Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO

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The effective design of an artificial photosynthetic system entails the optimization of several important interactions. Herein we report stopped-flow UV-visible (UV-vis) spectroscopy, X-ray crystallographic, density functional theory (DFT), and electrochemical kinetic studies of the $\text{Re}(\text{bipy-tBu})(\text{CO})_3(\text{L})$ catalyst for the reduction of CO_2 to CO. A remarkable selectivity for CO_2 over H^+ was observed by stopped-flow UV-vis spectroscopy of $[\text{Re}(\text{bipy-tBu})(\text{CO})_3]^{-1}$. The reaction with CO_2 is about 25 times faster than the reaction with water or methanol at the same concentrations. X-ray crystallography and DFT studies of the doubly reduced anionic species suggest that the highest occupied molecular orbital (HOMO) has mixed metal-ligand character rather than being purely doubly occupied d_z^2 , which is believed to determine selectivity by favoring CO_2 ($\sigma + \pi$) over H^+ (σ only) binding. Electrocatalytic studies performed with the addition of Brønsted acids reveal a primary H/D kinetic isotope effect, indicating that transfer of protons to Re-CO_2 is involved in the rate limiting step. Lastly, the effects of electrode surface modification on interfacial electron transfer between a semiconductor and catalyst were investigated and found to affect the observed current densities for catalysis more than threefold, indicating that the properties of the electrode surface need to be addressed when developing a homogeneous artificial photosynthetic system.

carbon dioxide reduction | electrochemistry | kinetics | electrocatalyst

The development of artificial photosynthetic systems is of immediate concern in view of the world's dependence on fossil fuels and the increasing emissions of CO_2 . Rapid industrial growth in developing nations will significantly increase the global energy demand in coming years, and although known reserves of fuels such as natural gas and coal are sufficient for the near future, they are becoming increasingly costly to obtain. As the use of fossil fuels is fundamentally unsustainable and generates greenhouse gases and other pollutants, the development of environmentally benign energy sources is important. Solar energy is an abundant alternative but suffers from being a diffuse energy source, and its availability varies by location and time of day. If we can capture solar energy and use CO_2 as a C_1 feedstock for liquid fuels, we can envision converting our global energy economy into a nearly carbon-neutral system (1).

Photosynthesis is one of the great triumphs of nature and is the cornerstone for advanced life on the planet. Mankind has yet to master nature's ability to store sunlight as chemical energy by splitting CO_2 and H_2O to form C—C, C—H, and O—O bonds. The energy-dense liquid fuels formed by this process would have the advantage of conforming to the existing infrastructure. Photosynthesis can be divided into two parts: water splitting and reduction of carbon dioxide. Water oxidation has been reviewed extensively by others (2–4).

Our laboratory is currently exploring the development of CO_2 reduction catalysts with the goal of implementing a directly photo-driven system. A few systems for the direct conversion

of solar energy into chemical energy using a CO_2 reduction catalyst at a semiconductor photoelectrode have been reported (5–9), and further development of this concept will require optimization of both the catalyst and the semiconductor components.

The reduction of CO_2 to useful products is inherently proton-dependent. This dependence is true not only for the production of carbohydrates by natural photosynthesis, but also for the synthetic production of other value-added products. The protons required are susceptible to competitive, direct reduction to H_2 , a process that occurs at a more positive (i.e., more favorable) thermodynamic potential. A functional artificial photosynthetic system therefore requires a catalyst that is kinetically selective for CO_2 reduction over H^+ reduction.

Recently, we have explored complexes of the type $\text{Re}(\text{bipy-R})(\text{CO})_3(\text{L})$ (where bipy-R is 4,4'-disubstituted-2,2'-bipyridine and L is a halide or a neutral ligand with $-\text{OTf}$) and reported that $\text{Re}(\text{bipy-tBu})(\text{CO})_3\text{Cl}$ **1** is a precatalyst for the electrochemical reduction of CO_2 to CO at high turnover frequency ($>200 \text{ s}^{-1}$) (10) compared with the previous reports on $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$ (11, 12). Complex **1** has one of the highest turnover frequencies reported for the reduction of CO_2 to CO, and exhibits nearly 100% faradic efficiency with very high turnover numbers. We have also successfully coupled the catalyst to a semiconductor electrode, p-type silicon (p-Si), which enables us to provide part of the thermodynamic energy for catalysis using solar illumination (8).

A fully operational photoelectrochemical device will require the coordination of photovoltaics, semiconductor electrodes, catalysts, and substrates. We believe that understanding the individual components of the system will accelerate research toward a functional device. Herein, we report detailed studies of the key components in an artificial photosynthetic system based on the $\text{Re}(\text{bipy-tBu})(\text{CO})_3(\text{L})$ catalyst (Fig. 1) that are widely applicable to homogeneous photoelectrochemical catalysis. The first is the interaction between the catalyst and the two potential substrates, CO_2 and H^+ . We show by stopped-flow UV-visible (UV-vis) spectroscopy that the active catalyst displays remarkable selectivity for CO_2 over H^+ . The origins of this desirable activity were further investigated through crystallographic and density

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Fig. 1. Schematic for a device using a p-Si/Re(bipy-tBu)(CO)₃Cl semiconductor/molecular catalyst junction to photoelectrochemically reduce CO₂.

functional theory (DFT) characterization of the reduced catalytic intermediate. We also show that CO₂ reduction is enhanced by the addition of Brønsted acids, and exhibits a primary H/D kinetic isotope effect (KIE). Whereas most electrocatalytic studies focus primarily on the catalyst/substrate interaction, it is important not to overlook the heterogeneous electron transfer from the electrode to the catalyst. To probe this interaction, we studied catalytic behavior at various electrode surfaces, including semiconductors.

Results and Discussion

Synthesis of [Re(bipy-tBu)(CO)₃]⁻¹. Previously published results (10) suggested that the doubly reduced [Re(bipy-tBu)(CO)₃]⁻¹ anion is the species that actively binds CO₂, rendering it the most immediately relevant intermediate in studies of CO₂/H⁺ selectivity. We observed that solutions of this species could be generated by reduction of **1** with KC₈. With careful handling, they could be maintained and characterized by a variety of techniques.

UV-Vis Stopped-Flow Spectroscopy: Probing the Selectivity of the Re Catalyst. Recently published results demonstrated the remarkable selectivity of the [Re(bipy-tBu)(CO)₃]⁻¹ anion toward CO₂ over H⁺ reduction (13). We investigated the CO₂/H⁺ selectivity in detail using stopped-flow UV-vis experiments to quantify their relative rates of reaction with the Re catalyst. Although the exact products are not well-defined in these stoichiometric reactions, the relative rates of the reactions are still informative. The UV-vis spectrum of the reduced Re anion contains a strong absorption at 570 nm (14,000 M⁻¹ cm⁻¹) that presumably arises from a coordinated bipyridine-based radical. The persistence of the anion was thus monitored at this absorption. The parent complex, **1**, however, has a λ_{max} at 384 nm (3,900 M⁻¹ cm⁻¹) (14). Solutions of the reduced complex were mixed in the stopped-flow apparatus with either CO₂-saturated tetrahydrofuran (THF) (0.20 M) (15) or with 0.20 M solutions of H₂O, CH₃OH, or CF₃CH₂OH (TFE) in THF.

The spectral changes for the CO₂ reaction show rapid and complete decay of Re anion (Fig. 2). The absorbance at 570 nm follows first-order kinetics over three half-lives, with *t*_{1/2} = 20 ms and a pseudo first-order rate constant of 35 s⁻¹ (Table 1). The reactions with water, CH₃OH, and TFE were much slower and were not complete at the end of monitoring. Control reactions mixing the Re anion with pure THF (no CO₂ or proton source) showed background degradation on this longer timescale. Remarkably, TFE did not appear to react with the Re anion on the timescale of the experiments (up to 150 s). These results mirror the electrochemical results that suggest that CO₂ is more readily reduced than H⁺ by the Re anion, and suggest that this selectivity may have its origin in the initial reaction of the substrate with the doubly reduced Re species.

The H₂O and CH₃OH reactions were more complicated than simple first-order decay of the Re anion. The absorbance at 570 nm did not fully bleach, and new absorbances are observed at approximately 520 and 370 nm (Fig. S1). Until more detailed

Fig. 2. Reaction of [Re(bipy-tBu)(CO)₃]⁻¹ in THF with a solution of 200 mM CO₂ in THF over 0.75 s in a stopped-flow UV-vis experiment. Scans were taken every 1.5 ms over the course of the experiment and the degradation of the peak at 570 nm was followed for the half-life and pseudo first-order rate constant determination.

kinetic analyses can be completed, we have estimated half-lives for these reactions to provide a comparison with the well-behaved CO₂ reaction: approximately 0.5 s for H₂O, approximately 1 s CH₃OH, and greater than or equal to 100 s for TFE. These values imply that the reaction with CO₂ is about 25 times faster than that with H₂O, and 50 times faster than that with CH₃OH. The slower reaction with TFE than with H₂O or CH₃OH is surprising given the higher acidity of TFE and suggests that these reactions may be more complicated than simple protonation of the Re anion. Still, the conclusion is very clear that the Re anion reacts much more quickly with CO₂ than with sources of H⁺.

Crystallography and DFT of the Re Anion: Origins of Selectivity. With stable solutions of the [Re(bipy-tBu)(CO)₃]⁻¹ species in hand, the source of CO₂ selectivity could be investigated through structural studies. Single crystals suitable for X-ray diffraction were grown from the vapor diffusion of pentane into a THF solution of the anion containing 18-crown-6 as a stabilizing agent. Upon

Table 1. Results from UV-vis stopped-flow experiments of [Re(bipy-tBu)(CO)₃]⁻¹

Reactant	Half-life (<i>t</i> _{1/2})	Pseudo first-order rate constant
CO ₂	0.02 s	35 s ⁻¹
H ₂ O	[0.5 s]	[~1 s ⁻¹]
CH ₃ OH	[1 s]	[~1 s ⁻¹]

The first three half-lives for the CO₂ reaction fit well to pseudo first-order kinetics. The H₂O and CH₃OH reactions, however, as described in the text, are more complex. The values given above in square brackets are rough estimates of the time for the first half-life of reaction, estimated from the spectral changes in Figs. S1 and S2.

reduction, complex **1** loses chloride and adopts a distorted trigonal bipyramidal structure ($\tau_5 = 0.46$) (16) in the solid state with the Re coordinated by three facial carbonyl ligands and a chelating bipyridine (Fig. 3, numbering scheme in Fig. S2, selected bond lengths and angles in Table S1, and crystallographic data and refinement information in Table S2). The potassium cation is encapsulated by the crown ether and has one bound THF molecule. It is also associated with the axial carbonyl [O3–K1, 2.945(7) Å]. The Re–N distance contracts and the bite angle of the bipyridine increases slightly compared with the unreduced starting material (Fig. S3). This behavior is indicative of an improved orbital overlap between the ligand and metal center in the anion.

To obtain a better understanding of the electronics of this reduced state, we employed DFT calculations using the Amsterdam Data Functional (ADF) program 2007.1. The calculated highest occupied molecular orbital (HOMO) is a hybrid involving both the ligand and the metal center, containing substantial π^* character (Fig. S4). This calculated orbital is consistent with the bond length alternation observed in the bipyridine rings of the Re anion crystal structure, which is similar to what is seen in crystal structures of reduced 2,2'-bipyridine (17), suggesting significant electron density on the ligand. The geometry of the HOMO diffuses the directional basicity of the Re anion, and thus other factors such as π interactions become important. We expect that the mixed character of the HOMO ($\text{bipy}^- + \text{Re}^0$) relative to a doubly occupied d_z^2 lone-pair is sufficient to cause CO_2 binding to be more favorable than H^+ binding. Similarly, a HOMO that is delocalized disfavors direct protonation of the Re d_z^2 orbital to produce a hydride.

The nature of the binding of CO_2 to the anion can also be better understood through DFT. The geometry-optimized electronic structure of a $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{CO}_2)\text{K}$ complex was calculated. The structure did not converge without the addition of a cation (H, Li, Na, K) to support the highly electronegative oxygen atoms. We observed that the d_z^2 orbital can form a σ bond to the carbon atom of CO_2 (HOMO), and the interaction with CO_2 can be further stabilized by a π interaction of the metal d_{xz} and d_{yz} orbitals with p orbitals on the CO_2 oxygen atoms (HOMO-4) (Fig. 4). This stabilizing interaction is clearly not available for the interaction with H^+ and is similar to that calculated by Fujita and coworkers for $[\text{Co}(\text{macrocycle})(\text{CO})_2(\text{CH}_3\text{CN})]^+$, but the Re complex forms an extended bonding interaction with the CO_2 oxygen atoms rather than with the carbon center (18).

Brønsted Acid Rate Enhancement and Kinetic Isotope Effects. Having established a marked selectivity for CO_2 over H^+ , we investigated the catalytic system in the presence of added proton sources. The parent catalyst system, **1**, has a very negative catalytic potential of -2.23 V (vs. Fc/Fc^+) relative to the thermodynamic potential of the reduction of CO_2 to CO (approximately -1.2 V vs. Fc/Fc^+ in

Fig. 3. Full structure of $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3][\text{K}(18\text{-crown-6})\cdot\text{THF}]$. Hydrogen atoms are omitted for clarity and ellipsoids are shown at 50% probability.

Fig. 4. Calculated orbitals of $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{CO}_2)\text{K}$ using ADF 2007.1 showing (A) the HOMO orbital where Re (d_z^2) forms a σ bond to the carbon atom of CO_2 (s and p_z), and (B) the HOMO-4 orbital that forms π interactions between the d_{yz} and d_{xz} orbitals of Re and the p orbitals of the oxygen atoms on CO_2 .

water at pH 7). The high overpotential creates a situation where catalysis can occur without an added proton source. Previous reports have suggested that the oxygen from CO_2 is transferred to an unknown oxide acceptor (19). The oxide acceptor can be a proton that can be extracted from acetonitrile (20) or even from the supporting electrolyte via Hoffman degradation (21). More recently, evidence pointing to protons as the oxide acceptor was reported by Wong et al. They showed that the catalytic current increased for the reduction of $\text{Re}(\text{bipy})(\text{CO})_3(\text{py})(\text{OTf})$ under CO_2 in the presence of increasing concentrations of weak Brønsted acids (22). In their study, the rate of electrocatalytic CO_2 reduction increased for the series: $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{phenol} < \text{TFE}$. In all cases, the faradic efficiency for the production of CO remained greater than 95%.

The CO_2 reduction behavior of the improved catalysts $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{MeCN})(\text{OTf})$ **2** and $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{py})(\text{OTf})$ **3** were studied in the presence of H_2O , CH_3OH , and TFE under an atmosphere of CO_2 . Under argon before the addition of protons, complex **2** exhibits one reversible reduction at -1.71 V followed by a quasireversible reduction at -1.94 V (vs. Fc/Fc^+). Complex **3** exhibits one reversible reduction at -1.64 V and one quasireversible reduction at -1.95 V (vs. Fc/Fc^+) (Fig. 5).

Given that **1** showed a substantial increase in the rate of catalysis over the original $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$ catalyst (10), we expected to see even higher current densities upon the addition of protons to **2** and **3** in the presence of CO_2 . Upon addition of CH_3OH or TFE, an increased i_{cat}/i_p was observed compared with the results of Wong et al., whereas for water a similar i_{cat}/i_p was observed (Table 2).

Fig. 5. $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{py})(\text{OTf})$ **2** under argon (black) and CO_2 (red). The solution is 1 mM in catalyst with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A 1 mm diameter glassy carbon electrode, a Pt wire counter electrode, and an Ag wire pseudo reference were used with ferrocene added as an internal reference.

Table 2. Summary of results for addition of Brønsted acids

Precatalyst	Brønsted acid	Highest i_{cat}/i_p *	CO ₂ solubility at highest i_{cat}/i_p
Re(bipy- <i>t</i> Bu)(CO) ₃ (MeCN)(OTf) 2	TFE	54.0 (1.6 M)	0.19 M
Re(bipy- <i>t</i> Bu)(CO) ₃ (MeCN)(OTf) 2	methanol	41.9 (9.9 M)	0.22 M
Re(bipy- <i>t</i> Bu)(CO) ₃ (MeCN)(OTf) 2	water	9.0 (10.0 M)	0.18 M
Re(bipy- <i>t</i> Bu)(CO) ₃ (py)(OTf) 3	TFE	62.0 (1.5 M)	0.27 M
Re(bipy- <i>t</i> Bu)(CO) ₃ (py)(OTf) 3	methanol	28.9 (8.0 M)	0.23 M
Re(bipy- <i>t</i> Bu)(CO) ₃ (py)(OTf) 3	water	8.2 (7.3 M)	0.19 M
Re(bipy)(CO) ₃ (py)(OTf) [†]	TFE	47.1 (0.77 M)	0.27 M
Re(bipy)(CO) ₃ (py)(OTf) [†]	phenol	39.5 (0.57 M)	0.30 M
Re(bipy)(CO) ₃ (py)(OTf) [†]	methanol	31.1 (7.20 M)	0.24 M
Re(bipy)(CO) ₃ (py)(OTf) [†]	water	11.4 (10.4 M)	0.17 M

*Acid concentration in parenthesis.

[†]From Wong et al. (22).

A normal primary H/D kinetic isotope effect was observed in these experiments (data for CH₃OH vs. CD₃OD in Fig. 6). For complex **2**, the KIE for H₂O/D₂O is 1.8(±0.1), the KIE for CH₃OH/CD₃OD is 1.8(±0.1), and the KIE for TFE/TFE-d₃ is 1.2(±0.1). The decreased KIE for TFE is attributed to an increased mismatch between the pK_a of the metal-bound CO₂ and the pK_a of the acid (23). The observation of a KIE suggests that proton transfer to the Re-CO₂ adduct is likely involved in the rate limiting step in this reaction.

The Brønsted acid experiments also suggest that the catalytic reaction is second-order in acid. A linear region can be observed in a plot of the ratio of catalytic current (i_{cat}) to noncatalytic current (i_p) vs. substrate concentration (Fig. S5). This behavior is expected for an EC' catalytic mechanism, in which the relationship between substrate concentration and current ratio can be described by Eq. 1 (24, 25), as follows:

$$\text{TOF} = k[\text{sub}]^x = \frac{F\theta n_p}{RT} \left(\frac{0.4463}{n_{\text{cat}}} \right)^2 \left(\frac{i_{\text{cat}}}{i_p} \right)^2. \quad [1]$$

All of the acids exhibit this behavior before tapering and establishing a steady i_{cat}/i_p . Catalytic currents do not plateau in the cyclic voltammograms under CO₂ (even at high H⁺ concentrations), but Eq. 1 applies because the catalytic current is scan rate independent. Additional experiments have established that the reaction is first-order in [CO₂] (22), leading to the rate equation

$$k_{\text{obs}} = k[\text{CO}_2][\text{H}^+]^2. \quad [2]$$

For all Brønsted acids, the production of CO was nearly quantitative (greater than 95% current efficiency) even at acid concen-

Fig. 6. KIE study for CH₃OH and CD₃OD addition to the catalytic reaction of [Re(bipy-*t*Bu)(CO)₃]⁻¹ with CO₂. In each case we see a significant increase in the catalytic current upon addition of the Brønsted acid. The x axis is offset for clarity. These data are representative of the results for H₂O/D₂O and TFE/TFE-d₃.

trations where i_{cat}/i_p was at its maximum, consistent with other data indicating that the catalyst remains very selective for CO₂ even in the presence of a large excess of H⁺. Together, the KIE and second-order [H⁺] dependence of this catalytic reaction provide strong evidence for H₂O formation from the second oxygen atom of the CO₂ substrate.

Interfacial Charge Transfer Studies. We then turned our attention to the heterogeneous charge transfer at the electrode/catalyst interface. In the system shown in Fig. 1, the electrons are generated via photoexcitation from the valence band to the conduction band of the p-Si electrode and move toward the interface between the p-Si and catalyst under the influence of a potential bias. They are then transferred to the catalyst, which goes on to reduce CO₂ to CO.

No reduction peaks are observed for **1** under dark conditions. Under polychromatic light illumination, two one-electron reduction peaks can be observed that are about 600 mV more positive than those obtained at glassy carbon or platinum electrodes (Fig. S64) (8). The limiting catalytic current density for the hydrogen-terminated p-Si/**1** junction was 2.9 mA/cm² (at 0.6 mM catalyst), which is lower than the 5.3 mA/cm² measured at glassy carbon. Given that (i) these TOFs are measured in identical conditions in the same electrochemical cell, (ii) cyclic voltammograms (CVs) of the Re catalyst under Ar have been shown to be stable at illuminated p-Si, (iii) the faradic efficiency for the reduction of CO₂ to CO is nearly 100% for both surfaces, and (iv) single crystalline silicon was used for this work, losses associated with the homogeneous catalysis and bulk semiconductor should be minimal and cannot account for the decrease in limiting catalytic current density. The lower current density for the hydrogen-terminated p-Si/**1** junction can only be explained if the limiting factor involves heterogeneous charge transfer and/or the interaction between the p-Si and complex **1**. This possibility was probed by modifying the surface of the photocathode to improve its charge transfer properties. Styrene and n-hexene were used separately to generate phenylethyl p-Si and hexyl p-Si surfaces using the method described by Buriak and Allen (26).

The current density for the photoelectrochemical reduction of CO₂ at a styrene-modified p-Si electrode in the presence of complex **1** scales with the illumination intensity (Fig. S6B and Table S3). A direct comparison of the photocatalytic current densities shows a more than threefold increase for the styrene-modified p-Si surface over both the hydrogen-terminated surface (Fig. S6C) and the hexene-modified surface with no appreciable change in the onset potential for the catalysis. The hydrogen-terminated and hexene-modified surfaces had very similar current densities under the same catalyst and substrate concentrations. Based on these data, the styrene-modified p-Si outperforms the other semiconductor surfaces, as well as the glassy carbon/**1** junction. The superior performance of the styrene-modified p-Si/**1** is attributed to improved charge transport via π interactions between the aromatic rings on the styrene-modified p-Si surface

and the bipyridine ligand of **1**. These results illustrate the importance of heterogeneous charge transfer between the electrode and catalyst, and the optimization of this interaction should not be overlooked in a homogeneous electrocatalytic system.

Concluding Remarks

This work reinforces the importance of considering not only the interactions of an electrocatalyst with the targeted catalytic substrate but also the heterogeneous electron transfer from the electrode surface to the catalyst. We have shown that the $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{L})$ electrocatalytic system is very selective for the reduction of CO_2 , and that the rate of catalysis can be enhanced by the addition of a proton source. Stopped-flow UV-vis experimental data indicate that CO_2 reacts about 25 times faster than water and about 50 times faster than methanol with $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3]^{-1}$. The reduced form presumed to be the active catalyst was studied by X-ray crystallography. The structural data, combined with DFT studies of the reduced complex, suggest that the HOMO contains mixed metal-ligand character. KIE and kinetic studies indicate that protons are involved in the rate-determining step for the reduction of CO_2 to CO by $\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{L})$. In addition, we have shown that the electrode surfaces make a large difference in the catalytic current density by controlling the electron transfer from the electrode to the catalyst. The catalytic current densities can be increased threefold by modifying the p-Si surface with phenylethyl groups as opposed to hexyl groups or hydrogen atoms. These results may help guide future catalyst design as well as the optimization of other artificial photosynthesis systems.

Materials and Methods

Complex **1** was synthesized by previously reported methods (10). Syntheses of complexes **2** and **3** are reported in the *SI Text* and the crystal structure of **3** is shown in *Fig. S7*. Reductions of complex **1** to the $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3]^{-1}$ were carried out using 2.1 equivalents of K^+C_8 in THF. DFT calculations were performed with the ADF program suite (27, 28), version 2007.1 using the triple- ζ Slater-type orbital basis set. Geometry optimized xyz coordinates for $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3]^{-1}$ and $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3(\text{CO}_2)(\text{K})]$ can be found in *Tables S4* and *S5*, respectively. Further experimental procedures, including electrochemical details and p-Si surface modification techniques, as well as additional references are included in the *SI Text*.

Stopped-flow measurements were performed using a Hi-Tech/TgK Scientific SF-61DX2 CryoStopped-Flow system. A xenon-lamp illuminated the mixing chamber (1 cm path length, fused UV silica) in conjunction with a diode array detector. Samples were prepared under a nitrogen atmosphere in a dry box and were transported to the stopped-flow apparatus in gas-tight syringes. The concentration of $[\text{Re}(\text{bipy-}t\text{Bu})(\text{CO})_3]^{-1}$ before mixing was 0.12 mM, CO_2 was at saturation (approximately 200 mM) in THF. H_2O , methanol, and TFE were all prepared at 200 mM in THF.

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