

Redox-Regulated Ethylene Binding to a Rhenium-Thiolate Complex

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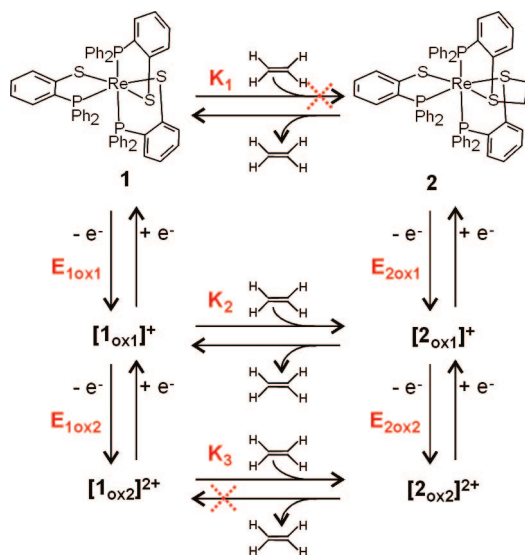
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In 2001 Wang and Stiefel proposed metal-assisted separation of ethylene from feedstock utilizing electrochemically regulated C–S bond formation/cleavage as an alternative to current energy intensive methods.¹ While initial results were promising, two major obstacles were revealed in further studies.^{2,3} First, the major products of alkene addition are the deleterious intraligand product dihydrotithiin 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

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



oxidation state dependent with **1** strongly favoring C–S bond cleavage while oxidation promotes C–S bond formation such that $K_3 > K_2 > K_1$.

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 $[1_{ox1}]^+$ and ethylene, k_f , and C–S bond cleavage for $[2_{ox1}]^+$, k_r , were determined as $(1.2 \pm 0.2) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ and $(3.0 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$, respectively. From these, K_2 was calculated as $4.0 \pm 0.8 \text{ M}^{-1}$. From the four redox potentials and the equilibrium constant K_2 , values for K_1 and K_3 were determined as $(1.9 \pm 0.4) \times 10^{-11} \text{ M}^{-1}$ and $(2.5 \pm 0.9) \times 10^9 \text{ M}^{-1}$, 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 $[2_{ox1}]^+$ or $[2_{ox2}]^{2+}$ result in rapid ethylene release. In contrast, the one electron oxidized complexes $[1_{ox1}]^+$ and $[2_{ox1}]^+$ exist in equilibrium as a function of ethylene concentration. A slow ethylene purge through fresh solutions of $[1_{ox1}]^+$ rapidly initiates C–S bond formation to yield $[2_{ox1}]^+$. As shown in Figure 1, the absorbance at 581 nm associated with $[1_{ox1}]^+$ rapidly decreases

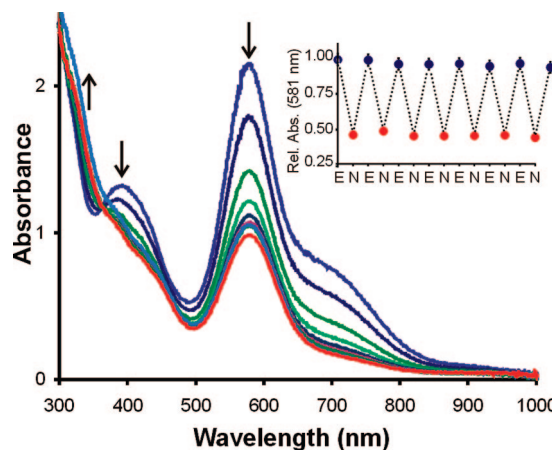


Figure 1. Electronic spectra recorded during slow ethylene purge through a solution of $[1_{ox1}]^+$ at room temperature. Data collected every 30 s for 3 min and after 10 min (red trace after dilution to original volume). The relative absorbance at 581 nm following alternating 10 min purges of ethylene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

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 $2.4 \pm 0.1 \text{ M}^{-1}$ consistent with its value from voltammetry studies. The C–S bonds of $[2_{ox1}]^+$ can be easily cleaved by nitrogen purge within 10 min restoring the initial spectrum of $[1_{ox1}]^+$. The C–S bond formation/cleavage cycle was repeated 7 times with no significant changes in efficiency, Figure 1 (inset).

The large value of K_3 indicates a stable C–S bond in $[2_{\text{ox}2}]^{2+}$. Solutions of $[2_{\text{ox}2}]^{2+}$ 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 $[1_{\text{ox}1}]^+$ in the initial electrochemical step. In the chemical step $[1_{\text{ox}1}]^+$ adds ethylene yielding $[2_{\text{ox}1}]^+$, which is subsequently oxidized to $[2_{\text{ox}2}]^{2+}$ 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 $[2_{\text{ox}2}]^{2+}$ 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 $[2_{\text{ox}1}]^+$ or **2**, which rapidly releases ethylene to give **1**.

In addition to electrochemical methods, $[2_{\text{ox}2}]^{2+}$ was prepared by chemical oxidation (2.0 equiv of AgPF_6) of **1** in ethylene saturated solution. The structure of $[2_{\text{ox}2}][\text{PF}_6]_2$ has been determined by single-crystal X-ray techniques with details provided in the Supporting Information.^{10–17} An ORTEP view of $[2_{\text{ox}2}]^{2+}$ is presented in Figure 2 with selected bond distances and angles provided in the figure caption.¹⁸

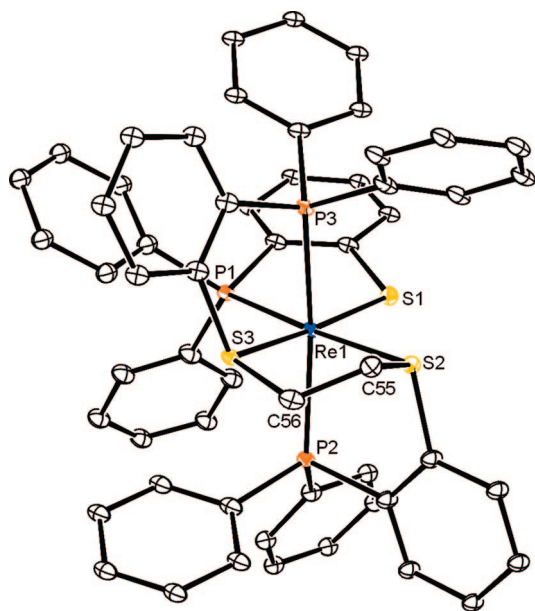


Figure 2. ORTEP representation of $[2_{\text{ox}2}]^{2+}$. Selected bond distances (Å): Re(1)–S(1) 2.209(3); Re(1)–S(2) 2.435(3); Re(1)–S(3) 2.433(3); Re(1)–P(1) 2.420(3); Re(1)–P(2) 2.456(3); Re(1)–P(3) 2.465(3); C(55)–C(56) 1.499(14); Selected bond angles (deg): S(1)–Re(1)–S(3) 170.00(9); P(1)–Re(1)–S(2) 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-trithiacyclononane.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 $[2_{\text{ox}2}][\text{PF}_6]_2$: orange plate, monoclinic, space group $C2/c$, $a = 29.009(18)$, $b = 22.577(18)$ Å, $c = 43.99(3)$ Å, $\beta = 96.182(17)^\circ$, $V = 28\,643(35)$ Å³, $\rho_{\text{calcd}} = 1.413$ g/cm³, $Z = 8$. Data were collected on a Bruker SMART APEX CCD using Mo K α radiation. For all 25 546 unique reflections ($R(\text{int}) = 0.073$), 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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