

Supplementary Material

Anodic Properties of Diarylethene Derivatives Having Organometallic Piano-Stool Tags

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Experimental

Materials. Compounds **4**¹³, **5**¹⁵, and **6**¹³ have been described in the literature.

Synthesis of Mn(CO)₃(η⁵-C₅H₄)(Et)C=C(C₆H₅)₂, **3.** TiCl₄ (1.14 g, 6 mmol) was added dropwise to a suspension of zinc powder (0.784 g, 12 mmol) in THF (20 mL) at 0 °C. The blue mixture obtained was heated at reflux for 2 h, whereupon the solution became black. The oil bath was removed. A second solution was prepared by dissolving benzophenone (0.728 g, 4 mmol) and propionylcymantrene (0.520 g, 2 mmol) in THF (10 mL). The latter solution was added dropwise to the first solution, and the resulting mixture was then heated for 4 h. After it was cooled to room temperature, the mixture was poured into 100 mL water and acidified to pH 1 with diluted aqueous HCl solution. After CH₂Cl₂ extraction (3x50 mL), washing with water (50 mL) and solvent removal, the crude product (1.17 g) was chromatographed on a silica gel column with 1:50 ethyl ether/petroleum ether as eluent to give the final compound (0.380 g, 46% yield).

Recrystallization from ethyl ether/pentane furnished yellow crystals, mp 102 °C. ¹H NMR (300 MHz, CD₃COCD₃): δ 7.39-7.17 (m, 10H, aromatic rings), 4.77 (t, *J* = 2.1 Hz, 2H, C₅H₄), 4.62 (t, *J* = 2.1 Hz, 2H, C₅H₄), 2.31 (q, 2H, *J* = 7.5 Hz, CH₂CH₃), 1.08 (t, 3H, *J* = 7.5 Hz, CH₂CH₃). ¹³C NMR (75.5 MHz, CD₃COCD₃): δ 15.4 (CH₃), 28.5 (CH₂), 82.8 and 85.7 (CH, C₅H₄), 105.1 (C_{ip}, C₅H₄), 127.7, 127.9, 129.3, 129.4, 129.5 and 130.1 (CH_{arom}), 132.9, 143.7, 144.2 and 144.4 (C_q of 2 C₆H₄ and C=C). IR (CH₂Cl₂) ν_{CO} 2017, 1932 cm⁻¹. MS (CI) : 410 [MH]⁺, 426 [M -3CO]⁺. Anal. Calcd for C₂₄H₁₉O₃Mn: C, 70.25, H, 4.67. Found: C, 69.75, H, 4.55.

Electrochemistry. Voltammetry and electrolysis experiments were carried out in a Vacuum Atmospheres drybox under nitrogen, using a Princeton Applied Research (PAR) Model 273A potentiostat interfaced to a personal computer. IR spectroelectrochemistry was conducted under Schlenk-type argon conditions using a fiber-optic IR 'dip' probe hooked up to an ATI-Mattson Infinity Series FTIR employing Winfirst software at a resolution of 4 cm⁻¹. Three-compartment

H-cells were used for the electrochemistry experiments, using 1 mm glassy carbon disks (Bioanalytical Systems) or platinum gauze for the working electrode and platinum as the auxiliary electrode. The disks were pretreated using a standard sequence of polishing with diamond paste (Buehler) of decreasing sizes (3 to 0.25 μm) interspersed by washings with nanopure water and finally vacuum drying. The reference electrode was a homemade Ag/AgCl electrode prepared by electrolytic deposition of AgCl onto a silver wire. However, all potentials are reported versus the $\text{FeCp}_2^{0/+}$ redox couple, the potential of which was obtained by using FeCp_2 as an internal standard. EPR spectra were recorded using a Bruker ESP 300E spectrometer.

Electrochemical “Switch” Preparation of $\text{Mn}(\text{CO})_2\text{P}(\text{OPh})_3(\eta^5\text{-C}_5\text{H}_4)(\text{Et})\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$.

In-situ scale. Operating at low room light levels, anodic electrolysis of a solution containing 1.0 mM $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4)(\text{Et})\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ (**3**) and 1.5 mM $\text{P}(\text{OPh})_3$ was carried out at a Pt basket in $\text{CH}_2\text{Cl}_2/0.05 \text{ M} [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ at 1.0 V vs ferrocene at room temperature under nitrogen. After about 30 min, 1.0 F had been passed and the color of the solution had gone from pale yellow to pink. A negative-going CV scan originating at $E_{\text{appl}} = 1.0 \text{ V}$ showed that the neutral starting material had been converted essentially quantitatively to cationic $[\text{Mn}(\text{CO})_2\text{P}(\text{OPh})_3(\eta^5\text{-C}_5\text{H}_4)(\text{Et})\text{C}=\text{C}(\text{C}_6\text{H}_5)_2]^+$ (see red curve in following figure). When the applied potential was reset to 0.1 V, reduction of the substituted product occurred, passing about 0.85 F. The resulting CV (green curve in the figure) showed that the neutral substitution product $\text{Mn}(\text{CO})_2\text{P}(\text{OPh})_3(\eta^5\text{-C}_5\text{H}_4)(\text{Et})\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ was the only electroactive compound in solution.

Preparative scale. A solution of the same electrolyte was prepared containing 3 mM $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4)(\text{Et})\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ (**3**) (40 mg) and 4.5 mM $\text{P}(\text{OPh})_3$ in a divided H-cell. After completing the “forward” and “backward” electrolyses as described above, the working compartment solution was transferred to a round-bottom flask and evaporated while being protected from excess light. A pentane extract of the product was evaporated to dryness. The yellow solid was spotted on an alumina column by dichloromethane and eluted with diethyl ether, trailing the unreacted phosphite as a yellow band. Evaporation gave a yellow powder (40%, un-optimized yield) identified by its IR spectrum ($\nu_{\text{CO}} = 1956, 1893 \text{ cm}^{-1}$) in CH_2Cl_2 .

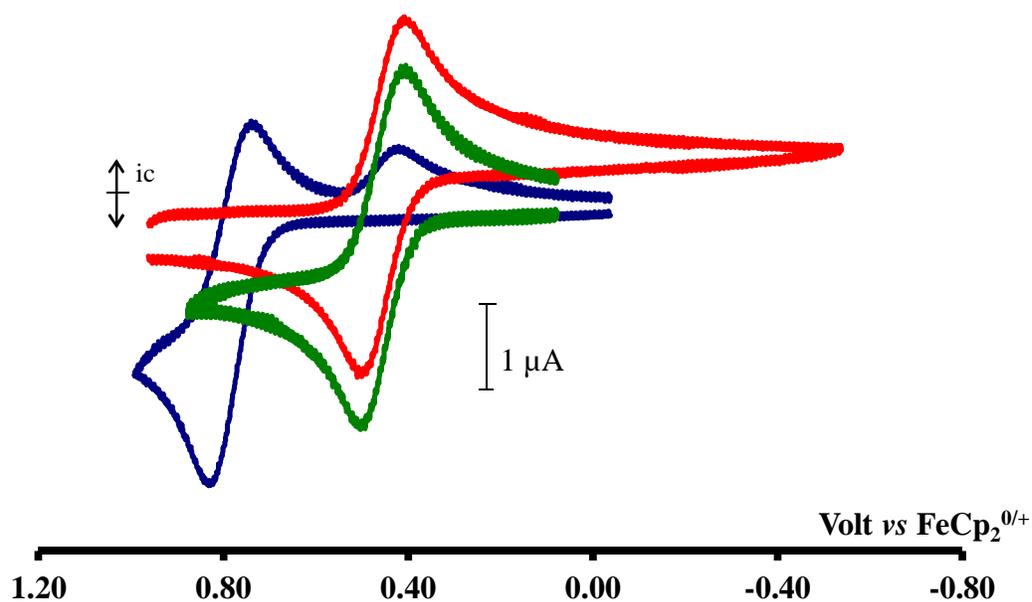


Figure S1. Cyclic voltammograms (200 mV s^{-1}) at glassy carbon electrode: (a) Blue: before electrolysis of solution that was 1 mM solution in **3** and 1.5 mM in $\text{P}(\text{OPh})_3$ (b) Red: after bulk anodic electrolysis at $E_{\text{appl}} = 1.0 \text{ V}$ (c) Green: after cathodic re-electrolysis at $E_{\text{appl}} = 0.1 \text{ V}$. Each CV scan was initiated at a rest potential of the cell: -0.1 V for (a), 1.0 V for (b), and 0.1 V for (c).

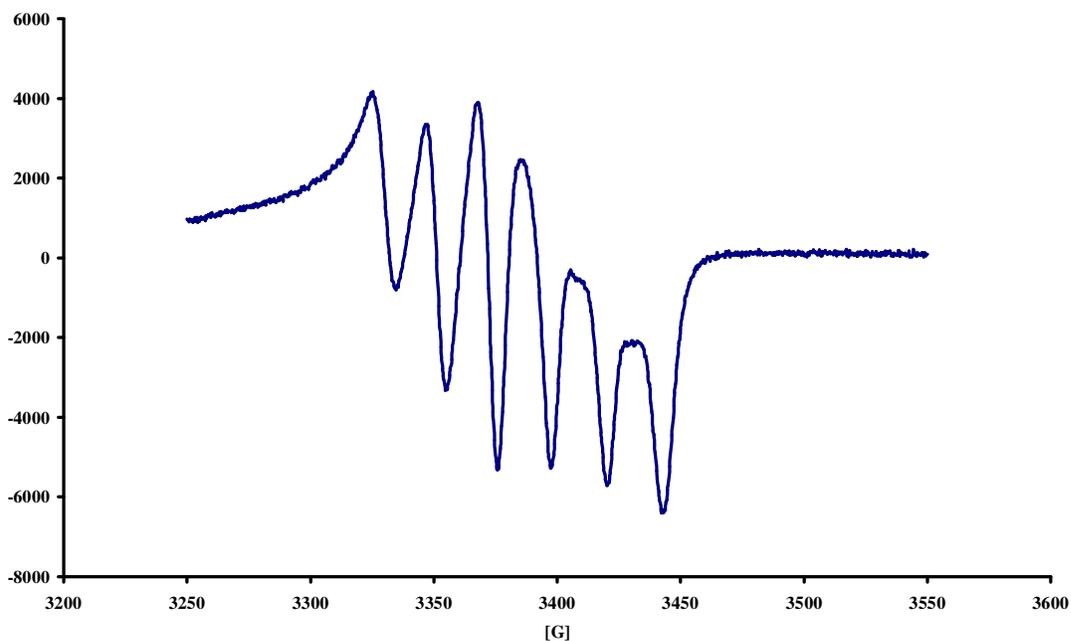


Figure S2. EPR spectrum of 3^+ at 77 K. Sample was prepared by one-electron electrolysis of 1.5 mM **3** in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ at 253 K. The spectrum is indicative of a radical having very small differences in the three principal g -values and ^{57}Mn ($I = 5/2$) hyperfine splittings.