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Re(bipy-tBu)$(CO)_3$Cl−improved Catalytic Activity for Reduction of Carbon Dioxide: IR-Spectroelectrochemical and Mechanistic Studies

Jonathan M. Smieja and Clifford P. Kubiak*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0358

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Five Re(bipy)$(CO)_3$Cl complexes were prepared and studied where bipy was 4,4′-dicarboxyl-2,2′-bipyridine (**1**), 2,2′-bipyridine (**2**), 4,4′-dimethyl-2,2′-bipyridine (**3**), 4,4′-di-*tert*-butyl-2,2′-bipyridine (**4**), and 4,4′-dimethoxy-2,2′-bipyridine (**5**). From this group, a significantly improved catalyst, Re(bipy-tBu)$(CO)_3$Cl (**4**), for the reduction of carbon dioxide to carbon monoxide was found. The complex shows two one-electron reductions under argon, one reversible at −1445 mV (vs SCE), and one irreversible at −1830 mV. Under CO_2 the second irreversible wave displays a large catalytic enhancement in current. Diffusion coefficients were determined using the Levich−Koutecky method (1.1×10^{-5} cm^2/s for the neutral complex and 8.1×10^{-6} cm^2/s for the singly reduced species), and a second order rate constant for the electrochemical reduction with CO_2 of 1000 M^{-1} s^{-1} was measured. Bulk electrolysis studies were performed to measure Faradaic efficiencies for the primary gaseous products, $\eta_{CO} = 99 \pm 2\%$ in acetonitrile.

Introduction

The catalytic conversion of carbon dioxide to liquid fuels is a critical goal that would positively impact the global carbon balance by both recycling CO_2 and producing a renewable fuel. One approach is to develop highly efficient carbon dioxide reduction catalysts that can catalyze the reaction of CO_2 to CO at low overpotentials with high selectivity. CO can then be used to prepare hydrogen (water-gas shift reaction) and the mixture of CO and H_2 (synthesis gas) can be used to synthesize liquid fuels by the well-proven Fischer−Tropsch process.[1] Researchers have been exploring this problem for several decades, with limited success, but the problem today is as important as ever.[2−16]

In general, there are three main classes of synthetic CO_2 reduction catalysts. These are (1) metal complexes with macrocyclic ligands, (2) metal complexes with phosphine ligands, and (3) metal complexes with bipyridine ligands.[5] Of these classes of catalysts, metal bipyridine complexes have shown reasonable activities and lifetimes. In particular, the complex Re(bipy)$(CO)_3$Cl (bipy = 2,2′-bipyridine) (**2**), reported by Lehn et al. in 1984, was reported to catalyze the reduction of CO_2 to CO on a glassy carbon electrode in a 9:1 DMF/H_2O solution during a 14 h experiment with 98% Faradaic efficiency and no significant decrease in performance from catalyst degradation.[17,18]

Photoreduction of CO_2 to CO has also been reported using Re(bipy)$(CO)_3$X complexes (where bipy = 2,2′-bipyridine and X is an anionic ligand).[18−23] In these experiments monochromatic light and a sacrificial donor (triethylamine, nitroethanol, or triethanolamine) were used to effect photocatalysis.

In the time since Lehn et al.'s original report of the Re(bipy)$(CO)_3$Cl catalyst many other synthetic CO_2

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*To whom correspondence should be addressed. E-mail: ckubiak@ucsd.edu.

(1) Underwood, A. J. V. *Ind. Eng. Chem.* **1940**, *32*, 449.
(2) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem.* **1993**, *361*, 149.
(3) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315.
(4) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.
(5) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, *38*, 89.
(6) Bhugun, I.; Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 1769.
(7) Bolinger, C. M.; Story, N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4582.
(8) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics* **1988**, *7*, 238.
(9) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H. H.; O'Toole, T. R.; Downard, A.; Pugh, J. R.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 4864.
(10) Dubois, D. L. *Comments Inorg. Chem.* **1997**, *19*, 307.
(11) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753.
(12) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.
(13) Haines, R. J.; Wittrig, R. E.; Kubiak, C. P. *Inorg. Chem.* **1994**, *33*, 4723.
(14) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181.
(15) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158.
(16) Raebiger, J. W.; Turner, J. W.; Noll, B. C.; Curtis, C. J.; Miedaner, A.; Cox, B.; DuBois, D. L. *Organometallics* **2006**, *25*, 3345.
(17) Hawecker, J.; Lehn, J. M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328.
(18) Hawecker, J.; Lehn, J. M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.
(19) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *J. Photochem. Photobiol., A* **1996**, *96*, 171.
(20) Hori, H.; Takano, Y.; Koike, K.; Sasaki, Y. *Inorg. Chem. Commun.* **2003**, *6*, 300.
(21) Kurz, P.; Probst, B.; Spingler, B.; Alberto, R. *Eur. J. Inorg. Chem.* **2006**, 2966.
(22) Sung-Suh, H. M.; Kim, D. S.; Lee, C. W.; Park, S. E. *Appl. Organomet. Chem.* **2000**, *14*, 826.

reduction catalysts have been reported as summarized in reference 5. The best of these catalysts in terms of rate constant (1000 M^{-1} s^{-1}) is the bimetallic Pd-phosphine developed by Dubois and co-workers, but this catalyst has a turnover number of only 8.[16] [Pd(tridentate)(solvent)]-$(BF_4)_2$ catalysts with more reasonable turnover numbers in the 100s or more have also been developed, but in that case the rate constant drops to only ~150 M^{-1} s^{-1}.[11,16]

Other complexes with modified bipyridine ligands have been reported, including Re(bipy-COOH)$(CO)_3$Cl (bipy-COOH = 4,4′-dicarboxyl-2,2′-bipyridine) (**1**),[24] Re(dmb)-$(CO)_3$Cl (dmb = 4,4′-dimethyl-2,2′-bipyridine) (**3**),[25−27] Re(bipy-tBu)$(CO)_3$Cl (bipy-tBu = 4,4′-di-*tert*-butyl-2,2′-bipyridine) (**4**),[28] and Re(bipy-OMe)$(CO)_3$Cl (bipy-OMe = 4,4′-dimethoxy-2,2′-bipyridine) (**5**),[23] but none of those complexes were studied for electrocatalytic reduction of CO_2.

In this study, all of the above complexes were studied by cyclic voltammetry to determine their relative reactivity in the catalytic reduction of carbon dioxide. In the end, we determined that Re(bipy-tBu)$(CO)_3$Cl (**4**) is the best catalyst in the group with a second order rate constant of 1000 M^{-1} s^{-1} and a Faradaic efficiency of 99 ± 2%; a marked improvement in rate of catalysis over the original Lehn catalyst (**2**). The catalyst also showed long-term stability, displaying no significant loss in activity over the course of a 5 h bulk electrolysis experiment. IR-spectroelectrochemical studies of this catalyst revealed several mechanistic details which suggest important considerations for future improvement of CO_2 reduction catalysts.

Results and Discussion

Electrochemical Studies. Electrochemical studies of a series of Re(bipyridyl)$(CO)_3$Cl complexes showed that the bipyridine ligand substituents affect the first and second reduction potentials. A series of five complexes with varying electron donating/withdrawing substituents in the 4,4′ positions of the bipyridine ligand were studied: COOH (**1**) < H (**2**) < Me (**3**) < t-Bu (**4**) < OCH_3 (**5**). It is convenient to consider the complexes in the above order because of increasing pK_a of the pyridine ligand on rate of catalysis (4-carboxylpyridine pK_a = 3.10, pyridine pK_a = 5.17 4-methylpyridine pK_a = 5.94, 4-*tert*-butylpyridine pK_a = 5.99, 4-methoxypyridine pK_a = 6.62).[29] This trend is reflected in the increasingly negative reduction potentials (Table 1) for the series, and it is also reflected in the ν(CO) values observed in the IR spectra (Table 2). All cyclic voltammograms (CVs) of these complexes displayed similar features under an atmosphere of argon, namely, a one electron quasi-reversible reduction wave followed by a one electron irreversible reduction wave at more negative potential. At slower scan rates it was also possible to see a small wave in the CV of **2** between the first and the second reductions, corresponding to the production of the [*fac*-Re(bipyridyl)$(CO)_3]_2$ dimer that has been reported previously.[30]

Table 1. Reduction Potentials for the Re(bipyridyl) Complexes in This Study[a]

complex	1st reduction potential (mV vs SCE)	2nd reduction potential (mV vs SCE)
Re(bipy-COOH)$(CO)_3$Cl (**1**)	−940	−1725
Re(bipy)$(CO)_3$Cl (**2**)	−1340	−1725
Re(dmb)$(CO)_3$Cl (**3**)	−1430	−1765
Re(bipy-tBu)$(CO)_3$Cl (**4**)	−1445	−1830
Re(bipy-OMe)$(CO)_3$Cl (**5**)	−1485	−1860

[a] First reduction potential is the $E_{1/2}$ for the reversible wave, and the second reduction is the peak maximum for the cathodic wave. All scans were performed at 100 mV/s in acetonitrile at 1.0 mM rhenium complex with 0.1 M TBAH and a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference (later adjusted to SCE for clarity).

Table 2. Selected Infrared Stretches for Complexes under Study

complex	υ(CO)/cm^{-1}	solvent	ref.
[Re(bipy-tBu)$(CO)_3$Cl] (**4**)	2023, 1916, 1898	MeCN	*a*
[Re(bipy-tBu)$(CO)_3Cl]^{\bullet-}$ (**4a**)	2005, 1895, 1878	MeCN	*a*
[Re(bipy-tBu)$(CO)_3]^{\bullet}$ (**4b**)	1983, 1865, 1850	MeCN	*a*
[Re(bipy-tBu)$(CO)_3]^{-}$ (**4c**)	1938, 1834 (br)	MeCN	*a*
[Re(bipy)$(CO)_3$Cl] (**2**)	2025, 1918, 1902	MeCN	*a*
[Re(bipy)$(CO)_3Cl]^{\bullet-}$ (**2a**)	1998, 1885, 1867	MeCN	33
[Re(bipy)$(CO)_3]^{-}$ (**2c**)	1947, 1843 (br)	MeCN	33
[Re(bipy-COOH)$(CO)_3$Cl] (**1**)	2037, 1935, 1911	MeCN	*a*
[Re(dmb)$(CO)_3$Cl] (**3**)	2023, 1916, 1899	MeCN	*a*
[Re(bipy-OMe)$(CO)_3$Cl] (**5**)	2022, 1914, 1896	MeCN	*a*
[Re(bipy-tBu)$(CO)_3$Cl] (**4**)	2020, 1916, 1893	THF	*a*
[Re(bipy-tBu)$(CO)_3Cl]^{\bullet-}$ (**4a**)	1995, 1882, 1867	THF	*a*
[Re(bipy-tBu)$(CO)_3]^{-}$ (**4c**)	1943, 1839	THF	*a*

[a] This work.

When acetonitrile solutions were saturated with CO_2, vast differences were observed in the second reduction wave from complex to complex. In order of increasing e^- donating ability, the Re(bipy-COOH)$(CO)_3$Cl (**1**) complex showed little to no current enhancement under CO_2 at the second reduction wave. **2** (Lehn's catalyst) showed a 3.4-fold current increase in peak current at 100 mV/s between the complex under argon and the complex under CO_2 at −1.73 V versus SCE. Re(dmb)$(CO)_3$Cl (**3**) showed a current enhancement under CO_2 that was slightly larger than **2**. **4** showed the largest catalytic current with an 18.4-fold increase in peak current at a scan rate of 100 mV/s under CO_2 at −1.83 V versus SCE (Figure 1). Re(bipy-OMe)$(CO)_3$Cl (**5**) showed almost no current enhancement under CO_2. **4** and **2** were compared directly at equal concentrations of analyte and CO_2 where **4** performed significantly better, showing more than 3.5 times more catalytic current at 100 mV/s than **2** at 100 mV more negative potential (Figure 2).

At the outset, these data make it clear that catalytic activity for CO_2 reduction depends on factors other than the electrocatalyst reduction potentials. We note, for instance, that although complex **5** has the most negative reduction potential and should have a more nucleophilic Re center for CO_2 reduction, it shows essentially no

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(23) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. *J. Am. Chem. Soc.* **2008**, *130*, 2023.

(24) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

(25) Fujita, E.; Hayashi, Y.; Kita, S.; Brunschwig, B. S. *Carbon Dioxide Utilization for Global Sustainability*; Elsevier: Maryland Heights, MO, 2004.

(26) Fujita, E.; Muckerman, J. T. *Inorg. Chem.* **2004**, *43*, 7636.

(27) Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **2003**, *125*, 11976.

(28) Yam, V. W. W.; Lau, V. C. Y.; Cheung, K. K. *Organometallics* **1995**, *14*, 2749.

(29) Brown, H. C.; Braude, E. A.; Nachod, F. C. *Determination of Organic Structures by Physical Methods*; Academic Press: New York, 1955.

(30) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414.

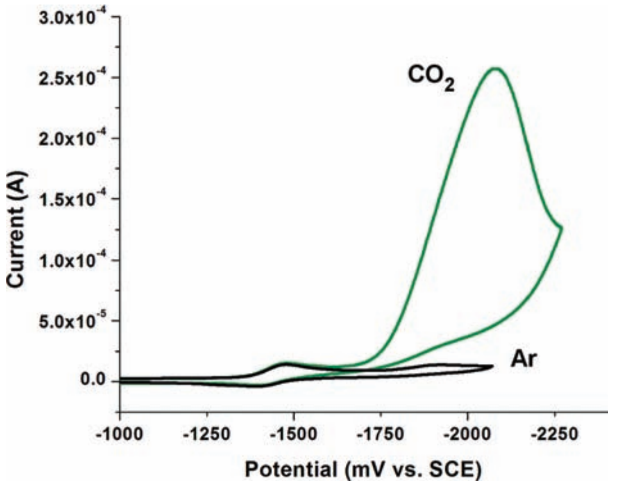

Figure 1. Re(bipy-tBu)(CO)$_3$Cl (**4**) under both argon and CO$_2$. Scan under CO$_2$ shows large current enhancement because of catalytic reduction of CO$_2$ to CO. Voltammograms taken at 100 mV/s in acetonitrile with 0.1 M TBAH, glassy carbon working electrode, Pt counter electrode, and a catalyst concentration of 0.5 mM. Scans with no catalyst present under CO$_2$ were also performed, and no Faradaic current was observed.

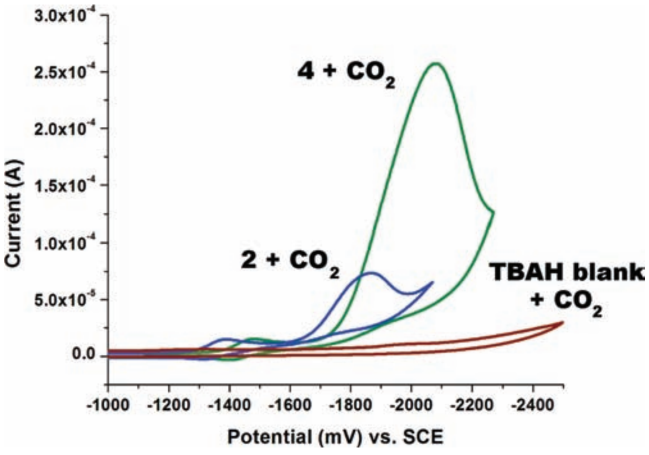

Figure 2. Catalytic comparison of **4** to **2** showing increased catalytic current of new catalyst. Voltammograms taken at 100 mV/s in acetonitrile with 0.1 M TBAH, glassy carbon working electrode, Pt counter electrode, and a catalyst concentration of 0.5 mM. Also included is a blank scan of acetonitrile with 0.1 M TBAH saturated with CO$_2$ that shows no catalytic current from the electrode surface.

catalytic current, pointing to a possible π donor versus σ donor effect. Experiments are ongoing in our laboratory to further examine this phenomenon by designing and testing new bipyridine ligands with a variety of substituents in the 4, 4′ positions.

Although the catalytic activity of **4** is 3.5 fold greater than **2** at the same catalyst concentration and only 100 mV more negative reduction potential, it was also noted that **4** shows a 1.4 fold increase in catalytic current over **2** at identical potentials (−1730 mV vs SCE at **2**′s maximum catalytic current).

Rotating disk electrode (RDE) experiments were carried out on Re(bipy-tBu)(CO)$_3$Cl (**4**) to determine the diffusion coefficients of the complex. The data obtained from these experiments display Levich−Koutecky behavior with linear fits having R^2 values of greater than 0.99 for both the first and the second reductions, indicating that the complex behaves well under the conditions of the experiment (Supporting Information, Figure S1). The Levich−Koutecky equation was used to obtain diffusion coefficients from that data 1.[31]

$$i_L = (0.620)nFAD^{2/3}\omega^{1/2}v^{-1/6}C \qquad (1)$$

In the above equation, i_L is the Levich current from the rotating disk experiment, n is the number of electrons (1 in this case), F is Faraday's constant, A is the electrode area, D is the diffusion coefficient, ω is the rotation rate, v is the kinematic viscosity of the solution, and C is the concentration of the analyte in solution. These data yielded diffusion coefficients of 1.1×10^{-5} cm^2/s for Re(bipy-tBu)(CO)$_3$Cl and 8.1×10^{-6} cm^2/s for the singly reduced species. These values are reasonable when compared to diffusion coefficients for other complexes in the literature.[13] From the diffusion coefficient of the complex, along with additional data from the experiment it was possible to calculate the second order rate constant for the CO$_2$ reduction using eq 2.[11,32]

$$i_c = nFA[\text{cat}](Dk[\text{Q}]^y)^{1/2} \qquad (2)$$

In the equation above, i_c is the catalytic current observed in the CV, n is the number of electrons (2 for this reaction reflecting the reduction of CO$_2$ to CO), F is Faraday's constant, A is the area of the electrode surface, D is the diffusion coefficient of the active catalytic species, k is the rate constant (the variable of interest in this case), Q is the concentration of substrate, and y is the order of the substrate in the reaction in question. A second order rate constant of 650 M^{-1} s^{-1} is obtained using this equation, and a similar value, 1000 M^{-1} s^{-1}, was obtained using the electrochemical simulation software DigiSim. The DigiSim fit as well as the assumed mechanism for the voltammograms can be found in the Supporting Information, Figure S2. When the same equations were used for the Lehn catalyst (**2**), a second order rate constant of 50 M^{-1} s^{-1} was obtained.

Controlled Potential Electrolysis (CPE). Additional catalytic experiments have been done involving the Re(bipy-tBu)(CO)$_3$Cl (**4**) complex to draw comparisons with the Lehn complex, **2**. Controlled potential electrolysis of both complexes were performed in an acetonitrile (MeCN) solution in a sealed cell developed in our laboratory with a carbon working electrode, platinum counter electrode, and Ag/AgCl pseudo reference (with internal ferrocene reference added). In the acetonitrile solution, complex **4** performed significantly better than complex **2** producing 2.2 times the CO in the first 15 min of CPE as measured by gas chromatography when held at −1850 mV versus SCE. It is also noteworthy that complex **4** retained high electrocatalytic activity for upward of 5 h in acetonitrile, outperforming complex **2**, which loses some catalytic activity in acetonitrile over the same time period.

Further CPE experiments were carried out to determine the Faradaic efficiency of **4** in acetonitrile. A solution of **4** in acetonitrile was held at a constant potential of −2000 mV (vs SCE) for 2 h, and GC samples were taken

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(31) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and applications*, 2nd ed.; Wiley: New York, 2001.

(32) Savéant, J. M.; Vianello, E. *Electrochim. Acta* **1962**, *8*, 905.

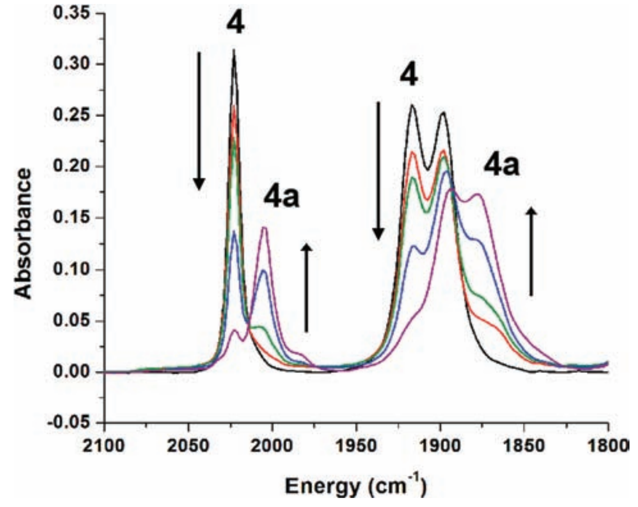

Figure 3. First reduction of **4** in the IR-SEC experiment in acetonitrile (arrows indicate whether the bands decrease or increase). 20−30 cm^{-1} shifts indicative of bipyridine-based reduction of the complex. Initial reduction of **4** leads to a negatively charged complex where the added electron density lies mostly on the bipyridine ligand.

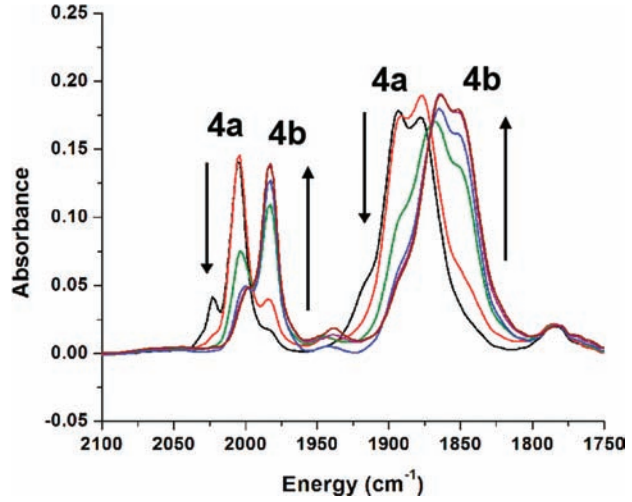

Figure 4. Second transition from **4a** to **4b** in the IR-SEC experiment in acetonitrile (arrows indicate whether the bands decrease or increase). This 20 cm^{-1} shift is due to a ligand to metal charge transfer and subsequent loss of Cl$^-$. This electron transfer is facilitated by the electron donating nature of the *tert*-butyl groups on the bipyridine ligand that destabilize the bipy•−.

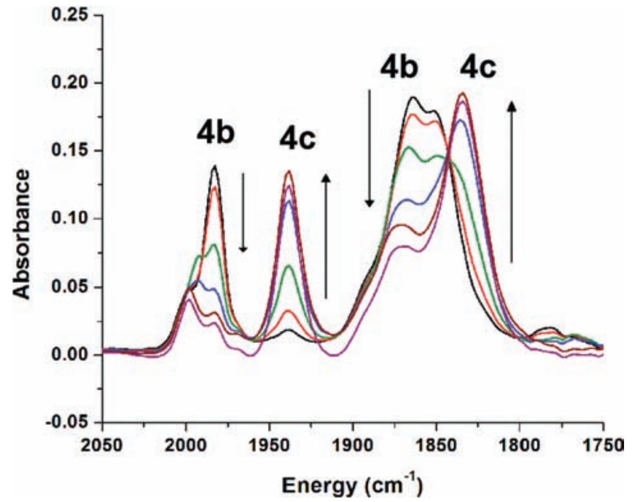

Figure 5. Second reduction in the IR-SEC experiment in acetonitrile (arrows indicate whether the bands decrease or increase). 40 cm^{-1} shift for the second reduction is indicative of a metal-based reduction of the complex forming the Re^{1-} five coordinate complex (**4c**).

every 30 min. The output from the GC was plotted and gave a linear plot for current passed versus CO produced. The data correspond to a Faradaic efficiency of 99 ± 2% in acetonitrile (Supporting Information, Figure S3).

Infrared Spectroelectrochemistry (FTIR-SEC). Infrared spectroelectrochemistry was performed on the Re(bipy)(CO)$_3$Cl (**2**) and Re(bipy-tBu)(CO)$_3$Cl (**4**) to compare the two species at various stages of reduction. Both complexes showed three carbonyl peaks at rest potential as expected from previous data on similar complexes (see Table 2).[33] The ν(CO) peaks for complex **4** appear at 2023 cm^{-1}, 1916 cm^{-1}, and 1898 cm^{-1}. These ν(CO) bands are typical of facial tricarbonyl systems: one higher energy stretch (A$_1$) is separated from the two lower energy stretches (split E), which overlap slightly.

When a voltage is applied to the solutions at the potential of the first reduction, for both **4** and **2**, each carbonyl peak in the spectrum shifts approximately 20 cm^{-1} to lower energy to create new species **4a** and **2a** (for **4a**, ν(CO) at 2005 cm^{-1}, 1894 cm^{-1}, and 1878 cm^{-1}) (Figure 3). This shift is indicative of a primarily bipyridine-based reduction of the complex as was concluded in previous studies.[30,33]

When all the unreduced complex was singly reduced, another species was produced from **4a** at potentials positive of that for the second reduction wave. This intermediate species shows ν(CO) modes that were again shifted 20−30 cm^{-1} lower in energy (ν(CO): 1983 cm^{-1}, 1865 cm^{-1}, and 1850 cm^{-1} [**4b**]) (Figure 4). The new species has been assigned as the neutral five coordinate bipy^{0}Re^0 complex with no bound Cl$^-$. Evidence for this species comes from a recent crystal structure determination in our laboratory of [Re(trip-bipy)(CO)$_3$] (trip-bipy = 6,6′-(2,4,6-triisopropylphenyl)-2,2′-bipyridine). Details will be published in a future manuscript.

At this potential Re(bipy)(CO)$_3$Cl$^{\bullet-}$ (**2a**) formed a significant amount of Re−Re dimer[33] while **4a** does not form measurable quantities of dimer in these experiments. Fujita et al. reported that with Re(dmb)(CO)$_3$(OTf) (OTf = trifluoromethanesulfonate) the formation of dimer happens very slowly[27] in UV−vis experiments at lower concentrations. When performing IR-SEC on **3** we noted a small amount of dimer formation, most likely because of the intermediate bulk of the methyl group when compared to the bulk in **2** and **4**. We also independently synthesized the dimer [Re(bipy-tBu)(CO)$_3$]$_2$ (**6**) via reflux of Re$_2$(CO)$_{10}$ with 2 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridine and obtained a liquid FTIR of the product in xylenes. This IR spectrum had a very similar ν(CO) signature to the reported [Re(bipy)(CO)$_3$]$_2$ IR by Turner et al.[33] This spectrum, however, does not match any of the major species observed in the IR-SEC of **4**, which provides additional evidence that dimer is not formed in the SEC or bulk electrolysis studies.

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(33) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. *Organometallics* **1996**, *15*, 3374.

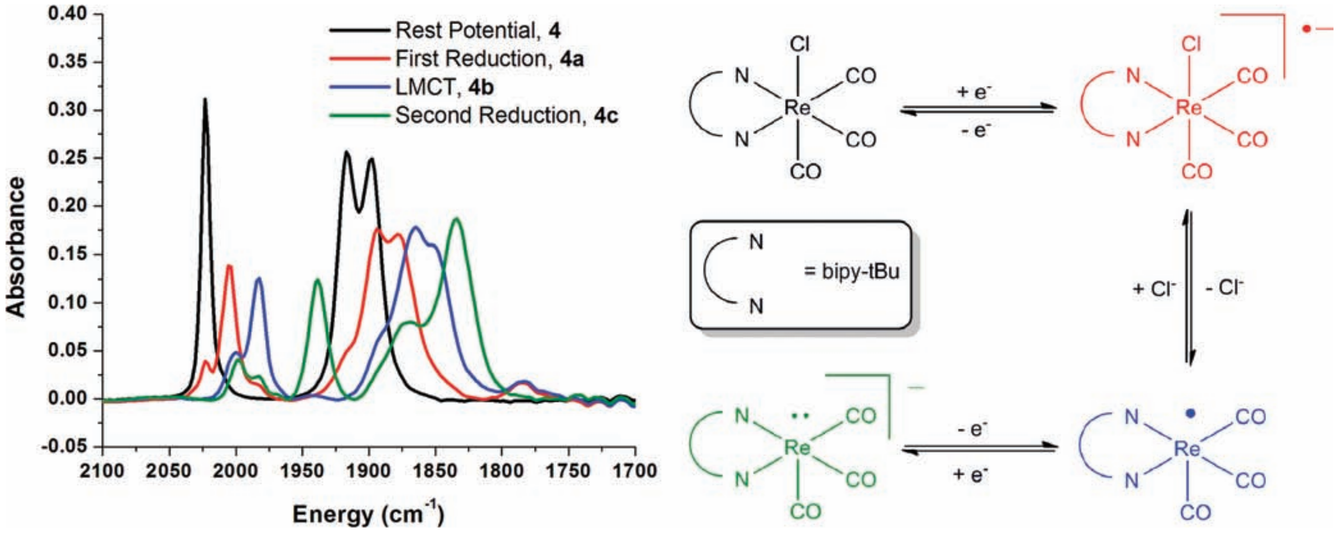

Figure 6. IR-SEC of **4** in acetonitrile with Bu_4NPF_6 electrolyte. **4a** is formed by the first reduction of the complex to the radical anion with added electron density mostly centered on the bipyridine ligand. **4b** follows through a ligand to metal charge transfer facilitated by the electron donating nature of the *tert*-butyl groups on the ligand. **4c** represents the second reduction of the complex to the five coordinate anion that acts as the active catalyst species.

We assign the next species, formed at potentials negative of the second reduction, in the IR-SEC of complex **4** as the two electron reduced $Re(bipy\text{-}tBu)(CO)_3^-$ with two ν(CO) modes at 1938 cm^{-1} and 1834 cm^{-1} (broad, overlapped) (**4c**) (Figure 5). The larger ν(CO) shift for the higher energy stretch is indicative of a mostly metal-based reduction of the complex as is expected for the second reduction. The four species observed in the IR-SEC experiments of **4** are displayed in Figure 6.

It is worthwhile here to note the difference between the IR-SEC reported here for **4** and that observed by Turner et al. for **2**. The main difference between Turner's study and ours is the assignment of the third species formed (**4b** in our study). We see no indication that **4b** is a result of a second reduction. Instead we invoke a ligand to metal charge transfer from the bipy to the Re center to explain the further shift in the ν(CO) in the singly reduced complex. This electron transfer is promoted by the donating nature of the *tert*-butyl groups on the bipy, which destabilize the bipy radical and allow electron occupancy of the d_{z^2} orbital after loss of Cl^-.

IR-SEC of **4** was also performed in CO_2-saturated CH_3CN demonstrating the production of CO at catalytic potentials. This CO production could be seen via the stretch at 2120 cm^{-1} indicative of dissolved CO in the acetonitrile solution (Supporting Information, Figure S4).

Conclusions

We have reported here an improved catalyst for the reduction of CO_2 to CO with high turnover number and frequency. This catalyst was identified in a systematic study of a series of $Re(bipyridyl)(CO)_3Cl$ complexes with varying degrees of electron donating/withdrawing substituents in the 4, 4′ positions of the bipyridine. We have seen by IR-SEC studies that the $Re(bipy\text{-}tBu)(CO)_3Cl$ complex forms a stable Re(0) radical, and significantly less dimer during electrolysis than does its $Re(bipy)(CO)_3Cl$ counterpart. This may also help explain the enhanced catalytic activity of **4**. Studies are ongoing in our laboratory to investigate the bulk electrocatalytic properties of the $Re(bipy\text{-}tBu)(CO)_3Cl$ complex in acetonitrile/water mixtures and also to study and compare its mechanism of catalysis with other complexes that appear to follow a similar mechanism.

Experimental Section

General Experimental Procedures. NMR spectra were recorded on a Jeol 500 MHz spectrometer at 298 K and data was manipulated using Jeol Delta software. ^1H chemical shifts are reported relative to solvent residual peaks. Mass spectrometry data was collected on a Finnigan LCQDECA in ESI positive ion mode. Infrared spectra were collected on a Bruker Equinox 55 spectrometer. Microanalyses were performed by Midwest Microlab, LLC, Indianapolis, IN for C, H, and N content, and all analyses were performed in duplicate.

Syntheses. Manipulations were performed open to air and solvents were not dried before use. Reagents were used as received. Chemicals were received from the following: $Re(CO)_5Cl$ (Strem), 2,2′-bipyridine (Aldrich), 4,4′-di-*tert*-butyl-2,2′-bipyridine (Aldrich), 4,4′-dicarboxy-2,2′-bipyridine (Strem), 4,4′-dimethoxy-2,2′-bipyridine (Aldrich), 4,4′-dimethyl-2,2′-bipyridine (Acros), and $Re_2(CO)_{10}$ (Acros).

[Re(4,4′-dicarboxyl-2,2′-bipyridine)(CO)$_3$Cl] (1). This complex was prepared with slight modifications to literature methods.[24] $Re(CO)_5Cl$ (0.200 g, 0.55 mmol) was dissolved in 50 mL of hot toluene and 20 mL of methanol. An equimolar amount of 4,4′-dicarboxy-2,2′-bipyridine (0.130 g, 0.55 mmol) was added to the solution, and the reaction mixture was stirred under reflux for 1 h with initial color change from clear to orange occurring in the first 15 min. The reaction mixture was removed from heat after the 1 h reflux, and the unreacted starting material was precipitated from solution in the freezer over a 1 h period. After that time, the white starting material was filtered, and the bright orange filtrate was rotary evaporated to dryness. ^1H NMR (acetonitrile-d_3): δ 6.80 (d, 2H, 5 and 5′ H's), δ 7.68 (s, 2H, 3 and 3′ H's), δ 7.84 (d, 2H, 6 and 6′ H's). IR (CH_3CN) ν(CO): 2037 cm^{-1}, 1935 cm^{-1}, 1911 cm^{-1}.

[Re(2,2′-bipyridine)(CO)$_3$Cl] (2). This complex was prepared with slight modifications to literature methods.[34] $Re(CO)_5Cl$ (0.3020 g, 0.83 mmol) was dissolved in 50 mL of hot toluene. An equimolar amount of 2,2′-bipyridine (0.130 g, 0.83 mmol) was

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(34) Worl, L. A.; Duesing, R.; Chen, P. Y.; Dellaciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.

then added to the hot solution, and the reaction mixture was stirred with reflux for 1 h. Within the first 5 min of applying heat the solution began to turn yellow, and the intensity of the color increased with time during reflux. After 1 h of reflux the mixture was removed from heat and put in a freezer for 1 h where all product precipitated from solution. After removing from the freezer, the bright yellow powder product was filtered from the slurry. The product was then put in the vacuum oven at 90 °C overnight to eliminate any residual solvent and water. Spectroscopically pure product was isolated from this reaction for an overall yield of 84%. ^{1}H NMR (acetonitrile-d_3): δ 7.44 (t, 2H, 5 and 5′ H's), δ 8.00 (t, 2H, 4 and 4′ H's), δ 8.23 (d, 2H, 6 and 6′ H's), δ 8.82 (d, 2H, 3 and 3′ H's). IR (CH_3CN) ν(CO): 2025 cm^{-1}, 1918 cm^{-1}, 1902 cm^{-1}. ESI-MS (*m*/*z*): 444.65 (100, $[M-Cl^-+H_2O]^+$), 484.90 (29, $[M+Na^+]^+$).

[Re(4,4′-dimethyl-2,2′-bipyridine)(CO)$_3$Cl] (3). $Re(CO)_5Cl$ (0.984 g, 2.72 mmol) was dissolved in 150 mL of hot toluene in a 250 mL round-bottom flask. An equimolar amount of 2,2′-dimethyl-2,2′-bipyridine (0.501 g, 2.72 mmol) was added, and the reaction was refluxed for 90 min. The solution turned yellow after 15 min of reflux, orange after that, and product precipitated after only 30 min of reflux. After removing from heat, the reaction mixture was placed in a freezer overnight to force all products from solution. The product was filtered and dried in a vacuum oven at 90 °C. Spectroscopically pure product was obtained from the reaction for a total yield of 94%. ^{1}H NMR (acetonitrile-d_3): δ 2.33 (s, 6H, CH_3), δ 7.22 (d, 2H, 5 and 5′ H's), δ 8.05 (s, 2H, 6 and 6′ H's), δ 8.60 (d, 2H, 3 and 3′ H's). IR (CH_3CN) ν(CO): 2025 cm^{-1}, 1918 cm^{-1}, 1902 cm^{-1}. ESI-MS (*m*/*z*): 472.62 (100, $[M-Cl^-+H_2O]^+$), 507.77 (60, $[M+NH_4{}^+]^+$), 455.10 (21, $[M-Cl^-]^+$. Anal. Calcd for **2**, $C_{15}H_{12}ClN_2O_3Re$: C, 36.77; H, 2.47; N, 5.72. Found: C, 36.72; H, 2.41; N, 5.75. X-ray quality crystals were grown from the vapor diffusion of pentane into a chloroform solution of **3** (Supporting Information, Figure S6).

[Re(4,4′-di-*tert*-butyl-2,2′-bipyridine)(CO)$_3$Cl] (4). $Re(CO)_5Cl$ (0.1075 g, 0.30 mmol) was dissolved in 50 mL of hot toluene. An equimolar amount of 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.0800 g, 0.30 mmol) was added to the hot solution, and the reaction mixture was stirred with reflux for 1 h. Once the solution reached reflux the mixture began to change color from clear, to yellow, and finally to orange. After 1 h of reflux the reaction mixture was removed from heat and cooled in a freezer. Solid did not precipitate from cold toluene in this reaction, so the solvent was removed in vacuo leaving a gold solid. This solid was then dissolved in acetone, and an equal amount of heptane was added. The acetone was removed by vacuum, leaving only heptane. The product immediately precipitated from heptane and was isolated by filtration. The yellow solid was dried overnight in a vacuum oven at 90 °C. Spectroscopically pure product was obtained from the reaction with an overall yield of 95%. ^{1}H NMR (acetonitrile-d_3): δ 1.45 (s, 18H, ^{t}Bu), δ 7.64 (dd, 2H, 5 and 5′ H's), δ 8.41 (d, 2H, 6 and 6′ H's), δ 8.88 (d, 2H, 3 and 3′ H's). IR (CH_3CN) ν(CO): 2023 cm^{-1}, 1916 cm^{-1}, 1898 cm^{-1}. ESI-MS (*m*/*z*): 556.69 (100, $[M-Cl^-+H_2O]^+$), 596.96 (54, $[M+Na^+]^+$). Anal. Calcd for **2**, $C_{21}H_{24}ClN_2O_3Re$: C, 43.93; H, 4.21; N, 4.88. Found: C, 43.91; H, 4.21; N, 4.89.

[Re(4,4′-dimethoxy-2,2′-bipyridine)(CO)$_3$Cl] (5). This complex was prepared with slight modifications to literature methods.[34] $Re(CO)_5Cl$ (0.101 g, 0.28 mmol) was dissolved in 50 mL of hot toluene. An equimolar amount of 4,4′-dimethoxy-2,2′-bipyridine (0.060 g, 0.28 mmol) was added, and a reflux condenser was attached. After 5 min of stirring with heat, the reaction mixture started to turn yellow. Reflux was continued for 2 h, and the reaction mixture was allowed to cool. The solution was put in a freezer for 1 h to precipitate the product. The yellow solid was filtered and washed with pentane before being dried overnight at 90 °C under vacuum. The spectroscopically pure product was weighed (0.126 g), and a yield of 85% was obtained for the reaction. ^{1}H NMR (acetonitrile-d_3): δ 4.01 (s, 6H, CH_3), δ 7.10 (dd, 2H, 5 and 5′ H's), δ 7.86 (d, 2H, 3 and 3′ H's), δ 8.74 (d, 2H, 6 and 6′ H's). IR (CH_3CN) ν(CO): 2022 cm^{-1}, 1914 cm^{-1}, 1896 cm^{-1}. ESI-MS (*m*/*z*): 504.48 (100, $[M-Cl^-+H_2O]^+$), 544.84 (18, $[M+Na^+]^+$). X-ray quality crystals were grown from the vapor diffusion of diethyl ether into an acetonitrile solution of **5** (Supporting Information, Figure S7).

[*fac*-Re(4,4′-di-*tert*-butyl-2,2′-bipyridine)(CO)$_3$]$_2$ (6). $Re_2(CO)_{10}$ (0.081 g, 0.124 mmol) was dissolved in 100 mL of hot xylenes with stirring. To the hot solution, 2 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.066 g, 0.248 mmol) was added, and the solution was refluxed for 72 h. Over the course of the reflux the solution turned from clear to dark purple. After 72 h, the reaction mixture was removed from heat, and an aliquot was taken for FTIR analysis. Solid product was obtained from the reaction mixture by recrystallization with copious amounts of diethyl ether. IR (xylenes) ν(CO): 1990 cm^{-1}, 1952 cm^{-1}, 1890 cm^{-1}, 1862 cm^{-1}.

Electrochemistry. Electrochemical experiments were performed using either a BAS CV-50 or BAS Epsilon potentiostat. A one compartment cell was used for all cyclic voltammetry experiments with a glassy carbon electrode (3 mm in diameter from BASi), a Pt wire counter electrode, and a Ag/AgCl reference with internal Fc/Fc^+ as an internal reference. All electrochemical experiments were performed with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte, and all solutions were purged with argon or CO_2 before CVs were taken. Re complex concentrations ranged from 0.5 to 1.5 mM, and experiments with CO_2 were performed at gas saturation ($\sim$ 0.25 M) in acetonitrile.[35,36]

A Teflon-shrouded glassy carbon rotating disk electrode was employed to determine the diffusion coefficient of Re(bipy-tBu)(CO)$_3$Cl (**4**), along with a Pt counter electrode and Ag/AgCl reference. A Pine Instruments, Inc., Model ASR2 electrode rotator was employed for all rotating disk experiments. In these experiments, a 70−75 mL, 5 mM solution of the rhenium complex with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) was used in a 100 mL round-bottom flask. CVs were taken from 0 to 2000 rpm rotation rates at potentials from 0 to −2500 mV versus SCE at 100 mV/s. In these scans, both reductions of the rhenium complex were seen. The absolute current heights for each reduction were tabulated for every scan rate to construct a Levich−Koutecky plot for the data. Data from both reduction peaks fit a linear plot of inverse current versus the negative square root of the rotation rate. A good linear fit for the data in this plot represents usable data for the calculation of diffusion coefficient. Data points from the line were then inserted in the Levich−Koutecky equation to calculate the diffusion coefficient for each species in the reduction pathway.

Bulk Electrolysis. Bulk electrolysis experiments were carried out in a single compartment cell with a carbon disk working electrode, a platinum cage counter electrode, and an Ag/AgCl reference electrode on the BAS Epsilon potentiostat. The bulk reductions were carried out in a 0.1 M TBAH/CH_3CN solution. The bulk electrolysis solution was purged with CO_2 for 20 min prior to electrolysis. Gas analysis for bulk electrolysis experiments were performed using 1 mL sample injection volume on a Hewlett-Packard 7890A Series gas chromatograph with a molsieve column (30 m × 0.53 mm ID × 25 μm film).

Cyclic Voltammetry Simulation. Cyclic voltammograms were simulated using Digisim software.[37] All simulations were done on cyclic voltammograms for the first reduction only, and then extended to the second reduction on full voltammograms. Catalyst and substrate concentrations were held constant in the simulations based on experimental details, and the diffusion

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(35) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870.

(36) Gennaro, A.; Isse, A. A.; Vianello, E. *J. Electroanal. Chem.* **1990**, *289*, 203.

(37) Rudolph, M. *J. Electroanal. Chem.* **1991**, *314*, 13.

coefficients of Re(bipyridyl) complexes were determined as described above using rotating disk electrode experiments.

Infrared Spectroelectrochemistry (FTIR-SEC). The design of the IR spectroelectrochemical cell used for the rhenium catalyst studies has been reported previously by our laboratory[38] and is based on a cell used by Mann and co-workers.[39−43] IR spectral changes accompanying thin-layer bulk electrolyses were measured using a flow-through spectroelectrochemical cell. All spectroelectrochemical experiments were carried out in a 0.1 M TBAH solution using acetonitrile, and all solutions were prepared under an atmosphere of dry nitrogen in a drybox. Blank acetonitrile solutions with 0.1 M TBAH were used for the FTIR solvent subtractions. A Pine Instrument Company Model AFCBP1 bipotentiostat was used to affect and monitor thin layer bulk electrolysis. The IR spectra were acquired using the Bruker Equinox 55 spectrometer mentioned above. For the CO_2(g) experiments, CO_2 was bubbled through the catalyst solution for 10 min prior to injection into the SEC cell.

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Supporting Information Available: Figures S1−S7 and a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Zavarine, I. S.; Kubiak, C. P. *J. Electroanal. Chem.* **2001**, *495*, 106.

(39) Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 4006.

(40) Bullock, J. P.; Palazotto, M. C.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1284.

(41) Bullock, J. P.; Palazzotto, M. C.; Mann, K. R. *Inorg. Chem.* **1990**, *29*, 4413.

(42) Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429.

(43) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Washington, J.; Kubiak, C. P. *Science* **1997**, *277*, 660.