

Electronic Supplementary Information (ESI) for:

**Exploiting a Dimeric Silver Transmetallating Reagent to Synthesize Macrocyclic
Tetracarbene Complexes**

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Experimental Section

All reactions were performed under a dry nitrogen atmosphere with the use of either a glovebox or standard Schlenk techniques unless otherwise noted. Solvents were dried on an Innovative Technologies (Newburgport, MA) Pure Solv MD-7 Solvent Purification System and degassed by three freeze-pump-thaw cycles on a Schlenk line to remove O₂ prior to use. DMSO-d₆, acetonitrile-d₃, and chloroform-d were degassed by three freeze-pump-thaw cycles prior to drying over activated molecular sieves. These NMR solvents were then stored under N₂ in a glovebox. (Me,EtTC^{Ph})(OTf)₄ and (Me,EtTC^{Ph})(I)₄,¹ were prepared as described previously. Characterization of [(Me,EtTC^{Ph})Fe(NCCH₃)₂](PF₆)₂ has been previously reported.² All other reagents were purchased from commercial vendors and used without purification. ¹H, ¹³C{¹H}, and ¹⁹F NMR spectra were recorded at ambient temperature, unless otherwise noted, on a Varian Mercury 300 MHz, Varian VNMRS 500 MHz narrow-bore broadband system or an INOVA 600 MHz narrow-bore broadband system. ¹H and ¹³C NMR chemical shifts were referenced to the residual solvent. ¹⁹F NMR chemical shifts are reported relative to an external standard of neat CFCl₃. Solution magnetic moments were measured by the method of Evans and were adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The ESI-MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Mass spectrometry sample solutions were prepared in acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. UV-vis measurements were taken inside a dry glovebox on an Ocean Optics USB4000 UV-vis system with 1 cm path length quartz crystal cell. Cyclic voltammetry measurements were made inside a dry glovebox using a BAS Epsilon electrochemical analyzer with a platinum working electrode, platinum wire counter electrode, and Ag/AgNO₃ reference electrode. All potentials were measured versus an external standard of ferrocene. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of $(^{\text{Me,Et}}\text{TC}^{\text{Ph}})(\text{PF}_6)_4$ (1b**).** $(^{\text{Me,Et}}\text{TC}^{\text{Ph}})(\text{I})_4$ (2.933 g, 1.997 mmol) and thallium hexafluorophosphate (2.790 g, 7.987 mmol) were added to a 100 mL round bottom flask followed by the addition of 10 mL of DMSO and 60 mL of acetonitrile. The slurry was allowed to stir for 24 h. The mixture was then filtered over Celite into a 500 mL filter flask. Water (200 mL) was added to the solution to yield a white precipitate that was collected on a 60 mL fine sintered glass frit as the pure white powder product (2.612 g, 85% yield). ^1H NMR (DMSO- d_6 , 499.74 MHz): δ 10.04 (s, 4H), 7.44 (m, 16H), 7.26 (t, $J = 7.5$ Hz, 8H), 7.17 (d, $J = 7.5$ Hz, 8H), 6.98 (d, $J = 7.5$ Hz, 8H), 6.63 (s, 4H), 4.67 (s, 8H). ^{13}C NMR (DMSO- d_6 , 125.66 MHz): δ 136.7, 132.7, 132.5, 131.0, 130.6, 130.2, 129.4, 123.1, 122.2, 55.9, 46.8. ^{19}F NMR (DMSO- d_6 , 470.39 MHz): δ -70.55 (d, $J = 705.6$ Hz). IR (neat): 3145, 3067, 1560, 1445, 1372, 1336, 1278, 1254, 1241, 1226, 1177, 1027, 765 cm^{-1} . ESI/MS (m/z): $[\text{M-PF}_6]^+$ 1395.36, $[\text{M-2PF}_6]^{2+}$ 625.19, $[\text{M-3PF}_6]^{3+}$ 368.48. Anal. Calcd for $\text{C}_{66}\text{H}_{56}\text{F}_{24}\text{N}_8\text{P}_4$: C, 51.44; H, 3.66; N, 7.27. Found: C, 50.64; H, 3.78; N, 7.17.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})(\text{H})_2\text{Ag}](\text{OTf})_3$ (2**).** $(^{\text{Me,Et}}\text{TC}^{\text{Ph}})(\text{OTf})_4$ (0.256 g, 0.165 mmol) (**1a**) and silver(I) triflate (0.0420 g, 0.160 mmol) were added to a 20 mL vial wrapped in aluminum foil and dissolved in 15 mL of DMSO while stirring and heating to 90 °C. After 10 min., triethylamine (0.165 g, 1.63 mmol) was added and allowed to stir for 24 h. The reaction mixture was cooled and brought out of the glovebox. The solution was added to a 200 mL beaker and quenched with 150 mL of water to yield a white precipitate. A white powder was collected on a 60 mL fine sintered glass frit. The product was dried by dissolving the white powder in methylene chloride (100 mL) followed by addition of anhydrous MgSO_4 , and filtration over a 60 mL medium sintered glass frit to remove the MgSO_4 . Volatiles were removed under reduced pressure to yield the pure white powder product (0.200 g, 80% yield). Single crystals suitable for single crystal X-ray diffraction can be grown via vapor diffusion of pentane into a solution of **2** in methylene chloride. ^1H NMR (CD_3CN , 60 °C, 499.74 MHz): δ 9.88 (s, 2H), 7.56 (m, 6H), 7.41 (m, 18H), 7.27 (m, 8H), 7.19 (d, $J = 7.5$ Hz, 4H), 6.78 (d, $J = 13.5$ Hz, 2H), 6.68 (d, $J = 6.5$ Hz, 4H), 5.90 (d, $J = 14.0$ Hz, 2H), 4.60 (dd, $J_1 = 15.5$ Hz, $J_2 = 8.0$ Hz, 2H), 4.44 (m, 4H), 4.31 (dd, $J_1 = 15.5$ Hz, $J_2 = 4.5$ Hz, 2H). ^{13}C NMR (CD_3CN , 60 °C, 125.66 MHz): δ 178.38 ($J_{\text{Ag-C}} = 202.4$ Hz), 138.37, 135.82, 134.41, 134.24, 132.66,

132.52, 132.39, 132.29, 132.14, 131.89, 131.42, 131.27, 130.49, 130.33, 130.31, 129.90, 127.42, 126.51, 125.05, 124.84, 122.37 (q, $J_{F-C} = 321.6$ Hz), 59.87, 50.25, 50.10. ^{19}F NMR (CD_3CN , 470.39 MHz): δ -79.14. IR (neat) 3116, 3056, 2964, 1663, 1635, 1552, 1489, 1445, 1359, 1333, 1249, 1223, 1152, 1076, 1057, 1027, 930, 836, 760, 697, 661 cm^{-1} . ESI/MS (m/z): $[\text{M-OTf}]^+$ 1364.86, $[\text{M-2OTf}]^{2+}$ 607.24, $[\text{M-H-3OTf}]^{2+}$ 533.27, $[\text{M-3OTf}]^{3+}$ 355.19. Electrochemistry (vs. ferrocene in CH_3CN with $(\text{TBA})(\text{PF}_6)$ as supporting electrolyte): -2181 mV (irr.), -2387 mV (irr.). Anal. Calcd for $\text{C}_{69}\text{H}_{54}\text{N}_8\text{O}_9\text{F}_9\text{S}_3\text{Ag}$: C, 54.73; H, 3.59; N, 7.40. Found: C, 53.86; H, 3.58; N, 7.61.

Synthesis of $\{(\text{Me},\text{EtTC}^{Ph})\text{Ag}\}_2\text{Ag}_2(\text{OTf})_4$ (3a**).** $(\text{Me},\text{EtTC}^{Ph})(\text{OTf})_4$ (0.580 g, 0.373 mmol) (**1a**) and silver(I) triflate (0.190 g, 0.742 mmol) were added to a 20 mL vial wrapped in aluminum foil and dissolved in 15 mL of DMSO while stirring and heating to 90 °C. After 10 min., triethylamine (0.165 g, 1.63 mmol) was added and allowed to stir for 24 h. The reaction mixture was cooled to rt and brought out of the glovebox. The solution was added to a 200 mL beaker and quenched with 150 mL of water to yield a white precipitate. A white powder was collected on a 60 mL fine sintered glass frit. The product was dried by dissolving the white powder in methylene chloride (100 mL) followed by addition of anhydrous MgSO_4 , and filtration over a 60 mL medium sintered glass frit to remove the MgSO_4 . Volatiles were removed under reduced pressure to yield the pure white powder product (0.534 g, 95% yield). Single crystals suitable for single crystal X-ray diffraction can be grown by layering an acetone solution of **3a** with water to give colorless needles. ^1H NMR (CD_3CN , 499.74 MHz): δ 7.64 (t, $J = 7.0$ Hz, 4H), 7.57 (t, $J = 7.0$ Hz, 8H), 7.47 (t, $J = 7.5$ Hz, 4H), 7.40 (t, $J = 7.0$ Hz, 4H), 7.36 (t, $J = 7.5$ Hz, 4H), 7.25 (t, $J = 7.5$ Hz, 8H), 7.19 (m, 16H), 7.08 (s, 8H), 6.97 (d, $J = 8.0$ Hz, 8H), 6.79 (m, 12H), 6.13 (m, 8H), 6.03 (d, $J = 15.0$ Hz, 4H), 5.14 (m, 4H), 4.94 (m, 4H), 4.41 (t, $J = 13.0$ Hz, 4H), 4.06 (d, $J = 14.0$ Hz, 4H). ^{13}C NMR (CD_3CN , 125.66 MHz): δ 183.18 ($^1J_{Ag-C}^{109} = 199.9$ Hz, $^1J_{Ag-C}^{107} = 168.5$ Hz), 176.96 ($^1J_{Ag-C}^{109} = 217.5$ Hz, $^1J_{Ag-C}^{107} = 189.8$ Hz), 136.92 (d, $J_{Ag-C} = 5.0$ Hz), 135.74 (d, $J_{Ag-C} = 5.0$ Hz), 135.21 (d, $J_{Ag-C} = 5.0$ Hz), 133.82 (d, $J_{Ag-C} = 5.0$ Hz), 132.15, 131.90, 131.86, 131.64, 131.62, 131.37, 131.29, 131.05, 130.53, 130.18, 130.05, 127.00, 126.42, 125.63, 125.55, 121.96 (q, $J_{F-C} = 320.4$ Hz), 61.90, 51.12, 49.11. ^{19}F NMR (CD_3CN , 470.39 MHz): δ -78.62. IR (neat): 2950, 2917, 2868, 2837, 1487, 1457, 1376, 1258, 1222, 1157, 1076, 1026, 973, 840, 763, 698

cm^{-1} . ESI/MS (m/z): $[\text{M}-2\text{OTf}]^{2+}$ 1321.10, $[\text{M}-3\text{OTf}]^{3+}$ 831.08, $[\text{M}-4\text{OTf}]^{4+}$ 586.07. Electrochemistry (vs. ferrocene in CH_3CN with $(\text{TBA})(\text{PF}_6)$ as supporting electrolyte): -1880 mV (rev.), -2490 mV (rev.). Anal. Calcd for $\text{C}_{136}\text{H}_{104}\text{N}_{16}\text{O}_{12}\text{F}_{12}\text{S}_4\text{Ag}_4$: C, 55.44; H, 3.69; N, 7.61. Found: C, 54.86; H, 3.89; N, 7.62.

Synthesis of $[\{(\text{Me},\text{EtTC}^{\text{Ph}})\text{Ag}\}_2\text{Ag}_2](\text{PF}_6)_4$ (3b**).** $(\text{Me},\text{EtTC}^{\text{Ph}})(\text{PF}_6)_4$ (1.455 g, 0.944 mmol) (**1b**) and silver(I) hexafluorophosphate (0.477 g, 1.89 mmol) were added to a 20 mL vial wrapped in aluminum foil and dissolved in 15 mL of DMSO while stirring and heating to 90 °C. After 10 min, triethylamine (0.477 g, 4.72 mmol) was added and allowed to stir for 48 h. The reaction mixture was cooled to rt and brought out of the glovebox. The solution was added to a 200 mL beaker and quenched with 150 mL of water to yield a white precipitate. The white powder was collected on a 60 mL fine sintered glass frit. The powder was then purified by dissolving in (40 mL) acetone in the sintered frit, filtering, and triturating with excess water (200 mL). The resulting fine powder was collected on a 60 mL fine sintered glass frit which yielded the pure white powder product (1.238 g, 90% yield). Single crystals suitable for X-ray diffraction can be grown by layering an acetone solution of **3b** with water to give colorless needles. ^1H NMR (CD_3CN , 499.74 MHz): δ 7.65 (t, $J = 7.5$ Hz, 4H), 7.58 (t, $J = 6.5$ Hz, 4H), 7.48 (t, $J = 8.0$ Hz, 8H), 7.41 (t, $J = 7.5$ Hz, 4H), 7.36 (t, $J = 8.0$ Hz, 4H), 7.26 (t, $J = 8.0$ Hz, 8H), 7.19 (m, 16H), 7.09 (s, 8H), 6.96 (d, $J = 7.0$ Hz, 8H), 6.79 (s, 8H), 6.62 (d, $J = 14.5$ Hz, 4H), 6.10 (d, $J = 7.5$ Hz, 8H), 6.02 (d, $J = 13.5$ Hz, 4H), 5.05 (td, $J_1 = 13.5$ Hz, $J_2 = 3.5$ Hz, 4H), 4.82 (dd, $J_1 = 15.5$ Hz, $J_2 = 2.0$ Hz, 4H), 4.44 (m, 4H), 4.03 (d, $J = 14.0$ Hz, 4H). ^{13}C NMR (CD_3CN , 125.66 MHz): δ 182.83 ($J^{109}_{\text{Ag-C}} = 214.9$ Hz, $J^{107}_{\text{Ag-C}} = 181.0$ Hz), 176.85 ($J^{109}_{\text{Ag-C}} = 218.7$ Hz, $J^{107}_{\text{Ag-C}} = 188.5$ Hz), 137.00 (d, $J_{\text{Ag-C}} = 5.8$ Hz), 135.91 (d, $J_{\text{Ag-C}} = 5.3$ Hz), 135.21 (d, $J_{\text{Ag-C}} = 5.3$ Hz), 133.95 (d, $J_{\text{Ag-C}} = 5.0$ Hz), 132.25, 131.99, 131.81, 131.71, 131.62, 131.47, 131.28, 131.11, 130.55, 130.20, 130.09, 126.91, 126.30, 125.53, 125.48, 61.85, 51.06, 49.16. ^{19}F NMR (CD_3CN , 470.39 MHz): δ -72.81 (d, $J = 705.6$ Hz). IR (neat): 2950, 2917, 2868, 2837, 1709, 1488, 1447, 1376, 1359, 1321, 1261, 1221, 1168, 1074, 1019, 827, 761, 739, 696 cm^{-1} . ESI/MS (m/z): $[\text{M}-2\text{PF}_6]^{2+}$ 1317.70, $[\text{M}-3\text{PF}_6]^{3+}$ 829.82, $[\text{M}-4\text{PF}_6]^{4+}$ 586.37. Electrochemistry (vs. ferrocene in CH_3CN with $(\text{TBA})(\text{PF}_6)$ as supporting electrolyte): -1848 mV (rev.), -2005 mV (rev.). Anal. Calcd for $\text{C}_{132}\text{H}_{104}\text{N}_{16}\text{F}_{24}\text{P}_4\text{Ag}_4$: C, 54.19; H, 3.58; N, 7.66. Found: C, 53.20; H, 3.83; N, 7.59.

General Transmetallation Reaction. $[\{({}^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Ag}\}_2\text{Ag}_2](\text{X})_4$ (**3**) and the corresponding metal salt was added to a 20 mL vial followed by 4 mL of methylene chloride and 4 mL of tetrahydrofuran. The reaction mixture was stirred and heated at the designated temperature overnight. After allowing the reaction to cool to rt the silver halide was filtered away over Celite (except $[\{({}^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Ru}(\text{DMSO})_2\}(\text{OTf})_2$ (**6**)). The remainder of the work-up for each complex is described separately below.

Synthesis of $[\{({}^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Pt}\}(\text{OTf})_2$ (4**).** The general transmetallation reaction was followed using dichlorobis(benzonitrile)platinum(II) (0.0170 g, 0.0360 mmol) and **3a** (0.0500 g, 0.0170 mmol) at rt. The volatiles were removed from the resulting solution under reduced pressure to yield the pure white powder (0.0460 g, 93% yield). Crystals suitable for single crystal X-ray diffraction were obtained by vapor diffusing pentane into a solution of **4** in methylene chloride. ^1H NMR (CD_3CN , 499.74 MHz): δ 7.43 (m, 12H), 7.35 (m, 12H), 7.22 (t, $J = 8.0$ Hz, 8H), 7.12 (d, $J = 7.0$ Hz, 8H), 5.98 (d, $J = 14.0$ Hz, 2H), 5.78 (d, $J = 13.5$ Hz, 2H), 4.74 (dd, $J_1 = 15.0$ Hz, $J_2 = 8.0$ Hz, 4H), 4.33 (dd, $J_1 = 15.0$ Hz, $J_2 = 8.0$ Hz, 4H). ^{13}C NMR (125.66 MHz, CD_3CN): δ 161.28 (s and Pt satellites, $J^{195}_{\text{Pt-C}} = 951.2$ Hz), 133.45, 132.27, 131.49, 130.92, 130.77, 129.94, 129.91, 127.55, 126.90, 122.11 (q, $J_{\text{F-C}} = 320.4$ Hz), 118.28, 59.26, 48.01. ^{19}F NMR (470.385 MHz, CD_3CN): δ -79.24. IR (neat) 3058, 2954, 1577, 1488, 1445, 1404, 1335, 1259, 1223, 1149, 1076, 1029, 925, 839, 764, 698 cm^{-1} . ESI/MS (m/z): $[\text{M-OTf}]^+$ 1301.38, $[\text{M-2OTf}]^{2+}$ 576.22; UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ): 323 (21000). Anal. Calcd for $\text{C}_{69}\text{H}_{54}\text{N}_8\text{O}_6\text{F}_6\text{Cl}_2\text{S}_2\text{Pt}$ (**4**· CH_2Cl_2): C, 53.98; H, 3.55; N, 7.30. Found: C, 54.86; H, 3.46; N, 7.65.

Synthesis of $[\{({}^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Pd}\}(\text{OTf})_2$ (5**).** The general transmetallation reaction was followed using palladium(II) iodide (0.0125 g, 0.0347 mmol) and **3a** (0.0500 g, 0.0170 mmol) at rt. The volatiles were removed from the resulting solution under reduced pressure to yield the pure white powder (0.0260 g, 70% yield). Crystals suitable for single crystal X-ray diffraction were obtained by vapor diffusing pentane into a solution of **5** in methylene chloride. ^1H NMR (CD_3CN , 499.74 MHz): δ 7.44 (m, 12H), 7.35 (m, 12H), 7.22 (t, $J = 8.0$ Hz, 8H), 7.10 (d, $J = 8.0$ Hz, 8H), 6.11 (d, $J = 13.5$ Hz, 2H), 5.68 (d, $J = 13.5$ Hz, 2H), 4.74 (dd, $J_1 = 14.5$ Hz, $J_2 = 8.0$ Hz, 4H), 4.31 (dd, $J_1 = 15.5$ Hz, $J_2 =$

8.0 Hz, 4H). ^{13}C NMR (125.66 MHz, CD_3CN): δ 168.07, 133.50, 132.59, 132.22, 131.44, 130.92, 130.77, 129.93, 127.50, 126.89, 122.13 (q, $J_{\text{F-C}} = 320.4$ Hz), 59.38, 48.26. ^{19}F NMR (470.385 MHz, CD_3CN): δ -79.30. IR (neat) 2916, 1593, 1489, 1444, 1401, 1375, 1332, 1262, 1221, 1145, 1075, 1029, 925, 842, 786, 763, 696 cm^{-1} . ESI/MS (m/z): $[\text{M-OTf}]^+$ 1211.32, $[\text{M-2OTf}]^{2+}$ 530.69; UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ): 278 (42000), 292 (35000). Anal. Calcd for $\text{C}_{68}\text{H}_{52}\text{N}_8\text{O}_6\text{F}_6\text{S}_2\text{Pd}$: C, 59.98; H, 3.85; N, 8.23. Found: C, 59.03; H, 3.79; N, 7.97.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Ni}](\text{OTf})_2$ (6). The general transmetallation reaction was followed using bis(triphenylphosphine)nickel(II)chloride (0.0267 g, 0.0410 mmol) and **3a** (0.0460 g, 0.0157 mmol) at rt. The volatiles were removed from the resulting solution under reduced pressure and to the remaining solids methanol was added (2 mL). The resulting mixture was filtered over Celite and the methanol was removed under reduced pressure to yield the product as a yellow powder (0.0467 g, 87% yield). Crystals suitable for single crystal X-ray diffraction were obtained by vapor diffusing pentane into a solution of **6** in methylene chloride. ^1H NMR (CD_3CN , 499.74 MHz): δ 7.43 (m, 12H), 7.35 (t, $J = 7.5$ Hz, 4H), 7.31 (d, $J = 6.5$ Hz, 8H), 7.23 (d, $J = 8.0$ Hz, 8H), 7.08 (d, $J = 7.5$ Hz, 8H), 6.34 (d, $J = 13.0$ Hz, 2H), 5.79 (d, $J = 13.5$ Hz, 2H), 4.85 (dd, $J_1 = 15.5$ Hz, $J_2 = 8.0$ Hz, 4H), 4.21 (dd, $J_1 = 15.0$ Hz, $J_2 = 8.0$ Hz, 4H). ^{13}C NMR (125.66 MHz, CD_3CN): δ 170.69, 133.47, 133.07, 132.05, 131.27, 130.89, 130.72, 129.98, 129.93, 127.51, 127.00, 122.00 (q, $J_{\text{F-C}} = 321.7$ Hz), 58.60, 47.42. ^{19}F NMR (470.385 MHz, CD_3CN): δ -73.96. IR (neat) 3057, 1593, 1489, 1460, 1399, 1366, 1342, 1326, 1263, 1221, 1180, 1144, 1075, 1028, 925, 862, 844, 788, 763, 735, 697 cm^{-1} . ESI/MS (m/z): $[\text{M-OTf}]^+$ 1163.32, $[\text{M-2OTf}]^{2+}$ 507.19; UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ): 344 (25000). Anal. Calcd for $\text{C}_{68}\text{H}_{52}\text{N}_8\text{O}_6\text{F}_6\text{S}_2\text{Ni}$: C, 62.16; H, 3.99; N, 8.53. Found: C, 61.76; H, 3.86; N, 8.16.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Rh}(\text{I})_2](\text{PF}_6)$ (7). The general transmetallation reaction was followed using rhodium(III) iodide (0.0146 g, 0.0301 mmol) and **3b** (0.0441 g, 0.0151 mmol) in THF (5 mL) and DMSO (1 mL) and was heated to 60 °C. The volatiles were removed from the resulting solution under reduced pressure to yield the pure red powder (0.0315 g, 72% yield). Crystals suitable for single crystal X-ray diffraction were

obtained by layering water into a solution of **7** in acetonitrile to yield red plates. ^1H NMR (CD_3CN , 599.77 MHz): δ 7.43 (m, 10H), 7.37 (m, 10H), 7.29 (t, $J = 7.8$ Hz, 4H), 7.22 (d, $J = 7.2$ Hz, 6H), 7.17 (t, $J = 7.8$ Hz, 6H), 7.09 (d, $J = 7.8$ Hz, 4H), 6.40 (s, 4H), 4.58 (s, 8H). ^{13}C NMR (150.83 MHz, CD_3CN): δ 167.37 ($J_{\text{Rh-C}} = 33.2$ Hz), 135.09, 132.31, 132.12, 131.75, 130.44, 129.79, 129.74, 128.38, 127.33, 50.57, 41.37. ^{19}F NMR (470.39 MHz, CD_3CN): δ -72.74 (d, $J = 705.6$ Hz). IR (neat) 3053, 2923, 2853, 1979, 1557, 1489, 1445, 1402, 1367, 1228, 1182, 1076, 1017, 833, 766, 740, 697 cm^{-1} . ESI/MS (m/z): $[\text{M-PF}_6]^+$ 1313.10, $[\text{M-2I-PF}_6]^{3+}$ 353.12; UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ): 463 (740). Anal. Calcd for $\text{C}_{66}\text{H}_{52}\text{N}_8\text{I}_2\text{PF}_6\text{Rh}$: C, 54.34; H, 3.59; N, 7.68. Found: C, 53.23; H, 4.07; N, 7.31.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Co}(\text{OTf})](\text{OTf})$ (8**).** The general transmetallation reaction was followed using cobalt(II) chloride (0.0060 g, 0.046 mmol) and **3a** (0.0660 g, 0.0200 mmol) at room temperature. The volatiles were removed from the resulting solution under reduced pressure and the remaining solids were dissolved into methylene chloride (2 mL). Purification was achieved by vapor diffusing pentane into this methylene chloride solution to yield light pink crystals that were suitable for single crystal X-ray diffraction (0.0400 g, 68% yield). ^{19}F NMR (470.39 MHz, CD_3CN): δ -78.46 (s), -121.26 (br). Evans' method (CDCl_3): 1.8 μB . IR (neat) 3056, 2924, 1603, 1594, 1488, 1444, 1388, 1341, 1325, 1275, 1247, 1223, 1150, 1074, 1027, 958, 923, 861, 845, 787, 763, 731, 697 cm^{-1} . UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ): 376 (17000). ESI/MS (m/z): $[\text{M-OTf}]^+$ 1164.26, $[\text{M-2OTf}]^{2+}$ 507.68. Electrochemistry (vs. ferrocene in CH_3CN with (TBA)(PF_6) as supporting electrolyte): -1500 mV (rev.). Anal. Calcd for $\text{C}_{69}\text{H}_{54}\text{N}_8\text{O}_6\text{F}_6\text{Cl}_2\text{S}_2\text{Co}$ (**7**· CH_2Cl_2): C, 59.23; H, 3.89; N, 8.01. Found: C, 59.00; H, 3.72; N, 7.96.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Ru}(\text{DMSO})_2](\text{OTf})_2$ (9**).** The general transmetallation reaction was followed using ruthenium(II) chloride tetradimethylsulfoxide (0.0570 g, 0.120 mmol) and **3a** (0.182 g, 0.0610 mmol). The reaction mixture was not filtered over Celite but instead over a 15 mL fine sintered glass frit. The solid was extracted with acetone (3 x 30 mL). The volatiles were removed under reduced pressure to yield white powdery product (0.075 g, 0.050 mmol, 40% yield). Crystals suitable for single crystal

X-ray diffraction can be obtained by slow evaporation of a 50/50 v/v methanol and acetone solution of the **9** to yield colorless plates. ^1H NMR (DMSO- d_6 , 499.74 MHz) δ 7.38 (m, 12H), 7.30 (t, $J = 7.5$ Hz, 4H), 7.25 (m, 8H), 7.16 (m, 16H), 6.28 (d, $J = 14.0$ Hz, 2H), 6.04 (d, $J = 13.5$ Hz, 2H), 4.52 (d, $J = 14.5$ Hz, 4H), 4.42 (d, $J = 14.0$ Hz, 4H). ^{13}C NMR (DMSO- d_6 , 125.66 MHz) δ 180.34, 134.43, 131.72, 130.94, 130.60, 129.44, 129.35, 128.74, 126.84, 125.78, 118.03, 56.55, 50.31. ^{19}F NMR (DMSO- d_6 , 470.39 MHz): δ -77.76. IR (neat) 3055, 2953, 1594, 1576, 1501, 1488, 1445, 1405, 1376, 1354, 1327, 1256, 1223, 1181, 1151, 1075, 1029, 925, 859, 839, 763, 697 cm^{-1} . ESI/MS (m/z): $[\text{M-OTf-DMSO}]^+$ 1285.15, $[\text{M-2OTf}]^{2+}$ 607.11, $[\text{M-2OTf-DMSO}]^{2+}$ 568.11, $[\text{M-2OTf-2DMSO}]^{2+}$ 529.11. Electrochemistry (vs. ferrocene in DMSO with (TBA)(PF₆) as supporting electrolyte): +687 mV (irr.). Anal. Calcd. for C₇₂H₆₄N₈O₈F₆S₄Ru: C, 57.17; H, 4.26; N, 7.41. Found: C, 57.10; H, 4.54; N, 8.10.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Fe}(\text{NCCH}_3)_2](\text{PF}_6)_2$ (10**).** The general transmetallation reaction was followed using iron(II) iodide (0.0302 g, 0.0974 mmol) and **3b** (0.143 g, 0.0487 mmol) at room temperature. Addition of acetonitrile followed by removal of volatiles under reduced pressure yielded the pure product as a red powder (0.124 g, 92% yield). The product can be crystallized by slow evaporation of diethyl ether into an acetonitrile solution of **10** to afford red crystals.

Synthesis of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{Cr}(\text{Cl})_2](\text{PF}_6)$ (11**).** The general transmetallation reaction was followed using chromium(II) chloride (0.0232 g, 0.0189 mmol) and **3b** (0.111 g, 0.00378 mmol) at room temperature. The product was purified by crystallization via vapor diffusion of diethyl ether into the filtered reaction mixture to afford blue crystals (0.0532 g, 58% Yield). Crystals suitable for X-ray diffraction can be grown by slow evaporation of an acetonitrile solution of **11** to yield blue plates. IR (neat) 2952, 1488, 1446, 1358, 1340, 1314, 1265, 1161, 1059, 1020, 836, 764, 735, 698 cm^{-1} . UV-vis (CH₃CN) λ_{max} , nm (ϵ): 570 (17). ESI/MS (m/z): $[\text{M-PF}_6]^+$ 1078.31, $[\text{M-PF}_6\text{-Cl}]^{2+}$ 521.67, $[\text{M-PF}_6\text{-2Cl}]^{3+}$ 336.12. Electrochemistry (vs. ferrocene in CH₃CN with (TBA)(PF₆) as supporting electrolyte): +1314 mV (irr.), -1995 mV (irr.). Anal. Calcd for C₆₇H₅₄N₈F₆Cl₄PCr (**11**·CH₂Cl₂): C, 61.43; H, 4.15; N, 8.55. Found: C, 61.41; H, 4.20; N, 8.66.

Synthesis of [(^{Me,Et}TC^{Ph})Au](OTf)₃ (12). The general transmetallation reaction was followed using hydrogen tetrachloroaurate(III) trihydrate (0.0283 g, 0.0719 mmol), **3a** (0.1057 g, 0.0330 mmol) and silver triflate (0.0185 g, 0.0720 mmol) at rt. The volatiles were removed from the resulting solution under reduced pressure and the remaining solids were dissolved into methylene chloride (2 mL). Purification was achieved by vapor diffusing pentane into this methylene chloride solution to yield white crystals that were suitable for single crystal X-ray diffraction (0.0540 g, 47% yield). ¹H NMR (CD₃CN, 499.74 MHz): δ 7.45 (m, 4H), 7.39 (m, 20H), 7.23 (t, *J* = 7.5 Hz, 8H), 7.15 (d, *J* = 7.0 Hz, 8H), 6.70 (bs, 2H), 5.92 (d, *J* = 14.0 Hz, 2H), 4.92 (dd, *J*₁ = 16.0 Hz, *J*₂ = 8.5 Hz, 4H), 4.47 (dd, *J*₁ = 15.5 Hz, *J*₂ = 8.0 Hz, 4H). ¹³C NMR (125.66 MHz, CD₃CN): δ 147.97, 135.06, 133.90, 132.29, 131.59, 131.52, 131.43, 130.09, 126.23, 125.55, 121.88 (q, *J*_{F-C} = 320.4 Hz), 59.61, 47.94. ¹⁹F NMR (470.385 MHz, CD₃CN): δ -74.00. IR (neat): 3060, 2258, 1634, 1593, 1576, 1493, 1445, 1427, 1346, 1251, 1223, 1148, 1074, 1027, 926, 842, 787, 765, 724, 697 cm⁻¹. ESI/MS (*m/z*): [M-OTf]⁺ 1451.18, [M-2OTf]²⁺ 652.64, [M-3OTf]³⁺ 385.12. Anal. Calcd for C₆₉H₅₂N₈F₉O₉S₃Au: C, 51.75; H, 3.27; N, 7.00. Found: C, 51.76; H, 3.06; N, 6.82.

Isolation of [(^{Me,Et}TC^{Ph})Ag}(AgCl)₂](OTf) (13). The general transmetallation reaction was followed using ruthenium(II) chloride tetradimethylsulfoxide (0.0096 g, 0.0198 mmol) and **3a** (0.0512 g, 0.0174 mmol). The solvent was then removed under reduced pressure. In one attempt to crystallize **9** by slow evaporation of a 50/50 v/v solution of methanol and acetone, **13** (0.0050 g, 0.0034 mmol) was co-crystallized as colorless block crystals. ¹H NMR (DMSO-*d*₆, 499.74 MHz): δ 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (m, 16H), 7.32 (m, 6H), 7.27 (m, 4H), 7.22 (t, *J* = 8.0 Hz, 4H), 7.04 (d, *J* = 7.0 Hz, 4H), 6.95 (d, *J* = 13.5 Hz, 2H), 6.79 (s, 4H), 5.73 (d, *J* = 13.5 Hz, 2H), 4.63 (dd, *J*₁ = 15.5 Hz, *J*₂ = 7.5 Hz, 2H), 4.31 (dd, *J*₁ = 15.0 Hz, *J*₂ = 6.5 Hz, 2H), 4.23 (dd, *J*₁ = 15.5 Hz, *J*₂ = 7.5 Hz, 2H), 4.16 (dd, *J*₁ = 15.0 Hz, *J*₂ = 6.5 Hz, 2H). ¹⁹F NMR (470.39 MHz, CD₃CN): δ -77.75. IR (neat) 2960, 1489, 1445, 1367, 1261, 1182, 1076, 1017, 830, 764, 739, 697 cm⁻¹. ESI/MS (*m/z*): [M-OTf]⁺ 1351.09, [M-OTf-Cl]²⁺ 658.05, [M-OTf-Cl-AgCl]²⁺ 586.11. Anal. Calcd for C₆₈H₅₄N₈F₃Cl₄O₃SAg₃ (**13**·CH₂Cl₂): C, 51.51; H, 3.43; N, 7.07. Found: C, 51.02; H, 3.67; N, 7.37.

Reaction of **13 and Ru(DMSO)₄Cl₂ to form [(^{Me,Et}TC^{Ph})RuCl(DMSO)](OTf) (**14**).**

Ruthenium(II) chloride tetradimethylsulfoxide (0.0016 g, 0.0034 mmol) and **13** (0.0050 g, 0.0034 mmol) were dissolved in a mixture of 2 mL of methylene chloride and 2 mL of THF. The mixture was stirred and heated at 70 °C for 18 hours. The mixture was filtered over Celite and ESI/MS data confirmed the presence of **14** and **13** was no longer present. ESI/MS (m/z): [M-OTf]⁺ 1171.42, [M-OTf-Cl-DMSO]²⁺ 529.19.

X-ray Structure Determinations. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on glass fibers or mounted on nylon CryoLoops (Hampton Research). Each crystal was frozen under a stream of N₂ while data were collected on a Bruker APEX diffractometer. Initial scans of each specimen were taken to obtain preliminary unit cell parameters and to assess the mosaicity (i.e. breadth of spots between frames) of the crystal to select the required frame width for data collection. For all cases frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker APEX2* software suite to carry out overlapping ϕ and ω scans at detector setting of $2\theta = 28^\circ$. Following data collection, reflections were sampled from all regions of the Ewald sphere to re-determine unit cell parameters for data integration. Following exhaustive review of collected frames the resolution of the dataset was judged, and, if necessary, regions of the frames where no coherent scattering was observed were removed from consideration for data integration using *Bruker SAINTplus* software. Data was integrated using a narrow frame algorithm and were subsequently corrected for absorption. Absorption corrections were performed for both samples using the *SADABS* program. Space group determination and tests for merohedral twinning were carried out using *XPREP*. In all cases, the highest possible space group was chosen.

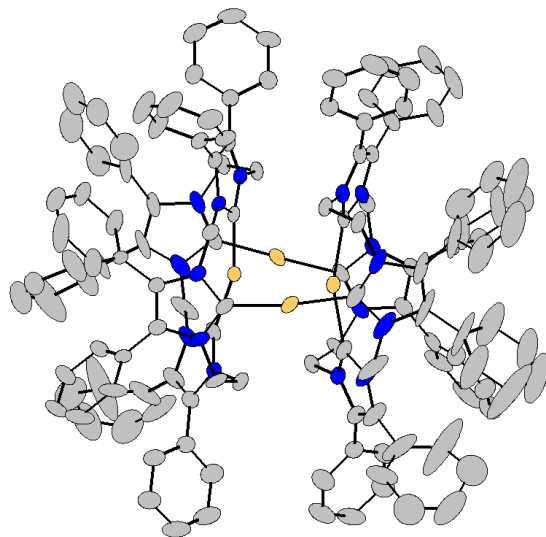


Figure S1. X-ray crystal structure of $[\{(\text{Me},\text{EtTC}^{\text{Ph}})\text{Ag}\}_2\text{Ag}_2](\text{OTf})_4$ (**3a**). Light yellow, blue, and gray ellipsoids (50% probability) represent Ag, N, and C, respectively. Counteranions, solvent molecules and H atoms have been omitted for clarity.

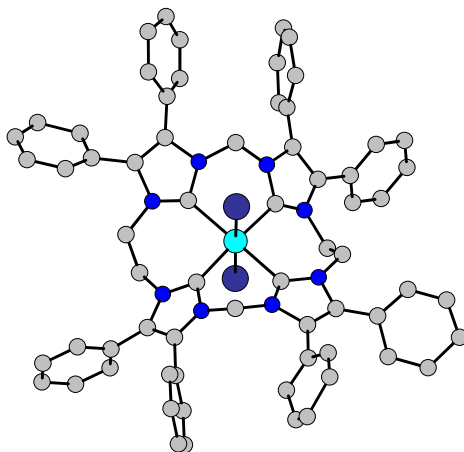


Figure S2. Graphical representation of $[\{(\text{Me},\text{EtTC}^{\text{Ph}})\text{Rh}(\text{I})_2\}]\text{PF}_6$ (**7**) based on X-ray analysis. Light blue, purple, blue, and gray spheres represent Rh, I, N, and C, respectively. Counteranions, solvent molecules and H atoms have been omitted for clarity.

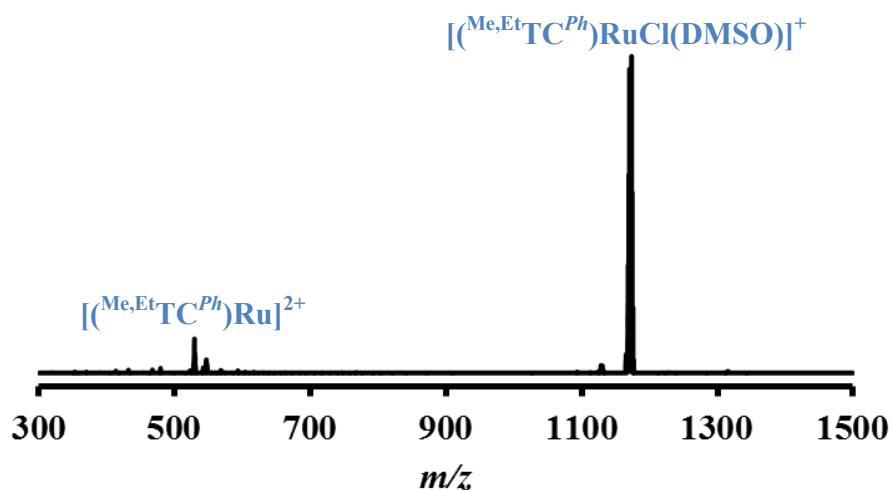


Figure S3. Electrospray ionization mass spectrum measured for an acetonitrile solution of $[(^{\text{Me,Et}}\text{TC}^{\text{Ph}})\text{RuCl}(\text{DMSO})](\text{OTf})$ (**14**).

References

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