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Supporting Information

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A Novel Approach to Ru^{II} –Complexes of "Large Surface" Ligands

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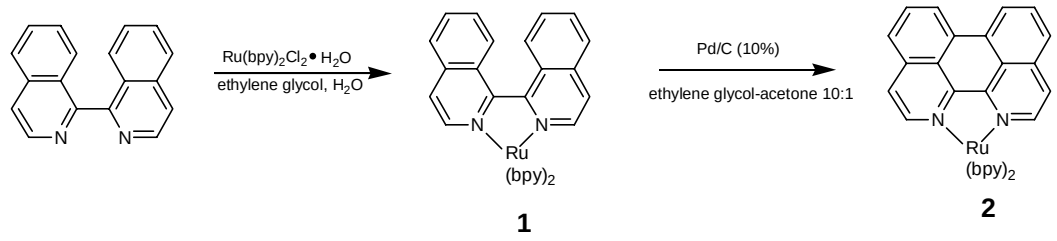
Supporting Information

General Methods and Procedures

All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury spectrometer(400 and 100 MHz, respectively), and all chemical shifts are reported relative to the residual solvent signal. Electrochemical measurements were performed with a BAS CV-50W system using a platinum working and auxiliary electrode, and a $Ag/AgNO_3$ reference electrode. The experiments were conducted using degassed MeCN solutions using 0.1 M $[n\text{-}Bu_4N^+][PF_6^-]$ as the supporting electrolyte, and the Ferrocene/Ferrocinium (Fc/Fc^+) couple as a reference. All chemicals were obtained from commercial sources and were used without further purification. The 10% Pd/C used for dehydrogenations was preactivated by heating to 150 ºC under vacuum for 1 h. The temperature for all dehydrogenations was carefully monitored as not to exceed 200 ºC to prevent ligand exchange. Metal complexes were isolated after column purification by solvent removal, dissolving the crude into H_2O, addition of a saturated aqueous solution of KPF_6, and extraction of the complex into CH_2Cl_2. Integration values are not provided for the unfused metal complexes, as their fluctional behavior results in multiple isomers and fractional integration values.

List of Abbreviations

biiq	1,1'-biisoquinoline
bpy	2,2'-bipyridine
dbiiq	dehydrobiisoquinoline
DMF	*N*,*N*-Dimethylformamide
EDTA	Ethylenediaminetetraacetic acid



1 **2**

Scheme 1. Synthesis of Ru(biiq)(bpy)$_2$ **1** and dehydrogenation to the fused Ru(dbiiq)(bpy)$_2$ **2**.

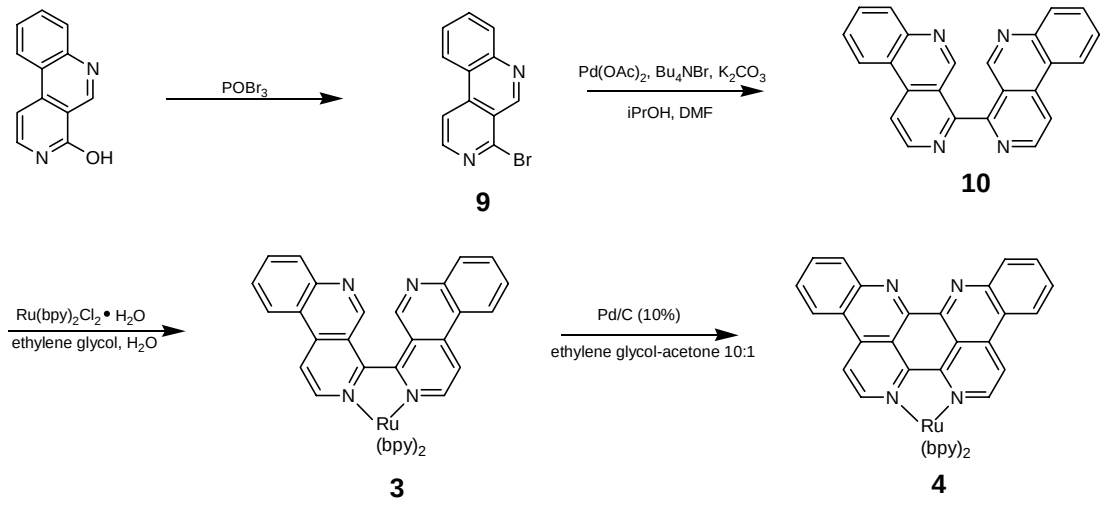
Ru(biiq)(bpy)$_2$•2PF$_6$ 1. Biisoquinoline (100 mg, 0.4 mmol) and Ru(bpy)$_2$Cl$_2$•5H$_2$O (184 mg, 0.35 mmol) were dissolved in a degassed 1:1 mixture of ethylene glycol and water (10 mL) under argon, and solution was heated to 80 ºC. After 4 h the solution was cooled to room temperature, diluted with water (25 mL) and washed with CH_2Cl_2. A saturated aqueous solution of KPF_6 was added, and the metal complex extracted into CH_2Cl_2. The organic layer was washed with water to remove the residual ethylene glycol. The organic solvent was removed under reduced pressure, and the crude purified by flash chromatography (silica, 3–4% H_2O, 0.1% sat. aq. KNO_3, in MeCN) to give Ru(biiq)(bpy)$_2$•2PF$_6$ **1** (320 mg, 94% yield). ^{1}H NMR (acetone-d$_6$) δ 8.82 (m), 8.75 (d, *J*=8.0 Hz), 8.62 (d, *J*=4.8 Hz), 8.30 (d, *J*=8.0 Hz), 8.25-7.98 (m), 7.90 (td, *J*=8.0 Hz, 1.1 Hz), 7.78 (td, *J*=8.0 Hz, 1.1 Hz), 7.72 (td, *J*=8.0 Hz, 1.1 Hz), 7.62-7.56 (m), 7.39-7.33 (m), 7.02 (d, *J*=4.8 Hz). (In good agreement with literature values; *J. Am. Chem. Soc.*, **1994**, *116*, 4801). ^{13}C NMR (acetone-d$_6$) δ 160.26, 159.64, 158.14, 157.76, 157.69, 157.44, 152.92, 152.52, 152.14, 152.11, 143.76, 143.41, 138.73, 138.68, 138.64, 137.32, 137.10, 132.85, 132.51, 129.61, 129.53, 129.46, 129.13, 128.59, 128.53, 128.46, 128.39, 128.21. 128.07. 127.83, 127.67, 126.94, 126.35, 125.14, 125.06, 124.78. UV / Vis (MeCN) λ_{max}(ε x 10^{-4}) 246 (62), 288 (71), 322 (22), 392 (17), 444 (11.5), 518 (12.5).

Ru(biiq)(bpy)$_2$•2PF$_6$ 2. Ru(biiq)(bpy)$_2$•2PF$_6$ **1** (20 mg, 0.02 mmol) was dissolved in ethylene glycol (4 mL) and acetone (0.5 mL) and added to a pressure tube containing 10% Pd / C (10 mg). The mixture was heated to 190 ºC. After 24 h it

was cooled to room temperature. The solids were removed by filtration, and washed with hot acetonitrile. The volatile substances were removed under reduced pressure, and the residual crude (in ethylene glycol) was purified by flash chromatography (silica, MeCN to remove the ethylene glycol, then increased to 4% H_2O, 0.1% sat. aq. KNO_3, in MeCN) to give $Ru(dbiiq)(bpy)_2 \cdot 2PF_6$ **2** (6 mg , 30% yield). ^1H NMR (acetone-d_6) δ 8.93 (d, *J*=7.3 Hz, 2H), 8.86 (d, *J*=8.4 Hz, 2H), 8.80 (d, *J*=8.1 Hz, 2H), 8.27 (t, *J*=8.1 Hz, 2H), 8.22 (d, *J*=8.4 Hz, 2H), 8.06-8.16 (m, 12 H), 8.01 (d, *J*=6.2 Hz, 2H), 7.66 (td, *J*=5.9, 1.1 Hz, 2H), 7.41 (td, *J*=5.9, 1.5 Hz, 2H). ^{13}C NMR (acetone-d_6) δ 157.7, 157.6, 155.5, 153.5, 152.2, 144.6, 139.0, 138.7, 136.1, 133.3, 130.0, 128.7, 128.6, 128.5, 126.7, 126.1, 125.7, 125.1. 124.9. UV / Vis (MeCN) $\lambda_{max}(\varepsilon \times 10^{-4})$ 242 (56), 286 (77), 440 (24.5), 468 (24.5), 552 (18.8). ESI–MS calcd. for $C_{38}H_{26}F_6N_6PRu$ 813.09, found 813.1 *m/z* $[M-PF_6]^+$.

An authentic sample was synthesized by an alternative process (see ref. 13 in manuscript).

$Ru(dbiiq)(bpy)_2 \cdot 2PF_6$ 2. 1,12-diazaperylene (15 mg, 0.06 mmol) and $Ru(bpy)_2Cl_2 \cdot 5H_2O$ (27 mg, 0.054 mmol) were dissolved in a degassed 1:1 mixture of ethanol and water (4 mL) under argon, and solution was heated to 80 ºC. After 4 h the solution was cooled to room temperature, diluted with water (25 mL) and washed with CH_2Cl_2. A saturated aqueous solution of KPF_6 was added, and the metal complex extracted into CH_2Cl_2. The organic solvent was removed under reduced pressure, to give $Ru(dbiiq)(bpy)_2 \cdot 2PF_6$ **2** (46 mg, 90% yield). The spectroscopic properties were identical to that of the complex synthesized by the dehydrogenation method.



Scheme S2. Synthesis of the "PreEilatin" ligand and metal complex, followed by dehydrogenation to form the Ru(Eilatin)$(bpy)_2$ complex.

1-Bromo-2,9-Diazaphenanthrene 9. 2,9-Diazaphenanthrene-1(2H)-one (Pyrlolidine)[1] (220 mg, 1.12 mmol) was mixed with $POBr_3$ (1 g, 3.36 mmol) under argon. It was heated under reflux to 135 ºC. After 3 h it was cooled to room temperature, quenched with cold water, and neutralized with NH_4OH. It was extracted into $CHCl_3$, washed with brine, dried over $MgSO_4$, and the solvent removed under reduced pressure. It was purified by flash chromatography (silica gel, $CHCl_3$) to give 262 mg of **9** (91% yield). ^1H NMR ($CDCl_3$) δ 9.67 (s, 1H) 8.65 (d, *J*=5.5 Hz, 1H), 8.53 (d, *J*=8.2 Hz, 1H), 8.33 (d, *J*=5.8 Hz, 1H), 8.26 (d, *J*=8.2 Hz, 1H), 7.91 (t, *J*=7.7 Hz, 1H), 7.77 (t, *J*=7.7 Hz, 1H).). ^{13}C ($CDCl_3$) δ 152.1, 147.9, 145.6, 145.3, 139.7, 131.5, 130.4, 128.2, 122.8, 121.0, 120.8, 115.4. MALDI-FTMS calcd. for $C_{12}H_8BrN_2$ 258.9861 (MH^+), found 258.9861 *m/z* MH^+.

PreEilatin 10. **9** (200 mg, 0.77 mmol), $Pd(OAc)_2$ (8.7 mg, 0.04 mmol), Bu_4NBr (124 mg, 0.38 mmol), and K_2CO_3 (106 mg, 0.77 mmol) were dissolved under argon in a degassed mixture of iPrOH (2.5 mL) and DMF(1.8 mL). The solution was heated to 115 ºC for 12 h. The solvents were removed under reduced pressure, and the

crude dissolved in $CHCl_3$. It was washed with aqueous EDTA (pH 7), then with brine, dried over $MgSO_4$, and the solvents removed. The crude was purified by flash chromatography (silica gel, 0–5% MeOH / $CHCl_3$) to give 150 mg of **10** (54% yield). ^{1}H NMR ($CDCl_3$) δ 9.32 (s, 1H), 9.15 (d, *J*=5.5 Hz, 1H), 8.77 (d, *J*=8.1 Hz, 1H), 8.72 (d, *J*=5.9 Hz, 1H), 8.23 (d, *J*=8.1 Hz, 1H), 7.97 (t, *J*=7.3 Hz, 1H), 7.89 (t, *J*=7.3 Hz, 1H).). ^{13}C ($CDCl_3$) δ 158.6, 152.3, 148.4, 146.4, 139.8, 132.3, 131.5, 129.0, 123.9, 123.0, 121.8, 117.1. ESI–MS calcd. for $C_{24}H_{12}N_4H$ 357 (MH^+), found 357 *m/z* MH^+.

Ru(PreEilatin)(bpy)$_2$•2PF$_6$ 3. 10 (30 mg, 0.0084 mmol) and $Ru(bpy)_2Cl_2 \bullet 5H_2O$ (41 mg, 0.0079 mmol) were dissolved under argon in a degassed 1:1 mixture of ethylene glycol and water (8 mL). The solution was heated to 100 ºC. After 3 h it was cooled to room temperature, diluted with water, and washed with CH_2Cl_2. A saturated aqueous solution of KPF_6 was added, and the metal complex extracted into CH_2Cl_2. It was purified by flash chromatography (silica, 4% H_2O, 0.1% sat. aq. KNO_3, in MeCN) to give 45 mg of Ru(PreEilatin)(bpy)$_2$•2PF$_6$ **3** (62% yield). ^{1}H NMR (acetone-d_6) δ 9.65 (s), 9.61 (s), 9.06 (d, *J*=6.2 Hz), 8.92 (d, *J*=7.3 Hz), 8.85 (m), 8.78 (d, *J*=8.1 Hz), 8.71 (d, *J*=5.5 Hz), 8.58 (d, *J*=6.6 Hz), 8.52 (d, *J*=6.2 Hz), 8.27 (m), 8.20 (dd, *J*=8.2 Hz, 1.1 Hz), 8.17 (m), 8.06 (m), 7.96 (td, *J*=8.4 Hz, 1.5 Hz), 7.90 (td, *J*=8.4 Hz, 1.5 Hz), 7.64 (m), 7.38 (m). ^{13}C NMR (acetone-d_6) δ 159.41, 158.91, 158.77, 158.18, 157.99, 157.85, 157.52, 154.24, 153.29, 152.00, 152.88. 152.35, 150.14, 149.99, 149.91, 149.65, 145.95, 145.76, 139.56, 139.25. 139.16, 139.05, 139.02, 139.01, 138.85, 133.17, 133.14, 130.93, 130.88, 129.81, 129.78, 128.86, 128.81, 128.79, 128.55, 127.73, 127.06, 125.38, 125.34, 125.28, 125.12, 124.78, 124.75, 124.61. 124.45, 123.95, 123.61, 122.18, 121.79, 121.77. 121.48, 119.85. UV / Vis (MeCN) λ_{max}(ε x 10^{-4}) 242 (58), 286 (73), 357 (24), 397 (13), 539 (8.5). ESI–MS calcd for $C_{44}H_{30}F_6N_8PRu$ 917, mass found 917 *m/z* $[M\text{-}PF_6]^+$.

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[1] P. Rocca, C. Cochennec, F. Marsais, L. Thomas-dit-Dumont, M. Mallet, A. Godard, G. Quéguiner, *J. Org. Chem.*, **1993**, *58*, 7832-7838.

Ru(Eilatin)(bpy)$_2$•2PF$_6$ 4. Ru(PreEilatin)(bpy)$_2$•2PF$_6$ **3** (16 mg, 0.015 mmol) was taken up as a suspension in ethylene glycol (2 mL) and acetone (0.2 mL) and added to a pressure tube containing 10% Pd / C (10 mg, preactivated as above). It was heated to 180 ºC for 1 h, at which point complete conversion was observed by both color change and by TLC. The solids were removed by filtration, and washed with hot acetonitrile. The volatile substances were removed under reduced pressure, and the crude (in ethylene glycol) was purified by flash chromatography (silica, MeCN to remove the ethylene glycol, then increased to 5% H_2O, 0.1% sat. aq. KNO_3, in MeCN) to give 15.6 mg of Ru(Eilatin)(bpy)$_2$•2PF$_6$ **4** (97% yield). UV / Vis λ_{max}(ε x 10^{-4}) (MeCN) 241 (68), 286 (73), 341 (22), 424 (33), 581 (10). (In good agreement with literature data; *Chem. Comm.* **1997**, *1*, 17.) ^{13}C NMR (acetonitrile-d$_3$) δ 157.6, 157.5, 154.8, 154.6, 152.4, 150.4, 147.1, 146.1, 139.2, 139.0, 136.9, 133.7, 131.8, 131.2, 129.0, 128.9, 125.4, 125.2, 124.7, 121.7, 121.5, 119.9, 118.2. ESI–MS calcd. for $C_{44}H_{28}F_6N_8PRu$ 915.1, found 915.1 *m/z* [M-PF$_6$]$^+$.

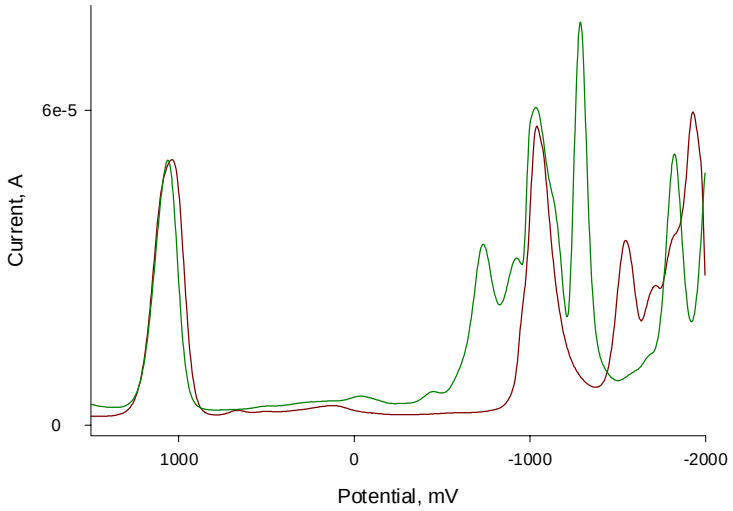
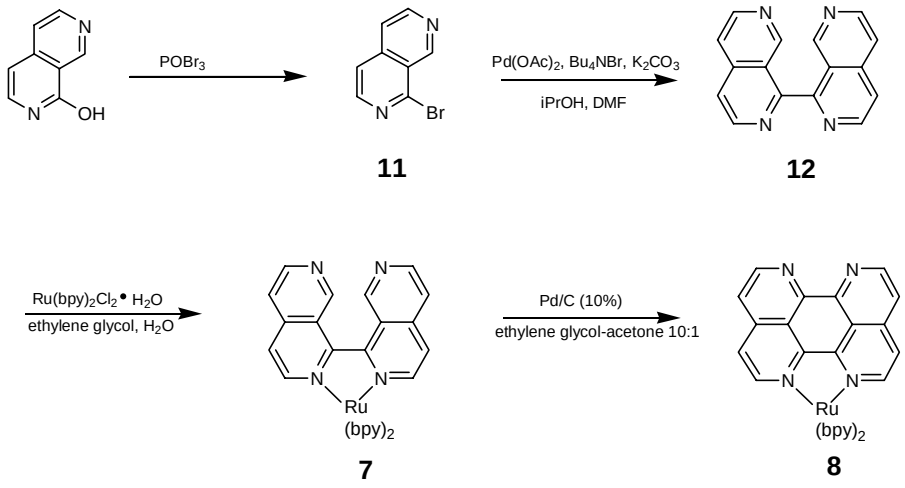


Figure S1. Square Wave Voltamogram of complexes **3** (red) and **4** (green).



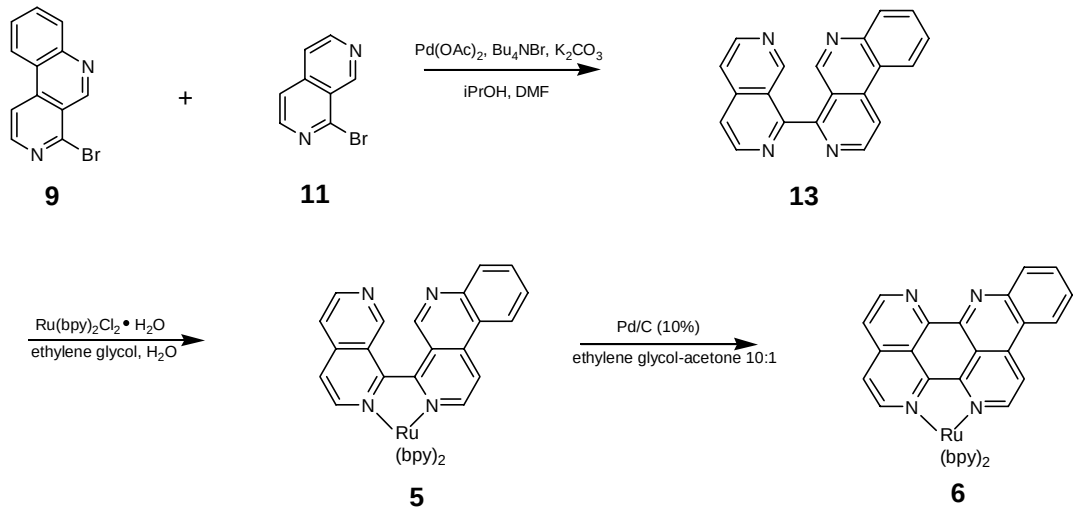
Scheme S3. Synthesis of the bisnaphthyridine ligand, metal complex, and final dehydrogenation to the fused product.

3-Bromo-2,7-naphthyridine 11. 3-Hydroxy-2,7-naphthyridine (200 mg, 1.37mmol) was combined with $POBr_3$ (ca. 1.2 g, 4.2 mmol) in anisole (5 mL) under argon and heated to 135 ºC. After 3 h, the solution was cooled to room temperature, and quenched with cold water. The solution was neutralized with ammonium hydroxide, and extracted into $CHCl_3$. The solvent was removed under reduced pressure and the crude purified by flash chromatography (silica, $CHCl_3$) to yield 3-Bromo-2, 7-naphthyridine **11** (250 mg, 87% yield). ^1H NMR ($CDCl_3$) δ 9.70 (s, 1H), 8.83 (d, *J*=5.5 Hz, 1H), 8.46 (d, *J*=5.5 Hz, 1H), 7.63 (t, *J*=5.9 Hz, 2H). ^{13}C ($CDCl_3$) δ 153.4, 147.7, 146.0, 145.0, 140.4, 119.5, 118.8. MALDI-FTMS calcd. for $C_8H_5BrN_2$ 208.9709 (MH^+), found 208.9709 *m/z* MH^+.

Bisnaphthyridine 12. 11 (50 mg, 0.24 mmol), $Pd(OAc)_2$ (2.7 mg, 0.011 mmol), Bu_4NBr (39 mg, 0.11 mmol), and K_2CO_3 (33 mg, 0.24 mmol) were dissolved under argon in a degassed solution of iPrOH (1.25 mL) and DMF (0.9 mL). The solution was heated to 115 ºC for 12 h. The solvents were removed under reduced pressure, and the crude dissolved in $CHCl_3$. It was washed with

aqueous EDTA (pH 7), then with brine, dried over $MgSO_4$, and the solvents removed. The crude was purified by flash chromatography (silica gel, gradient of 0–5% MeOH in $CHCl_3$) to give 15 mg of **12** (49% yield). ^1H NMR ($CDCl_3$) δ 9.52 (s, 1H), 8.94 (d, *J*= 5.5 Hz, 1H), 8.80 (d, *J*=5.9 Hz, 1H), 7.87 (d, *J*=5.9 Hz, 1H), 7.82 (d, *J*=5.9 Hz, 1H). ^{13}C ($CDCl_3$) δ 157.3, 152.2, 146.5, 145.4, 139.6, 120.0, 119.3.

Ru(dbisnaphthyridine)(bpy)$_2$•2PF$_6$ 8. 12 (14 mg, 0.054 mmol) and $Ru(bpy)_2Cl_2•5H_2O$ (17 mg, 0.032 mmol) were dissolved in a degassed mixture of 1:1 ethylene glycol and water (4 mL) under argon. The solution was heated to 80 ºC. After 2 h it was cooled to room temperature, diluted with water (10 mL) and washed with CH_2Cl_2. A saturated aq. solution of KPF_6 was added, and the metal complex extracted into CH_2Cl_2. The product (**7**) was dried down, and due to the propensity of the metal center to oxidize, was carried on to the next step without purification. ESI–MS calcd. for **7** $C_{36}H_{26}F_6N_8PRu$ 817.1, found 817.0 *m/z* $[M\text{-}PF_6]^+$. The crude was taken up as a suspension in ethylene glycol (2 mL) and acetone (0.2 mL) and added to a pressure tube containing 10% Pd / C (10 mg). It was heated to 180 ºC for 1 h, at which point complete conversion was observed by both color change and by TLC. The solids were removed by filtration, and washed with hot acetonitrile. The volatile substances were removed, and the residual crude (in ethylene glycol) was purified by flash chromatography (silica, MeCN to remove the ethylene glycol, then increased to 10% H_2O, 4% sat. aq. KNO_3, in MeCN) to give 9 mg of Ru(dbisnaphthyridine)(bpy)$_2$•2PF$_6$ **8** (30% yield). ESI–MS calcd. for $C_{36}H_{24}F_6N_8PRu$ 815.08, found 815.1*m/z* $[M\text{-}PF]^+$.



9 **11** **13** **5** **6**

Scheme S4. Synthesis of the debenzo-eilatin ligand, metal complex, and final dehydrogenation to the fused product.

Debenzo-Preeilatin 13. 11 (50 mg, 0.24 mmol), **9** (22 mg, 0.085 mmol), $Pd(OAc)_2$ (2.7 mg, 0.011 mmol), Bu_4NBr (39 mg, 0.11 mmol), and K_2CO_3 (33 mg, 0.24 mmol) were dissolved under argon in a degassed mixture of iPrOH (1.25 mL) and DMF (0.9 mL). The solution was heated to 115 ºC for 12 h. The solvents were removed under reduced pressure, and the crude was dissolved in $CHCl_3$, washed with aqueous EDTA (pH 7), brine, dried over $MgSO_4$, and the solvents removed. It was purified by flash chromatography (silica, 0–5% MeOH in $CHCl_3$) to give 8 mg of **12** (30% yield). ^{1}H NMR ($CDCl_3$) δ 9.81 (s, 1H), 9.75 (s, 1H), 9.22 (d, *J*= 5.8 Hz, 1H), 9.08 (d, *J*=5.8 Hz, 1H), 8.85 (d, *J*=5.5 Hz, 1H), 8.77 (d, *J*=8.3 Hz, 1H), 8.68 (d, *J*=5.8 Hz, 1H), 8.42 (d, *J*=8.3 Hz, 1H), 8.03-7.9 (m, 4H). ESI–MS calcd. for $C_{20}H_{13}N_4$ 309.1, found 309.4 *m/z* MH^+.

Ru(Debenzo-Eilatin)(bpy)$_2$•2PF$_6$ 6. **13** (8 mg, 0.026 mmol) and $Ru(bpy)_2Cl_2 \cdot 5H_2O$ (12 mg, 0.023 mmol) were dissolved in a degassed 1:1 mixture of ethylene glycol and water (4 mL) under argon. The solution was heated to 80 ºC. After 2 h the solution was cooled to room temperature, diluted with water

(10 mL) and washed with CH_2Cl_2. A saturated aq. solution of KPF_6 was added, and the metal complex (**5**) extracted into CH_2Cl_2. It was dried down, and carried on to the next step without further purification. ESI-MS (calcd. for **5** $C_{40}H_{26}F_6N_8PRu$ 867.1, found 866.9 *m/z* $[M\text{-}PF_6^+]$.)

The crude was taken up as a suspension in ethylene glycol (2 mL) and acetone (0.2 mL) and added to a pressure tube containing 10% Pd/C (10 mg). It was heated to 180 ºC for 0.5 h, at which point complete conversion was observed by both color change and by TLC. The catalyst was removed by filtration, and washed with hot acetonitrile. The crude (in ethylene glycol) was purified by flash chromatography (silica, neat MeCN to remove the ethylene glycol, then increased to 10% water, 1% sat. aq. KNO_3, 89% MeCN) to give 11 mg of Ru(Debenzo-eilatin)$(bpy)_2 \cdot 2PF_6$ **6** (47% yield). ESI–MS calcd. for $C_{40}H_{28}F_6N_8PRu$ 865.1, found 865.0 *m/z* $[M\text{-}PF_6]^+$.