

Supporting Information:

Redox-Regulated Ethylene Binding to a Rhenium-Thiolate Complex

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Crystallographic Studies

A long, thin orange plate $0.41 \times 0.06 \times 0.01 \text{ mm}^3$ crystal of $[\mathbf{2}_{\text{ox2}}][\text{PF}_6]_2$ was mounted on a 0.05 mm CryoLoop with Paratone oil for collection of x-ray data on a Bruker SMART APEX CCD diffractometer. The SMART^[1] software package (v 5.632) was used to acquire a total of 1,868 thirty-second frame ω -scan exposures of data at 100K to a $2\theta \text{ max} = 50.54^\circ$ using monochromated $\text{MoK}\alpha$ radiation ($0.71073 \text{ \AA}$) from a sealed tube and a monocapillary. Frame data were processed using SAINT^[2] (v 6.45) to determine final unit cell parameters: $a = 29.009(18) \text{ \AA}$; $b = 22.577(18) \text{ \AA}$; $c = 43.99(3) \text{ \AA}$; $\beta = 96.182(17)^\circ$; $V = 28,643(35) \text{ \AA}^3$; $D_{\text{calc}} = 1.413 \text{ Mg/m}^3$, $Z = 8$ to produce raw hkl data that were then corrected for absorption (transmission min./max. = $0.81/0.94$; $\mu = 2.009 \text{ mm}^{-1}$) using SADABS^[3] (v 2.10). The structure was solved by Patterson methods in the space group $C 2/c$ using SHELXS-90^[4] and refined by least squares methods on F^2 using SHELXL-97^[5] incorporated into the SHELXTL^[6] (v 6.14) suite of programs. The asymmetric unit of $[\mathbf{2}_{\text{ox2}}][\text{PF}_6]_2$ contains two crystallographically independent cation molecules. All non-hydrogen atoms in both cations, as well as the hexafluorophosphate anions were refined with anisotropic atomic displacement parameters. The structural model has one full occupancy and three partial occupancy chlorobenzene solvate molecules. Disorder in the full occupancy solvate was modeled using a full occupancy chlorine atom, Cl4, and two, 50% occupancy groups of carbon atoms, C150–C155, (the second group of atoms being generated by symmetry). A second disordered chlorobenzene was modeled with two 25% occupancy chlorine atoms (Cl3a and Cl3b) and half-occupancy carbon atoms C140–C145. All non-hydrogen atoms in the chlorobenzene solvates were refined isotropically. $[\mathbf{2}_{\text{ox2}}][\text{PF}_6]_2$ also crystallizes with highly disordered partial occupancy chlorobenzene molecules of solvation for which suitable models could not be obtained during refinement and these contributions were subtracted from the data using the program SQUEEZE.^[7] Hydrogen atoms were placed in their geometrically generated positions and refined as a riding model. Methylene and phenyl H's were included as fixed contributions with $U(\text{H}) = 1.2 \times U_{\text{eq}}$ (attached C atom). For all 25,546 unique reflections ($R(\text{int}) = 0.073$) the final anisotropic full matrix least-squares refinement on F^2 for 1,282 variables converged at $R1 = 0.125$ and $wR2 = 0.184$ with a GOF of 1.09. CCDC#699464

Electrochemical Methods

Electrochemical and spectroelectrochemical measurements were carried out in a 10 mL cell custom designed cell as described previously.^[8] All measurements were recorded in dry, freshly distilled dichloromethane containing 0.10 M tetrabutyl ammonium hexafluorophosphate as supporting electrolyte. A platinum mesh working electrode was employed for bulk electrolysis, while a glassy carbon electrode (area = 0.071 cm^2) was used for square wave and cyclic voltammetry methods. In all cases, a Pt counter electrode and a Ag/Ag^+ pseudo reference electrode was used. All data is scaled to a reference of ferrocenium/ferrocene, which is observed at +577 mV versus the pseudo reference. For square wave voltammograms, the initial potential was held for 15 s prior to initiation of the scan.

Cyclic voltammetry (CV) experiments were conducted on three independent samples at room temperature with an analyte concentration of 1.0 mM. Data were collected at 100, 150, 200, 300, 400, 600, 800, and 1000 mV/s. For each scan rate, a background voltammogram was collected on the solvent and supporting electrolyte prior to sample addition. The background data were subtracted from the measured sample data prior to analysis. For each sample, the CV was collected in a small (-1.2 to 0.30 V) and large (-1.2 to 0.90 V) window under an atmosphere of nitrogen or ethylene. For each set of data, the CV results over all scan rates were fit simultaneously using the DigiSim software package.^[9] Data analysis under nitrogen and ethylene in the small window is described below. Data analysis in the larger window did not yield satisfactory results due to competing decomposition reactions of $[\mathbf{1}_{\text{ox2}}]^{2+}$.

Simulation Under Nitrogen: The data was fit as a single, one electron redox event. Uncompensated resistance was estimated using the method of Bond *et al.*^[10] The diffusion coefficient was treated as a variable parameter with an initial setting of $10^{-6} \text{ cm}^2/\text{s}$. The standard rate constant (k_s) was treated as a variable parameter with an initial guess estimated by equations 1 and 2.^[11] The standard half potential was estimated based on the potentials of minimum and maximum current and allowed to refine freely. The transfer coefficient, α , was set to 0.7. Average fitting parameter for the three independent trials are listed in Table S1.

$$k_s = \psi^* a \quad (1)$$

$$a = (\pi D_0 f v)^{1/2} \quad (2)$$

Simulation Under Ethylene: The data was fit according to an ECEE mechanism with $E_{1\text{ox1}}$, $E_{2\text{ox1}}$, and $E_{2\text{ox2}}$ as the three redox events and a single chemical step associated with the equilibrium constant K_2 (k_f and k_r). All available parameters from the simulation under nitrogen were used as initial settings. The diffusion coefficients of all species were treated as single, variable parameter. The concentration of ethylene was set to the literature value (0.4642 M) for saturated dichloromethane solutions.^[12] The parameters K_2 and k_f were estimated from UV-visible studies and allowed to freely refine. Average fitting parameter for the three independent trials are listed in Table S1. The rate constant, k_r , was calculated from K_2 and k_f .

Table S1. Cyclic voltammetry simulation parameters

<u>Nitrogen Atmosphere; E Mechanism</u>					
	E_{1ox1} (V)	α	k_s (cm/s)	D_o (cm ² /s)	R_{uncomp} (Ω)
trial 1	-0.34	0.700	0.0780	3.48E-06	1500
trial 2	-0.33	0.700	0.0804	4.28E-06	1200
trial 3	-0.33	0.700	0.0792	4.07E-06	1300
<u>Ethylene Atmosphere; ECEE Mechanism</u>					
	E_{1ox1} (V)	α	k_s (cm/s)	D_o (cm ² /s)	R_{uncomp} (Ω)
trial 1	-0.34	0.700	0.0780	3.30E-06	1500
trial 2	-0.340	0.700	0.0800	5.07E-06	1200
trial 3	-0.35	0.700	0.0788	5.26E-06	1300
	E_{2ox2} (V)	α	k_s (cm/s)	D_o (cm ² /s)	R_{uncomp} (Ω)
trial 1	-0.97	0.700	0.0943	3.30E-06	1500
trial 2	-0.97	0.700	0.0930	5.07E-06	1200
trial 3	-0.97	0.700	0.0934	5.26E-06	1300
	E_{2ox1} (V)	α	k_s (cm/s)	D_o (cm ² /s)	R_{uncomp} (Ω)
trial 1	-1.00	0.700	0.0753	3.30E-06	1500
trial 2	-1.00	0.700	0.0737	5.07E-06	1200
trial 3	-1.00	0.700	0.0746	5.26E-06	1300
	K_2	k_f (M ⁻¹ s ⁻¹)	k_r (s ⁻¹)		
trial 1	4.01	0.128	0.0318		
trial 2	4.02	0.132	0.0328		
trial 3	4.00	0.103	0.0259		

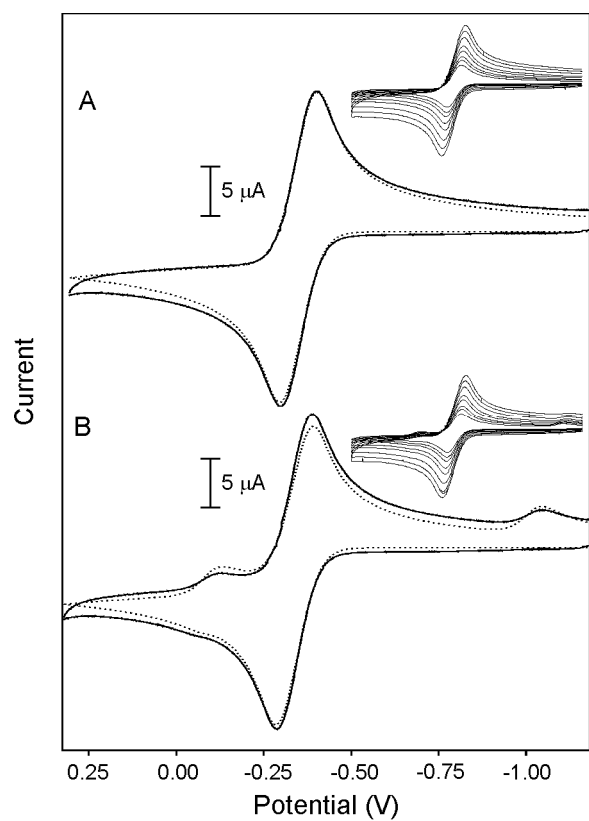


Figure S1. Experimental (—) and simulated (···) cyclic voltammograms of **1** under an atmosphere of N₂ (A) or ethylene (B) at a scan rate of 200 mV/s. Insets show experimental voltammograms at multiple scan rates from 100 to 1000 mV/s.

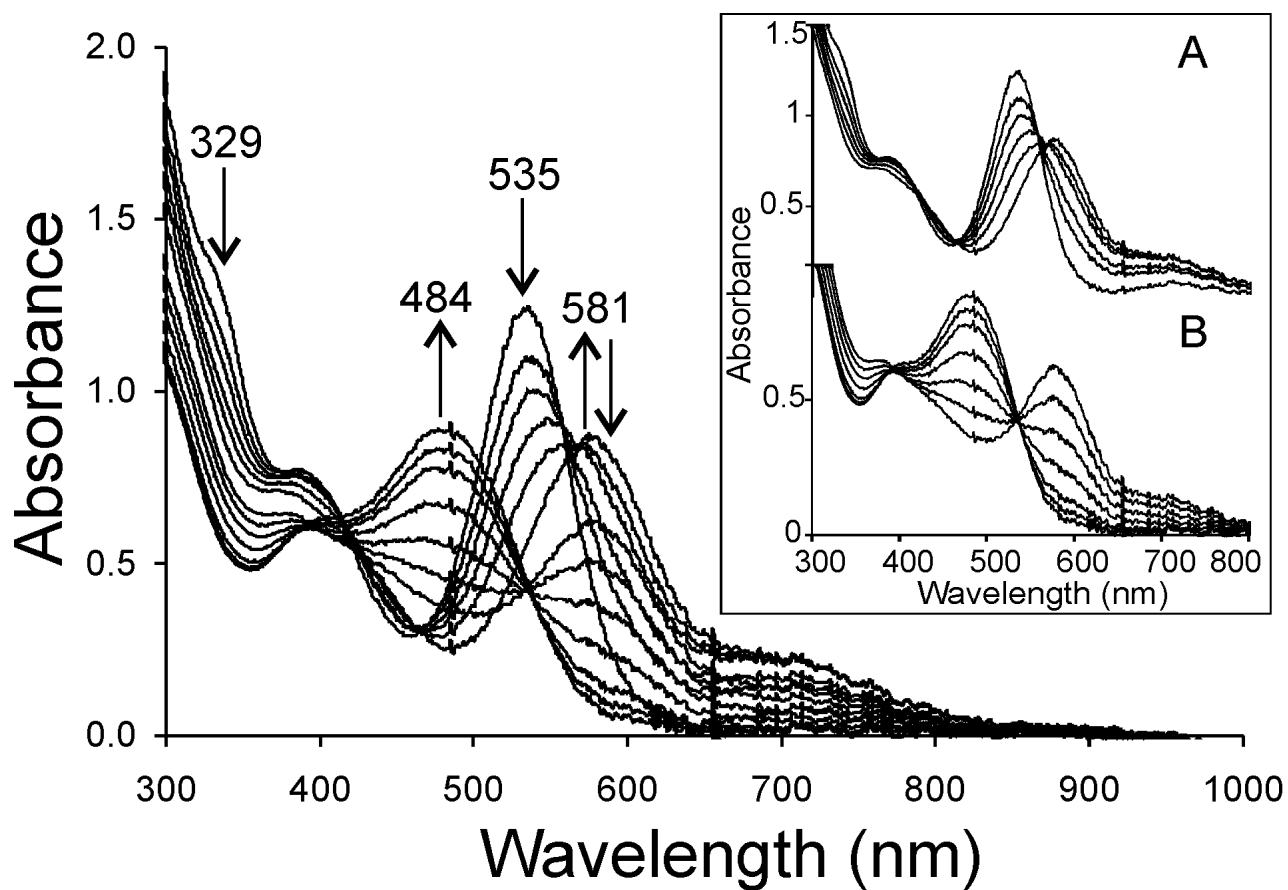


Figure S2. Electronic spectra obtained during bulk oxidation of **1** to $[2_{ox2}]^{2+}$ under an ethylene atmosphere at an applied potential of 20 mV. Data recorded at -15 °C in CH_2Cl_2 approximately every 0.15 electron equivalents. Insets A and B highlight changes during the initial and latter stages of oxidation, respectively.

References for Supporting Information

- [1] *SMART* (v.5632), Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2005.
- [2] *SAINT* (v6.45a), Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2003.
- [3] G. M. Sheldrick, *SADABS* (v2.10), *Area Detector Absorption Correction*, University Gottingen: Gottingen, Germany, 2003.
- [4] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
- [5] G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*, University Gottingen: Gottingen, Germany, 1997.
- [6] *SHELXTL* (v6.14), *Program Library for Structure Solution and Molecular Graphics*, Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2000.
- [7] A. L. Spek, *SQUEEZE*, University of Utrecht: Utrecht, The Netherlands, 1992.
- [8] C. A. Grapperhaus, S. Poturovic, *Inorg. Chem.* **2004**, *43*, 3292.
- [9] M. Rudolph, S. W. Feldberg, *DigiSim*, Bioanalytical Systems, Inc.: West Lafayette, IN, 2004.
- [10] A. L. Bond, K. B. Oldham, G. A. Snook, *Anal. Chem.* **2000**, *72*, 3492.
- [11] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, **1980**.
- [12] P. Wasserscheid, C. Hilgers, W. Keim, *J. Mol. Catal. A: Chem.* **2004**, *214*, 83.