClN_2C_{22}H_{22}]^+$ m/z = 451.050952, found m/z = 451.051132.

Synthesis of $[Ru(dmbpy)_2(btz)][PF_6]_2$ (1b).

$[RuCl_2(dmbpy)_2]$ (30.9 mg, 57.2 μmol) and btz (20.9 mg, 66.7 μmol) were dissolved in 8 mL EtOH and solution degassed by bubbling with N_2. The dark purple reaction mixture was then heated at reflux for 4 hours. After cooling to room temperature, the solvent was evaporated and the orange residue purified by silica gel column chromatography using a 7:1:0.5 $MeCN:H_2O:KNO_3$(aq) solvent system. The bright orange band was collected and the solvent evaporated. The orange residue was redissolved in MeCN, filtered to remove KNO_3 and the solvent evaporated once more. The product was dissolved in 8mL EtOH and an excess of NH_4PF_6 was added which caused an orange precipitate to form. This was filtered and washed with small portions of H_2O and Et_2O and allowed to dry. Yield 40.8 mg (66.3 %)

^{1}H NMR (400 MHz) CD_3CN δ_H 2.54 (s, 6H, C*H*$_3$ dmbpy), 2.57 (s, 6H, C*H*$_3$ dmbpy), 5.51 (s, 4H, C*H*$_2$ of btz), 7.12 – 7.14 (m, 4H, *Ph*), 7.20 (dd, $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 5.8 Hz, 2H, dmbpy-*H*$_5$), 7.26 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 5.8 Hz, 2H, dmbpy-*H*$_5$'), 7.34 – 7.41 (m, 6H, *Ph*), 7.67 (d, $^3J_{HH}$ = 5.8 Hz, 2H, dmbpy-*H*$_6$), 7.69 (d, $^3J_{HH}$ = 5.8 Hz, 2H, dmbpy-*H*$_6$'), 8.30 (br s, 2H, dmbpy-*H*$_3$), 8.32 (s, 2H, C*H*N_3), 8.33 (br s, 2H, dmbpy-*H*$_3$'). ^{13}C NMR (100.6 MHz) CD_3CN δ_C 20.7 (*C*H_3 dmbpy), 20.8 (*C*H_3 dmbpy) 55.8 (*C*H_2), 123.8 (*C*HN_3), 124.7 (*C*H, dmbpy-C_3), 125.0 (*C*H, dmbpy-C_3'), 127.9 (*C*H, 4-dmbpy-C_5), 128.5 (*C*H, Ph), 128.5 (*C*H, dmbpy-C_5'), 129.5 (*C*H, Ph), 129.6 (*C*H, Ph), 134.5 (*C*, Ph), 141.0 (*C*, CN_3), 150.4 (*C*, 4-dmbpy-C_4), 150.6 (*C*, dmbpy-C_4'), 151.7 (*C*H, dmbpy-C_6), 151.9 (*C*H, dmbpy-C_6'), 157.4 (*C*, dmbpy-C_2), 157.9 (*C*, dmbpy-C_2'). ESI-MS m/z $[RuN_{10}C_{42}H_{40}]^{2+}$ predicted 393.123497, found 393.125224.

Synthesis of $[Ru(phen)_2(btz)][PF_6]_2$ (1d).

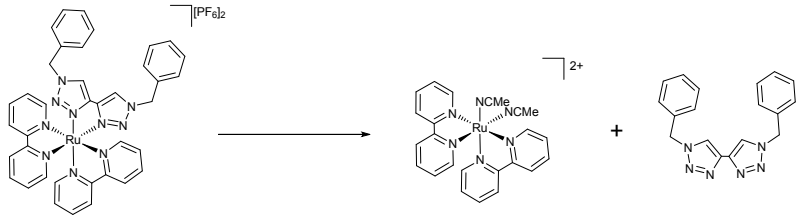
$[RuCl_2(phen)_2]$ (100 mg, 0.19 mmol) was dissolved in 8 mL EtOH and the solution degassed by bubbling with N_2. $AgPF_6$ (99.1 mg, 0.39 mmol) and btz (654 mg, 0.21 mmol) were added to the dark purple reaction mixture and this was heated at reflux for 6 hours. After cooling to room temperature, the solvent was evaporated and the residue purified by silica gel column chromatography using a 7:1:0.5 $MeCN:H_2O:KNO_3$(aq) solvent system. The bright orange fractions were collected and the solvent evaporated. The residue was redissolved in MeCN, filtered to remove KNO_3 and the solvent evaporated once more. The product was then dissolved in a minimum amount of MeOH and an excess of NH_4PF_6 was added which caused an orange-red precipitate to form. This was filtered and washed with small portions of H_2O and Et_2O and allowed to dry. Yield 9.9 mg (4.9 %)

^{1}H NMR (400 MHz) CD_3CN δ_H 5.39 (d, $^2J_{HH}$ = 14.9 Hz, 2H, C*H*H of btz), 5.45 (d, $^2J_{HH}$ = 15.1 Hz, 2H, CH*H* of btz), 7.02 (d, *J* = 7.1 Hz, 4H, *Ph*), 7.27 – 7.39 (m, 6H, *Ph*), 7.59 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.2 Hz, 2H, phen), 7.85 (dd, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.3 Hz, 2H, phen), 8.11 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, phen), 8.23 (d, $^3J_{HH}$ = 8.9 Hz, 2H, phen), 8.28 (d, $^3J_{HH}$ = 8.9 Hz, 2H, phen), 8.31 (s, 2H, C*H*N_3), 8.36 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, phen), 8.56 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 8.2 Hz, 2H, phen), 8.70 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 8.3 Hz, 2H, phen); ^{13}C NMR (100.6 MHz) CD_3CN δ_C 55.8 (*C*H_2), 123.9 (*C*HN_3), 125.7 (*C*H, phen), 126.5 (*C*H, phen), 128.3 (*C*H, *Ph*), 128.3 (*C*H, phen), 129.4 (*C*H, *Ph*), 129.6 (*C*H, *Ph*), 131.0 (*C*, phen), 131.3 (*C*, phen) 134.3 (*C*, *Ph*), 137.1 (*C*H, phen), 137.2 (*C*H, phen-C_4'), 141.2 (*C*, CN_3), 148.6 (*C*, phen), 149.2 (*C*, phen), 153.5 (*C*H, phen), 153.9 (*C*H, phen).

References

1. C. E. Welby, S. Grkinic, A. Zahid, B. S. Uppal, E. A. Gibson, C. R. Rice and P. I. P. Elliott, *Dalton Trans*., 2012, **41**, 7637-7646.
2. B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334-3341.
3. M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233-241.

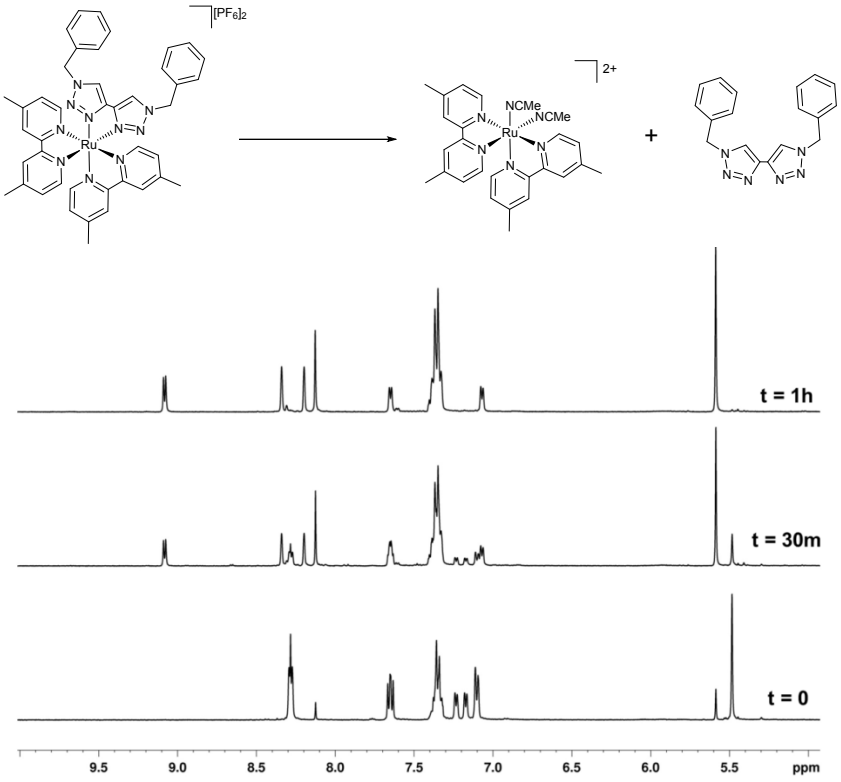
Photolysis reactions



NMR data for *cis*-$[Ru(bpy)_2(MeCN)_2]^{2+}$ (2a):

^{1}H NMR (400 MHz) CD_3CN δ_H 7.27 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $H_{5'}$-bpy), 7.61 (d, $^3J_{HH}$ = 5.6 Hz, 2H, $H_{6'}$-bpy), 7.86 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H_5-bpy), 7.96 (t, $^3J_{HH}$ = 7.9 Hz, 2H, $H_{4'}$-bpy), 8.29 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H_4-bpy), 8.39 (d, $^3J_{HH}$ = 8.2 Hz, 2H, $H_{3'}$-bpy), 8.53 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_3-bpy), 9.32 (d, $^3J_{HH}$ = 5.6 Hz, 2H, H_6-bpy). ^{13}C NMR (100.6 MHz) CD_3CN δ_C 124.1 (*C*H, $C_{3'}$-bpy), 124.4 (*C*H, C_3-bpy), 127.3 (*C*H, $C_{5'}$-bpy), 128.0 (*C*H, C_5-bpy), 138.5 (*C*H, $C_{4'}$-bpy), 138.9 (*C*H, C_4-bpy), 152.7 (*C*H, $C_{6'}$-bpy), 153.8 (*C*H, C_6-bpy), 157.7 (*C*, C_2-bpy), 158.5 (*C*, $C_{2'}$-bpy)

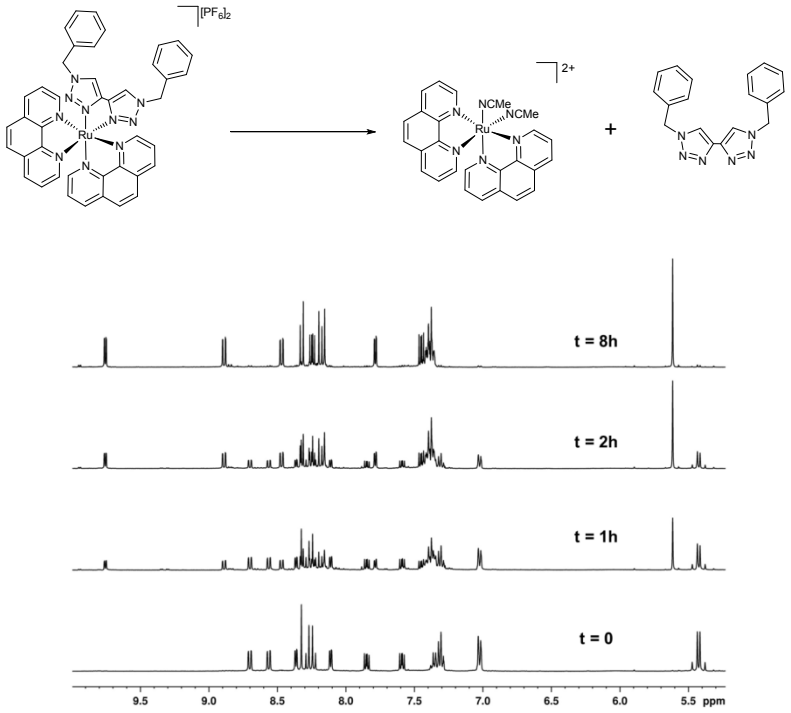
Photolysis of $[Ru(dmbpy)_2(btz)]^{2+}$ (1b)



NMR data for *cis*-$[Ru(dmbpy)_2(MeCN)_2]^{2+}$ (2b):

^{1}H NMR (400 MHz) CD_3CN δ_H 2.47 (s, 6H, CH_3), 2.71 (s, 6H, CH_3), 7.10 (d, $^3J_{HH}$ = 6.1 Hz, 2H, $H_{5'}$-bpy), ~7.37 ($H_{6'}$-bpy), 7.68 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H_5-bpy), 8.22 (s, 2H, $H_{3'}$-bpy), 8.37 (s, 2H, H_3-bpy), 9.11 (d, $^3J_{HH}$ = 5.7 Hz, 2H, H_6-bpy); ^{13}C NMR (100.6 MHz) CD_3CN δ_C 20.7 (*C*H_3'-4-Dmbpy), 21.0 (*C*H_3-4-Dmbpy), 124.7 (*C*H, $C_{3'}$-4-Dmbpy), 125.1 (*C*H, C_3-4-Dmbpy), 127.9 (*C*H, $C_{5'}$-4-Dmbpy), 128.7 (*C*H, C_5-4-Dmbpy), 150.9 (*C*, $C_{4'}$-4-Dmbpy), 151.2 (*C*, C_4-4-Dmbpy), 151.6 (*C*H, $C_{6'}$-4-Dmbpy), 153.0 (*C*H, C_6-4-Dmbpy), 157.3 (*C*, C_2-4-Dmbpy), 158.1 (*C*, $C_{2'}$-4-Dmbpy).

Photolysis of $[Ru(phen)_2(btz)]^{2+}$ (1c)



NMR data for *cis*-$[Ru(phen)_2(MeCN)_2]^{2+}$ (2c):

^{1}H NMR (400 MHz) CD_3CN δ_H 5.61 (s, 4H, CH_2 of btz), 7.34 – 7.43 (m, 10H, *Ph*), 7.45 (dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 8.2 Hz, 2H, phen), 7.79 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, phen), 8.15 (s, 2H, C*H*N_3), 8.19 (d, $^3J_{HH}$ = 8.9 Hz, 2H, phen-), 8.25 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, phen), 8.32 (d, $^3J_{HH}$ = 8.9 Hz, 2H, phen), 8.47 (dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 8.3 Hz, 2H, phen), 8.89 (dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, phen), 9.76 (dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, phen); ^{13}C NMR (100.6 MHz) CD_3CN δ_C 54.1 (*C*H_2), 121.8 (*C*HN_3), 125.7 (*C*H, phen), 126.6 (*C*H, phen), 128.3 (*C*H, phen), 128.4 (*C*H, phen), 128.5, 128.9, 129.5 (*C*H, *Ph*), 131.0 (*C*, phen-C_3'), 131.4 (*C*, phen) 136.4 (*C*, *Ph*), 137.4 (*C*H, phen), 137.9 (*C*H, phen), 139.6 (*C*, CN_3), 148.7 (*C*, phen), 149.2 (*C*, phen), 153.7 (*C*H, phen), 154.7 (*C*H, phen).