Supporting Information

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Photochemistry of RuII 4,4′-Bi-1,2,3-triazolyl (btz) Complexes: Crystallographic Characterization of the Photoreactive Ligand-Loss Intermediate trans-[Ru(bpy)(κ^2-btz)(κ^1-btz)(NCMe)]^{2+}

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Photochemical conversion of [Ru(bpy)(btz)\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1a) in acetonitrile

Photochemical conversion of [Ru(dmbpy)(btz)\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1b) in acetonitrile

Photochemical conversion of [Ru(dmeobpy)(btz)\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1c) in acetonitrile

Photochemical conversion of [Ru(phen)(btz)\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1d) in acetonitrile

Photochemical conversion of [Ru(bpy)(btz\textsubscript{Ph})\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1a\textsubscript{Ph}) in acetonitrile

Photochemical conversion of [Ru(bpy)(btz\textsubscript{Pr})\textsubscript{2}][PF\textsubscript{6}\textsubscript{2}] (1a\textsubscript{Pr}) in acetonitrile

DFT atomic coordinates for cis/trans-[Ru(bpy)(btz)(NCMe)\textsubscript{2}]\textsuperscript{2+}

and cis/trans-[Ru(bpy)\textsubscript{6}(NCMe)\textsubscript{2}]\textsuperscript{2+}

Table S1. X-ray Crystallographic data for complexes 1d, 1e, 2a and 3d.
Photochemical conversion of [Ru(bpy)(btz)₂][PF₆]₂ (1a) in acetonitrile

**Figure S1.** ¹H NMR spectra recorded during photochemical conversion of 1a in d₃-acetonitrile (* signals for 2a)

**Trans-[Ru(bpy)(κ¹-btz)(κ²-btz)(MeCN)]²⁺ 2a:**

¹H NMR (500 MHz) CD₃CN δH 5.07 (s, 2H, CH₂ of κ¹-btz), 5.40 (s, 2H, CH₂ of κ¹-btz), 5.81 (d, JHH = 15.0 Hz, 2H, CH₂ of κ²-btz), 5.87 (d, JHH = 15.0 Hz, 2H, CH₂ of κ²-btz), 6.86 (d, JHH = 7.6 Hz, 2H, Ph of κ¹-btz), 7.05 (s, 1H, CHN of κ²-btz), 7.29 (t, JHH = 7.5 Hz, 2H, Ph of κ¹-btz), 7.34 – 7.57 (m, 18H, Ph of κ¹-btz), 7.58 (s, 1H, CHN of κ¹-btz), 8.07 (t, JHH = 7.8 Hz, 2H, H₄-bpy), 8.21 (d, JHH = 8.0 Hz, 2H, H₃-bpy), 8.29 (s, 2H, CHN of κ²-btz), 9.96 (d, JHH = 5.6 Hz, 2H, H₆-bpy).

¹³C NMR (100.6 MHz) CD₃CN δC 53.6 (CH₂ of κ¹-btz), 54.7 (CH₂ of κ¹-btz), 55.5 (CH₂ of κ²-btz), 122.4 (CHN of κ²-btz), 122.6 (CH, bpy-C₃), 125.2 (CHN of κ²-btz), 125.9 (CH, bpy-C₃), 126.5 (CH of Ph), 127.7 (CHN of κ²-btz), 128.0, 128.3, 128.5, 128.6, 128.9, 129.1, 129.1, 129.2 (CH of Ph), 133.7, (C, ipso-Ph of κ²-btz), 134.0 (CN of κ²-btz), 134.3 (C, ipso-Ph of κ²-btz), 135.2 (C, ipso-Ph of κ²-btz), 137.7 (CH, bpy-C₂), 141.3 (CN of κ²-btz), 142.6 (CN of κ¹-btz), 155.6 (CH, bpy-C₆), 158.7 (C, bpy-C₅).

**trans-[Ru(bpy)(btz)(MeCN)]²⁺ 3a:**

¹H NMR (400 MHz) CD₃CN δH 5.91 (s, 4H, CH₃), 7.46 – 7.57 (m, 10H, Ph), 7.80 (t, JHH = 6.6 Hz, 2H, H₄-bpy), 8.21 (t, JHH = 7.9 Hz, 2H, H₄-bpy), 8.48 (d, JHH = 8.1 Hz, 2H, H₃-bpy), 8.50 (s, 2H, CHN), 10.2 (d, JHH = 5.6 Hz, 2H, H₆-bpy).

¹³C NMR (100.6 MHz) CD₃CN δC 56.2 (CH₃), 123.5 (CHN), 123.7 (CH, C₁-bpy), 127.2 (CH, C₂-bpy), 129.1, 129.7, 129.8 (CH, Ph), 134.7 (C, ipso, Ph), 139.0 (CH, C₁-bpy), 141.8 (C, CN), 156.1 (CH, C₆-bpy), 159.1 (C, C₇-bpy).
Photochemical conversion of [Ru(dmbpy)(btz)_2][PF_6]_2 (1b) in acetonitrile

Trans-[Ru(4-Me bpy)(κ^2-btz)(κ^2-btz)(MeCN)]^{2+} 3b:

\(^1\)H NMR (500 MHz) CD_3CN \( \delta \)H 2.60 (s, 6H, 4-Me bpy), 5.07 (s, 2H, CH_2 of κ^1-btz), 5.42 (s, 2H, CH_2 of κ^1-btz), 5.81 (d^*, \( J_{HH} = 15.0 \) Hz, 2H, CH_2 of κ^2-btz), 5.87 (d^*, \( J_{HH} = 15.0 \) Hz, 2H, CH_2 of κ^2-btz), 6.88 (d, \( J_{HH} = 7.3 \) Hz, 2H, Ph of κ^1-btz), 7.08 (s, 1H, CHN of κ^1-btz), 7.30 (t, \( J_{HH} = 7.8 \) Hz, 2H, Ph of κ^1-btz), 7.34 – 7.57 (m, 18H, Ph of κ^2-btz {10H} + Ph of κ^1-btz {6H} + H_4-Me bpy (2H)), 7.59 (s, 1H, CHN of κ^1-btz), 8.09 (br s, 2H, H_4-Me bpy), 8.27 (s, 2H, CHN of κ^2-btz), 9.70 (d, \( J_{HH} = 5.8 \) Hz, 2H, H_4-Me bpy); \(^{13}\)C NMR (125.8 MHz) CD_3CN \( \delta \)C 25.6 (CH_2, 4-Me bpy), 58.9 (CH_2 of κ^1-btz), 60.0 (CH_2 of κ^2-btz), 60.8 (CH_2 of κ^2-btz), 127.7 (CHN of κ^2-btz), 128.3 (CH, 4-Me bpy-C_4), 128.6 (CH, 4-Me bpy-C_3), 130.7 (CHN of κ^1-btz), 132.0 (CH of Ph), 133.0 (CHN of κ^1-btz), 133.6, 133.8, 133.9, 134.1, 134.2, 134.4, 134.5, 134.5 (CH of Ph), 139.1, (C, ipso-Ph of κ^1-btz), 139.3 (CN_1 of κ^1-btz), 139.7 (C, ipso-Ph of κ^2-btz), 140.6 (C, ipso-Ph of κ^2-btz), 146.6 (CN_1 of κ^2-btz), 147.9 (CN_1 of κ^1-btz), 155.3 (C, 4-Me bpy-C_3), 160.0 (CH, 4-Me bpy-C_2), 163.6 (C, 4-Me bpy-C_3).

trans-[Ru(4-Me bpy)(btz)(MeCN)]^{2+} 4b:

\(^1\)H NMR (400 MHz) CD_3CN \( \delta \)H 2.67 (s, 6H, 4-Me bpy), 5.90 (s, 4H, CH_2), 7.44 – 7.55 (m, 10H, Ph), 7.63 (d, \( J_{HH} = 5.7 \) Hz, 2H, H_4-Me bpy), 8.33 (br s, 2H, H_4-Me bpy), 8.48 (s, 2H, CHN), 9.95 (d, \( J_{HH} = 5.8 \) Hz, 2H, H_4-Me bpy); \(^{13}\)C NMR (100.6 MHz) CD_3CN \( \delta \)C 20.9 (CH_2, 4-Me bpy), 56.2 (CH_2), 123.4 (CHN), 124.4 (CH, C_2-Me bpy), 127.9 (CH, C_4-Me bpy), 129.1, 129.7, 129.8 (all CH of Ph), 134.7 (Cipso of Ph), 141.9 (CN_1 of Ph), 151.4 (C, C_2-Me bpy), 155.2 (CH, C_5-Me bpy), 158.6 (C, C_2-Me bpy).

Figure S3. \(^1\)H NMR spectra recorded during photochemical conversion of 1b in d_3-acetonitrile (* signals for 2b)
Photochemical conversion of [Ru(dmebpy)(btz)]2+PF62 (1c) in acetonitrile

**Figure S4.** 1H NMR spectra recorded during photochemical conversion of 1c in d3-acetonitrile (* signals for 2c)

**Trans-[Ru(4-OMeBpy)(κ1-btz)(κ2-btz)(MeCN)]2+ 3c:**

1H NMR (400 MHz) CD3CN δH 4.06 (s, 6H, 4-OMeBpy), 5.09 (s, 2H, CH2 of κ1-btz), 5.43 (s, 2H, CH2 of κ1-btz), 5.80 (d, JHH = 15.0 Hz, 2H, CH2 of κ2-btz), 6.90 (d, JHH = 7.7 Hz, 2H, Ph of κ1-btz), 6.86 (d, JHH = 15.0 Hz, 2H, CH2 of κ2-btz), 5.89 (s, 4H, C-H), 6.96 (dd, JHH = 6.5 Hz, JHH = 2.7 Hz, 2H, Hc-4-OMeBpy), 7.13 (s, 1H, CHN, of κ1-btz), 7.31 – 7.44 (m, 12H, Ph{10H of free btz} + Ph of κ1-btz [5H]), 6.60 (s, 1H, CHN, of κ1-btz), 7.79 (d, JHH = 2.7 Hz 2H, Hc-4-OMeBpy), 8.25 (s, 2H, CHN, of κ2-btz), 9.62 (d, JHH = 6.5 Hz, 2H, Hc-4-OMeBpy).

**trans-[Ru(4-OMeBpy)(btz)(MeCN)]2+ 4c:**

1H NMR (400 MHz) CD3CN δH 4.12 (s, 6H, 4-OMeBpy), 5.89 (s, 4H, CH2), 7.31 – 7.44 (m, 12H, Ph {10H of free btz} + Hc-4-OMeBpy [2H]), 7.44 – 7.55 (m, 10H, Ph), 8.00 (br s, 2H, Hc-4-OMeBpy), 8.49 (s, 2H, CHN), 9.87 (d, JHH = 6.4 Hz, 2H, Hc-4-OMeBpy); 13C NMR (100.6 MHz) CD3CN δC 56.1 (btz-CH2), 57.2 (OMe), 110.6 (CH, C4-4-OMeBpy), 113.3 (CH, C8-4-OMeBpy), 123.4 (CHN), 129.1, 129.7, 129.8 (all CH of Ph), 134.8 (Cipso of Ph), 141.9 (CN), 156.5 (CH, Cc-4-OMeBpy), 160.0 (C, Cc-4-OMeBpy), 168.3 (C, Cc-4-OMeBpy).
Photochemical conversion of [Ru(phen)(btz)]2[PF$_6$]$_2$ (1d) in acetonitrile

Figure S5. $^1$H NMR spectra recorded during photochemical conversion of 1d in d$_3$-acetonitrile (* signals for 2d)

[Ru(phen)(κ$^1$-btz)(κ$^2$-btz)(MeCN)]$^{2+}$ 3d:

$^1$H NMR (400 MHz) CD$_3$CN δ$_H$ 4.99 (s, 2H, CH$_2$ of κ$^1$-btz), 5.31 (s, 2H, CH$_2$ of κ$^1$-btz), 5.85 (d, $^2$J$_{HH}$ = 14.9 Hz, 2H, CH$_2$ of κ$^2$-btz), 5.91 (d, $^2$J$_{HH}$ = 15.0 Hz, 2H, CH$_2$ of κ$^2$-btz), 6.75 (d, $^2$J$_{HH}$ = 7.6 Hz, 2H, Ph of κ$^1$-btz), 6.88 (s, 1H, CH$_3$ of κ$^2$-btz), 7.19 – 7.60 (m, 19H, Ph of κ$^1$-btz), 7.82 (dd, $^3$J$_{HH}$ = 5.2, 8.4 Hz, 2H, Phen-H$_5$), 8.16 (s, 2H, Phen-H$_3''$), 8.35 (s, 2H, Phen-H$_3''$), 8.61 (d, $^2$J$_{HH}$ = 8.1 Hz, 2H, Phen-H$_6$), 10.2 (d, $^2$J$_{HH}$ = 5.1 Hz, 2H, Phen-H$_6$); $^{13}$C NMR (100.6 MHz) CD$_3$CN δ$_C$ 54.0 (CH$_2$ of κ$^1$-btz), 55.1 (CH$_2$ of κ$^1$-btz), 56.1 (CH$_2$ of κ$^2$-btz), 123.1 (CH$_3$ of κ$^2$-btz), 125.5 (CH$_3$ of κ$^1$-btz), 125.6 (CH, Phen-C$_5$), 127.8 (CH, Phen-C$_7$), 128.3 (CH$_3$ of κ$^1$-btz), 128.7, 128.8, 129.0, 129.1, 129.4, 129.8 (CH of Ph), 129.5 (CH$_3$ of κ$^1$-btz), 129.6, 129.7, 129.8 (CH of Ph), 130.5 (C, Phen-C$_3$), 134.1 (C, ipso-Ph of κ$^1$-btz), 134.9 (C, ipso-Ph of κ$^2$-btz), 135.7 (C, ipso-Ph of κ$^1$-btz), 137.1 (C, Phen-C$_3$), 142.1 (CH$_3$ of κ$^2$-btz), 143.0 (CH$_3$ of κ$^2$-btz), 150.0 (C, Phen-C$_2$), 156.6 (CH, Phen-C$_6$).

trans-[Ru(phen)(btz)(MeCN)]$^{2+}$ 4d:

$^1$H NMR (500 MHz) CD$_3$CN δ$_H$ 5.96 (s, 4H, CH$_2$), 7.48 – 7.54 (m, 10H, Ph), 8.15 (dd, $^2$J$_{HH}$ = 5.2, 8.1 Hz, 2H, Phen-H$_5$), 8.26 (s, 2H, Phen-H$_6$), 5.85 (s, 2H, CH$_3$N$_i$), 5.77 (d, $^2$J$_{HH}$ = 8.1 Hz, 2H, Phen-H$_5$), 10.4 (d, $^2$J$_{HH}$ = 5.3 Hz, 2H, Phen-H$_6$); $^{13}$C NMR (125.8 MHz) CD$_3$CN δ$_C$ 58.7 (CH$_3$), 124.0 (CH$_3$N$_i$), 126.4 (CH, Phen-C$_5$), 128.5 (CH, Phen-C$_7$), 129.5, 130.1, 130.2 (CH, Ph), 131.3 (C, Phen-C$_3$), 135.2 (C, ipso-Ph), 138.2 (CH, Phen-C$_3$), 142.5 (C, CN$_i$), 150.3 (C, Phen-C$_2$), 156.9 (CH, Phen-C$_6$).

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Photochemical conversion of \([\text{Ru(bpy)(btz}^\text{Ph})_2]\)[PF$_6$]$_2$ (1a$^{\text{Ph}}$) in acetonitrile
Photochemical conversion of \([\text{Ru(bpy)}(\text{btz}^{\text{Pr}})_2][\text{PF}_{6}]_2\) (1a^{Pr}) in acetonitrile

Figure S7. \(^1\text{H}\) NMR spectra recorded during photochemical conversion of 1a^{Pr} in d\(_3\)-acetonitrile.
Atomic coordinates for DFT optimised geometries

Trans-[Ru(bpy)(btz)(NCMe)2]2+

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 3.02063148 | -3.77418300 | -0.66144602 |
| C    | 1.69170112  | -3.95659097  | -0.29778676 |
| C    | 0.86086763  | -2.84844197  | -0.13369893 |
| N    | 1.33598598  | -1.58833072  | -0.32176487 |
| C    | 2.62061674  | -1.41545542  | -0.67297167 |
| C    | 3.49309108  | -2.48071662  | -0.85356602 |
| C    | -1.23067978 | -4.13879612  | 0.48313933 |
| C    | -2.57720831 | -4.12262606  | 0.82671121 |
| C    | -3.23191489 | -2.89972878  | 0.92204364 |
| C    | -2.51623515 | -1.73602328  | 0.67223248 |
| N    | -1.21510247 | -1.74817681  | 0.34045215 |
| C    | -0.56395870 | -2.93768765  | 0.24129654 |
| N    | 0.45049487  | 0.01706714   | 1.94522164 |
| N    | 2.35478924  | 1.90801319   | -0.68957532 |
| N    | 2.52938940  | 3.22866154   | -0.76745053 |
| C    | 1.38069955  | 3.89855005   | -0.50506839 |
| C    | 0.45202693  | 2.91295250   | -0.25672079 |
| N    | 1.10196347  | 1.71264397   | -0.38346017 |
| N    | -2.70172758 | 1.58915848   | 0.54808722 |
| N    | -3.05029694 | 2.87646035   | 0.58829357 |
| C    | -2.00080115 | 3.68511424   | 0.30240725 |
| C    | -0.94938758 | 2.82463575   | 0.07890812 |
| N    | -1.43419716 | 1.55298623   | 0.24310823 |
| C    | 3.85907400  | 3.78067379   | -1.04298476 |
C: -4.44074856  3.25384440  0.85758234
Ru: -0.05220341 -0.04498473 -0.03388263
H:  3.67279293 -4.62976180 -0.79293351
  1.30946227 -4.95710275 -0.14584535
  2.94182012 -0.39103037 -0.80861666
  4.52023413 -2.28981413 -1.13900657
  -0.70900115 -5.08343317  0.40671572
  -3.10291629 -5.05123064  1.01636067
  -4.28025332 -2.83868759  1.18706969
  -2.97999194 -0.76034524  0.73578960
  1.32179403  4.97445864 -0.51544774
  -2.08613892  4.75915288  0.28279816
  3.74594463  4.74432965 -1.53542315
  4.38675069  3.09374639 -1.69993472
  4.41181121  3.90208830 -0.11127022
  -4.45493102  4.21439970  1.36879609
  -4.88229209  2.49278066  1.49595091
  -4.99630383  3.32185199 -0.07790416
  0.73576683  0.01666812  3.06006586
  1.09478605  0.00800897  4.46870554
  0.20490188  0.14517159  5.08665314
  1.55969777 -0.94451093  4.73196595
  1.80065537  0.81232013  4.68632306
  -0.55596904 -0.15176687  2.01119633
  -0.84159884 -0.24615206 -3.12196416
  -1.20391041 -0.36969926 -4.52441227
  -2.28915804 -0.33018673 -4.63968210
  -0.75970198  0.44211394 -5.10406864
  -0.84442289 -1.32023800 -4.92425744
Cis-[Ru(bpy)(btz)(NCMe)$_2$]$^{2+}$

|   |     |     |     |
|---|-----|-----|-----|
| C | -1.84845869 | 2.33260892 | 3.44395683 |
| C | -1.38342501 | 2.98127272 | 2.30702035 |
| C | -0.70588221 | 2.25959622 | 1.32361696 |
| N | -0.49976854 | 0.92181772 | 1.46061238 |
| C | -0.94113612 | 0.30232810 | 2.56797521 |
| C | -1.61879460 | 0.96737693 | 3.57972523 |
| C | -0.28309547 | 4.21268864 | -0.23013272 |
| C | 0.27891407 | 4.69483376 | -1.40558712 |
| C | 0.96269370 | 3.81151428 | -2.23376815 |
| C | 1.05588312 | 2.47967215 | -1.85579923 |
| N | 0.51486878 | 2.00751717 | -0.72192765 |
| C | -0.15345296 | 2.86294529 | 0.09682384 |
| N | 0.88053252 | -2.83164970 | 1.25741015 |
| N | 0.20206736 | -3.98201113 | 1.23754237 |
| C | -0.90309716 | -3.8956456 | 0.45633486 |
| C | -0.89380700 | -2.61003644 | -0.02536452 |
| N | 0.22035700 | -2.00004349 | 0.49818289 |
| N | -2.04952609 | 0.17001196 | -1.84590238 |
| N | -3.03249990 | -0.66783841 | -2.18169399 |
| C | -2.87188387 | -1.88634452 | -1.60843548 |
| C | -1.71004237 | -1.77786028 | -0.87839199 |
| N | -1.24953099 | -0.49743191 | -1.06144355 |
| C | 0.71614423 | -5.14844774 | 1.96094636 |
| C | -4.13324955 | -0.20292902 | -3.03059368 |
| Ru | 0.54118525 | 0.00759445 | -0.10465332 |
| H | -2.37449736 | 2.88672405 | 4.21270362 |
| H | -1.54533180 | 4.04476244 | 2.19342566 |
| H | -0.73040644 | -0.75647337 | 2.63489482 |
| H | -1.95275390 | 0.42158113 | 4.45355558 |
| H | -0.81908991 | 4.88758873 | 0.42367267 |
|  | x      | y      | z      |
|---|--------|--------|--------|
| H | 0.18300853 | 5.74184500 | -1.66819506 |
| H | 1.41880566 | 4.14080392 | -3.15915320 |
| H | 1.57376348 | 1.75633187 | -2.47014907 |
| H | -1.57619544 | -4.72906836 | 0.31468717 |
| H | -3.56816887 | -2.69460208 | -1.76073367 |
| H | -0.12229574 | -5.75700241 | 2.29378621 |
| H | 1.27799423 | -4.79412123 | 2.82140228 |
| H | 1.36577420 | -5.73398042 | 1.31031268 |
| H | -4.41667878 | -0.99793119 | -3.71811924 |
| H | -3.78136671 | 0.65974132 | -3.59023842 |
| H | -4.98639059 | 0.07835712 | -2.41306670 |
| N | 2.29081587 | 0.28691656 | 0.92535946 |
| C | 3.26837063 | 0.42202290 | 1.51621893 |
| C | 4.50263232 | 0.58595891 | 2.26645626 |
| N | 1.61376495 | -0.73141525 | -1.70710092 |
| C | 2.22862037 | -1.17052819 | -2.57581490 |
| C | 3.00935900 | -1.71858511 | -3.67350580 |
| H | 5.27958315 | 1.01567965 | 1.63063932 |
| H | 4.34142246 | 1.25138628 | 3.11720080 |
| H | 4.84828757 | -0.38087594 | 2.63844132 |
| H | 4.07604167 | -1.58096103 | -3.48392619 |
| H | 2.80993556 | -2.78667269 | -3.78286084 |
| H | 2.75280518 | -1.21874764 | -4.61002182 |
Trans-[Ru(bpy)$_2$(NCMe)$_2$]$^{2+}$

| atom  | x          | y          | z          |
|-------|------------|------------|------------|
| C     | 2.87105070 | -3.98696725| -0.00860583|
| C     | 1.49814799 | -4.04542147| 0.19288230 |
| C     | 0.73287202 | -2.88183479| 0.10239100 |
| N     | 1.31515360 | -1.67392449| -0.12378961|
| C     | 2.63284152 | -1.63909869| -0.37846913|
| C     | 3.44529663 | -2.76352069| -0.33492174|
| C     | -1.51470124| -4.03849531| 0.14883569 |
| C     | -2.88240292| -3.97108303| -0.08385873|
| C     | -3.44296444| -2.74189949| -0.41332605|
| C     | -2.62350207| -1.62186214| -0.43074680|
| N     | -1.31222889| -1.66596978| -0.14562023|
| C     | -0.74146315| -2.87809843| 0.08583572 |
| N     | -0.00654789| -0.17002450| 2.06375316 |
| Ru    | 0.00286940 | -0.00030745| 0.02547614 |
| H     | 3.47240226 | -4.88608319| 0.05650589 |
| H     | 1.02850312 | -4.99921860| 0.39272272 |
| H     | 3.04197680 | -0.67524330| -0.64348811|
| H     | 4.50209255 | -2.67279133| -0.55385913|
| H     | -1.05452751| -4.99645665| 0.35034410 |
| H     | -3.48966819| -4.86764442| -0.03942099|
| H     | -4.49410056| -2.64427942| -0.65564571|
| H     | -3.02139949| -0.65377904| -0.69861598|
| C     | -0.01065000| -0.22128429| 3.21401195 |
| C     | -0.01505589| -0.27962416| 4.66724735 |
| H     | -1.01582174| -0.07197074| 5.05258073 |
| H     | 0.29147585 | -1.27123660| 5.00681976 |
| H     | 0.67651099 | 0.45960434 | 5.07778418 |
| N     | 0.01496200 | 0.16180869 | -2.01419667|
| C     | 0.02489314 | 0.19424333 | -3.16500918|
| C     | 0.03852991 | 0.22466414 | -4.61873891|
| H     | -0.96831637| 0.39743106 | -5.00483914|
H  0.69154927  1.02389938  -4.97527805
H  0.40436407  -0.72635854  -5.01233039
C  2.87291626  3.97703968  -0.05939160
C  1.50547944  4.02207707  -0.30024193
C  0.73631382  2.86760387  -0.14792866
N  1.31254425  1.67615089  0.16647106
C  2.62114270  1.65991593  0.46608712
C  3.43523870  2.78046951  0.37186332
C  -1.51143746  4.02016880  -0.27793127
C  -2.87703201  3.96956124  -0.02782231
C  -3.43409471  2.76709180  0.39403165
C  -2.61660736  1.64792643  0.47255481
N  -1.31013675  1.67043425  0.16436917
C  -0.73869136  2.86563754  -0.14347004
H  3.47800337  4.86899470  -0.17315751
H  1.04233694  4.95966472  -0.57756233
H  3.02085387  0.71589661  0.80794116
H  4.48424991  2.70773579  0.63154220
H  -1.05234523  4.96207418  -0.54666910
H  -3.48473968  4.86129976  -0.12769159
H  -4.48117304  2.68936522  0.65996079
H  -3.01171772  0.69945713  0.80799772
Cis-[Ru(bpy)$_2$(NCMe)$_2$]$^{2+}$

geometry

|   |   |   |   |
|---|---|---|---|
| C | -2.80437659 | 2.28698751 | -2.80473044 |
| C | -2.17596090 | 2.91009995 | -1.73383449 |
| C | -1.26226436 | 2.19959848 | -0.95481602 |
| N | -0.97240528 | 0.89864739 | -1.23179712 |
| C | -1.58346148 | 0.30308813 | -2.26997360 |
| C | -2.50319003 | 0.95698491 | -3.07746205 |
| C | -0.71891969 | 4.09655736 | 0.63123607 |
| C | -0.00673842 | 4.56065481 | 1.72975700 |
| C | 0.86721972  | 3.69391928 | 2.37855205 |
| C | 0.99200739  | 2.39536609 | 1.90421440 |
| N | 0.30083232  | 1.93693323 | 0.84588373 |
| C | -0.55111047 | 2.77942620 | 0.20077748 |
| C | 0.08039792  | -4.55788981 | -1.71670711 |
| C | -0.72378686 | -4.08079160 | -0.68924781 |
| C | -0.57469391 | -2.76639881 | -0.24387017 |
| N | 0.34477688  | -1.93789571 | -0.80916286 |
| C | 1.12467598  | -2.40900512 | -1.79798851 |
| C | 1.02576750  | -3.70657364 | -2.28015084 |
| C | -2.36336674 | -2.87222348 | 1.54165341 |
| C | -3.06639926 | -2.24264904 | 2.56120927 |
| C | -2.76173684 | -0.92124925 | 2.86885458 |
| C | -1.76538824 | -0.28115795 | 2.14558024 |
| N | -1.08169696 | -0.88272385 | 1.15728465 |
| C | -1.37281392 | -2.17621318 | 0.84796933 |
| Ru| 0.44360200  | -0.00138816 | 0.02270153 |
| H | -3.51519448 | 2.83283518  | -3.41380651 |
| H | -2.39977001 | 3.94477999  | -1.51144254 |
| H | -1.31746763 | -0.72945328 | -2.45176199 |
| H | -2.96779668 | 0.42813444  | -3.90048216 |
| H | -1.39985365 | 4.76086886  | 0.11605773 |
| H | -0.13289951 | 5.58169437  | 2.07082227 |
Table S1 X-ray Crystallographic data for complexes 1d, 1e, 2a and 3d.

|          | 1d                      | 1e                      | 2a                      | 3d                      |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|
| Formula  | C₅₁,H₄₅.₅₉F₂₅N₁₄.₄₉O₁₂.₅₁P₂Ru | C₄₉H₄₁F₁₂N₁₉OP₂Ru     | C₃₅H₅₀.₅₁F₁₂N₁₇.₃P₂Ru | C₂₉H₅₀F₂₇N₁₆P₂Ru     |
| M_r / g mol⁻¹ | 1260.99                  | 1246.98                | 1323.62                 | 969.69                  |
| Temperature / K | 150                      | 150                    | 150                     | 150                     |
| Space group | P42bc                    | P42bc                  | P1                      | P21/c1                  |
| a / Å      | 22.5345(6)               | 22.4167(10)            | 12.4144(3)              | 34.2603(9)              |
| b / Å      | 22.5345(6)               | 22.4167(10)            | 14.3194(3)              | 9.3177(2)               |
| c / Å      | 20.6805(3)               | 20.6681(9)             | 17.5321(4)              | 11.9338(3)              |
| a / °      | 90                       | 90                     | 92.0042(11)             | 90                      |
| β / °      | 90                       | 90                     | 98.6530(10)             | 93.351(1)               |
| γ / °      | 90                       | 90                     | 108.1437(10)            | 90                      |
| V / Å³     | 10501.6(5)               | 10385.9(8)             | 2916.82(11)             | 3803.08(16)             |
| Dc / g cm⁻¹ | 1.595                    | 1.595                  | 1.507                   | 1.694                   |
| Z          | 8                       | 8                      | 2                       | 4                       |
| μMo / mm⁻¹ | 0.457                    | 0.462                  | 3.501                   | 0.598                   |
| 2θmax     | 33.160                   | 28.280                 | 68.24                   | 29.570                  |
| N_ref     | 19704                    | 11575                  | 10624                   | 10666                   |
| R₁        | 0.0439 (14247)           | 0.0459 (8307)          | 0.0512 (9376)           | 0.0353 (8918)           |
| wR₂       | 0.0977 (19704)           | 0.1087 (11575)         | 0.1550 (10624)          | 0.0832 (10666)          |
| S         | 1.015                    | 1.030                  | 1.039                   | 1.030                   |

X-ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(Kα) (1d, 1e and 4d) or a Bruker D8 Venture Cu(Kα) (2a) radiation source and a cold stream of N₂ gas. Summarized crystal and refinement data are presented in Table S1. Preliminary scans were employed to assess crystal quality, lattice symmetry, ideal exposure time etc. prior to collecting a full sphere of diffraction intensity data using SMART operating software.[1] Intensities were then integrated from several series of exposures, merged and corrected for Lorentz and polarisation effects using SAINT software.[2] Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix non-linear least squares on all F² data, using SHELXS-97 and SHELXL software respectively (as implemented in the SHELXTL suite of programs).[3] Empirical absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.[4] All structures were refined until convergence (max shift/esd < 0.01) and in each case, the final Fourier difference map showed no chemically sensible features. In some cases the structures contained disordered solvents which were restrained using DELU and SIMU in the least squares refinement. Structure 1d contained substitutional disorder of acetonitrile and diethyl ether solvent molecules which was modeled using the PART instruction and 2a contained a disordered acetonitrile molecule which as best modeled as half-occupancy and restrained using DELU, SIMU and ISOR for one of the carbon atoms.

Computational Details

The structures of cis- and trans-[Ru(bpy)₂(NCMe)₂]²⁺ and cis- and trans-3a (benzyl substituents simplified to methyl) were optimized in the gas phase at the B3LYP[27] level if theory using the Stuttgart-Dresden relativistic small core potential[5] for Ru and 6-311G* basis sets[6] for all other atoms. Calculations were carried in using the NWChem 6.1 software package.[7]
Syntheses

Synthesis of [RuCl(p-cymene)(dmbpy)][PF₆].

[RuCl₂(p-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 NH₄PF₆ was added and the volume of the solution reduced by half in vacuo. An orange precipitate was observed to form which was filtered and washed with 10 mL Et₂O. Yield = 153.5 mg (78 %)

¹H NMR (500 MHz) CD₃CN δ_H 1.02 (s, 3H, CH(CH₃)), 1.04 (s, 3H, CH(CH₃)), 2.20 (s, 3H, p-cymene CH₃), 2.59 (s, 6H, 4-Me bpy), 2.64 (sp, 3_J_HH = 7.2 Hz, 1H, CH(CH₃)₂), 5.68 (d, 3_J_HH = 6.2 Hz, 2H, p-cymene Ar-CH), 5.89 (d, 3_J_HH = 6.2 Hz, 2H, p-cymene Ar-CH) 7.53 (d, 3_J_HH = 5.9 Hz, 2H, 4-Me bpy-H₃), 8.17 (s, 2H, 4-Me bpy-H₃), 9.14 (d, 3_J_HH = 6.0 Hz, 2H, 4-Me bpy-H₆). ¹³C NMR (125.8 MHz) CD₃CN δ_c 18.5 (CH₃, p-cymene), 20.9 (CH₃, 4-Me bpy), 21.7 (CH₃, CH(CH₃)₂), 31.4 (CH, CH(CH₃)₂), 84.5 (CH, p-cymene Ar), 86.8 (CH, p-cymene Ar), 103.8 (C, p-cymene Ar-C(CH₃)), 105.0 (C, p-cymene Ar-C(CH₃)₂), 124.8 (CH, 4-Me bpy-C₃), 128.9 (CH, 4-Me bpy-C₃), 153.2 (C, 4-Me bpy-C₄), 154.8 (C, 4-Me bpy-C₅), 155.1 (CH, 4-Me bpy-C₆). HRMS-ESI calculated for [RuClN₂C₂H₂₆]⁺ m/z = 455.082252, found m/z = 455.082790.

Synthesis of [RuCl(p-cymene)(phen)][PF₆].

[RuCl₂(p-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 NH₄PF₆ was added and the volume of the solution reduced by half in vacuo. An orange precipitate was observed to form which was filtered and washed with 10 mL Et₂O. Yield = 109.2 mg (75 %)

¹H NMR (500 MHz) CD₃CN δ_H 1.01 (s, 3H, CH(CH₃)), 1.02 (s, 3H, CH(CH₃)), 1.05 (s, 3H, CH(CH₃)), 2.19 (s, 3H, p-cymene CH₃), 2.71 (sp, 3_J_HH = 7.0 Hz, 1H, CH(CH₃)₂), 5.86 (d, 3_J_HH = 6.4 Hz, 2H, p-cymene Ar-CH), 6.05 (d, 3_J_HH = 6.4 Hz, 2H, p-cymene Ar-CH), 8.06 (dd, 3_J_HH = 5.3 Hz, 8.2 Hz, 2H, phen), 8.18 (s, 2H, phen), 8.78 (dd, 3_J_HH = 0.9 Hz, 3_J_HH = 8.3 Hz, 2H, phen), 9.69 (dd, 3_J_HH = 1.0 Hz, 3_J_HH = 5.3 Hz, 2H, phen).

¹³C NMR (125.8 MHz) CD₃CN δ_c 18.4 (CH₃, p-cymene), 21.7 (CH₃, CH(CH₃)₂), 31.4 (CH, CH(CH₃)₂), 84.5 (CH, p-cymene Ar), 86.3 (CH, p-cymene Ar), 103.0 (C, p-cymene Ar-C(CH₃)), 106.0 (C, p-cymene Ar-C(CH₃)₂), 126.9 (CH, phen), 128.1 (CH, phen), 131.2 (C, phen), 139.4 (CH, phen), 146.3 (C, phen), 155.9 (CH, phen). HRMS-ESI calculated for [RuClN₂C₂H₂₂]⁺ m/z = 451.050952, found m/z = 451.051132.

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