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Supporting Information

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“Synthesis and Ligand Exchange Kinetics of the Solvated Trigonal Prismatic Clusters $[W_6CCl_{12}L_6]^{2+}$ (L = DMF, py)”

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Experimental Section

Compounds. Pyridine and pyridine-d_5 were dried by distilling from CaH_2 under N_2 and storing over 3 Å molecular sieves. Anhydrous DMF was purchased from Aldrich and stored over 3 Å molecular sieves. The starting compound $(Bu_4N)_2[W_6CCl_{18}]$ was prepared by the procedure in Ref. 2a. All other compounds were used as received from various chemical suppliers.

$(Bu_4N)_2[W_6CCl_{12}(O_3SCF_3)_6]$ (1). A small three-neck flask was dried at 150 °C for 24 h, fitted with two L-shaped gas-inlet adaptors with Teflon-stopcocks, and then purged with N_2 for 30 min. Powdered $(Bu_4N)_2[W_6CCl_{18}]$ (1.0 g, 0.45 mmol) and neat triflic acid (4.0 mL, 45 mmol) were sequentially added to the flask. The solution quickly turned from dark green to black. After capping the third neck not fitted with an adaptor, the N_2 flow was routed through a KOH trap and oil bubbler and reduced to one bubble per second. The solution was heated at 100 °C for 8 h with vigorous stirring. While still hot, the mixture was dried under increased N_2 flow until the remaining black solid was no longer oily (ca. 1 h). The solid was dissolved in 4 mL of nitromethane and diluted to 100 mL with diethylether. Black distorted-tetrahedron shaped crystals of the product (1.2 g, 91% yield), suitable for X-ray analysis, were formed by cooling the solution at -28 °C for 2 days. UV-visible spectrum (MeCN) λ_{max} (ε_M) 268 (19 100), 304 (10 300), 390 (3040), 455 (2080), 581 (1410), 725 (628) nm. ES$^-$-MS (MeCN): m/z 1218 ($[W_6CCl_{12}(CF_3SO_3)_6]^{2-}$). IR: ν_{SO} 1234, 1189, 1157 cm^{-1}. Anal. Calcd. for $C_{39}H_{72}Cl_{12}F_{18}N_2O_{18}S_6W_6$: C, 16.04; H, 2.49; N, 0.96; S, 6.59. Found: C, 16.33; H, 2.46; N, 0.95; S, 6.94.

$[W_6CCl_{12}(DMF)_6](BF_4)_2\cdot DMF$ (2). Under a dinitrogen atmosphere, a solution of Cp_2Co (13.0 mg, 0.0685 mmol) in 2 mL of DMF was added to a solution of **1** (100 mg, 0.0342 mmol) in 4 mL of DMF, resulting in a color change from green-black to red-brown. In air, the resulting solution was diluted to 50 mL with water. Addition of $(Bu_4N)(BF_4)$ (500 mg, 1.51 mmol) induced formation of a brown precipitate, which was collected by filtration, washed with water (3 × 25 mL), dried in air, and dissolved in 2 mL of DMF. Diffusion of diethylether vapor into the solution afforded black block-shaped crystals of **2**. The supernatant solution was decanted and the crystals were washed with diethylether (3 × 5 mL) and dried in air to yield 63 mg (83%) of product. UV-Vis spectrum (DMF) λ_{max} (ε_M) 422 (3090), 587 (1570), 981 (465) nm. ^{1}H NMR (400 MHz, NO_2Me-d_3, δ): 8.11 (s, 1H, –CHO–), 3.37 (s, 3H, $–CH_3$), 3.22 (s, 3H, $–CH_3$). ES$^+$-MS (MeCN): m/z 990 ($[W_6CCl_{12}(DMF)_6]^{2+}$). IR: ν_{CO} 1639 cm^{-1}. Anal. Calcd. for $C_{22}H_{49}B_2Cl_{12}F_8N_7O_7W_6$: C, 11.87; H, 2.22; N, 4.41. Found: C, 11.85; H, 2.21; N, 4.29.

$[W_6CCl_{12}(py)_6](CF_3SO_3)_2\cdot Py$ (3). Under a dinitrogen atmosphere, compound **1** (300 mg, 0.102 mmol) was heated in 4 mL of pyridine at 90 °C for 3 days, inducing a gradual color change from green-black to brown-black and formation of a small amount of black, crystalline powder. The resulting mixture was slowly concentrated to 1 mL *in vacuo* and cooled to –28 °C for 24 h. The black solid was collected by decanting the brown supernatant, washed with 2 mL of cold pyridine, and dissolved in a minimum amount of hot pyridine (90 °C, ca. 4 mL). The green-black solution was then cooled slowly to room temperature, then to –28 °C for 24 h, affording black rectangular prism-shaped crystals of **3**. The supernatant solution was decanted and the crystals were washed with diethylether (3 × 5 mL) and dried under nitrogen to yield 183 mg (72%) of product. UV-visible spectrum (Py) λ_{max} (ε_{M}) 320 (11 600), 333 (9890), 534 (2420), 615 (2280), 829 (638) nm. ^{1}H NMR (400 MHz, Py-d_5, δ): 8.08 (d, J = 5.2 Hz, 2H, –py), 7.75 (t, J = 7.2 Hz, 2H, –py), 6.85 (t, J = 7.6 Hz, 1H, –py). ES$^+$-MS (MeCN): m/z 1008 ($[W_6CCl_{12}(py)_6]^{2+}$). Anal. Calcd. for $C_{43}H_{40}Cl_{12}F_6N_8O_6S_2W_6$: C, 20.90; H, 1.63; N, 4.54. Found: C, 21.28; H, 1.64; N, 4.23.

Kinetics Measurements. Kinetics measurements were performed on 0.5 mL aliquots of 12.3 mM solutions of **3** in pyridine-d_5 containing a few crystals of hexamethylbenzene as an internal standard. The solutions were flame-sealed in dry NMR tubes under vacuum. The low solubility **3** prevented utilizing the variable temperature capabilities of the NMR instrument, as the compound crystallizes above the solvent level during the experiments. Heating cycles were performed by completely immersing the tube in a temperature-controlled oil bath, followed by immersing the tube in ice-water to stop the reaction. The data were fit to exponential decay models and the estimated rates were as follows: 30 °C ($k = 2.7 \times 10^{-5}$ s^{-1}), 40 °C ($k = 1.2 \times 10^{-4}$ s^{-1}), 50 °C ($k = 4.4 \times 10^{-4}$ s^{-1}), 60 °C ($k = 1.4 \times 10^{-3}$ s^{-1}). Water was rigorously excluded since even trace water inhibits the reaction. Results were verified by performing a kinetics measurement at 40 °C using dimethylzirconocene as an internal desiccant ($k = 1.0 \times 10^{-4}$ s^{-1}).[S1] Unfortunately, $Cp_2Ze(CH_3)_2$ was not stable under the reaction conditions at higher temperatures. Activation parameters were calculated using the kinetics data and the Eyring equation: $\Delta S^{\ddagger} = 6.0 \pm 1.7$ cal K^{-1} mol^{-1} and $\Delta H^{\ddagger} = 25.9 \pm 0.5$ kcal mol^{-1}.

Additional Crystallographic Details. Single crystals of compounds **1**, **2**, and **3** were coated with Paratone-N oil and mounted on Kapton loops. The crystals were then quickly transferred to a Siemens SMART diffractometer and cooled in a stream of nitrogen gas. A full hemisphere of data was collected for all compounds. Data were integrated and corrected for Lorentz and polarization effects using SAINT 7.07b and were corrected for absorption effects using SADABS 2.10. Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods and expanded through successive difference Fourier maps. They were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for the central carbon atom of **1** and **3** refined NPD if anisotropic and were modeled best as isotropic. One of the three distinct triflate ligands of **1** was disordered over two sites that share one oxygen and two fluorine atoms. The shared C, O, and F atoms were refined isotropically. The DMF solvate molecule of **2** was extensively disordered. A vacancy large enough to contain a single DMF molecule is evident from the structure. The only peak of significant

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[S1] D. A. Dobbs, R. G. Bergman, *Organometallics* **1994,** *13*, 4594.

electron density residing in the center of this vacancy was modeled as an isotropic nitrogen atom. All other thermal parameters were refined anisotropically. In all structures, hydrogen atoms were inserted at idealized positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens).

Other Physical Measurements. UV-visible absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer, and infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory. Mass spectrometric measurements were performed on a Micromass Quattro triple quadrapole mass spectrometer equipped with an electrospray ionization source. NMR spectra were recorded on a Bruker AV-400 MHz instrument and peaks were referenced to residual solvent peaks. Electrochemical measurements were conducted with a Bioanalytical Systems CV-50 potentiostat with platinum-disk working, platinum-wire auxiliary, and silver-wire reference electrodes. Samples were measured at a scan rate of 100 mV/s (unless otherwise noted) in a supporting electrolyte of 0.1 M $(Bu_4N)(PF_6)$ in DMF. Ferrocene was added after each measurement as an internal reference.

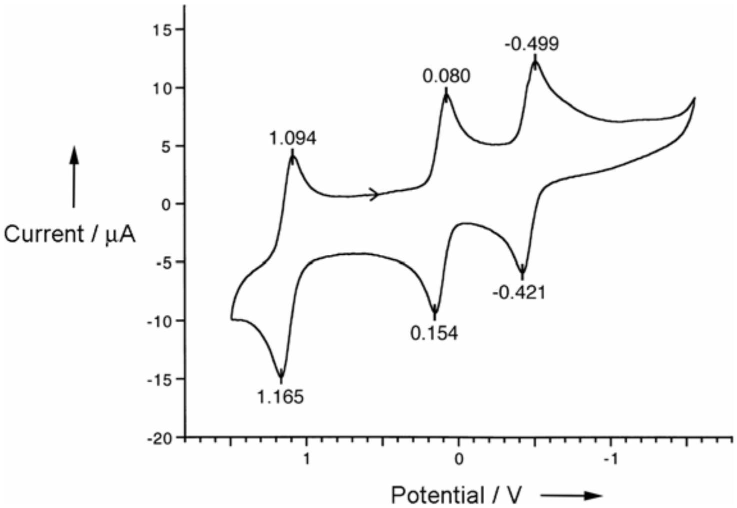

Figure S1. Cyclic voltammogram of **1** in nitromethane.

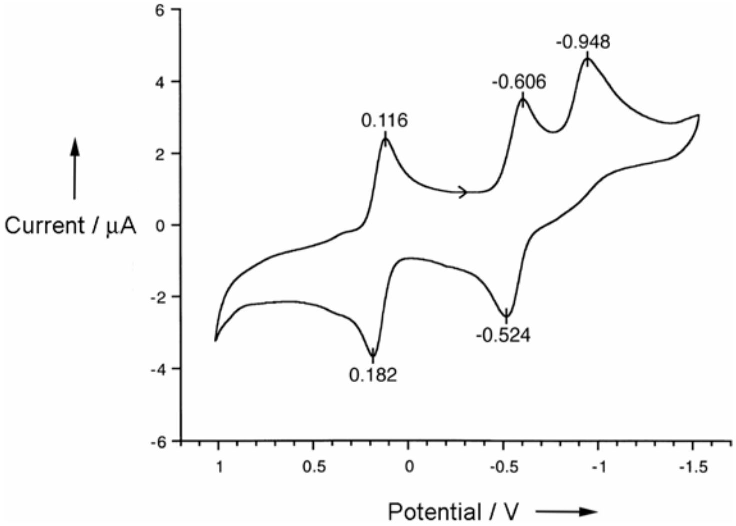

Figure S2. Cyclic voltammogram of **1** in DMF.

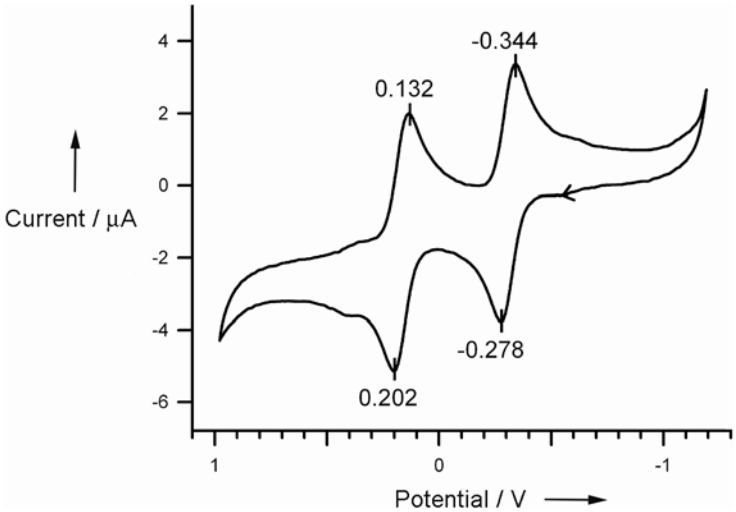

Figure S3. Cyclic voltammogram of **2** in DMF.

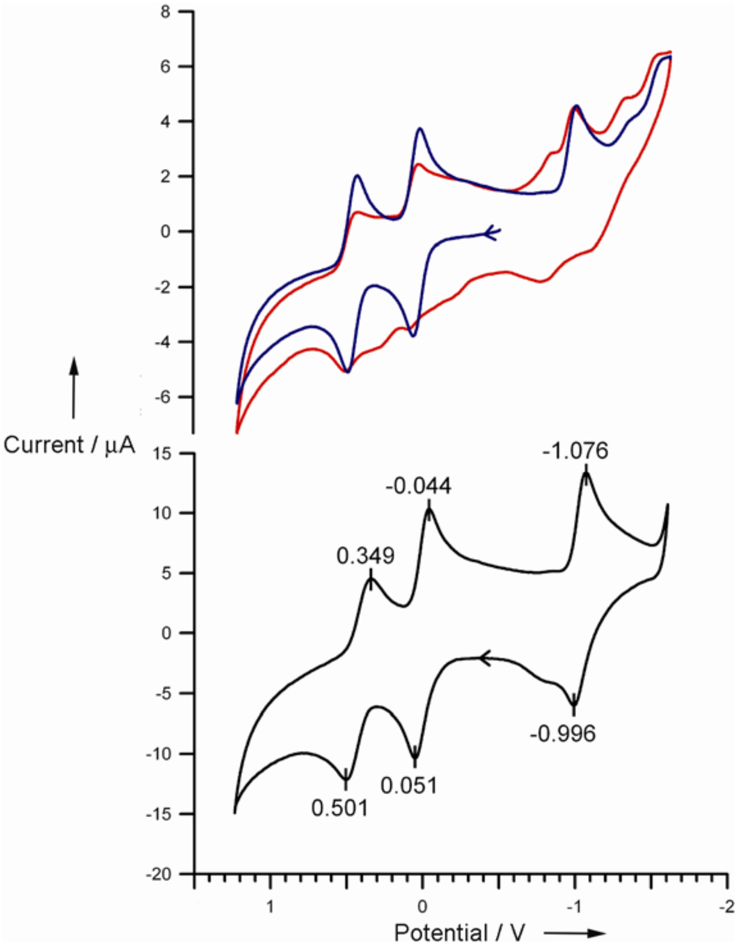

Figure S4. Cyclic voltammograms of **3** in DMF. Top: Scan rate = 100 mV/s, blue = first cycle, red = second cycle. Bottom: Scan rate = 700 mV/s.

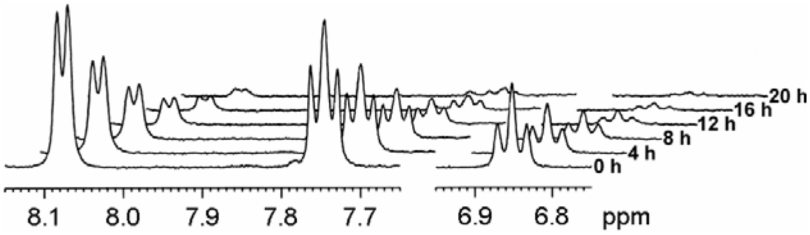

Figure S5. NMR spectra of **3** in Py-d_5 at 4 h time intervals at 30 °C.