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Redox-Regulated Ethylene Binding to a Rhenium-Thiolate Complex

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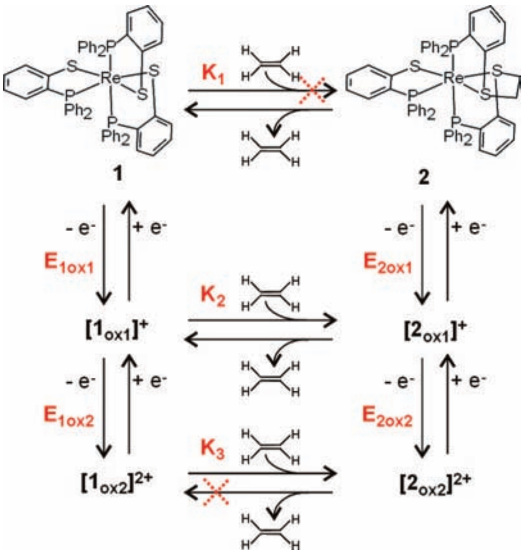
In 2001 Wang and Stiefel proposed metal-assisted separation of ethylene from feedstock utilizing electrochemically regulated C−S bond formation/cleavage as an alternative to current energy intensive methods.[1] While initial results were promising, two major obstacles were revealed in further studies.[2,3] First, the major products of alkene addition are the deleterious intraligand product dihydrodithiin and complex degradation (the desired interligand addition is only a minor product).[2] Second, the reduction potential required for ethylene release is significantly more negative than originally anticipated making electrochemical release energy-intensive.[3] Herein we report a system that overcomes these obstacles with rapid and reversible C−S bond formation/cleavage in a redox-regulated process.

Previously we reported irreversible C−S bond formation between Ru(DPPBT)$_3$ (DPPBT = 2-diphenylphosphino-benzenethiolate) and alkenes (and selected ketones) upon oxidation.[4,5] Once formed, the C−S bond was stable in all accessible metal oxidation states precluding C−S bond cleavage. In the current study, we report reversible C−S bond formation/cleavage between ethylene and the rhenium analogue [Re(DPPBT)$_3$] (**1**) and its oxidized derivatives, Scheme 1. The equilibrium constants for ethylene binding are oxidation state dependent with **1** strongly favoring C−S bond cleavage while oxidation promotes C−S bond formation such that $K_3 > K_2 > K_1$.

Scheme 1. Square Representation of **1**, **2**, and Oxidized Derivatives



The equilibrium constants K_1, K_2, and K_3 were evaluated by cyclic voltammetric methods in ethylene saturated solutions. The synthesis of **1** was previously reported by Dilworth et al., and two reversible one electron oxidations were noted.[6] Cyclic voltammograms recorded under nitrogen reveal these two events at −340 mV (E_{1ox1}) and 420 mV (E_{1ox2}) versus ferrocene. Repeating the measurements in the presence of ethylene revealed two additional events for complex **2** at −100 mV (E_{2ox2}) and −1010 mV (E_{2ox1}) with currents that are scan rate dependent, Figure S1. The scan rate dependence was simulated using the DigiSim software package as described in the Supporting Information.[7,8] Average rate constant values for C−S bond formation between $[\mathbf{1}_{\mathbf{ox1}}]^+$ and ethylene, k_f, and C−S bond cleavage for $[\mathbf{2}_{\mathbf{ox1}}]^+$, k_r, were determined as $(1.2 \pm 0.2) \times 10^{-1}$ M^{-1} s^{-1} and $(3.0 \pm 0.4) \times 10^{-2}$ s^{-1}, respectively. From these, K_2 was calculated as 4.0 ± 0.8 M^{-1}. From the four redox potentials and the equilibrium constant K_2, values for K_1 and K_3 were determined as $(1.9 \pm 0.4) \times 10^{-11}$ M^{-1} and $(2.5 \pm 0.9) \times 10^{9}$ M^{-1}, respectively.

The large differences in equilibrium constants can be exploited in solution studies. In the most reduced form, **1** and **2**, equilibrium strongly favors **1**. As such, no spectral changes are observed upon ethylene addition to solutions of **1**. Likewise, solutions of **2** generated by reduction of $[\mathbf{2}_{\mathbf{ox1}}]^+$ or $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ result in rapid ethylene release. In contrast, the one electron oxidized complexes $[\mathbf{1}_{\mathbf{ox1}}]^+$ and $[\mathbf{2}_{\mathbf{ox1}}]^+$ exist in equilibrium as a function of ethylene concentration. A slow ethylene purge through fresh solutions of $[\mathbf{1}_{\mathbf{ox1}}]^+$ rapidly initiates C−S bond formation to yield $[\mathbf{2}_{\mathbf{ox1}}]^+$. As shown in Figure 1, the absorbance at 581 associated with $[\mathbf{1}_{\mathbf{ox1}}]^+$ rapidly decreases to approximately one-half of its initial value within 2.5 min with no further significant changes thereafter. Assuming ethylene saturation (0.4642 M in CH_2Cl_2),[9] K_2 is estimated as 2.4 ± 0.1 M^{-1} consistent with its value from voltammetry studies. The C−S bonds of $[\mathbf{2}_{\mathbf{ox1}}]^+$ can be easily cleaved by nitrogen purge within 10 min restoring the initial spectrum of $[\mathbf{1}_{\mathbf{ox1}}]^+$. The C−S bond formation/cleavage cycle was repeated 7 times with no significant changes in efficiency, Figure 1 (inset).

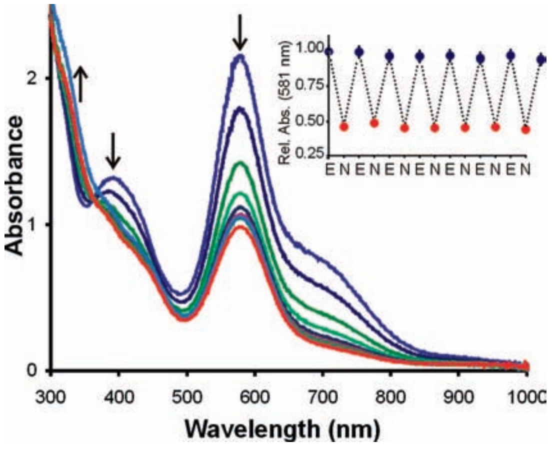


Figure 1. Electronic spectra recorded during slow ethylene purge through a solution of $[\mathbf{1}_{\mathbf{ox1}}]^+$ at room temperature. Data collected every 30 s for 3 min and after 10 min (red trace after dilution to original volume). The relative absorbance at 581 nm following alternating 10 min purges of ethylene (E) and N_2 (N) is shown in the inset.

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The large value of K_3 indicates a stable C−S bond in $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$. Solutions of $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ were prepared by bulk oxidation of **1** under an ethylene atmosphere via an ECE mechanism. In situ monitoring of the electronic spectra, Figure S2, reveals oxidation of **1** to $[\mathbf{1}_{\mathbf{ox1}}]^{+}$ in the initial electrochemical step. In the chemical step $[\mathbf{1}_{\mathbf{ox1}}]^{+}$ adds ethylene yielding $[\mathbf{2}_{\mathbf{ox1}}]^{+}$, which is subsequently oxidized to $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ to complete the ECE process. Once formed, the C−S bond cannot be cleaved in this oxidation state. No significant changes in the UV−visible spectrum of $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ are observed upon prolonged standing at room temperature, N_2 purging, or exposure to vacuum via repeated cycles of freeze−pump−thaw. C−S bond cleavage is only facilitated by reduction to $[\mathbf{2}_{\mathbf{ox1}}]^{+}$ or **2**, which rapidly releases ethylene to give **1**.

In addition to electrochemical methods, $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ was prepared by chemical oxidation (2.0 equiv of $AgPF_6$) of **1** in ethylene saturated solution. The structure of $[\mathbf{2}_{\mathbf{ox2}}][\mathbf{PF}_{\mathbf{6}}]_{\mathbf{2}}$ has been determined by single-crystal X-ray techniques with details provided in the Supporting Information.[10−17] An ORTEP view of $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$ is presented in Figure 2 with selected bond distances and angles provided in the figure caption.[18]

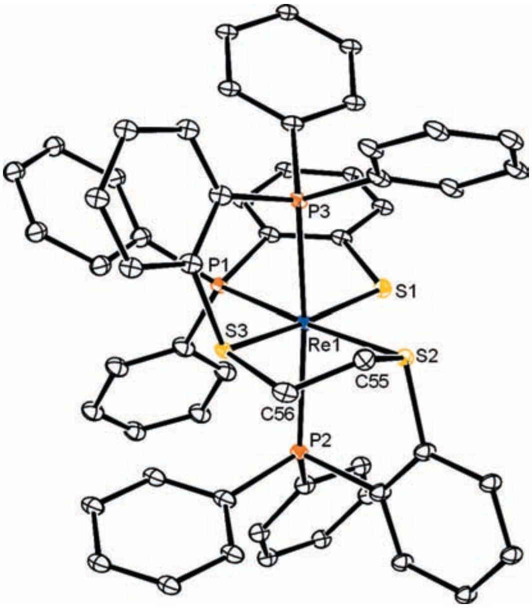

Figure 2. ORTEP representation of $[\mathbf{2}_{\mathbf{ox2}}]^{2+}$. Selected bond distances (Å): Re(1)−S(1) 2.209(3); Re(1)−S(2) 2.435(3); Re(1)−S(3) 2.433(3); Re(1)−P(1) 2.420(3); Re(1)−P(2) 2.456(3); Re(1)−P(3) 2.465(3); C(55)–C(56) 1.499(14); Selected bond angles (deg): S(1)−Re(1)−S(3) 170.00(9); P(1)−Re(1)−S(2) 174.01(9); P(2)−Re(1)−P(3) 162.68(9); S(3)−Re(1)−S(2) 84.37(10).

The stability of the C−S bonds as a function of oxidation state was previously noted for Re (and Tc) complexes of 1,4,7-trithiacylcononane.[19] Theoretical investigations by Rothlisberger related this effect to π-donation from a metal "t_{2g}" orbital to a C−S σ^*.[20,21] In our system, we propose similar changes in bonding are responsible for the remarkably large changes in K as a function of oxidation state and complex charge.

In summary, through the facile control of oxidation state by electrochemical or chemical methods, ethylene can be in a "locked on", "locked off", or in dynamic equilibrium with **1** or its oxidized derivatives. The system is robust with no apparent changes in efficiency after several cycles of C−S bond formation/cleavage. Although metal−dithiolenes were previously reported to display "locked on" and "locked off" modes, multiple cycles could not be realized. In fact, even C−S bond cleavage has been challenging. Recently reported studies with mixed-ligand Mo−dithiolenes yield partial ethylene release after reflux in chloroform for 21 h.[22] Equilibrium binding of alkenes, including ethylene at low temperatures, to ReS_4^- has been noted by Goodman and Rauchfuss.[23] In our current system, the kinetics of C−S bond formation/cleavage are much faster than those of metal−dithiolenes and allow facile trap and release of ethylene over the period of several minutes at 258 K. Thermodynamic control coupled with rapid C−S bond formation/cleavage are ideal for metal-assisted ethylene separation as first proposed by Wang and Stiefel. Yet, our system is not subject to the complications that hindered their original system.

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Supporting Information Available: Experimental procedures, voltammetry fitting parameters, cyclic voltammograms, and UV−visible spectra in PDF format. X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystal data for $[\mathbf{2}_{\mathbf{ox2}}][\mathbf{PF}_{\mathbf{6}}]_{\mathbf{2}}$: orange plate, monoclinic, space group *C*2/*c*, a = 29.009(18), b = 22.577(18) Å, c = 43.99(3) Å, β = 96.182(17)°, V = 28 643(35) Å^3, ρ_{calcd} = 1.413 g/cm^3, Z = 8. Data were collected on a Bruker SMART APEX CCD using Mo Kα radiation. For all 25 546 unique reflections (R(int) = 0.073), the final anisotropic full-matrix least-squares refinement on F^2 for 822 variables converged at R1 = 0.125, wR2 = 0.184 with a GOF of 1.09. CCDC-699464 contains the supplementary crystallographic data for this paper. Data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request.cif.
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