

Electronic Supplementary Information for

Diruthenium Aryl Compounds – Tuning of Electrochemical Responses and Solubility

Lyndsy A. Miller-Clark, Peter E. Christ and Tong Ren*

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* To whom correspondence should be addressed. Email: tren@purdue.edu.

^a *Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*

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1. Synthesis

Ru₂(DiMeOap)₄(C₆H₄-4-NMe₂) (1a). 4-Bromo-N,N-dimethylaniline (217 mg, 1.1 mmol) was dissolved in 5 mL THF and treated with 0.58 mL ⁿBuLi (1.5 mmol) at 0°C. The aryllithium solution was then cannula-transferred to a 30 mL solution of Ru₂(DiMeOap)₄Cl in THF (125 mg, 0.11 mmol). An immediate color change from green to black was observed. The reaction was stirred for 1 hour at room temperature. Upon exposure to atmosphere, the color of the solution remained black. After filtering over Celite and the removal of solvents, the crude product mixture was run through a deactivated (with triethylamine) silica pad. The filtrate was collected, solvents removed, and recrystallized using a 1/15 (v/v) acetone/pentane recrystallization at -20°C. The black solid was collected with a frit and purified by column chromatography. The black band was collected with 1:1 THF/hexanes (v/v), and a deep black solid was isolated. Single crystals suitable for X-ray diffraction were grown by slow evaporation of **1a** in acetone. Yield: 57 mg (43% based on Ru). Elem. Anal. Found (Calcd) for C₆₀H₆₆N₉O₁₀Ru₂ (**1a**·2H₂O·0.5THF): C, 56.36 (56.78); H, 5.29 (5.38); N, 9.44 (9.61). ESI-MS (*m/z*, based on ¹⁰¹Ru): [M+H]⁺ = 1241.1. UV-Vis (in THF) λ / nm (ε / M⁻¹ cm⁻¹): 465 (6200), 581 (5900), 760 (3400), 858 (3800). μ_{eff} (21°C) = 3.9 μ_B. Electrochemistry (THF, vs Fc⁺⁰) E_{1/2} / V, ΔE_p / mV, *i*_{backward}/*i*_{forward}: 0.09, 68, 0.92; -0.26, 66, 0.91; -1.63, 70, 0.99.

Ru₂(DiMeOap)₄(C₆H₄-4-OMe) (3a). 4-Bromoanisole (0.14 mL, 1.1 mmol) was dissolved in 5 mL THF and then treated with 0.57 mL ⁿBuLi (1.5 mmol) at 0°C. The aryllithium solution was then cannula-transferred to a 30 mL solution of Ru₂(DiMeOap)₄Cl in THF (126 mg, 0.11 mmol). A color change from dark green to dark red was observed. The reaction mixture stirred for 1 hour at room temperature. Upon exposure to atmosphere, the color changed to a brown. After filtering over Celite and the solvent was removed, the crude product mixture was first recrystallized using 1:20 THF/hexanes (v/v) recrystallization at -20°C. The solid was

collected and final purification was achieved via column chromatography on deactivated (with triethylamine) silica. The light brown band was collected with 1:1 THF/hexanes (v/v), and a dark brown solid was isolated. Single crystals suitable for X-ray diffraction were grown by layering pentane over a concentrated solution of **3a** in THF. Yield: 38 mg (28% based on Ru). Elem. Anal. Found (calcd) for $C_{63}H_{71}N_8O_{12}Ru_2$ (**3a**·2H₂O·1THF): C, 56.65 (56.71); H, 5.27 (5.36); N, 8.12 (8.40). ESI-MS (m/z , based on ^{101}Ru): [M^+] = 1225.9. UV-Vis (in THF) λ / nm ($\epsilon / M^{-1} cm^{-1}$): 473 (6900), 634 (1500), 833 (3400). $\mu_{eff}(21^\circ C) = 4.0 \mu_B$. Electrochemistry (THF, vs $Fc^{+/0}$) $E_{1/2} / V$, $\Delta E_p / mV$, $i_{backward}/i_{forward}$: -0.20, 67, 0.92; -1.59, 67, 0.99.

$Ru_2(DiMeOap)_4(C_6H_3-3,5-(OMe)_2)$ (4a**)**. 1-Bromo-3,5-dimethoxybenzene (165 mg, 0.76 mmol) was dissolved in 5 mL THF and treated with 0.4 mL $nBuLi$ (1 mmol) at $-78^\circ C$. The aryllithium solution was then cannula-transferred to a 30 mL solution of $Ru_2(DiMeOap)_4Cl$ in THF (125 mg, 0.11 mmol). A color change from green to red brown was observed. The reaction mixture stirred for 1 hour at room temperature. Upon exposure to atmosphere, the color changed to a green-black. After filtering over Celite and removal of the solvent, the crude mixture was purified by column chromatography on deactivated (w/ triethylamine) silica. The green band was eluted with 1:1 EtOAc/hexanes (v/v), and a dark green solid was isolated. Single crystals suitable for X-ray diffraction were grown by layering hexanes over a concentrated solution of **4a** in ethyl acetate (EtOAc). Yield: 81.2 mg (59% based on Ru). Elem. Anal. Found (Calcd) for $C_{76}H_{105}N_8O_{24}Ru_2$ (**4a**·4.5EtOAc·5.5H₂O): C, 53.13 (53.48); H, 6.09 (6.21); N, 6.18 (6.40). ESI-MS (m/z , based on ^{101}Ru): [M^+] = 1257.5. UV-Vis (in THF) λ / nm ($\epsilon / M^{-1} cm^{-1}$): 471 (6500), 650 (1700), 815 (4100). $\mu_{eff}(21^\circ C) = 3.5 \mu_B$. Electrochemistry (THF, vs $Fc^{+/0}$) $E_{1/2} / V$, $\Delta E_p / mV$, $i_{backward}/i_{forward}$: -0.18, 60, 0.89; -1.56, 69, 0.98.

Ru₂(DiMeOap)₄(C₆H₄-4-CF₃) (5a). 4-Bromobenzotrifluoride (0.1 mL, 0.71 mmol) was dissolved in 5 mL THF and then treated with 0.4 mL ⁿBuLi (1 mmol) at -78°C. The aryllithium solution was then cannula transferred to a 30 mL solution of Ru₂(DiMeOap)₄Cl in THF (126 mg, 0.11 mmol). No immediate color change was observed, with the solution remaining a dark green. The reaction stirred for 1 h at room temperature. Upon exposure to atmosphere, the color of the solution remained dark green. After filtering over Celite and solvent removal, the crude product mixture was purified by column chromatography on deactivated (w/ triethylamine) silica. The dark green band was eluted with 1:1 EtOAc/hexanes (v/v), and a dark green solid collected after removal of solvents. Single crystals suitable for X-ray diffraction were grown by layering hexanes over a concentrated solution of **5a** in ethyl acetate. Yield: 116 mg (84% based on Ru). Elem. Anal. Found (Calcd) for C₇₇H₉₇N₈O₉F₃Ru₂ (**5a**·0.5EtOAc·2.5C₆H₁₄): C, 60.42 (59.91); H, 5.92 (6.28); N, 6.99 (7.35). ESI-MS (*m/z*, based on ¹⁰¹Ru): [M+H]⁺ = 1265.6. UV-Vis (in THF) λ / nm (ε / M⁻¹ cm⁻¹): 472 (5700), 675 (1800), 820 (3500). μ_{eff} (21°C) = 3.8 μ_B. Electrochemistry (THF, vs Fc⁺⁰) E_{1/2} / V, ΔE_p / mV, *i*_{backward}/*i*_{forward}: -0.12, 65, 0.99; -1.45, 67, 0.98.

Ru₂(DiMeOap)₄(Ph) (6a). Bromobenzene (0.09 mL, 0.86 mmol) was dissolved in 5 mL THF and treated with 0.5 mL ⁿBuLi (1.25 mmol) at 0°C. The aryllithium solution was then cannula-transferred to a 30 mL solution of Ru₂(DiMeOap)₄Cl in THF (102 mg, 0.088 mmol). A color change from green to red-brown was observed. The reaction mixture stirred for 1.5 hours at room temperature, and after exposure to air changed back to dark green. After filtering over Celite and removing the solvent, the crude product mixture was purified by column chromatography on deactivated (w/ triethylamine) silica. The green band was eluted with 1:1 THF/hexanes (v/v), and a dark green solid was collected from the filtrate. Yield: 95 mg (91% based on Ru). Elem. Anal. Found (Calcd) for C₆₈H₇₁N₈O_{11.5}Ru₂ (**6a**·2.5THF·1H₂O): C, 58.84

(58.57); H, 5.55 (5.71); N, 8.04 (8.04). ESI-MS (m/z , based on ^{101}Ru): $[\text{M}^+] = 1196.4$. UV-Vis (in THF) λ / nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$): 472 (6200), 649 (1700), 829 (3400). μ_{eff} (21°C) = 4.3 μ_{B} . Electrochemistry (THF, vs $\text{Fc}^{+/0}$) $E_{1/2} / \text{V}$, $\Delta E_{\text{p}} / \text{mV}$, $i_{\text{backward}}/i_{\text{forward}}$: -0.18, 76, 0.97; -1.56, 77, 0.97.

$\text{Ru}_2(m\text{-}^i\text{PrOap})_4(\text{C}_6\text{H}_4\text{-4-NMe}_2)$ (1b). 4-Bromo-*N,N*-dimethylaniline (178 mg, 0.87 mmol) was dissolved in 10 mL THF and treated with 0.4 mL $n\text{BuLi}$ (1 mmol) at 0°C. The aryllithium solution was cannula-transferred to a 70 mL THF solution of $\text{Ru}_2(m\text{-}^i\text{PrOap})_4\text{Cl}$ (103 mg, 0.087 mmol). Upon addition an immediate color change from dark green to black was observed. The reaction mixture stirred for 1 hour at room temperature. Upon exposure to air, the solution stayed black. After filtering over Celite and removal of solvent, the crude mixture was purified by column chromatography on deactivated (with triethylamine) silica. The black band was eluted with 1:5 EtOAc/hexanes (v/v), and a black microcrystalline solid obtained after condensing. Yield: 50 mg (45% based on Ru). Elem. Anal. Found (Calcd) for $\text{C}_{84}\text{H}_{144}\text{N}_9\text{O}_{31}\text{Ru}_2$ (1b·17H₂O·5EtOAc): C 50.89 (51.0); H 6.91 (7.34); N 5.98 (6.37). ESI-MS (m/z , based on ^{101}Ru): $[\text{M}^+] = 1232.1$. UV-Vis (in THF) λ / nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$): 465 (4700), 580 (4300), 760 (2800), 830 (2900). μ_{eff} (21°C) = 3.5 μ_{B} . Electrochemistry (THF, vs $\text{Fc}^{+/0}$), $E_{1/2} / \text{V}$, $\Delta E_{\text{p}} / \text{mV}$, $i_{\text{backward}}/i_{\text{forward}}$: 0.00, 60, 0.37; -0.38, 70, 0.85; -1.70, 80, 0.30.

$\text{Ru}_2(m\text{-}^i\text{PrOap})_4(\text{C}_6\text{H}_4\text{-4-OMe})$ (3b). 4-Bromoanisole (0.1 mL, 1.1 mmol) was dissolved in 5 mL THF and then treated with 0.4 mL $n\text{BuLi}$ (1.5 mmol) at 0°C. The aryllithium solution was then cannula-transferred to a 70 mL solution of $\text{Ru}_2(m\text{-}^i\text{PrOap})_4\text{Cl}$ in THF (90.4 mg, 0.08 mmol). A color change from dark green to brown was observed. The reaction mixture stirred for 3 hours at room temperature. Upon exposure to atmosphere, no color change was observed. After filtering over Celite and solvent removed, the crude product mixture was purified by column

chromatography on deactivated (with triethylamine) silica. The light brown band was collected with 1:5 THF/hexanes (v/v), and a dark brown solid was isolated. This solid was noted to be relatively unstable in ambient conditions, degrading to $\text{Ru}_2(m\text{-}^i\text{PrOap})_4\text{Cl}$ and an unknown yellow impurity. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of **3b** in diethyl ether. Yield: 20 mg (21% based on Ru). Elem. Anal. Found (Calcd) for $\text{C}_{83}\text{H}_{113}\text{N}_8\text{O}_{13}\text{Ru}_2$ (**3b**·3H₂O·5THF): C 61.14 (61.05); H 7.02 (6.97); N 6.59 (6.86). ESI-MS (m/z , based on ¹⁰¹Ru): [M⁺] = 1218.5. UV-Vis (in THF) λ / nm (ϵ / M⁻¹ cm⁻¹): 473 (6200), 649 (1500), 813 (3000). μ_{eff} (21°C) = 3.6 μ_{B} . Electrochemistry (THF, vs Fc⁺⁰), $E_{1/2}$ / V, ΔE_{p} / mV, $i_{\text{backward}}/i_{\text{forward}}$: -0.20, 74, 0.88; -1.61, 80, 0.97.

Ru₂(*m*-^{*i*}PrOap)₄(C₆H₄-3,5-(OMe)₂) (4b). 1-Bromo-3,5-(dimethoxy)-benzene (200 mg, 0.91 mmol) was dissolved in 10 mL THF and was treated with 0.4 mL ^{*n*}BuLi (1 mmol) at -78°C. The ligand solution was warmed slightly and was cannula-transferred to a 30 mL THF solution of $\text{Ru}_2(m\text{-}^i\text{PrOap})_4\text{Cl}$ (149 mg, 0.131 mmol). An immediate color change to red-brown from dark green was observed upon addition. The reaction mixture was stirred for 1.5 hours at room temperature. Upon exposure to air, the solution changed back to dark green. After filtering over Celite and removal of the solvent, the crude mixture was first purified using a 1/20 (v/v) THF/hexanes recrystallization at -20°C. The dark green solid that was collected was then run through a Celite plug with 1:5 THF/hexanes (v/v). The filtrate was collected, and solvents were removed to give a dark green solid. Single crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated solution of **4b** in THF. Yield: 86 mg (53% based on Ru). Elem. Anal. Found (Calcd) for $\text{C}_{79}\text{H}_{104}\text{N}_8\text{O}_6\text{Ru}_2$ (**4b**·2.5C₆H₁₄·1THF): C 64.83 (64.36); H 6.80 (7.09); N 7.29 (7.51). ESI-MS (m/z , based on ¹⁰¹Ru): [M⁺] = 1249.0. UV-Vis (in THF) λ / nm (ϵ

/ M⁻¹ cm⁻¹): 469 (6300), 648 (1900), 800 (4200). μ_{eff} (21°C) = 3.4 μ_{B} . Electrochemistry (THF, vs Fc⁺⁰), $E_{1/2}$ / V, ΔE_p / mV, $i_{\text{backward}}/i_{\text{forward}}$: -0.19, 79, 0.84; -1.58, 85, 0.98.

Ru₂(*m*-^{*i*}PrOap)₄(C₆H₄-4-CF₃) (5b). 4-Bromobenzotrifluoride (0.1 mL, 0.71 mmol) was dissolved in 5 mL THF and then treated with 0.4 mL ^{*n*}BuLi (1 mmol) at -78°C. The aryllithium solution was then warmed to room temperature and 4.5 mL of the solution was transferred via syringe to a 60 mL THF solution of Ru₂(*m*-^{*i*}PrOap)₄Cl (106 mg, 0.092 mmol). An immediate color change from dark green to red-brown was observed upon addition. The reaction mixture was stirred for 2 hours at room temperature. Upon exposure to air, the solution changed back to dark green. After filtering over Celite and removal of the solvent, the crude mixture was purified first with a hexanes recrystallization at -20°C followed by final purification by column chromatography on deactivated (w/ triethylamine) silica. The green band was collected with 1:5 EtOAc/hexanes (v/v), and a dark green solid was isolated. Yield: 79 mg (68% based on Ru). Elem. Anal. Found (Calcd) for C₈₃H₁₁₆N₈O₂₀F₃Ru₂ (**5b**·6H₂O·5EtOAc): C 55.08 (55.23); H 6.45 (6.48); N 5.96 (6.21). ESI-MS (m/z , based on ¹⁰¹Ru): [M⁺] = 1257.0. UV-Vis (in THF) λ / nm (ϵ / M⁻¹ cm⁻¹): 466 (5300), 668 (1800), 810 (3200). μ_{eff} (20°C) = 3.9 μ_{B} . Electrochemistry (THF, vs Fc⁺⁰), $E_{1/2}$ / V, ΔE_p / mV, $i_{\text{backward}}/i_{\text{forward}}$: -0.13, 64, 0.86; -1.48, 80, 0.96.

2. X-ray structural analysis

Crystals suitable for X-ray diffraction analysis were grown by layering hexanes over a concentrated solution of either **2a**, **4a**, or **5a** in ethyl acetate or of **3a** or **4b** in THF. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of either **1a** in acetone, **2b** in hexanes or of **3b** in Et₂O. Single crystals of **2a**, **3a**, **4a**, **5a**, **3b**, and **4b** were coated with paraffin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident

beam monochromator, a Photon II area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K. Single crystals of **1a** and **2b** were coated with paraffin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I- μ -S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-III C14 area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 150 K. In some of the structures, **2b** and **4b**, only part of the solvent molecules were sufficiently resolved to model, and were included as partially occupied. Based on the XRD data it was not possible to determine whether the remaining volume remained unoccupied, or if additional highly disordered solvate molecules are present. A complete removal of the partially occupied solvent molecules via the Squeeze procedure did not substantially improve the overall quality of the structure, and we thus decided to include the resolved fraction of the void content as partially occupied solvate molecules.

Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3¹ and SADABS². The space groups were assigned using XPREP within the SHELXTL suite of programs^{3,4} and solved by direct methods using ShelXS⁴ or dual methods using ShelXT⁵ and refined by full matrix least squares against F^2 with all reflections using Shelxl2018⁶ using the graphical interface Shelxle.⁷ Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2123249-2123256 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data for compounds **1a**, **2a**, **3a**, **4a**, and **5a**.

	1a	2a	3a	4a	5a
Chemical formula	$C_{60}H_{61}N_9O_8Ru_2 \cdot 2(C_3H_6O)$	$C_{62}H_{65}N_8O_8Ru_2$	$C_{59}H_{59}N_8O_9Ru_2$	$C_{60}H_{61}N_8O_{10}Ru_2 \cdot C_4H_8O_2$	$C_{59}H_{56}F_3N_8O_8Ru_2$
Fw, g/mol	1355.48	1252.36	1226.28	1344.41	1264.26
Space group	<i>Pbca</i>	<i>I4</i>	<i>P2₁/c</i>	<i>P$\bar{1}$</i>	<i>P2₁/n</i>
<i>a</i> , Å	17.2181(8)	12.4116(2)	20.7861(9)	12.3210(4)	12.7603(5)
<i>b</i> , Å	24.2357(12)	12.4116(2)	15.6582(6)	12.9177(5)	21.0504(8)
<i>c</i> , Å	29.5233(16)	18.2620(6)	17.0761(7)	19.6606(7)	19.8667(7)
α °	90	90	90	108.3490(19)	90
β °	90	90	100.676(2)	91.745(2)	91.8246(15)
γ °	90	90	90	92.703(2)	90
V, Å ³	12319.9(11)	2813.22(13)	5461.6(4)	2963.37(19)	5333.7(3)
Z	8	2	4	2	4
T, K	150	150	150	150	150
λ , Å	1.54178	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} , g/cm ³	1.462	1.479	1.491	1.507	1.574
<i>R</i>	0.032	0.024	0.030	0.036	0.041
<i>R_w</i> (<i>F</i> ²)	0.077	0.055	0.073	0.086	0.082

Table S2 Crystal data for compounds **2b**, **3b**, and **4b**.

	2b	3b	4b
Chemical formula	$C_{66}H_{73}N_8O_4Ru_2 \cdot 0.815(C_6H_{14})$	$C_{63}H_{67}N_8O_5Ru_2 \cdot C_4H_{10}O$	$C_{64}H_{69}N_8O_6Ru_2 \cdot 1.316(C_5H_{12})$
Fw, g/mol	1314.73	1292.50	1343.20
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a , Å	10.6576(4)	13.5208(4)	10.5619(12)
b , Å	17.2858(6)	14.1761(5)	34.317(6)
c , Å	19.4972(7)	17.9369(6)	18.756(3)
α °	107.2809(15)	67.298(1)	90
β °	94.7543(16)	86.515(1)	104.369(6)
γ °	96.8966(15)	74.075(1)	90
V , Å ³	3378.2(2)	3045.98(18)	6585.6(16)
Z	2	2	4
T , K	150	150	150
λ , Å	1.54178	0.71073	0.71073
ρ_{calcd} , g/cm ³	1.293	1.409	1.355
R	0.046	0.035	0.050
$R_w(F^2)$	0.122	0.074	0.135

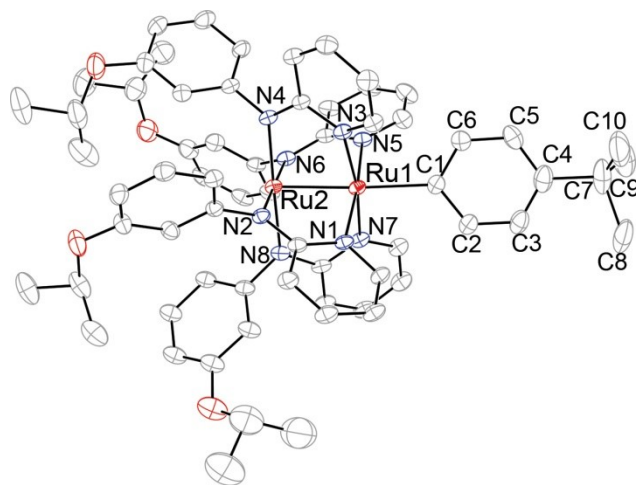


Fig. S1 ORTEP plot of **2b** at 30% probability level. Solvent molecules, ligand disorder, and H atoms removed for clarity.

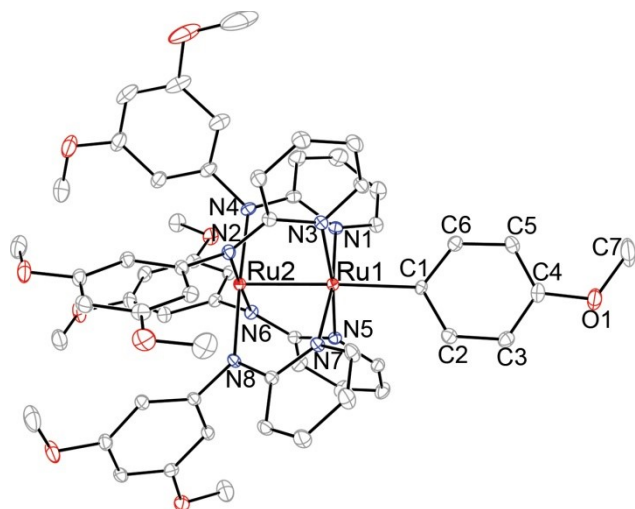


Fig. S2 ORTEP plot of **3a** at 30% probability level. H atoms removed for clarity.

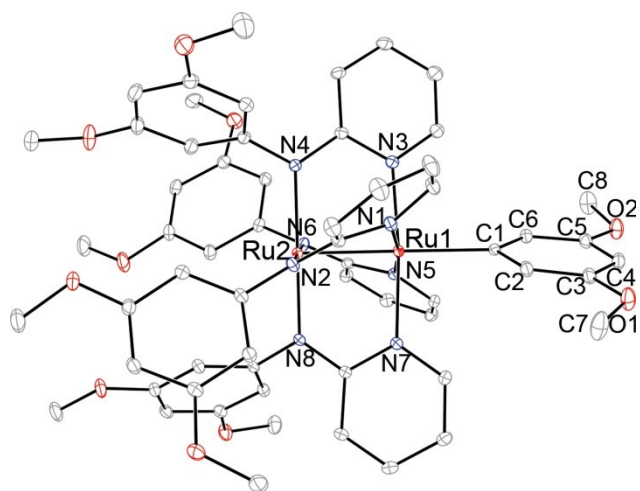


Fig. S3 ORTEP plot of **4a** at 30% probability level. H atoms removed for clarity.

Table S3 Selected Bond Lengths (Å) and Angles (°) for Compounds **2b**, **3a**, and **4a**

	2b	3a	4a
Ru1–Ru2	2.3399(4)	2.3365(2)	2.3407(2)
Ru1–C1	2.184(4)	2.193(2)	2.207(4)
Ru2–Ru1–C1	176.3(1)	178.03(6)	177.07(5)

Ru1–N1	2.114(3)	2.133(2)	2.134(2)
Ru1–N3	2.136(3)	2.116(2)	2.121(2)
Ru1–N5	2.124(3)	2.076(2)	2.104(2)
Ru1–N7	2.092(3)	2.111(2)	2.146(2)
Ru2–N2	2.049(3)	2.036(2)	2.046(2)
Ru2–N4	2.032(3)	2.026(2)	2.036(2)
Ru2–N6	2.033(3)	2.049(2)	2.041(2)
Ru2–N8	2.045(3)	2.038(2)	2.023(2)

3. Absorption Details for 1b–5b

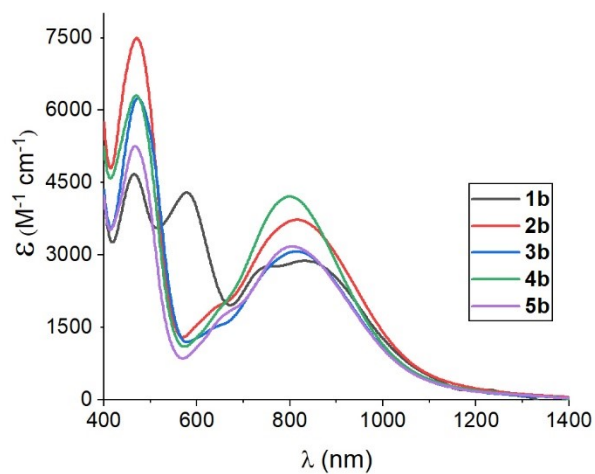


Fig. S4 Vis-NIR absorption spectra of **1b–5b** as THF solutions.

Table S4 Solubility comparisons between **2a/2b** and $\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}^t\text{Bu})$

Solvent	2a	2b	$\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}^t\text{Bu})$
Pentane	Sparingly soluble	Sparingly soluble	Insoluble
Hexanes	Soluble	Soluble	Insoluble

Diethyl Ether	Very soluble	Very soluble	Sparingly soluble
DCM	Very soluble	Very soluble	Soluble
THF	Very soluble	Very soluble	Soluble

*Sparingly soluble = < 1.0 mg / 2 mL solvent; soluble = 1.0 – 4.0 mg / 1 mL solvent; very soluble = > 8.0 mg / 1 mL solvent

4. Electrochemistry details for 1b–5b

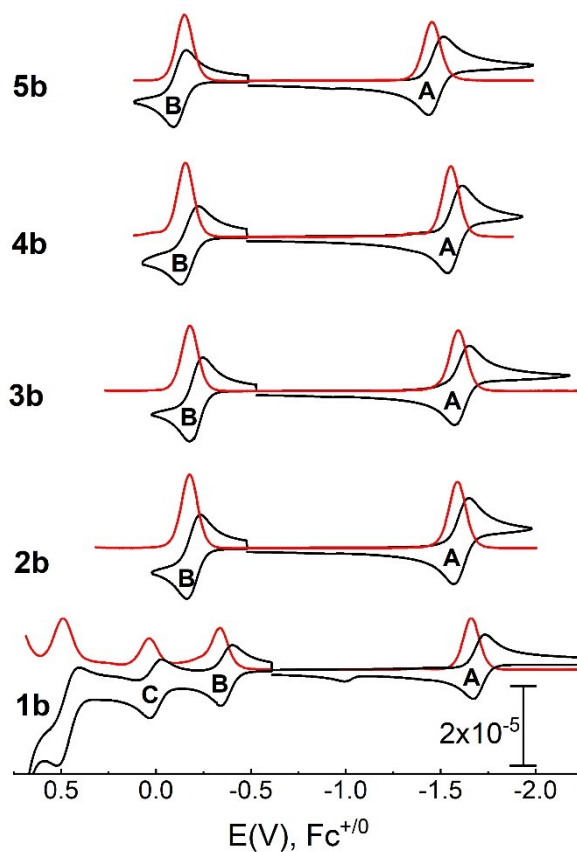
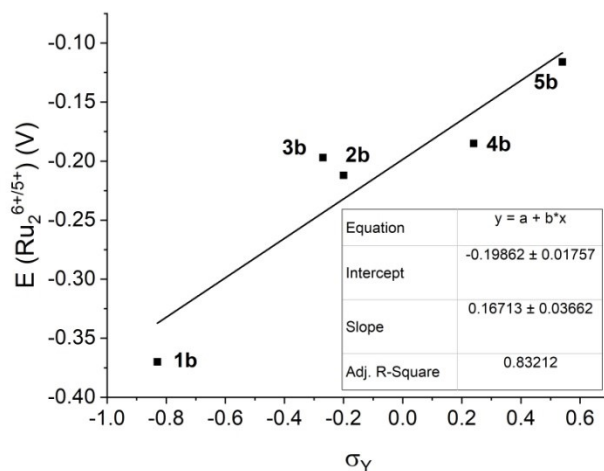


Fig. S5 Cyclic (black) and differential pulse (red) voltammograms of compounds **1b–5b** (1.0 mM) recorded in 0.10 M THF solutions of Bu_4NPF_6 at a scan rate of 0.1 V/s.

Table S5 Electrochemical Data from DPV (in V vs $\text{Fc}^{+/0}$) for **1b–5b**

	C	B	A
1b	0.00	− 0.37	− 1.70
2b	−	− 0.21	− 1.61
3b	−	− 0.20	− 1.61
4b	−	− 0.19	− 1.58
5b	−	− 0.13	− 1.48

**Fig. S6** Hammett plot of **1b–5b** oxidation potentials ($E(\text{Ru}_2^{6+/5+})$) versus σ_Y . The squares are measured potentials and the solid line is the linear best-fit line.**Table S6** Electrochemical data from CV (V vs. Ag/AgCl) in THF.

Compound	C	B ($\text{Ru}_2^{6+/5+}$)	A ($\text{Ru}_2^{5+/4+}$)
$\text{Ru}_2(\text{ap})_4\text{Cl}^8$	−	0.46	-0.834
$\text{Ru}_2(\text{DiMeOap})_4\text{Cl}^9$	−	0.56	-0.75
1a	0.58	0.23	-1.15
2a	−	0.29	-1.11
3a	−	0.28	-1.11
4a	−	0.31	-1.10
5a	−	0.36	-0.97
6a	−	0.30	-1.08
$\text{Ru}_2(m\text{-}^i\text{PrOap})_4\text{Cl}^{10}$	−	0.55	-0.77
1b	0.61	0.24	-1.11
2b	−	0.32	-1.09
3b	−	0.28	-1.13
4b	−	0.29	-1.09
5b	−	0.37	-0.98
$\text{Ru}_2(\text{ap})_4(\text{C}_2\text{-C}_6\text{H}_5)^{11}$	−	0.44	-0.88
$\text{Ru}_2(3\text{-O}^i\text{Buap})_4(\text{C}_2\text{-C}_6\text{H}_5)^{11}$	−	0.43	-0.87

5. Room Temperature Magnetism Data (Evans Method)

Table S6 Room temperature magnetism data using Evans method.¹² Solvent: CDCl₃; reference: ferrocene

Compound	$\Delta\delta$ (Hz)	[Ru ₂] (mM)	χ_M (emu/mol)	μ_{eff} (B.M.)
1a	24	3.23	5.84×10^{-3}	3.9
2a	21	2.90	5.76×10^{-3}	3.9
3a	24	3.11	6.14×10^{-3}	4.0
4a	21	3.62	4.62×10^{-3}	3.5
5a	17	2.45	5.36×10^{-3}	3.8
6a	27	3.04	7.07×10^{-3}	4.3
1b	18	3.20	4.55×10^{-3}	3.5
2b	29	3.51	6.60×10^{-3}	4.1
3b	15	2.46	4.90×10^{-3}	3.6
4b	14	2.67	4.11×10^{-3}	3.4
5b	23	3.18	5.78×10^{-3}	3.9

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