Supporting information

Unusually Slow Internal Conversion in N-Heterocyclic Carbene/Carbanion Cyclometallated Ru(II) Complexes: A Hammett Relationship

William T. Kender and Claudia Turro*

Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210

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Scheme S1. General synthetic scheme for 1 – 6 where (i) excess glyoxal, RT, overnight followed by NH₄Cl, formaldehyde H₃PO₄ for 6hrs, (ii) 40°C, Mel (neat) for 2 hr, (iii) 1.1 eq (RuCl₂(p-cymene))₃, excess Cs₂CO₃, 6 hr, and (iv) 3 eq bpy in minimal CH₃CN, reflux overnight followed by water, hexanes, and excess NH₄PF₆.

The complete syntheses of complexes 1₁, 3₁, 2 and 6₁ were accomplished following methods previously described, while 2, 4, and 5 were prepared using a modified version of the published routes for the ruthenium synthesis. The syntheses of the ligands for 2₃, 4₄ and 5₅ have been previously described.

The general reaction scheme for the conversion of dichloro(p-cymene)ruthenium(II) dimer to the cyclometallated p-cymene piano stool complex is as follows: The imidazolium salt (~0.5 mmol) and ruthenium starting material (~0.25 mmol) were added to a round bottom flask with Cs₂CO₃ (~1 mmol). Dried and degassed THF was added and the reaction was left to reflux overnight under the positive pressure of argon. The next day the solution was a dark orange color.
in all cases. This was passed through two short plugs of neutral alumina with dichloromethane as the solvent. The orange fractions were collected and concentrated to give an orange solid.

**Synthesis of Ru(II)(p-cymene)(NHC-Me)Cl**

The –Me substituent complex used 106 mg (0.17 mmol) ruthenium(p-cymene) dimer, 87 mg (0.29 mmol) ligand, and 541 mg of Cs₂CO₃ (1.66 mmol) to give a final weight of 118 mg (0.27 mmol, 77% yield). ^1^H NMR (400 MHz, CDCl₃) shown in Figure S1: 7.84 (1H, d, 1.3 Hz), 7.30 (1H, d, 2.1Hz), 6.96 (1H, d, 6.4Hz), 6.95 (1H, s), 6.70 (1H, dd, 1.2/7.0 Hz), 5.50 (1H, d, 6.0 Hz), 5.45 (1H, d, 6.1 Hz), 5.43 (1H, d, 6.1 Hz), 5.40 (1H, d, 6.0 Hz), 4.04 (3H, s), 2.32 (7H, m), 0.92 (3H, d, 6.9 Hz), 0.82 (3H, d, 6.9 Hz). MS-ESI monoisotopic weight of [M-Cl]^+ : Found – 407.14, Calculated – 407.11 shown in Figure S2.

![Figure S1](image_url)  
*Figure S1. ^1^H NMR data (400 MHz, CDCl₃) of Ru(II)(p-cymene)(NHC-Me)Cl*
Figure S2. MS-ESI data of Ru(II)(p-cymene)(NHC-Me)⁺

**Synthesis of Ru(II)(p-cymene)(NHC-Cl)Cl**

The –Cl substituent complex used 174 mg (0.28 mmol) ruthenium(p-cymene) dimer, 183 mg (0.57 mmol) ligand, and 562 mg of Cs₂CO₃ (1.72 mmol) to give a final weight of 186 mg (0.40 mmol, 71% yield). ¹H NMR (400 MHz, CDCl₃) shown in Figure S3: 7.96 (1H, d, 2.3 Hz), 7.30 (1H, d, 2.0Hz), 6.98 (1H, d, 3.0 Hz), 6.97 (1H, d, 3.0 Hz), 6.87 (1H, dd, 7.9/2.2 Hz), 5.52 (1H, d, 6.1Hz), 5.47 (1H, d, 5.6Hz), 5.45 (1H, d, 5.6Hz), 5.41 (1H, d, 6.1 Hz), 4.03 (3H, s), 2.33 (4H, m), 0.92 (3H, d, 7.0 Hz), 0.81 (3H, d, 7.0 Hz). Add in MS-ESI data here. MS-ESI monoisotopic weight of [M-Cl]⁺: Found – 427.09, Calculated – 427.05 shown in Figure S4.
Figure S3. $^1$H NMR data (400 MHz, CDCl$_3$) of Ru(II)(p-cymene)(NHC-Cl)Cl

Figure S4. MS-ESI data of Ru(II)(p-cymene)(NHC-Cl)$^+$
Synthesis of Ru(II)(p-cymene)(NHC-CO₂Et)Cl

The –CO₂Et substituent complex used 197 mg (0.32 mmol) ruthenium(p-cymene) dimer, 168 mg (0.47 mmol) ligand, and 247 mg of Cs₂CO₃ (0.76 mmol) to give a final weight of 135 mg (0.27 mmol, 42% yield). ¹H NMR (400 MHz, CDCl₃) shown in Figure S5: 8.71 (1H, d, 1.8 Hz), 7.65 (1H, dd, 1.8/8.0Hz), 7.38 (1H, d 2.1 Hz), 7.09 (1H, d, 8.0 Hz), 7.00 (1H, d, 2.1 Hz), 5.58 (1H, d, 6.1 Hz), 5.53 (1H, d, 6.1 Hz), 5.51 (1H, d, 5.9 Hz), 5.42 (1H, d, 5.9Hz), 4.38 (2H, q, 7.1 Hz), 4.06 (3H,s), 2.35 (m 1H 3.3Hz), 2.33 (3H, s), 1.42 (3H, t, 7.1Hz), 0.92 (3H, d, 7.0 Hz), 0.80 (3H, d, 7.0 Hz). MS-ESI monoisotopic weight of [M-Cl]⁺: Found – 465.15, Calculated – 465.11 shown in Figure S6.

**Figure S5.** ¹H NMR data (400 MHz, CDCl₃) of Ru(II)(p-cymene)(NHC-CO₂Et)Cl
The general reaction scheme for the conversion of the cyclometallated p-cymene piano stool complex to the cyclometallated bipyridine complex is as follows: 2,2’bipyridine (0.53 mmol), and the p-cymene complex (0.20 mmol) were added to a 1:1 water/acetonitrile mixture (15 mL). This was refluxed for 5 hours while monitoring via alumina TLC (eluting with dichloromethane/acetonitrile 10:1). When the reaction had completed, the heat was turned off and hexanes was added to the solution (30 mL). Then ammonium hexafluorophosphate was added to the solution (1 mmol) and a purple precipitate formed rapidly. This was then filtered, washed with hexanes and water, and dried under reduced pressure. The complexes were then dissolved in acetonitrile and crystalized via the slow diffusion of diethyl ether. This yielded single crystal diffraction quality crystals all of which were purple in color.
Synthesis of Ru(II)(bpy)$_2$(NHC-Me)PF$_6$

The –Me substituent complex used 78 mg (0.18 mmol) of Ru(II)(p-cymene)(NHC-Me)Cl, 56 mg (0.36 mmol) 2,2'-bipyridine, and 1.6 g of NH$_4$PF$_6$ (1 mmol) for a final weight of 100 mg (0.14 mmol, 78% yield). $^1$H NMR (400 MHz, CD$_3$CN) shown in Figure S7: 8.37 (1H, dt, 1.1/8.2 Hz), 8.33 (2H, dq, 0.9/8.3), 8.26 (1H, dt, 0.9/8.2 Hz), 8.05 (1H, dq, 0.8/5.8 Hz), 7.99 (1H, d, 5.6 Hz), 7.89 (3H, m), 7.81 (1H, dt, 1.5/7.86 Hz), 7.72 (1H, td, 1.5/7.8 Hz), 7.68 (1H, d, 2.0 Hz), 7.53 (1H, dq, 5.4 Hz/0.8), 7.30 (2H, m), 7.17 (3H, m), 6.94 (1H, d, 2.1 Hz), 6.62 (1H, d, 7.4 Hz), 6.07 (1H, s), 2.99 (3H, s), 1.98 (3H, s). MS-ESI monoisotopic weight of M$^+$: Found – 585.184, Calculated – 585.134 shown in Figure S10.

Figure S7. $^1$H NMR data (400 MHz, CD$_3$CN) of complex 2
Synthesis of Ru(II)(bpy)_2(NHC-Cl)PF_6

The –Cl substituent complex used 94 mg (0.20 mmol) Ru(II)(p-cymene)(NHC-Cl)Cl, 96 mg (0.61 mmol) 2,2'-bipyridine, and 1.6 g of NH_4PF_6 (1 mmol) for a final weight of 10 mg (0.013 mmol, 7% yield). ^1H NMR (400 MHz, CD_3CN) shown in Figure S8: 8.31 (3H, m), 8.29 (1H, dt, 8.2/1.1 Hz), 8.01 (1H, dq, 5.8/0.7 Hz), 7.99 (1H, dq, 5.9/0.6 Hz), 7.90 (3H, m), 7.84 (1H, td, 7.7/1.5 Hz), 7.77 (1H, td, 7.9/1.5 Hz), 7.70 (1H, d, 2.1 Hz), 7.53 (1H, qd, 0.8/5.6 Hz), 7.32 (2H, m), 7.25 (1H, d, 8.2 Hz), 7.20 (2H, m), 6.98 (1H, d, 2.1 Hz), 6.83 (1H, dd, 2.4/8.2 Hz), 6.16 (1H, d, 2.3 Hz), 3.0 (3H, s). MS-ESI monoisotopic weight of M^+: Found – 605.1141, Calculated – 605.0794 shown in Figure S10.

![Figure S8. ^1H NMR data (400 MHz, CD_3CN) of complex 4](image-url)
Synthesis of Ru(II)(bpy)$_2$(NHC-CO$_2$Et)PF$_6$

The –CO$_2$Et substituent complex used 64 mg (0.13 mmol) Ru(II)(p-cymene)(NHC-CO$_2$Et)Cl, 54 mg (0.35 mmol) 2,2’-bipyridine, and 1.6 g of NH$_4$PF$_6$ (1 mmol) for a final weight of 20 mg (0.025 mmol, 20% yield). $^1$H NMR (400 MHz, CD$_3$CN) shown in Figure S9: 8.36 (3H, m), 8.26 (1H, m), 8.02 (1H, d, 5.6 Hz), 7.94 (4H, m), 7.83 (1H, dt, 1.9/7.8 Hz), 7.77 (1H, d, 2.2 Hz), 7.74 (1H, dt, 1.1/8.0 Hz), 7.56 (1H, d, 5.7 Hz), 7.51 (1H, dd, 1.6/7.6 Hz), 7.34 (3H, m), 7.0 (1H, d, 2.1 Hz), 6.92 (1H, d, 1.5 Hz), 4.11 (2H, dq, 1.5/7.3 Hz), 3.03 (3H, s), 1.2 (3H, 7.3 Hz).

MS-ESI monoisotopic weight of M$: Found – 643.1972, Calculated – 643.1395 shown in Figure S10.

Figure S9. $^1$H NMR data (400 MHz, CD$_3$CN) of complex 5
Figure S10. MS-ESI for complexes 1-6
Crystallography

Table S1. Crystallographic details for 1 (CCDC 1894199).

| Property                      | Value                              |
|-------------------------------|------------------------------------|
| Empirical formula             | C_{34}H_{33}F_{6}N_{6}O_{2}PRu     |
| Formula weight                | 803.70                             |
| Temperature/K                 | 150(2)                             |
| Crystal system                | triclinic                          |
| Space group                   | P-1                                |
| a/Å                           | 9.2133(3)                          |
| b/Å                           | 13.1226(4)                         |
| c/Å                           | 15.7060(5)                         |
| α/°                           | 111.0380(10)                       |
| β/°                           | 93.8870(10)                        |
| γ/°                           | 106.1970(10)                       |
| Volume/Å³                     | 1671.83(9)                         |
| Z                             | 2                                  |
| ρ_{calc}/g/cm³                | 1.597                              |
| μ/mm⁻¹                        | 0.593                              |
| F(000)                        | 816.0                              |
| Crystal size/mm³              | 0.31 × 0.12 × 0.08                 |
| Radiation                     | MoKα (λ = 0.71073)                 |
| 2Θ range for data collection/°| 5.874 to 55.806                    |
| Index ranges                  | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected         | 100732                             |
| Independent reflections       | 7985 [R_{int} = 0.0257, R_{sigma} = 0.0119] |
| Data/restraints/parameters    | 7985/0/611                         |
| Goodness-of-fit on F²         | 1.062                              |
| Final R indexes [I>=2σ(I)]    | R₁ = 0.0203, wR₂ = 0.0527          |
| Final R indexes [all data]    | R₁ = 0.0212, wR₂ = 0.0535          |
| Largest diff. peak/hole / e Å⁻³| 0.53/-0.54                        |

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{ij} tensor.

| Atom  | x      | y      | z      | U(eq)    |
|-------|--------|--------|--------|----------|
| Ru(1) | 3049.2(2) | 5916.8(2) | 8147.4(2) | 16.30(4) |
| P(1)  | -426.5(5) | 1557.8(3) | 3833.1(3) | 30.42(9) |
| F(3)  | -1773.4(12) | 604.2(9) | 2998.0(7) | 41.7(2)  |
| F(5)  | 928.8(14) | 2508.2(9) | 4662.3(7) | 49.2(3)  |
| N(3)  | 2446.1(12) | 5855.1(9) | 9391.9(7) | 17.9(2)  |
| N(5)  | 757.1(13) | 4989.6(9) | 7422.5(7) | 19.2(2)  |
| N(4)  | 2856.5(12) | 7526.2(9) | 8803.2(7) | 18.1(2)  |
| N(6)  | 3072.1(13) | 4241.5(9) | 7593.9(7) | 19.4(2)  |
|    |    |    |    |    |    |
|----|----|----|----|----|----|
| F(6) | -725.7(16) | 758.6(10) | 4401.3(9) | 63.8(4) |
| F(1) | -113.5(15) | 2380.1(11) | 3272.2(8) | 54.0(3) |
| F(2) | 799.7(14) | 1000.8(11) | 3360.2(9) | 58.4(3) |
| O(1) | 8060.3(12) | 7955.5(10) | 10956.5(8) | 33.5(2) |
| N(1) | 5565.1(14) | 6698.8(10) | 7274.8(8) | 19.8(2) |
| F(3) | 799.7(14) | 1000.8(11) | 3360.2(9) | 58.4(3) |
| O(2) | 8060.3(12) | 7955.5(10) | 10956.5(8) | 33.5(2) |
| N(2) | 5565.1(14) | 6698.8(10) | 7274.8(8) | 19.8(2) |
| C(1) | 3997.8(16) | 6189.0(11) | 7089.0(9) | 20.9(2) |
| C(2) | 436.6(15) | 3831.1(11) | 6965.2(8) | 21.6(2) |
| C(3) | 4888(2) | 6296.0(13) | 5803.6(11) | 31.5(3) |
| C(4) | 6337.3(16) | 7044.3(11) | 8201.1(9) | 21.3(2) |
| C(5) | 5334.4(15) | 6705(1) | 8764.9(9) | 19.2(2) |
| C(6) | 6027.0(15) | 7039.5(11) | 9686.3(9) | 21.6(2) |
| C(7) | 7587.0(16) | 7657.9(12) | 8511(1) | 25.5(3) |
| C(8) | 8533.1(16) | 7980.5(12) | 9442.3(11) | 26.2(3) |
| C(9) | 7888.2(16) | 7657.9(12) | 8511(1) | 25.5(3) |
| C(10) | 2028(2) | 5403.2(15) | 5803.6(11) | 31.5(3) |
| C(11) | 2500.5(14) | 6888.0(11) | 10044.7(9) | 18.6(2) |
| C(12) | 2268.8(17) | 7008.3(12) | 10936.5(9) | 24.1(3) |
| C(13) | 1933.1(18) | 6050.5(14) | 11159(1) | 27.9(3) |
| C(14) | 1860.3(17) | 2249.3(12) | 6672.3(10) | 26.6(3) |
| C(15) | 2135.7(16) | 4932.4(12) | 9624.1(10) | 22.5(3) |
| C(16) | 2782.9(14) | 7837.4(11) | 9721.5(9) | 18.2(2) |
| C(17) | 3997.8(16) | 6189.0(11) | 7089.0(9) | 20.9(2) |
| C(18) | 3081.4(16) | 9790.3(12) | 10493.8(10) | 25.1(3) |
| C(19) | 3054.1(17) | 9455.8(12) | 8971.9(10) | 25.4(3) |
| C(20) | 2957.7(16) | 8331.2(12) | 9642.1(10) | 22.7(3) |
| C(21) | 436.6(15) | 3831.1(11) | 6965.2(8) | 21.6(2) |
| C(22) | 4257.0(18) | 2774.5(13) | 7360.5(11) | 29.7(3) |
| C(23) | 4527.0(18) | 7371.1(9) | 7371.1(9) | 23.4(3) |
| C(24) | -1846.5(17) | 4772.0(13) | 6868.5(10) | 26.7(3) |
| C(25) | -379.9(16) | 5436.8(12) | 7371.1(9) | 23.4(3) |
| C(26) | 5334.4(15) | 6705(1) | 8764.9(9) | 19.2(2) |
| C(27) | 1630.0(18) | 2249.3(12) | 6672.3(10) | 26.6(3) |
| C(28) | 2902.0(19) | 1929.5(12) | 6823.4(11) | 30.4(3) |
| C(29) | 4257.0(18) | 7371.1(9) | 7371.1(9) | 23.4(3) |
| C(30) | 4301.9(17) | 3913.1(12) | 7729.9(10) | 25.3(3) |
| C(31) | 9553.7(19) | 8747.4(17) | 11377.8(12) | 37.3(4) |
| C(32) | -3749(2) | 65.9(15) | 6459.7(14) | 44.7(4) |
| C(33) | -4577(11) | -569(10) | 7016(8) | 40.8(17) |
| C(34A) | -3439(16) | 1115(3) | 6743(7) | 67(2) |
| C(34) | -3540(20) | -610(13) | 5467(11) | 55(3) |
| C(33A) | -3730(40) | -620(20) | 5555(19) | 50(5) |
| O(2A) | -2680(20) | 1021(8) | 6945(5) | 58(4) |
Table S3. Crystallographic details for 2 (CCDC 1894201).

| Property                        | Value                           |
|---------------------------------|---------------------------------|
| Empirical formula               | C$_{34}$H$_{33}$F$_{6}$N$_{6}$OPRu |
| Formula weight                  | 787.70                          |
| Temperature/K                   | 150(2)                          |
| Crystal system                  | triclinic                       |
| Space group                     | P-1                             |
| a/Å                             | 9.1317(4)                       |
| b/Å                             | 13.2504(6)                      |
| c/Å                             | 15.7409(7)                      |
| α/°                             | 112.344(2)                      |
| β/°                             | 93.886(2)                       |
| γ/°                             | 106.329(2)                      |
| Volume/Å³                       | 1657.51(13)                     |
| Z                               | 2                               |
| ρcalc g/cm$^3$                   | 1.578                           |
| μ/mm$^{-1}$                     | 0.594                           |
| F(000)                          | 800.0                           |
| Crystal size/mm$^3$             | 0.35 $\times$ 0.12 $\times$ 0.04 |
| Radiation                       | MoKα ($λ = 0.71073$)            |
| 2Θ range for data collection/°  | 5.708 to 55.776                 |
| Index ranges                    | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected           | 100150                          |
| Independent reflections         | 7891 [R$_{int} = 0.0325$, R$_{sigma} = 0.0131$] |
| Data/restraints/parameters      | 7891/0/602                      |
| Goodness-of-fit on F$^2$        | 0.848                           |
| Final R indexes [I>=2σ (I)]     | R$_1 = 0.0228$, wR$_2 = 0.0862$ |
| Final R indexes [all data]      | R$_1 = 0.0251$, wR$_2 = 0.0909$ |
| Largest diff. peak/hole / e Å$^3$ | 0.50/-0.44                    |

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalized U$_{ij}$ tensor.

| Atom  | x      | y      | z      | U(eq)  |
|-------|--------|--------|--------|--------|
| Ru(1) | 8134.2(2) | 5972.9(2) | 8171.6(2) | 14.66(6) |
| P(1)  | 4489.1(5)  | 1493.6(4)  | 3787.2(3)  | 29.12(11) |
| F(5)  | 3089.0(15) | 522.5(11)  | 2958.9(8)  | 42.4(3)   |
| F(3)  | 5890.4(15) | 2462.6(11) | 4613.3(9)  | 47.3(3)   |
| N(3)  | 7555.4(15) | 5937.2(11) | 9424.7(9)  | 17.6(2)   |
| F(6)  | 4253.6(18) | 710.5(12)  | 4352.9(10) | 56.5(4)   |
| N(6)  | 8145.4(15) | 4293.8(11) | 7598.2(9)  | 18.2(2)   |
| N(5)  | 5801.2(15) | 5022.8(11) | 7454.0(9)  | 17.7(2)   |
| N(4)  | 7930.8(14) | 7577.6(11) | 8843.7(9)  | 16.9(2)   |
| F(1)  | 4743.8(17) | 2306.7(12) | 3233.1(9)  | 49.4(3)   |
|   |   |   |   |   |
|---|---|---|---|---|
| N(1) | 10589.9(1) | 6715.0(11) | 7247.7(9) | 20.9(3) |
| F(4) | 5697.5(18) | 935.6(14) | 3276.1(11) | 55.7(4) |
| F(2) | 3289.9(17) | 2075.1(13) | 4287.7(10) | 53.6(3) |
| N(2) | 8540.9(16) | 5954.5(12) | 6167.6(9) | 23.7(3) |
| C(5) | 10474.2(18) | 6782.8(13) | 8761.9(11) | 17.7(3) |
| C(21) | 5473.2(17) | 3862.4(12) | 6972.1(10) | 17.8(3) |
| C(16) | 7771.3(16) | 7888.2(12) | 9753.7(10) | 17.5(3) |
| C(11) | 7493.8(16) | 6949.9(13) | 10069.2(10) | 17.7(3) |
| C(1) | 9009.9(18) | 6209.9(13) | 7086.6(11) | 19.1(3) |
| C(26) | 6790.9(17) | 3448.9(12) | 6435.8(11) | 23.0(3) |
| C(22) | 4009.8(18) | 3139.8(14) | 6435.8(11) | 23.0(3) |
| C(4) | 11422.7(17) | 7081.8(13) | 8443.0(11) | 25.0(3) |
| C(17) | 7841.4(17) | 9005.7(13) | 10326.6(11) | 21.0(3) |
| C(18) | 8038.6(18) | 9830.1(13) | 9965.6(11) | 23.4(3) |
| C(15) | 7283.3(18) | 5027.9(13) | 9655.5(11) | 22.0(3) |
| C(9) | 13008.2(18) | 7699.4(14) | 8443.0(11) | 25.0(3) |
| C(6) | 11255.6(17) | 7149.3(12) | 9685.1(11) | 19.6(3) |
| C(20) | 8065.1(18) | 8382.5(13) | 8492.0(11) | 21.4(3) |
| C(14) | 6931.1(19) | 5076.5(15) | 10505.6(12) | 25.5(3) |
| C(25) | 4650.4(18) | 5464.0(14) | 7413.8(11) | 22.0(3) |
| C(19) | 8116.1(19) | 9499.1(14) | 9026.1(13) | 24.8(3) |
| C(12) | 7158.5(18) | 7057.4(14) | 10940.0(11) | 23.1(3) |
| C(30) | 9399.8(18) | 3974.6(14) | 7730.8(12) | 23.0(3) |
| C(27) | 6673(2) | 2290.3(13) | 6669.5(11) | 24.7(3) |
| C(7) | 12848.9(18) | 7770.0(13) | 9995.1(12) | 23.7(3) |
| C(24) | 3164.9(18) | 4788.1(15) | 6900.8(12) | 24.6(3) |
| C(29) | 9344(2) | 2834.7(14) | 7354.2(13) | 27.2(3) |
| C(8) | 13715.8(18) | 8036.7(15) | 9367.0(13) | 27.2(3) |
| C(13) | 6862(2) | 6108.9(16) | 11158.9(12) | 26.2(3) |
| C(23) | 2842.8(19) | 3610.8(15) | 6395.8(12) | 26.0(3) |
| C(2) | 11100(2) | 6761.6(16) | 6448.3(13) | 28.1(3) |
| C(28) | 7969(2) | 1977.1(14) | 6815.5(12) | 26.9(3) |
| C(10) | 6938(2) | 5414.8(18) | 5649.6(13) | 30.6(4) |
| C(3) | 9823(2) | 6291.6(16) | 5777.2(13) | 29.3(3) |
| O(1) | 1509(10) | 1142(4) | 6704(6) | 59.0(13) |
| C(31) | 13622(2) | 8171.6(18) | 10999.9(14) | 32.1(4) |
| C(32) | 1227(2) | 100.7(17) | 6433.7(15) | 37.9(4) |
| C(33) | 570(8) | -541(7) | 7016(5) | 32.9(15) |
| C(34) | 1423(8) | -616(5) | 5485(4) | 41.9(17) |
| O(1A) | 2150(70) | 1079(15) | 6862(15) | 77(11) |
| C(33A) | 420(40) | -380(30) | 6890(30) | 59(7) |
| C(34A) | 1400(60) | -450(50) | 5300(40) | 121(14) |
Table S5. Crystallographic details for 4 (CCDC 1894198).

| Parameter                  | Value                     |
|----------------------------|---------------------------|
| Empirical formula          | C₃₂H₂₇ClF₆N₇PRu           |
| Formula weight             | 791.09                    |
| Temperature/K              | 150(2)                    |
| Crystal system             | triclinic                 |
| Space group                | P-1                       |
| a/Å                        | 9.3307(4)                 |
| b/Å                        | 13.2508(7)                |
| c/Å                        | 14.7242(8)                |
| α/°                        | 67.278(2)                 |
| β/°                        | 84.131(2)                 |
| γ/°                        | 73.857(2)                 |
| Volume/Å³                  | 1612.96(14)               |
| Z                          | 2                         |
| ρcalc g/cm³                | 1.629                     |
| µ/mm⁻¹                     | 0.689                     |
| F(000)                     | 796.0                     |
| Crystal size/mm³           | 0.31 × 0.15 × 0.08        |
| Radiation                  | MoKα (λ = 0.71073)        |
| 2Θ range for data collection/° | 5.692 to 55.762 |
| Index ranges               | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19 |
| Reflections collected      | 97311                     |
| Independent reflections    | 7689 [Rint = 0.0291, Rsigma = 0.0125] |
| Data/restraints/parameters | 7689/0/565                |
| Goodness-of-fit on F²      | 1.108                     |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0348, wR₂ = 0.0938 |
| Final R indexes [all data] | R₁ = 0.0370, wR₂ = 0.0960 |
| Largest diff. peak/hole / e Å⁻³ | 2.17/-0.98 |

Table S6. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 4. Ueq is defined as 1/3 of of the trace of the orthogonalized Uij tensor

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| Ru(1) | 6211.8(2) | 6089.8(2) | 6859.4(2) | 21.90(7) |
| Cl(1) | 1901.6(9) | 7983.6(7) | 3636.7(6) | 50.93(19) |
| N(4)  | 6615(2)  | 7664.6(15) | 6212.9(14) | 25.0(4)  |
| N(5)  | 8218(2)  | 5161.7(16) | 7680.2(14) | 26.3(4)  |
| N(3)  | 7291(2)  | 6009.6(16) | 5560.2(14) | 24.5(4)  |
| N(6)  | 5970(2)  | 4462.5(16) | 7453.7(14) | 24.8(4)  |
| C(5)  | 4158(2)  | 6824.0(17) | 6182.1(16) | 23.6(4)  |
| N(1)  | 3435(2)  | 6861.7(18) | 7752.3(16) | 32.7(4)  |
| C(6)  | 3762(3)  | 7103.8(19) | 5208.6(18) | 29.1(5)  |
| C(26) | 7062(3)  | 3653.7(18) | 8075.2(16) | 25.4(4)  |
|   | N(2)    | C(17)   | C(21)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   | C(13)   | C(14)   | C(16)   | C(4)   | C(12)   | C(11)   | C(20)   |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| N(2) | 5038(3) | 6357(2) | 8891.3(17) | 40.9(5) |
| C(17) | 7336(3) | 9009(2) | 4725(2) | 32.1(5) |
| C(21) | 8340(3) | 4042.1(19) | 8191.9(16) | 25.9(4) |
| C(20) | 6232(3) | 8488(2) | 6588.7(19) | 31.2(5) |
| C(13) | 8707(3) | 6112(3) | 3785(2) | 36.7(5) |
| C(14) | 8343(3) | 5130(2) | 4411(2) | 34.8(5) |
| C(16) | 7190(2) | 7923.3(18) | 5287.8(17) | 25.4(4) |
| C(4) | 2977(3) | 7126.8(19) | 6780.1(18) | 28.1(4) |
| C(12) | 8349(3) | 7046(2) | 4051.7(18) | 33.5(5) |
| C(11) | 7628(2) | 8488(2) | 6588.7(19) | 31.2(5) |
| C(15) | 7643(3) | 5111(2) | 5285.5(18) | 29.6(5) |
| C(1) | 4935(3) | 6416.8(19) | 7954.5(17) | 29.0(5) |
| C(9) | 1521(3) | 7663(2) | 6446(2) | 37.1(6) |
| C(30) | 4765(3) | 4154(2) | 7320.2(18) | 33.3(5) |
| C(25) | 9346(3) | 5584(2) | 7747(2) | 33.4(5) |
| C(19) | 6389(3) | 9571(2) | 6069(2) | 36.7(5) |
| C(7) | 2318(3) | 7641(2) | 4871(2) | 36.0(5) |
| C(18) | 6933(3) | 9840(2) | 5120(2) | 37.7(6) |
| C(8) | 1190(3) | 7927(2) | 5474(2) | 41.9(6) |
| C(27) | 6922(3) | 2557(2) | 8593.8(18) | 34.1(5) |
| C(22) | 9569(3) | 3344(2) | 8789.2(19) | 35.6(5) |
| C(29) | 4572(3) | 3081(2) | 7819(2) | 39.1(6) |
| C(3) | 3622(4) | 6759(3) | 9248(2) | 51.2(8) |
| C(24) | 10594(3) | 4930(3) | 8325(2) | 40.7(6) |
| C(10) | 6412(4) | 6042(3) | 9426(2) | 54.2(8) |
| C(2) | 2633(4) | 7070(3) | 8534(2) | 45.6(7) |
| C(28) | 5652(3) | 2274(2) | 8481(2) | 39.2(6) |
| C(23) | 10701(3) | 3795(3) | 8859(2) | 42.7(6) |
| N(7) | 8838(4) | 7799(3) | 8450(3) | 73.4(10) |
| C(32) | 8490(4) | 8613(3) | 8555(3) | 55.9(8) |
| C(31) | 8060(11) | 9670(5) | 8682(5) | 141(3) |
| P(1) | 7022(2) | 9864.1(9) | 1552.3(7) | 51.5(5) |
| F(1) | 7606(7) | 10234(5) | 2294(3) | 101.2(17) |
| F(4) | 8376(18) | 8807(5) | 1773(8) | 167(6) |
| F(5) | 7878(12) | 10603(4) | 693(3) | 58(3) |
| F(3) | 6139(4) | 9120(2) | 2407.6(19) | 74.4(12) |
| F(2) | 5661(8) | 10971(4) | 1386(6) | 87(3) |
| F(6) | 6369(11) | 9548(7) | 781(3) | 151(5) |
| P(1A) | 8094(8) | 9650(4) | 1271(4) | 59(2) |
| F(3A) | 7440(20) | 8798(18) | 1370(30) | 209(19) |
| F(4A) | 9420(50) | 8741(14) | 1878(14) | 110(10) |
| F(6A) | 9010(30) | 9379(17) | 337(13) | 119(11) |
| F(1A) | 7900(50) | 9630(30) | 2225(14) | 156(19) |
| F(2A) | 6160(40) | 10585(19) | 890(20) | 272(17) |
| F(5A) | 8630(60) | 10664(19) | 792(16) | 135(10) |
### Table S7. Crystallographic details for 5 (CCDC 1894200).

| Property                        | Value                        |
|---------------------------------|------------------------------|
| Empirical formula               | C_{33}H_{29}F_{6}N_{6}O_{2}PRu |
| Formula weight                  | 787.66                       |
| Temperature/K                   | 150(2)                       |
| Crystal system                  | triclinic                    |
| Space group                     | P-1                          |
| a/Å                             | 13.7995(5)                   |
| b/Å                             | 14.5814(6)                   |
| c/Å                             | 19.5017(7)                   |
| α/°                             | 72.9320(10)                  |
| β/°                             | 71.4990(10)                  |
| γ/°                             | 84.0230(10)                  |
| Volume/Å³                       | 3557.1(2)                    |
| Z                               | 4                            |
| ρ calc g/cm³                    | 1.471                        |
| μ/mm⁻¹                          | 0.555                        |
| F(000)                          | 1592.0                       |
| Crystal size/mm³                | 0.31 × 0.23 × 0.04           |
| Radiation                       | MoKα (λ = 0.71073)           |
| 2Θ range for data collection/°  | 5.658 to 55.018              |
| Index ranges                    | -17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25 |
| Reflections collected           | 155023                       |
| Independent reflections         | 16307 [R_int = 0.0308, R_sigma = 0.0159] |
| Data/restraints/parameters      | 16307/0/1031                 |
| Goodness-of-fit on F²           | 1.062                        |
| Final R indexes [I>=2σ (I)]     | R_I = 0.0329, wR_2 = 0.0882  |
| Final R indexes [all data]      | R_I = 0.0385, wR_2 = 0.0931  |
| Largest diff. peak/hole / e Å⁻³ | 1.43/-0.80                  |

### Table S8. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 5. U(eq) is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

| Atom  | x      | y      | z      | U(eq)  |
|-------|--------|--------|--------|--------|
| Ru(1) | 6418.9(2) | 3101.4(2) | 6452.9(2) | 21.16(5) |
| Ru(1X) | -985.0(2) | 7346.6(2) | 7901.7(2) | 24.44(5) |
| P(1X) | -3202.1(5) | 8902.9(5) | 5377.1(4) | 37.77(14) |
| P(1) | -2808(4) | 10107(3) | 10328(2) | 43.4(7) |
| N(4X) | -315.7(13) | 7974.4(13) | 6779.5(10) | 25.5(4) |
| N(3) | 7331.3(13) | 2005.5(12) | 6901.5(10) | 24.2(3) |
| F(1X) | -3428.9(15) | 8107.8(11) | 5033.7(11) | 55.4(4) |
| N(4) | 6022.9(13) | 3148.2(13) | 7544.3(10) | 24.9(3) |
| N(3X) | -124.3(14) | 8430.2(14) | 7929.9(10) | 28.0(4) |
| Element (X) | Atomic Number (Z) | Atomic Mass (Da) | Position | Structure |
|------------|------------------|------------------|----------|-----------|
| N(6)       | 7                | 6801.4(13)       | 2855.5(12)| 5409.9(10)| 23.0(3) |
| N(5)       | 7                | 5315.6(13)       | 2077.3(12)| 6617.2(10)| 24.3(3) |
| O(1)       | 8                | 10890.0(16)      | 9700.5(12)| 4602.5(11)| 57.5(5) |
| F(3X)      | 9                | -2333.0(13)      | 8230.2(14)| 8023.9(11)| 28.0(4) |
| N(6X)      | 7                | -1650.0(15)      | 6967.1(15)| 9043.9(11)| 32.2(4) |
| O(2)       | 8                | 10517.3(14)      | 3532.4(15)| 6210.0(11)| 47.0(5) |
| C(5)       | 6                | 7548.3(17)       | 4079.2(15)| 6173.2(11)| 25.9(4) |
| N(2)       | 7                | 4768.7(16)       | 4681.7(15)| 6046.2(12)| 35.0(4) |
| N(1)       | 7                | 6243.8(16)       | 5168.3(15)| 5929.0(11)| 30.9(4) |
| F(6X)      | 9                | -901.3(18)       | 5382.8(15)| 7826.3(11)| 37.7(5) |
| N(1X)      | 7                | -901.3(18)       | 5382.8(15)| 7826.3(11)| 37.7(5) |
| C(26)      | 6                | 6245.0(15)       | 2194.0(14)| 5334.6(12)| 23.0(4) |
| F(2X)      | 9                | -4395.3(16)      | 9084.0(17)| 5655.7(15)| 80.5(7) |
| F(5X)      | 9                | -3217(3)         |         |          |         |
| F(4X)      | 9                | -2009.3(16)      | 8733.2(17)| 5043.2(17)| 85.6(7) |
| C(21)      | 6                | 5424.5(16)       | 1745.2(14)| 6016.5(12)| 23.7(4) |
| C(27)      | 6                | 6444.9(17)       | 1973.7(16)| 4654.9(13)| 27.3(4) |
| C(4)       | 6                | 7266.3(18)       | 5049.5(16)| 5944.5(13)| 29.5(4) |
| N(2X)      | 7                | -2397.0(17)      | 5853.5(15)| 7759.6(12)| 37.9(5) |
| C(9)       | 6                | 7922(2)          | 5811.4(17)| 5745.2(14)| 36.6(5) |
| C(11X)     | 6                | 511.4(16)        | 8905.7(16)| 7250.4(13)| 28.5(4) |
| C(1)       | 6                | 5700.9(17)       | 4346.8(16)| 6112.0(12)| 27.8(4) |
| F(6)       | 9                | -2204(6)         | 11101(6) | 9773(4)  | 59.8(16) |
| C(28)      | 6                | 7229.0(18)       | 2435.5(16)| 4038.6(13)| 29.5(4) |
| C(1X)      | 6                | -1537.1(19)      | 6168.6(17)| 7808.7(12)| 32.0(5) |
| C(18X)     | 6                | 632.6(19)        | 8962.3(18)| 5287.0(13)| 35.4(5) |
| C(5X)      | 6                | 245.5(18)        | 6416.7(18)| 7890.8(12)| 32.5(5) |
| C(17X)     | 6                | 838.1(19)        | 9190.6(17)| 5864.1(14)| 32.9(5) |
| C(7)       | 6                | 9237.5(18)       | 4665.5(18)| 5983.2(13)| 33.4(5) |
| C(30)      | 6                | 7565.4(16)       | 3301.0(16)| 4799.7(12)| 27.0(4) |
| C(15)      | 6                | 8043.8(18)       | 1489.6(16)| 6511.2(14)| 31.1(5) |
| C(11)      | 6                | 7278.2(17)       | 1898.6(15)| 7626.2(13)| 27.9(4) |
| C(16)      | 6                | 6507.0(17)       | 2513.0(16)| 8000.6(13)| 29.1(4) |
| C(6)       | 6                | 8559.1(17)       | 3915.1(16)| 6182.4(13)| 28.7(4) |
| C(29X)     | 6                | -3518(2)         | 9414(2)   | 7607.1(18) | 41.0(6) |
| C(29)      | 6                | 7789.6(17)       | 3109.8(17)| 4115.7(13)| 29.8(4) |
| O(2X)      | 8                | 3196.1(16)       | 6906(2)   | 7732.3(16) | 77.9(8) |
| C(30X)     | 6                | -2667.4(18)      | 8821.8(18)| 7470.7(15)| 32.9(5) |
| C(10)      | 6                | 3906(2)          | 4088(2)   | 6195.5(17) | 43.4(6) |
| C(8)       | 6                | 8915(2)          | 5611.0(18)| 5764.0(14)| 37.5(5) |
| C(20)      | 6                | 5320.1(17)       | 3751.4(17)| 7852.8(14)| 31.1(5) |
| O(1X)      | 8                | 3698.5(19)       | 5407(3)   | 7876.5(17) | 100.9(12) |
| C(25)      | 6                | 4595.3(17)       | 1683.1(17)| 7263.6(13)| 30.2(5) |
|      |      |      |      |      |      |
|------|------|------|------|------|------|
| C(24)| 3965.3(18)| 962.2(18)| 7339.7(14)| 36.3(5)|      |
| C(20X)| -494.5(19)| 7760.8(18)| 6203.2(13)| 31.7(5)|      |
| C(15X)| -54.1(19)| 8618(2)| 8549.6(14)| 39.2(6)|      |
| C(22)| 4803.8(18)| 1029.4(16)| 6055.0(14)| 30.6(5)|      |
| C(12)| 7930(2)| 1279.0(19)| 7968.7(15)| 38.3(5)|      |
| C(6X)| 4803.8(18)| 1029.4(16)| 6055.0(14)| 30.6(5)|      |
| C(13)| 8665(2)| 1279.0(19)| 7968.7(15)| 38.3(5)|      |
| C(31)| 10293(2)| 4471(2)| 6034.4(14)| 40.5(6)|      |
| F(1)| -3474(5)| 9173(8)| 10873(5)| 73.1(16)|      |
| C(21X)| -2468.9(18)| 7516.3(19)| 9315.6(14)| 34.7(5)|      |
| C(17)| 6288(2)| 2468.7(19)| 8754.9(14)| 41.4(6)|      |
| C(24X)| -1678(2)| 6150(3)| 10309.5(16)| 56.1(8)|      |
| C(25X)| -1280(2)| 6295(2)| 9540.9(15)| 44.6(6)|      |
| C(27X)| -3708(2)| 8803(2)| 10582.7(16)| 60.3(9)|      |
| C(19)| 5081(2)| 3740(2)| 8598.7(15)| 40.0(6)|      |
| C(4X)| 88(2)| 5499.8(19)| 7845.2(13)| 39.0(6)|      |
| C(12X)| 1236.1(19)| 9540(2)| 7192.1(15)| 39.3(6)|      |
| C(28X)| -4036(2)| 9408(2)| 8338.1(19)| 48.3(7)|      |
| C(7X)| 1992(2)| 5836(3)| 7846.1(14)| 51.4(8)|      |
| F(4)| -2221(9)| 9611(9)| 9689(6)| 104(4)|      |
| C(2)| 5651(2)| 5986.6(18)| 5760.7(16)| 40.6(6)|      |
| C(2X)| -1367(3)| 4606.3(19)| 7791.0(16)| 50.2(7)|      |
| C(18)| 5568(2)| 3090(2)| 9057.7(15)| 47.2(7)|      |
| C(14X)| 641(2)| 9248(2)| 8525.2(16)| 49.3(7)|      |
| C(23X)| -2483(3)| 6712(3)| 10582.7(16)| 60.3(9)|      |
| C(3X)| -2298(3)| 4900(2)| 7746.1(16)| 48.0(7)|      |
| C(9X)| 822(3)| 4775(2)| 7802.1(16)| 52.0(8)|      |
| C(8X)| 1780(3)| 4954(2)| 7802.0(16)| 58.0(9)|      |
| C(22X)| -2884(2)| 7398(2)| 10086.2(16)| 49.6(7)|      |
| C(13X)| 1305(2)| 9707(2)| 7836.6(17)| 48.6(7)|      |
| C(32)| 11528(2)| 3258(3)| 6280.1(18)| 54.0(8)|      |
| C(10X)| -3302(2)| 6423(2)| 7703.4(18)| 49.0(7)|      |
| C(31X)| 3032(2)| 5984(3)| 7823.4(19)| 66.4(11)|      |
| F(3)| -3524(7)| 10264(5)| 9818(4)| 118(3)|      |
| C(33)| 11581(3)| 2195(3)| 6487(3)| 81.1(12)|      |
| F(5)| -2122(5)| 9862(5)| 10874(3)| 93(2)|      |
| F(2)| -3544(5)| 10665(4)| 10863(5)| 110(3)|      |
| C(32X)| 4216(3)| 7134(5)| 7685(4)| 113(2)|      |
| C(33X)| 4229(5)| 8051(6)| 7622(6)| 188(5)|      |
| P(1A)| -2576(8)| 10060(6)| 10337(5)| 80(3)|      |
Density Functional Theory

Calculated electron densities of ground and triplet states of 1 – 6.

![Graphical representation of electron density plots for the ground state frontier molecular orbitals of 1.](image)

**Figure S11.** Electron density plots for the ground state frontier molecular orbitals of 1.
**Figure S12.** Electron density plots for the ground state frontier molecular orbitals of 3.

**Figure S13.** Electron density plots for the ground state frontier molecular orbitals of 4.
**Figure S14.** Electron density plots for the ground state frontier molecular orbitals of 5.

**Figure S15.** Electron density plots for the ground state frontier molecular orbitals of 6.
**Figure S16.** Electron density plots for lowest optimized triplet state molecular orbitals of 1.

**Figure S17.** Electron density plots for lowest optimized triplet state molecular orbitals of 2.

**Figure S18.** Electron density plots for lowest optimized triplet state molecular orbitals of 3.
Figure S19. Electron density plots for lowest optimized triplet state molecular orbitals of 4.

Figure S20. Electron density plots for lowest optimized triplet state molecular orbitals of 5.

Figure S21. Electron density plots for lowest optimized triplet state molecular orbitals of 6.
Table S9. Summary Singlet Excited State Transitions from TD-DFT Calculations for 1.

| Excited State | Transition | Coefficient | Parentage | Energy (eV) | λ (nm) | Oscillator Strength (f) |
|---------------|------------|-------------|-----------|------------|--------|------------------------|
| 1             | 137→140   | -0.12003    | HOMO-2→LUMO | 1.96       | 634    | 0.0060                 |
|               | 139→140   | 0.67118     | HOMO→LUMO  |            |        |                        |
|               | 139→1401  | 0.13785     | HOMO→LUMO+1|            |        |                        |
| 5             | 137→140   | 0.36795     | HOMO-2→LUMO | 2.39       | 519    | 0.0991                 |
|               | 137→1401  | 0.20871     | HOMO-2→LUMO+1|          |        |                        |
|               | 138→140   | -0.15359    | HOMO-1→LUMO |            |        |                        |
|               | 138→141   | 0.52204     | HOMO-1→LUMO+1|          |        |                        |
|               | 139→140   | 0.11120     | HOMO→LUMO  |            |        |                        |
| 6             | 137→141   | 0.55717     | HOMO-2→LUMO+1|          |        |                        |
|               | 138→140   | 0.27999     | HOMO-1→LUMO |            |        |                        |
|               | 138→141   | -0.17728    | HOMO-1→LUMO+1|          |        |                        |
|               | 139→141   | 0.19012     | HOMO→LUMO  |            |        |                        |
|               | 139→144   | -0.10378    | HOMO→LUMO+4|            |        |                        |
| 15            | 137→143   | 0.17315     | HOMO-2→LUMO+3|          |        |                        |
|               | 138→143   | 0.66216     | HOMO-1→LUMO+3|          |        |                        |
|               | 139→145   | 0.10770     | HOMO→LUMO+5|            |        |                        |
| 19            | 137→144   | 0.16674     | HOMO-2→LUMO+4|          |        |                        |
|               | 137→145   | 0.65873     | HOMO-2→LUMO+5|          |        |                        |
|               | 138→145   | -0.11906    | HOMO-1→LUMO+5|          |        |                        |
| 20            | 137→143   | 0.25978     | HOMO-2→LUMO+3|          |        |                        |
|               | 137→144   | 0.40720     | HOMO-2→LUMO+4|          |        |                        |
|               | 138→145   | 0.38647     | HOMO-1→LUMO+5|          |        |                        |
|               | 139→144   | -0.10339    | HOMO→LUMO  |            |        |                        |
|               | 139→146   | 0.11514     | HOMO→LUMO+6|            |        |                        |

Table S10. Summary Singlet Excited State Transitions from TD-DFT Calculations for 2.

| Excited State | Transition | Coefficient | Parentage | Energy (eV) | λ (nm) | Oscillator Strength (f) |
|---------------|------------|-------------|-----------|------------|--------|------------------------|
| 1             | 135→136   | 0.67282     | HOMO→LUMO | 1.94       | 638    | 0.0058                 |
|               | 135→137   | -0.15803    | HOMO→LUMO+1|            |        |                        |
| 5             | 133→136   | 0.31584     | HOMO-2→LUMO | 2.39       | 519    | 0.0947                 |
|               | 133→137   | -0.27572    | HOMO-2→LUMO+1|          |        |                        |
|               | 134→136   | 0.20683     | HOMO-1→LUMO |            |        |                        |
|               | 134→137   | 0.50482     | HOMO-1→LUMO+1|          |        |                        |
| 6             | 133→136   | -0.24241    | HOMO-2→LUMO | 2.55       | 487    | 0.0516                 |
|               | 133→137   | 0.49196     | HOMO-2→LUMO+1|          |        |                        |
|               | 134→136   | 0.16032     | HOMO-1→LUMO |            |        |                        |
| Table S11. Summary Singlet Excited State Transitions from TD-DFT Calculations for 3. |
|-----------------------------------|-----------------|-------------------------------------------------|-----------------|-----------------|-----------------|
| Excited State | Transition | Coefficient | Description | Energy (eV) | λ (nm) | Oscillator Strength (f) |
| 1 | 131→132 | 0.67105 | HOMO→LUMO | 1.96 | 632 | 0.0052 |
| 131→133 | -0.17303 | HOMO→LUMO+1 | | | | |
| 5 | 129→132 | 0.25625 | HOMO-2→LUMO | 2.40 | 516 | 0.0982 |
| 129→133 | -0.38512 | HOMO-2→LUMO+1 | | | | |
| 130→132 | 0.28022 | HOMO-1→LUMO | | | | |
| 130→133 | 0.42633 | HOMO-1→LUMO+1 | | | | |
| 6 | 129→132 | -0.28000 | HOMO-2→LUMO | 2.56 | 484 | 0.0521 |
| 129→133 | 0.40596 | HOMO-2→LUMO+1 | | | | |
| 130→132 | 0.10631 | HOMO-1→LUMO | | | | |
| 130→133 | 0.41856 | HOMO-1→LUMO+1 | | | | |
| 131→133 | -0.15579 | HOMO→LUMO+1 | | | | |
| 131→136 | 0.11223 | HOMO→LUMO+4 | | | | |
| 21 | 128→133 | 0.37257 | HOMO-3→LUMO+1 | 3.61 | 343 | 0.1104 |
| 129→135 | 0.16503 | HOMO-2→LUMO+3 | | | | |
| 129→137 | -0.29490 | HOMO-2→LUMO+5 | | | | |
| 129→138 | 0.10730 | HOMO-2→LUMO+6 | | | | |
| 130→135 | 0.16502 | HOMO-1→LUMO+3 | | | | |
| 130→136 | 0.29135 | HOMO-1→LUMO+4 | | | | |
| 131→136 | 0.10839 | HOMO→LUMO+4 | | | | |
| 138→132 | 0.20555 | HOMO→LUMO+6 | | | | |
Table S12. Summary Singlet Excited State Transitions from TD-DFT Calculations for 4.

| Excited State | Transition | Coefficient | Parentage                  | Energy (eV) | λ (nm) | Oscillator Strength (f) |
|---------------|------------|-------------|----------------------------|-------------|--------|-------------------------|
| 1             | 139→140    | 0.68088     | HOMO→LUMO                  | 2.02        | 615    | 0.0058                  |
| 1             | 139→141    | -0.11856    | HOMO→LUMO+1                |             |        |                         |
| 5             | 137→140    | -0.27603    | HOMO-2→LUMO                | 2.44        | 508    | 0.0978                  |
| 5             | 137→141    | 0.37557     | HOMO-2→LUMO+1              |             |        |                         |
| 5             | 138→140    | 0.25969     | HOMO-1→LUMO                |             |        |                         |
| 5             | 138→141    | 0.44043     | HOMO-1→LUMO+1              |             |        |                         |
| 6             | 137→140    | 0.24478     | HOMO-2→LUMO                | 2.60        | 477    | 0.0536                  |
| 6             | 137→141    | 0.43043     | HOMO-2→LUMO+1              |             |        |                         |
| 6             | 138→140    | -0.14617    | HOMO-1→LUMO                |             |        |                         |
| 6             | 138→141    | -0.40536    | HOMO-1→LUMO+1              |             |        |                         |
| 6             | 139→141    | -0.16175    | HOMO-1→LUMO+1              |             |        |                         |
| 6             | 139→144    | 0.11068     | HOMO-1→LUMO+1              |             |        |                         |

Table S13. Summary Singlet Excited State Transitions from TD-DFT Calculations for 5.

| Excited State | Transition | Coefficient | Description                  | Energy (eV) | λ (nm) | Oscillator Strength (f) |
|---------------|------------|-------------|------------------------------|-------------|--------|-------------------------|
| 1             | 150→151    | 0.67300     | HOMO→LUMO                   | 2.02        | 614    | 0.0054                  |
| 1             | 150→152    | -0.16469    | HOMO→LUMO+1                 |             |        |                         |
| 5             | 148→151    | -0.21784    | HOMO-2→LUMO                 | 2.45        | 507    | 0.0925                  |
| 5             | 148→152    | 0.43746     | HOMO-2→LUMO+2               |             |        |                         |
| 5             | 149→151    | -0.28697    | HOMO-1→LUMO                 |             |        |                         |
| 5             | 149→152    | -0.39359    | HOMO-1→LUMO+2               |             |        |                         |
| 6             | 148→151    | -0.27252    | HOMO-2→LUMO                 | 2.60        | 477    | 0.0580                  |
| 6             | 148→152    | 0.37032     | HOMO-2→LUMO+1               |             |        |                         |
| 6             | 149→152    | 0.46113     | HOMO-1→LUMO+1               |             |        |                         |
| 6             | 150→152    | 0.15643     | HOMO→LUMO+1                 |             |        |                         |
| 6             | 150→156    | -0.10080    | HOMO→LUMO+1                 |             |        |                         |
| 30            | 143→152    | 0.15361     | HOMO-7→LUMO+1               | 4.32        | 287    | 0.0815                  |
| 30            | 144→151    | -0.33324    | HOMO-6→LUMO                 |             |        |                         |
| 30            | 145→151    | 0.57545     | HOMO-5→LUMO                 |             |        |                         |
| Excited State | Transition | Coefficient | Parentage | Energy (eV) | λ (nm) | Oscillator Strength (f) |
|--------------|------------|-------------|-----------|------------|--------|------------------------|
| 1            | 141→144   | -0.10120    | HOMO-1→LUMO+1 | 2.08       | 595    | 0.0085                 |
|              | 142→143   | -0.40970    | HOMO→LUMO   |            |        |                        |
|              | 142→144   | 0.55898     | HOMO→LUMO+1 |            |        |                        |
| 8            | 140→144   | -0.15329    | HOMO-2→LUMO+1 | 2.51       | 493    | 0.0846                 |
|              | 140→145   | 0.50978     | HOMO-2→LUMO+2 |            |        |                        |
|              | 141→144   | -0.36096    | HOMO-1→LUMO+1 |            |        |                        |
|              | 141→145   | -0.24246    | HOMO-1→LUMO+2 |            |        |                        |
| 21           | 139→143   | -0.22597    | HOMO-3→LUMO | 3.65       | 340    | 0.110                  |
|              | 140→147   | -0.10574    | HOMO-2→LUMO+4 |            |        |                        |
|              | 140→149   | 0.47729     | HOMO-2→LUMO+6 |            |        |                        |
|              | 141→147   | -0.20371    | HOMO-1→LUMO+4 |            |        |                        |
|              | 141→148   | -0.31781    | HOMO-1→LUMO+5 |            |        |                        |
| 22           | 139→143   | 0.61092     | HOMO-3→LUMO | 3.75       | 331    | 0.1215                 |
|              | 139→144   | -0.15860    | HOMO-3→LUMO+1 |            |        |                        |

Table S14. Summary Singlet Excited State Transitions from TD-DFT Calculations for 6.
| Orbital | Atom | OMe | Me | H  | Cl  | CO₂Et | NO₂ |
|---------|------|-----|----|----|-----|-------|-----|
| HOMO-2  | Ru   | 0.74| 0.72| 0.70| 0.74| 0.67  | 0.72|
| HOMO    | Ru   | 0.54| 0.59| 0.61| 0.61| 0.64  | 0.66|
| LUMO    | Ru   | <0.03| <0.03| <0.03| <0.03| <0.03 | <0.03|
| LUMO+1  | Ru   | <0.03| 0.07 | 0.07| 0.07| 0.07  | <0.03|

Table S15. Percent Contribution from the Ruthenium Center to Frontier Orbitals from NBO Calculations for the Ground State of 1.

| MO      | 1   | 2   | 3   | 4   | 5   | 6   |
|---------|-----|-----|-----|-----|-----|-----|
| HOMO-2  | 74  | 72  | 70  | 74  | 67  | 72  |
| HOMO    | 54  | 59  | 61  | 61  | 64  | 66  |
| LUMO    | 3   | 3   | 3   | 3   | 3   | 3   |
| LUMO+1  | 3   | 7   | 7   | 7   | 7   | 3   |

Table S16. Percent Ru Contribution to Frontier Orbitals in the Ground State of 1 – 6 from Mulliken Population Analysis.

| Orbital | Spin | Atom | OMe | Me  | H   | Cl  | CO₂Et | NO₂ |
|---------|------|------|-----|-----|-----|-----|-------|-----|
| HSOMO   | α    | Ru   | <0.03| <0.03| <0.03| <0.03| <0.03| <0.03|
| LSOMO   | α    | Ru   | 0.04 | 0.10 | 0.18 | 0.11 | 0.18  | 0.29|

Table S17. Percent Contribution from the Ruthenium Center to Frontier Orbitals from NBO Calculations for the Lowest Triplet Excited State of 1.
Figure S22. Difference spectra upon oxidation (black) and reduction (red) of (a) 1, (b) 2, (c) 3, (d) 4, and (e) 6 at the indicated potentials vs Fe$^{+/0}$ in degassed CH$_3$CN (0.1 M N$^\text{Bu}_4$PF$_6$).
Nanosecond Transient Absorption Spectroscopy

Figure S23. Nanosecond transient absorption spectra of (a) 1 with $\lambda_{exc} = 575$ nm, (b) 2 with $\lambda_{exc} = 550$ nm, (c) 3 with $\lambda_{exc} = 550$ nm (lifetime measured at 585 nm), and (d) 4 with $\lambda_{exc} = 575$ nm (lifetime measured at 545 nm) in degassed CH$_3$CN at 298 K.
Figure S24. Femtosecond transient absorption spectra of 1 in CH$_3$CN at 298 K collected at various delay times following (a) 550 nm, (b) 640 nm, and (c) 670 nm excitation (irf = 85 fs).
Figure S25. Femtosecond transient absorption spectra of 2 in CH$_3$CN at 298 K collected at various delay times following (a) 400 nm, (b) 550 nm, (c) 620 nm, and (d) 670 nm excitation (irf = 85 fs).
Figure S26. Femtosecond transient absorption spectra of 3 in CH$_3$CN at 298 K collected at various delay times following (a) 400 nm, (b) 550 nm, (c) 620 nm, and (d) 650 nm excitation (irf = 85 fs).
Figure S27. Femtosecond transient absorption spectra of 4 in CH$_3$CN at 298 K collected at various delay times following (a) 400 nm, (b) 550 nm, (c) 600 nm, and (d) 640 nm excitation (irf = 85 fs).
Figure S28. Femtosecond transient absorption spectra of 5 in CH$_3$CN at 298 K collected at various delay times following (a) 400 nm, (b) 550 nm, (c) 600 nm, and (d) 650 nm excitation (irf = 85 fs).
Figure S29. Femtosecond transient absorption spectra of 5 in CH$_3$CN at 298 K collected at various delay times following (a) 400 nm, (b) 550 nm, (c) 620 nm, and (d) 650 nm excitation (irf = 85 fs).
Figure S30. TRIR difference spectra of 1 in CD$_3$CN at various delay times following (a) 400 nm and (b) 585 nm (irf = 185 fs).
Figure S31. TRIR difference spectra of 2 in CD$_3$CN at various delay times following (a) 400 nm and (b) 585 nm (irf = 185 fs).
Figure S32. TRIR difference spectra of 3 in CD$_3$CN at various delay times following (a) 400 nm and (b) 585 nm (irf = 185 fs).
Figure S33. TRIR difference spectra of 4 in CD$_3$CN at various delay times following (a) 400 nm and (b) 585 nm (irf = 185 fs).

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