Published in final edited form as:

Catal Today. 2014 April 15; 225: 149–157. doi:10.1016/j.cattod.2013.10.091.

Reduction of CO₂ using a Rhenium Bipyridine Complex Containing Ancillary BODIPY Moieties

Justin J. Teesdale[§], Allen J. Pistner[§], Glenn P.A. Yap[§], Ying-Zhong Ma[†], Daniel A. Lutterman^{†,*}, and Joel Rosenthal^{§,*}

[§]Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716

[†]Chemical Sciences Division Oak Ridge National Laboratory, Oak Ridge, TN, 37831

Abstract

The reduction of carbon dioxide to chemical fuels such as carbon monoxide is an important challenge in the field of renewable energy conversion. Given the thermodynamic stability of carbon dioxide, it is difficult to efficiently activate this substrate in a selective fashion and the development of new electrocatalysts for CO₂ reduction is of prime importance. To this end, we have prepared and studied a new *fac*-Re^I(CO)₃ complex supported by a bipyridine ligand containing ancillary BODIPY moieties ([Re(BB2)(CO)₃Cl]). Voltammetry experiments revealed that this system displays a rich redox chemistry under N₂, as [Re(BB2)(CO)₃Cl] can be reduced by up to four electrons at modest potentials. These redox events have been characterized as the Re^{I/0} couple, and three ligand based reductions – two of which are localized on the BODIPY units. The ability of the BB2 ligand to serve as a non-innocent redox reservoir is manifest in an enhanced electrocatalysis with CO₂ as compared to an unsubstituted Re-bipyridine complex lacking BODIPY units ([Re(bpy)(CO)₃Cl]). The second order rate constant for reduction of CO₂ by [Re(BB2)(CO)₃Cl] was measured to be $k = 3400 \text{ M}^{-1}\text{s}^{-1}$ at an applied potential of -2.0 V versus SCE, which is roughly three times greater than the corresponding unsubstituted Re-bipyridine homologue. Photophysical and photochemical studies were also carried out to determine if [Re(BB2)(CO)₃Cl] was a competent platform for CO₂ reduction using visible light. These experiments showed that this complex supports unusual excited state dynamics that precludes efficient CO₂ reduction and are distinct from those that are typically observed for *fac*-Re^I(CO)₃ complexes.

Keywords

BODIPY; carbon dioxide; catalysis; electrochemistry; photochemistry; rhenium bipyridine derivatives

© 2013 Elsevier B.V. All rights reserved.

*luttermanda@ornl.gov; joelr@udel.edu.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Introduction

The electrochemical production of fuels from carbon dioxide is an important step toward the development of schemes for artificial photosynthesis.^{1,2} In particular, the renewable production of liquid fuels is critical to addressing societal needs pertaining to transportation,³ which account for nearly 30% of US energy demand.⁴ An attractive approach in this regard is the efficient reduction of CO₂ to CO, coupled to the production of synthetic petroleum using existing Fisher-Tropsch methods.^{5–7} In this way, the renewable generation of CO represents a key energy storing reaction for the production and distribution of versatile chemical fuels.

Renewable production of carbon-based fuels can be accomplished by interfacing electrocatalysts for CO₂ reduction with a photovoltaic assembly^{8–10} or a conventional electrolyzer powered by an alternative source of electricity. Of the several major classes of homogenous electrocatalysts for CO₂ reduction,¹¹ metal polypyridyl complexes based on ruthenium,^{12–17} and rhenium^{18–25} have been particularly well studied. One of the earliest metal complexes of this type that was shown to efficiently catalyze the electrochemical conversion of CO₂ to CO was Lehn's Re-bipyridine system (**[Re(bpy)(CO)₃Cl]**).²⁶ This compound, which is shown in Chart 1, has been reported to drive this process with reasonable turnover number (TON) and a Faradaic efficiency (FE) that approached unity. More recently, Kubiak demonstrated that the activity of Lehn's Re-complex could be vastly improved by utilizing a modified bpy ligand containing *tert*-butyl groups at the 4- and 4'-positions.²⁷ The improved kinetics observed for this system are believed to be due to a combination of two factors: (1) increased electron donation by the alkyl substituted bipyridine ligand engenders greater nucleophilicity to the Re center, leading to enhanced activation of CO₂, and (2) the bulky *tert*-butyl groups at the bpy 4- and 4'-positions sterically inhibits Re^I—Re^I dimerization, which can occur during electrocatalysis and decrease the amount of active [Re⁰(bpy)(CO)₃][–] available to activate CO₂ near the electrode surface.²⁸

Given the stereoelectronic factors that are attendant with enhanced CO₂ electrocatalysis by Re-bipyridine complexes, we rationalized that an assembly supported by a bulky bpy ligand bearing redox active moieties might also serve as an improved platform for CO₂ reduction, as compared to Lehn's unsubstituted **[Re(bpy)(CO)₃Cl]** complex. Toward this end, we recently developed a 2,2'-bipyridine derivative containing boron-dipyrromethane moieties appended to the 4 and 4'-positions of the ligand.²⁹ This bpy-BODIPY construct (**BB2**) is highly sterically encumbered and supports a notable redox chemistry, as each of the BODIPY units can be reversibly reduced by a single electron at modest potentials. In the present study we report the first transition-metal complex supported by **BB2** – the BODIPY appended rhenium complex (**[Re(BB2)(CO)₃Cl]**) shown in Chart 1. We have undertaken a detailed study of the structural, electrochemical and photochemical properties of this platform. Cyclic voltammetry revealed that **[Re(BB2)(CO)₃Cl]** supports a rich redox chemistry and can be reduced by up to four electrons at modest potentials, with three of these redox events being ligand centered. Moreover, the ability of the BODIPY appended ligand of **[Re(BB2)(CO)₃Cl]** to serve as a redox reservoir by storing multiple reducing equivalents, manifests in enhanced electrocatalytic activity with CO₂ as compared to the

corresponding unsubstituted homologue ($[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$). Since complexes of this type are also excellent photocatalysts for CO_2 reduction, we have also probed the ability of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ to drive the photochemical generation of CO. The BODIPY chromophores appended to the bipyridine ligand of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ are excellent light absorbers in the visible region, and the photophysics of this system were surveyed from 300 – 700 nm. Unlike for traditional *fac*- $\text{Re}^{\text{I}}(\text{CO})_3$ complexes, the presence of the BODIPY units on the bipyridine ligand of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ gives rise to excited state dynamics that are distinct from that of more commonly studied rhenium-bipyridine complexes. Implications for the future development and photochemical investigation of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ and related systems is also discussed.

Experimental

General Materials and Methods

Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N_2 using flasks fitted with Suba-Seal rubber septa or in nitrogen filled glove box. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were purchased from Sigma Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Solvents for synthesis were of reagent grade or better.

^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent ($\text{CDCl}_3 = \delta$ 7.26) and carbon spectra are referenced to the carbon resonances of the solvent ($\text{CDCl}_3 = \delta$ 77.23). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. High resolution mass spectrometry was performed at the University of Delaware Mass Spectrometry Facility. Both compound **1**³⁰ and $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ ³¹ were synthesized using previously published methods.

[2,2'-bipyridine]-4,4'-dicarbonyl chloride (**2**)

This compound was prepared with slight modifications to a literature method.²⁹ [2,2'-bipyridine]-4,4'-dicarboxylic acid (**1**) (0.50 g, 2.2 mmol) was suspended in 20 mL of thionyl chloride heated to reflux with stirring under an atmosphere of N_2 . After 24 hours all material was dissolved in the SOCl_2 , which appeared as a dark yellow solution. Following removal of the SOCl_2 under reduced pressure, the resulting material was dried in vacuo for 30 min. The reaction product was used immediately in the following reaction, assuming a quantitative yield.

4,4'-bis(BODIPY)-2,2'-bipyridine (BB2)

This compound was prepared using a modified literature method.²⁹ The [2,2'-bipyridine]-4,4'-dicarbonyl chloride (**2**) synthesized in the previous step was dissolved in 100 mL of CHCl_3 that had been sparged with N_2 for 45 min. To this solution was added 2,4-dimethyl-3-ethylpyrrole (2.11 mL, 15.6 mmol). The reaction mixture was then heated under N_2 to 50 °C with stirring for 90 min. After approximately 25 min the solution became dark

brown in color. After 90 min the solvent was removed by rotary evaporation and the residue was dissolved in 200 mL of 5% CH₂Cl₂ in toluene. Triethylamine (2.48 mL, 17.8 mmol) was added to the reaction, which was stirred under air for 30 min at room temperature. The solution was then heated to 50 °C and 3.85 mL (31.2 mmol) of BF₃•OEt₂ was added. The reaction was stirred for an additional 90 min at 50 °C, after which time, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica, eluting first with CH₂Cl₂ and followed by CH₂Cl₂ and CH₃OH (99:1). Analytically pure material (0.780 g; 46%) was afforded by a second silica column purification using CH₂Cl₂ and CH₃OH (99:1) as the mobile phase. ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, *J* = 4.9 Hz, 1H), 8.53 (s, 1H), 7.35 (d, *J* = 4.8 Hz, 1H), 2.55 (s, 6H), 2.30 (d, *J* = 7.6 Hz, 4H), 1.38 (s, 6H), 0.99 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 156.51, 155.05, 150.38, 145.84, 138.13, 136.72, 133.65, 130.10, 124.35, 121.54, 53.79, 17.40, 14.96, 12.96, 12.66. HR-ESI-MS: [M+H]⁺ *m/z*: calcd for C₄₄H₅₁B₂F₄N₆, 761.4297; found 761.4302

Re[4,4'-bis(BODIPY)-2,2'-bipyridine](CO)₃Cl ([Re(BB2)(CO)₃Cl])

This compound was prepared with slight modifications to a literature method.²⁷ Re(CO)₅Cl (0.040 g, 0.11 mmol) and **BB2** (0.084 g, 0.11 mmol) were dissolved in 50 mL of toluene and heated at reflux under air overnight for 14 hrs. After allowing the resulting dark red solution to cool to room temperature, the majority of the solvent was removed by rotary evaporation until only 2–3 mL of solvent remained and the resulting precipitate was isolated by filtration and dried in vacuo to deliver 0.106 g of the title compound as a scarlet powder (90%). ¹H NMR (400 MHz, CDCl₃) δ 9.24 (d, *J* = 5.6 Hz, 1H), 8.19 (s, 1H), 7.60 (dd, *J* = 5.6, 1.5 Hz, 1H), 2.52 (d, *J* = 5.1 Hz, 6H), 2.29 (dq, *J* = 19.0, 7.5 Hz, 4H), 1.46 (s, 3H), 1.30 (s, 3H), 0.96 (dt, *J* = 19.4, 7.5 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 197.04, 157.08, 156.55, 156.19, 154.23, 148.72, 138.15, 136.77, 134.94, 134.39, 132.90, 129.80, 129.28, 127.92, 123.95, 32.27, 30.05, 29.71, 23.04, 17.38, 14.89, 14.77, 14.48, 13.30, 13.07. HR-ESI-MS: [M+H]⁺ *m/z*: calcd for C₄₇H₅₁B₂ClF₄N₆O₃Re, 1067.3391; found 1067.3443. *v*_{max} (KBr)/cm⁻¹ 2021.50, 1920.95, 1906.39 (s, C≡O).

Electrochemistry

Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-720D bipotentiostat. Cyclic voltammetry (CV) was performed using a standard three-electrode configuration. The working electrode was a polished glassy carbon electrode (GCE, 3.0 mm diameter CH Instruments) and a piece of platinum wire was used as the counter electrode. All potentials were measured against a silver wire pseudo reference with a ferrocene internal standard and were adjusted to the saturate calomel electrode (SCE) via the relation Fc/Fc⁺ = 460 mV + SCE. Unless otherwise stated, the electrolyte was 0.1M TBAPF₆, the sample concentration was 1.0 mM, and all CV experiments were carried out using a scan rate of 100 mV/s.

Controlled potential electrolysis (CPE) experiments were performed in a single-compartment cell using the same three-electrode setup employed for CV measurements. These consisted of a polished glassy carbon working electrode, a platinum mesh counter electrode, and a Ag/AgCl reference electrode (1.0 M KCl, CH Instruments) or a silver wire

pseudo reference. Prior to electrolysis the solution was sparged with MeCN saturated CO₂ gas for approximately 30 min, following which, the cell was sealed and electrolysis initiated. The headspace of the electrolysis cell was sampled periodically by manually removing 1.0 mL aliquots using a gas-tight syringe. These aliquots were analyzed by manual injection into a gas-sampling loop of a Shimadzu GC-2014 gas chromatograph (GC). This GC was equipped with two 10 port injection valves in line with HaySepT 80/100 columns. Quantification of CO was accomplished using a flame ionization detector (FID) with methanizer after passage through a HaySepD 80/100 column using helium (99.999%) as the carrier gas. Quantification of H₂ was accomplished using a thermal conductivity detector (TCD) after passage through a packed MolSieve 5A 60/80 column, using argon as the carrier gas (99.999%).

X-ray Structure Determination

[Re(BB2)(CO)₃Cl] consistently deposited as red, multiple, crystal masses and the results herein represent the best of several trials. A crystal was sectioned and mounted on plastic mesh with viscous oil flash-cooled to 200 K. Data were collected on a Bruker-AXS Apex 2 Duo CCD diffractometer with Gobel mirror focussed Cu-K α radiation ($\lambda=1.54178$ Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω , from three different sections of the Ewald sphere. No symmetry higher than triclinic was observed and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with numerical absorption corrections. The structure was solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 6.12 program library.³²

Two molecules of [Re(BB2)(CO)₃Cl] and one disordered molecule of methylene chloride solvent were located in the asymmetric unit and rigid bond displacement restraints were applied. One ethyl group was found disordered with a refined site occupancy of 72/28. The disordered solvent molecule was treated as a rigid body with idealized geometry and with a refined site occupancy ratio of 52/48.

Computations

Geometry optimizations and frequency calculations were performed using the Gaussian09 (G09) program package,³³ with the Becke three-parameter hybrid exchange and the Lee–Yang–Parr correlation functionals (B3LYP). The 6-31G* basis set was used for H, B, C, N, O, and F, along with the Stuttgart/Dresden (SDD) energy-consistent pseudopotentials for Re. Crystallographic coordinates were used as starting points for geometry optimizations. All geometry optimizations were performed in C₁ symmetry with subsequent vibrational frequency analysis to confirm that each stationary point was a minimum on the potential energy surface. Molecular orbital were visualized using Visual Molecular Dynamics (VMD) software.

UV-vis Absorption

UV/visible absorption spectra were acquired on an Agilent 8453 Diode Array UV-vis spectrometer using screw cap quartz cuvettes (6q) of 1 cm pathlength from Starna. All absorption spectra were recorded at room temperature and all samples were prepared in DMF.

Steady-State Fluorescence Measurements

Spectra were recorded on an automated Photon Technology International (PTI) QuantaMaster 40 fluorometer equipped with a 75-W Xenon arc lamp, a LPS-220B lamp power supply and a Hamamatsu R2658 photomultiplier tube. Samples for fluorescence analysis were prepared in an analogous method to that described above for the preparation of samples for UV-vis spectroscopy. Samples were excited at $\lambda_{\text{ex}} = 500$ nm and emission was monitored from 510–800 nm with a step size of 1 nm and integration time of 0.5 seconds. Reported spectra are the average of at least three individual acquisitions.

Emission quantum yields were calculated using Ru(phen)₃Cl₂ in water ($\Phi_{\text{ref}} = 0.072$)³⁴ as the reference actinometer using the expression below:³⁵

$$\Phi_{\text{em}} = \Phi_{\text{ref}} \left(\frac{A_{\text{ref}}}{A_{\text{em}}} \right) \left(\frac{I_{\text{em}}}{I_{\text{ref}}} \right) \left(\frac{\eta_{\text{em}}}{\eta_{\text{ref}}} \right)^2$$

The Φ_{em} and Φ_{ref} represent the emission quantum yield of the sample and the reference, respectively, A_{ref} and A_{em} are the measured absorbance of the reference and sample at the excitation wavelength, respectively, I_{ref} and I_{em} are the integrated emission intensities of the reference and sample, respectively, and η_{ref} and η_{em} are the refractive indices of the solvents of the reference and sample, respectively ($\eta_{\text{ref}} = 1.33$ and ($\eta_{\text{em}} = 1.43$). The optical density of the samples and references were kept around 0.1 at $\lambda_{\text{ex}} = 500$ nm.

Time-resolved Fluorescence Measurements

Time correlated single photon counting (TCSPC) experiments were performed on an IBH (Jobin Yvon Horiba) model 5000F instrument equipped with single monochromators on both the excitation and emission sides of the instrument. The excitation light source was a NanoLED with a short 1.3 ns pulse width at 458 nm. Emission signals were collected on a picosecond photon detection module (TBX-04) at an angle perpendicular to excitation for samples and blanks. Data was collected at 550 nm and averaged (30,000 counts) to obtain the decay profile. Decay analysis and curve fitting routines to determine sample lifetimes were performed by the software (DAS6) provided by the manufacturer (IBH).

Photocatalytic CO₂ Reduction and Headspace Analysis

The experimental setup for picosecond time- correlated single-photon-counting (TCSPC) measurements has been described in detail previously³⁶ and only a brief account will be given here. The detection system includes an actively quenched single photon avalanche photodiode (PDM 50CT module, Micro Photon Devices) and a TCSPC module (PicoHarp 300, PicoQuant). The light source was an optical parametric amplifier pumped by a 250 kHz

Ti:Sapphire regenerative amplifier. Excitation was at 500 nm with typically 50 fs (full width at half maximum, fwhm) pulse duration and ~4 nJ pulse energy. Fluorescence emission was selected by using a 5 nm (fwhm) bandpass filter centered at 550 nm, which were chosen according to the peak wavelength of the fluorescence emission spectra. The instrument response function (IRF) showed a fwhm of ~40 ps as recorded at the excitation wavelength using a dilute water suspension of coffee creamer. A 4.0-ps channel time was chosen and typically more than 10,000 counts were collected in the peak channel in order to obtain an acceptable signal-to-noise ratio. The polarization of the excitation beam was set to the magic angle (54.7) with respect to an emission linear polarizer, which enables us to eliminate any depolarization contribution. Quantitative analysis of the time-resolved fluorescence data were performed by employing a least squares deconvolution fitting algorithm with explicit consideration of the finite IRF (FluoFit, PicoQuant) and a reduced chi-squares (χ^2) value was used to judge the quality of each fit.

Photocatalytic CO₂ Reduction and Headspace Analysis

Samples (1.5 mM) were prepared in 5:1 DMF:triethanol amine to a total volume of 3 mL in a 8 mL cuvette. The samples were charged with a stir bar and the system was sealed with a rubber septum which was tightened with a copper wire. The sample solution and cuvette headspace was saturated with CO₂ by sparging for 25 minutes. The samples were irradiated with light from a 200 W Xe arc lamp (Oriel Instruments Model 66057). The wavelength of light was controlled by passing it through a long pass filter ($\lambda > 400$ or 495 nm) that was immersed in water. Light was focused onto the stirred sample and irradiated for 17 hrs. After irradiation, aliquots were analyzed by gas chromatography coupled to a methanizer and flame ionization detector (GC-FID) for CO production and a known quantity of CO was injected for normalization purposes.

Results and Discussion

Study of the BODIPY appended Re-bipyridine complex began with the synthesis of the necessary 4,4'-bis(BODIPY)-2,2'-bipyridine ligand (**BB2**), following the pathway shown in Scheme 1. In previous work, we demonstrated that **BB2** could be prepared in modest yield via condensation of compound **2** with 2,4-dimethyl-3-ethylpyrrole, BF₃•OEt₂ and NEt₃ at elevated temperature (~75 °C).²⁹ We have found that this reaction can be adapted to run at lower temperatures with slightly longer reaction times. These modified conditions are commensurate with vastly improved yields for **BB2**, as carrying out this condensation at 50 °C in CHCl₃ more than doubles the yield for preparation **BB2** to approximately 45%.

Metallation of **BB2** was readily accomplished by heating a toluene solution of the ligand and Re(CO)₅(Cl) at reflux for 14 hours. Crystallization of the reaction product allowed for isolation of [Re(**BB2**)(CO)₃Cl] in 90% yield. The solid-state structure of this complex was determined by X-ray crystallography. Single crystals of [Re(**BB2**)(CO)₃Cl] were grown by slow evaporation of a saturated CH₂Cl₂ solution of the complex. Crystal parameters for [Re(**BB2**)(CO)₃Cl] are provided in Table 1. The structure (Figure 1) reveals that the BODIPY moieties that comprise the **BB2** ligand are significantly canted with respect to the bipyridine backbone. The dihedral angles between each BODIPY unit and the bipyridine

bridge were measured to be 73.8° and 83.2°. NMR data recorded for this complex demonstrates that the orthogonal orientation between the BODIPY and bipyridine frameworks is not simply a result of crystal packing. As shown in Figure 2, both the methyl and ethyl groups on the BODIPY moieties are inequivalent for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ as judged by ^1H NMR spectroscopy. This inequivalency is not observed for the free **BB2** ligand, and is due to one half of the BODIPY unit being oriented toward the axial chloride ligand, while the other halves are oriented toward the axial carbonyl. The methyl substituents at the 1- and 7-positions of the BODIPY framework hinder rotation about the indacenebipyridine bond under ambient conditions. This molecular topology limits the extent of π -communication between the BODIPY sites and bipyridine spacer, however, the direct linkage of the bpy bridge to the 8-position of the indacenes manifests in strong coupling through the σ -framework of the ligand.

With $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in hand, we sought to characterize the redox behavior of this metal complex. Cyclic voltammetry (CV) experiments conducted in MeCN containing 0.1 M TBAPF₆ under an atmosphere of N₂ revealed two quasi-reversible reductions at approximately -0.85 V and -1.0 V, as well as a broad reduction wave centered at -1.6 V vs. SCE (Figure 3A). These results are distinct from those observed for simpler Re bipyridine complexes which do not bear BODIPY groups on the bpy ligand. For comparison, a CV trace recorded for Lehn's unsubstituted Re bipyridine complex ($[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$)²⁶ are reproduced in Figure 3. This complex only displays two reduction waves centered at approximately -1.4 V and -1.8 V. Both these reduction waves correspond to single electron redox events based on an internal ferrocene standard and have been ascribed to reduction of the bipyridine ligand and Re^{I/0} couple, respectively.^{26,27,37,38} Notably, both of these waves occur at potentials that are more negative than the corresponding redox events for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ (*vide infra*).

Based on these designations, the third redox feature observed for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ at -0.85 V can be attributed to the near simultaneous reduction of each BODIPY moiety on the **BB2** ligand by a single electron. This assignment is consistent with redox properties of the free **BB2** ligand, which show two closely separated single electron reductions at -1.15 V and -1.22 V versus SCE.²⁹ Furthermore, the stoichiometry for this process is supported by experiments that employ an internal ferrocene standard and by noting that the reduction wave at -0.85 V is roughly twice as large as the subsequent single-electron bipyridine reduction that follows at -1.0 V. These designations are buttressed by DFT calculations performed for the $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ complex. As shown in Figure 4, the frontier orbitals for this system are all localized on the **BB2** ligand and are close in energy.

The ability of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ to electrochemically activate carbon dioxide was probed by studying the voltammetry of this complex in the presence of CO₂. As shown in Figure S1, the CV profile obtained for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in MeCN under an atmosphere of CO₂ is significantly altered compared to the corresponding trace recorded under N₂. Both ligand redox waves are shifted to slightly more positive potentials, as reduction of the BODIPY moieties occurred at approximately -0.75 V, followed by the reduction of the bipyridine ligand at -0.9 V. Most notably, a large increase in current is observed upon scanning to more negative potentials, consistent with an electrocatalytic process taking place at

potentials more negative than -1.65 V (Figures 3b and S1). The onset of this catalytic wave, which maximizes at approximately -2.0 V at a scan rate of 100 mV/s suggests that reduction of the Re^{I} center triggers CO_2 catalysis. This mechanistic pathway is consistent with that proposed for other Re bipyridine based CO_2 reduction electrocatalysts.

A comparison of the CVs obtained for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ under 1 atm of CO_2 (Figure 3b) suggests that the activity of these complexes are similar. This result is somewhat surprising considering that reduction of the bipyridine ligand and Re^{I} center of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ occurs at potentials that are approximately 350 mV more positive than those for the unsubstituted complex (*vide supra*). By contrast, other Re-bipyridine complexes that display ligand reduction waves at potentials more positive than -1.1 V generally display very little electrocatalytic activity with CO_2 .^{27,39} The improved performance of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in this regard may result from storage of electron equivalents on the BODIPY units of the supporting ligand. Since both BODIPY moieties are reduced at potentials at which electrocatalysis is observed, the ability of the indacene π -systems to serve as redox reservoirs may increase the overall reducing power of the $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ complex and assist in CO_2 activation.

In order to more rigorously quantify the observed electrocatalysis, we subjected the voltammetry data of Figure 3 to a Foot-of-the-Wave analysis, as has been developed by Savéant.⁴⁰⁻⁴² Using this method, we were able to determine the second order rate constant for CO_2 reduction for both Re-bipyridine complexes using Equation 1.

$$\frac{i}{i_p^0} = \frac{2.24 \sqrt{\frac{RT}{F\nu}} 2kC_A^0}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]} \quad (1)$$

In the equation above, i is the current in the presence of substrate (i.e., CO_2), i_p^0 is the current in the absence of substrate, k is the second order rate constant, which we sought to determine, C_A^0 is the concentration of the substrate (0.270 M in MeCN),⁴³ E is the potential at which the current was measured, and E_{PQ}^0 is the peak potential of the catalytic redox couple in the absence of substrate.

Analysis of the voltammetry data for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in Figure S1 was carried out by constructing a plot of i/i_p^0 versus $(1 + \exp[(F/RT)(E - E_{PQ}^0)])^{-1}$ as shown in Figure S2. Based on Equation 2, the slope of the linear regression that is fit to this data has a slope that is approximate to $2.24((RT/F\nu)2kC_A^0)^{1/2}$, which allows for the second order constant (k) to be determined. Under the conditions employed for this study, the rate constant for CO_2 reduction by $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ was determined to be approximately $k = 3400 \text{ M}^{-1}\text{s}^{-1}$ at an applied potential of -2.0 V. By contrast, carrying out the same analysis for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ leads to a rate constant of $k = 1100 \text{ M}^{-1}\text{s}^{-1}$ at the same potential (Figures S3 and S4). Based on these results, it is clear that the **BB2** framework engenders an enhanced catalysis, as the BODIPY appended catalyst is roughly three times more active than the analogous unsubstituted complex. This enhancement is presumably due to the steric bulk

imparted by the large indacene units, which impedes formation of reduced $\text{Re}^{\text{I}}\text{---Re}^{\text{I}}$ dimers. Furthermore, recent work has shown that non-innocent ligand reservoirs can significantly alter metal-ligand bonding in *fac*- $\text{Re}^{\text{I}}(\text{CO})_3$ complexes.⁴⁴ As such, the ability of the BODIPY appended ligand of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ to store multiple reducing equivalents during electrocatalysis may manifest in enhanced nucleophilic character at the metal center, while providing an electron reservoir that helps to drive the two electron reduction of CO_2 to CO.

Controlled potential electrolysis (CPE) experiments were performed in order to confirm and quantify the products of CO_2 electrocatalysis. The electrolyses were carried out using a single-compartment cell equipped with a glassy carbon working electrode for 1.0 mM solutions of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in CO_2 saturated MeCN containing 0.1 M TBAPF₆. After initiating the electrolysis at -2.0 V versus SCE, the headspace of the electrochemical cell was periodically analyzed by gas chromatography. This analysis showed that $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ quickly catalyzed the production of CO over the first 10 min of the CPE experiment with associated current densities of approximately 0.3 mA/cm^2 . Although $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ catalyzed CO production, current densities associated with this process quickly decay to negligible levels after 15 – 20 minutes. This quick decay in catalysis is not due to decomposition of the rhenium complex in solution, but rather, is a result of deposition of reduced $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ onto the working electrode, which is apparent from a simple visual inspection of the glassy carbon surface. Passivation of the working electrode is also evident by comparing CVs recorded for a 1.0 mM solution of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ before and after an 60 min CPE experiment. As shown in Figure S5, all redox waves are suppressed after electrolysis at -2.0 V, however, polishing the glassy carbon electrode completely restores the expected CV response (Figure S5). We note that this deposition is not typically observed for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ or other simple Re-bipyridine complexes, which retain their electrocatalytic activity over several hours.²⁷ This behavior is also distinct from that displayed by vinyl substituted Re-bipyridine complexes that can be electrodeposited on electrode surfaces.^{45,46} The rapid deposition of $\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}$ onto the working electrode may be due to formation of π - π interactions between the large, planar BODIPY units of the **BB2** ligand and the glassy carbon surface.

Rhenium bipyridyl complexes have been shown to be excellent photocatalysts for conversion of CO_2 to CO. As initially demonstrated by Lehn and coworkers, excitation of the metal-to-ligand charge transfer (MLCT) transition of platforms such as $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ in the presence of a sacrificial reductant such as triethanol amine (TEOA) leads to formation of a reduced rhenium complex that can activate CO_2 .²⁶ A major limitation of such complexes, however, is their lack of significant absorption features in the visible region. The inability of these systems to harvest solar energy at wavelengths longer than $\sim 450 \text{ nm}$ is a critical impediment to the use of sunlight to drive CO_2 reduction, since the solar power spectrum is most intense from approximately $425 - 600 \text{ nm}$. Since BODIPY^{47–51} and other polypyrrole derivatives^{52–55} can absorb light throughout the visible region we rationalized that $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ might support an improved photocatalysis with CO_2 using sunlight, as compared to *fac*- $\text{Re}^{\text{I}}(\text{CO})_3$ frameworks lacking indacene units.⁵⁶

Figure 5 presents the UV-vis absorption and emission profiles of the BODIPY containing **BB2** ligand and the corresponding Re complex (**[Re(BB2)(CO)₃Cl]**). The **BB2** ligand displays a UV-vis spectrum that is typical of that observed for BODIPY derivatives, with a strong absorption centered at 526 nm and a sharp fluorescence peak centered at 549 nm. This ligand is highly emissive, as the quantum yield of fluorescence for **BB2** was measured to be $\Phi_{\text{Fl}} = 0.70$ with an associated lifetime of $\tau_{\text{Fl}} = 3.7$ ns. Both these values are typical of BODIPY derivatives derived from substituted pyrrole precursors.^{29, 57, 58} **[Re(BB2)(CO)₃Cl]** also displays a strong BODIPY absorption band at 529 nm along with a characteristic MLCT transition, which is centered at approximately 375 nm and extends out to nearly 450 nm. The observation that the BODIPY $S_0 \rightarrow S_1$ transition of the **BB2** ligand is shifted bathochromically by less than 5 nm upon incorporation into the *fac*-Re^I(CO)₃ complex, suggests the preservation of this BODIPY excited state in **[Re(BB2)(CO)₃Cl]**. The emission properties of this complex are perturbed relative to the free **BB2** ligand, however, as the BODIPY fluorescence is significantly quenched. The emission quantum yield of **[Re(BB2)(CO)₃Cl]** was measure to be $\Phi_{\text{Fl}} = 0.02$ with an associated lifetime of $\tau_{\text{Fl}} = 335$ ps, which demonstrates that depopulation of the pyromethene excited state occurs rapidly for the BODIPY appended rhenium complex. These results suggest that the pendant BODIPY moieties of **[Re(BB2)(CO)₃Cl]** can efficiently sensitize the *fac*-Re^I(CO)₃ center by either an electron transfer⁵⁹ or energy transfer mechanism.

Once the basic photophysics of **[Re(BB2)(CO)₃Cl]** had been characterized, we probed the ability of this complex to photochemically activate CO₂ using visible light. Irradiation of a CO₂ saturated solution of **[Re(BB2)(CO)₃Cl]** (1.5 mM) in DMF/ TEOA (5:1) with light of $\lambda_{\text{ex}} = 500$ nm resulted in the generation of negligible levels of CO as judged by gas chromatography. The observation that excitation of the BODIPY units of **[Re(BB2)(CO)₃Cl]** does not induce CO₂ reduction is somewhat surprising given that the BODIPY excited state is so efficiently quenched by the Re center. Direct excitation of the MLCT transition of **[Re(BB2)(CO)₃Cl]** provided a similar result, as repeating the photolysis experiment with light of $\lambda_{\text{ex}} = 400$ nm did not lead to appreciable CO₂ reduction. This result is particularly surprising since prior work has shown that incorporation of BODIPY units into *fac*-Re^I(CO)₃ complexes does not abolish the MLCT derived photocatalysis common to this class of compounds.⁵⁶ As such, the lack of photochemistry observed for **[Re(BB2)(CO)₃Cl]** indicates that directly linking the BODIPY units onto the bipyridine ligand of systems such as **[Re(bpy)(CO)₃Cl]**, significantly perturbs the photophysics inherent to the rhenium complex. More detailed time-resolved absorption experiments should be helpful in illuminating these unusual excited state dynamics.

Summary and Future Directions

The conversion of CO₂ to CO is a process of potential import for the storage and distribution of renewable energy resources. In this work, we have described a new electrocatalyst for this reaction. This system (**[Re(BB2)(CO)₃Cl]**) is comprised of a *fac*-Re^I(CO)₃ center supported by a non-innocent bipyridine ligand with appended BODIPY moieties. Electrochemical experiments reveal that **[Re(BB2)(CO)₃Cl]** supports a rich redox chemistry and can be reduced by up to four electrons at modest potentials, with each BODIPY unit serving as a

redox reservoir. The ability of **BB2** to store multiple electron equivalents is manifest in enhanced activity for electrocatalytic CO₂ reduction relative to Lehn's unsubstituted Re-bipyridine homologue ([**Re(bpy)(CO)₃Cl**]). Foot-of-the-wave analysis shows that the rate constant for activation of CO₂ by [**Re(BB2)(CO)₃Cl**] is approximately three times greater than for [**Re(bpy)(CO)₃Cl**] at -2.0 V. It is notable that this enhancement is realized despite the fact that the BODIPY appended complex is reduced at potentials that are roughly 350 mV more positive than the corresponding unsubstituted variant.

In addition to the voltammetric analyses, CPE experiments confirm that [**Re(BB2)(CO)₃Cl**] is an electrocatalyst for conversion of CO₂ to CO. These CPE experiments also reveal that while this system is stable in MeCN solution under electrolysis conditions, deposition of [**Re(BB2)(CO)₃Cl**] leads to passivation of the working electrode surface.

A combination of photophysical and photocatalysis studies conducted for [**Re(BB2)(CO)₃Cl**] showed that coupling of BODIPY units directly to the bipyridine backbone significantly attenuates the photochemistry that is typically observed for *fac*-Re^I(CO)₃ complexes in the presence of CO₂. Future transient absorption experiments are required to determine the manner in which the BODIPY units perturb the excited state dynamics of this system. It will also be interesting to see if the photochemistry of this and related systems, can be altered by changing the positions to which BODIPY moieties are attached to the bipyridine ligand of *fac*-Re^I(CO)₃ complexes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Research reported in this publication was supported by an Institutional Development Award (IDeA) from the National Institute of General Medical Sciences of the National Institutes of Health under grant number P20GM103541. JR was supported through a DuPont Young Professor award. JR also thanks the University of Delaware Research Foundation and the donors of the American Chemical Society's Petroleum Research Fund for financial support. DAL was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. The authors thank the Ohio Supercomputer Center for support. NMR and other data were acquired at UD using instrumentation obtained with assistance from the NSF and NIH (NSF-MIR 0421224, NSF-CRIF MU CHE-0840401 and CHE-0541775, NIH P20 RR017716).

References

1. Olah GA, Goeppert A, Prakash GKS. J. Org. Chem. 2009; 74:487–498. [PubMed: 19063591]
2. Olah GA, Prakash GKS, Goeppert A. J. Am. Chem. Soc. 2011; 133:12881–12898. [PubMed: 21612273]
3. Centi G, Perathoner S. Catal. Today. 2009; 148:191–205.
4. Annual Energy Review 2011. US Energy Information Administration; 2012 Sep.
5. Rofer-DePoorter CK. Chem. Rev. 2012; 81:447–474.
6. Vennestrøm PNR, Osmundsen CM, Christensen CH, Taarning E. Angew. Chem. Int. Ed. 2011; 50:10502–10509.
7. Takeshita T, Yamaji K. Energy Policy. 2008; 36:2773–2784.
8. Kumar B, Smieja JM, Kubiak CP. J. Phys. Chem. C. 2010; 114:14220–14223.
9. Kumar B, Smieja JM, Sasayama AF, Kubiak CP. Chem. Commun. 2012; 48:272–274.

10. Smieja JM, Benson EE, Kumar B, Grice KA, Seu CS, Miller AJM, Mayer JM, Kubiak CP. *Proc. Natl. Acad. Sci. USA.* 2012; 109:15646–15650. [PubMed: 22652573]
11. Benson EE, Kubiak CP, Sathrum AJ, Smieja JM. *Chem. Soc. Rev.* 2008; 38:89–99. [PubMed: 19088968]
12. Ishida H, Tanaka K, Tanaka T. *Organometallics.* 1987; 6:181–186.
13. Nagao H, Mizukawa T, Tanaka K. *Inorg. Chem.* 1994; 33:3415–3420.
14. Takeuchi KJ, Thompson MS, Pipes DW, Meyer TJ. *Inorg. Chem.* 1984; 23:1845–1851.
15. Concepcion JJ, Jurss JW, Norris MR, Chen Z, Templeton JL, Meyer TJ. *Inorg. Chem.* 2010; 49:1277–1279. [PubMed: 20058918]
16. Chen Z, Chen C, Weinberg DR, Kang P, Concepcion JJ, Harrison DP, Brookhart MS, Meyer TJ. *Chem. Commun.* 2011; 47:12607–12609.
17. Chen Z, Concepcion JJ, Brennaman MK, Kang P, Norris MR, Hoertz PG, Meyer TJ. *Proc. Natl. Acad. Sci. USA.* 2012; 109:15606–15611. [PubMed: 22685210]
18. Sullivan BP, Meyer TJ. *Organometallics.* 1986; 5:1500–1502.
19. O'Toole TR, Sullivan BP, Bruce MRM, Margerum LD, Murray RW, Meyer TJ. *J. Electroanal. Chem. Interfacial Electrochem.* 1989; 259:217–239.
20. O'Toole TR, Margerum LD, Westmoreland TD, Vining WJ, Murray RW, Meyer TJ. *Chem. Commun.* 1985:1416–1417.
21. Agarwal J, Sanders BC, Fujita E, Schaefer IIIHF, Harrop TC, Muckerman JT. *Chem. Commun.* 2012; 48:6797–6799.
22. Agarwal J, Johnson RP, Li G. *J. Phys. Chem. A.* 2011; 115:2877–2881. [PubMed: 21410231]
23. Agarwal J, Fujita E, Schaefer HF, Muckerman JT. *J. Am. Chem. Soc.* 2012; 134:5180–5186. [PubMed: 22364649]
24. Sullivan BP, Meyer TJ. *Organometallics.* 1986; 5:1500–1502.
25. Sullivan BP, Meyer TJ. *Chem. Commun.* 1984:1244–1245.
26. Hawecker J, Lehn J-M, Ziessel R. *Chem. Commun.* 1984:328–330.
27. Smieja JM, Kubiak CP. *Inorg. Chem.* 2010; 49:9283–9289. [PubMed: 20845978]
28. Benson EE, Kubiak CP. *Chem. Commun.* 2012; 48:7374–7376.
29. Rosenthal J, Nepomnyashchii AB, Kozhukh J, Bard AJ, Lippard SJ. *J. Phys. Chem. C.* 2011; 115:17993–18001.
30. Uhlich MA, Sommer P, Bühr C, Schürch S, Reymond J-L, Darbre. *Chem. Commun.* 2009:6237–6239.
31. Worl LA, Duesing R, Chen P, Ciana LD, Meyer TJ. *Dalton Trans.* 1991:849–858.
32. Sheldrick GM. *Acta Cryst.* 2008; A64:112–122.
33. Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, GA.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, HP.; Izmaylov, AF.; Bloino, J.; Zheng, G.; Sonnenberg, JL.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, JA., Jr; Peralta, JE.; Ogliaro, F.; Bearpark, M.; Heyd, JJ.; Brothers, E.; Kudin, KN.; Staroverov, VN.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, JC.; Iyengar, SS.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, JM.; Klene, M.; Knox, JE.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Martin, RL.; Morokuma, K.; Zakrzewski, VG.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Dapprich, S.; Daniels, AD.; Farkas, Ö.; Foresman, JB.; Ortiz, JV.; Cioslowski, J.; Fox, DJ. *Gaussian 09, Revision A.01.* Wallingford CT: Gaussian, Inc.; 2009.
34. Juris A, Balzani V, Barigelli F, Campagna S, Belser P, Von Zelewsky A. *Coord. Chem. Rev.* 1988; 84:85–277.
35. Calvert JM, Caspar JV, Binstead RA, Westmoreland TD, Meyer TJ. *J. Am. Chem. Soc.* 1982; 104:6620.
36. Ma Y, Shaw R, Yu X, O'Neil HM, Hong K. *J. Phys. Chem. B.* 2012; 116:14451–14460. [PubMed: 23140246]
37. Sullivan BP, Bolinger CM, Conrad D, Vining WJ, Meyer TJ. *Chem. Commun.* 1985:1414–1416.

38. Johnson FPA, George MW, Hartl F, Turner JJ. *Organometallics*. 1996; 15:3374–3387.
39. Juris A, Campagna S, Bidd I, Lehn J-M, Ziessel R. *Inorg. Chem.* 1988; 27:4007–4011.
40. Costentin C, Drouet S, Robert M, Saveant J-M. *J. Am. Chem. Soc.* 2012; 134:11235–11242. [PubMed: 22670885]
41. Costentin C, Drouet S, Robert M, Saveant J-M. *J. Am. Chem. Soc.* 2012; 134:19949–19950.
42. Costentin C, Drouet S, Robert M, Saveant J-M. *Science*. 2012; 338:90–94. [PubMed: 23042890]
43. Tomita Y, Teruya S, Koga O, Hori Y. *J. Electrochem. Soc.* 2000; 147:4164–4167.
44. Roy S, Blane T, Lilio A, Kubiak CP. *Inorg. Chim. Acta*. 2011; 374:134–139.
45. O'Toole TR, Sullivan BP, Bruce MRM, Margerum LD, Murray RW, Meyer TJJ. *Electroanal. Chem. Interfacial Electrochem.* 1989; 259:217–239.
46. O'Toole TR, Margerum LD, Westmoreland TD, Vining WJ, Murray RW, Meyer TJ. *Chem. Commun.* 1985:1416–1417.
47. Loudet A, Burgess K. *Chem. Rev.* 2007; 107:4891–4932. [PubMed: 17924696]
48. Ziessel R, Ulrich G, Harriman A. *New J. Chem.* 2007; 31:496–501.
49. Lazarides T, McCormick TM, Wilson KC, Lee S, McCamant DW, Eisenberg RJ. *Am. Chem. Soc.* 2011; 133:350–364.
50. Turfan B, Akkaya EU. *Org. Lett.* 2002; 4:2857–2859. [PubMed: 12182573]
51. Nepomnyashchii AB, Pistner AJ, Bard AJ, Rosenthal J. *J. Phys. Chem. C*. 2013; 117:5599–5609.
52. Lee CY, Hupp JT. *Langmuir*. 2010; 26:3760–3765. [PubMed: 19886633]
53. Leonardi MJ, Topka MR, Dinolfo PH. *Inorg. Chem.* 2012; 51:13114–13122. [PubMed: 23215151]
54. Pistner AJ, Yap GPA, Rosenthal J. *J. Phys. Chem. C*. 2012; 116:16918–16924.
55. Pistner AJ, Lutterman DA, Ghidui MJ, Ma Y-Z, Rosenthal J. *J. Am. Chem. Soc.* 2013; 135:6601–6607. [PubMed: 23594346]
56. Andrade GA, Pistner AJ, Yap GPA, Lutterman DA, Rosenthal J. *ACS Catal.* 2013; 3:1685–1692. [PubMed: 24015374]
57. Nepomnyashchii AB, Broring M, Ahrens J, Bard AJ. *J. Am. Chem. Soc.* 2011; 133:8633–8645. [PubMed: 21563824]
58. Rosenthal J, Lippard SJ. *J. Am. Chem. Soc.* 2010; 132:5536–5537. [PubMed: 20355724]
59. Jones G, Kumar S, Klueva O, Pacheco D. *J. Phys. Chem. A*. 2003; 107:8429–8434.

Highlights

- A new rhenium bipyridine complex with ancillary BODIPY units (**[Re(BB2)(CO)₃Cl]**) was prepared and the structure determined
- **[Re(BB2)(CO)₃Cl]** supports an intriguing redox chemistry and can store multiple electrons
- **[Re(BB2)(CO)₃Cl]** displays a higher TOF for reduction of CO₂ to CO versus similar rhenium complexes
- **[Re(BB2)(CO)₃Cl]** supports an unusual photochemistry that is of interest to the photocatalytic reduction of CO₂

Figure 1. Solid-State structure of $[\text{Re}(\text{BB}2)(\text{CO})_3\text{Cl}]$ shown from (a) the front and (b) in profile. Thermal ellipsoids are shown at the 30% probability level (F, green; B, orange; C, black; N, blue; O, red). Hydrogen atoms and a cocrystallized CH_2Cl_2 solvent molecule are omitted for clarity.

Figure 2.
Comparison of ^1H NMR spectra recorded for **BB2** and $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ in CDCl_3 .

Figure 3.

Cyclic voltammograms recorded for 1.0 mM solutions of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ (red) and $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ (black) in MeCN containing 0.1 M TBAPF₆ under an atmosphere of (a) N₂, and (b) CO₂. A polarization curve recorded for CO₂ saturated MeCN in the absence of a Re complex is shown in blue. All voltammograms were recorded using a glassy carbon working electrode and a Pt auxiliary electrode at a scan rate of 100 mV/s.

Figure 4.

Calculated frontier molecular orbitals for $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$ by DFT. The calculated LUMO and LUMO+1 are nearly isoenergetic.

Figure 5. Absorbance (solid lines) and emission (dashed lines) spectra recorded for **BB2** (green) and **[Re(BB2)(CO)₃Cl]** (orange) in DMF. Emission spectra were recorded using $\lambda_{\text{ex}} = 500$ nm.

Scheme 1.
Synthesis of $[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]$.

Re(bpy)(CO)₃Cl

Chart 1.

Re(BB2)(CO)₃Cl

Table 1Crystallographic Data for $2[\text{Re}(\text{BB2})(\text{CO})_3\text{Cl}]\cdot\text{CH}_2\text{Cl}_2$

Formula	$\text{C}_{47.5}\text{H}_{51}\text{B}_2\text{Cl}_2\text{F}_4\text{N}_6\text{O}_3\text{Re}$
F_w	1108.66
Crystal System	Triclinic
Space Group	P_{-1}
a	14.4395(8) Å
b	16.3930(9) Å
c	22.5783(12) Å
α	82.748(4)°
β	89.828(4)°
γ	73.525(4)°
V	5081.0(5) Å ³
Z	4
Temp	200(2) K
D_{calcd}	1.449 g/cm
2θ range	144.86°
μ (Cu K α)	6.141 mm ⁻¹
Reflections	49241
Unique	14814
R (int)	0.2102
R_1	0.0801
wR_2	0.1746