

Splitting CO₂ into CO and O₂ by a single catalyst

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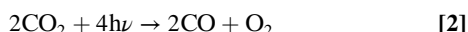
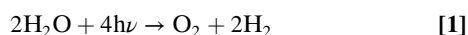
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Edited by Jack Halpern, University of Chicago, Chicago, IL, and approved April 25, 2012 (received for review February 23, 2012)

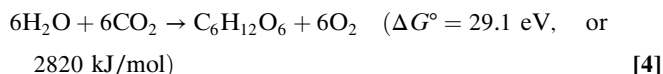
The metal complex [(tpy)(Mebim-py)Ru^{II}(S)]²⁺ (tpy = 2,2':6',2''-terpyridine; Mebim-py = 3-methyl-1-pyridylbenzimidazol-2-ylidene; S = solvent) is a robust, reactive electrocatalyst toward both water oxidation to oxygen and carbon dioxide reduction to carbon monoxide. Here we describe its use as a single electrocatalyst for CO₂ splitting, CO₂ → CO + 1/2 O₂, in a two-compartment electrochemical cell.

artificial photosynthesis | polypyridyl Ru complexes | proton coupled electron transfer | single-site catalysis | solar fuels

Rising energy prices, diminishing reserves of petroleum, and environmental concerns are driving new thinking about our energy future. Given its availability, with approximately 10,000 times the daily energy input required to meet current energy consumption, solar energy could be the ultimate answer. However, solar energy is diffuse, spread over the earth's surface, and requires vast collection areas for large-scale applications (1). A more difficult challenge is the intermittency of the sun as an energy source. Meeting the challenge of providing power at night will require energy storage on massive scales at levels exceeding the ability of existing or foreseeable energy storage technologies (2, 3). The only realistic alternative is energy storage in chemical bonds and the increasingly popular concept of "solar fuels." Solar fuels mimic natural photosynthesis in using solar energy and artificial photosynthesis to convert readily available sources, water and carbon dioxide, into high-energy fuels. Target reactions include water splitting into hydrogen and oxygen and reduction of carbon dioxide to carbon monoxide, other oxygenates, or hydrocarbons (Eqs. 1–3), as follows:

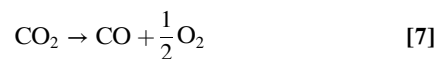
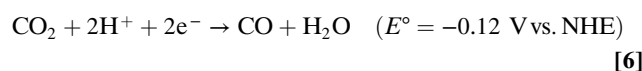
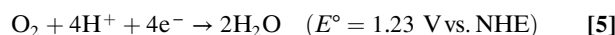


Carrying out these reactions presents a major challenge in chemical reactivity given their multiphoton, multielectron, multiatom character. It is reassuring that similar hurdles have been overcome in natural photosynthesis, in which light-driven reduction of CO₂ to carbohydrates by water occurs (Eq. 4). However, photosynthesis in green plants took 2–3 billion years to evolve and utilizes a complex architecture that utilizes thousands and thousands of atoms and multiple integrated assemblies (4, 5).



A simplifying factor, suggesting a mechanistic approach, comes with recognition that the target energy storage reactions can be split into constituent "half reactions" which are shown for CO₂ splitting in Eqs. 5 and 6. Photosynthesis in green plants occurs in the thylakoid membrane and uses physically separated molecular assemblies for light-driven water oxidation (Photosystem II) and CO₂ reduction (Photosystem I and the Calvin cycle) (6, 7). Electron/proton equilibration occurs by intra- or transmembrane electron/proton transfer channels driven by free energy gradients.

Application of a "half-reaction" strategy in artificial photosynthesis poses similar challenges. In both water oxidation and CO₂ reduction, mechanisms involving one-electron reactions are energetically untenable. They result in •OH on oxidation or CO₂•[−] on reduction at potentials too high to be of interest in solar fuels half-reaction with $E^\circ = 2.72 \text{ V vs. NHE}$ (E° is the standard electrode potential) for the •OH + H⁺ + e[−] → H₂O couple and $E^\circ = -1.90 \text{ V}$ for the CO₂ + e[−] → CO₂•[−] couple. By comparison, $E^\circ = 1.23 \text{ V}$ for water oxidation to oxygen in Eq. 5 and $E^\circ = -0.12 \text{ V}$ for CO₂ reduction to CO in Eq. 6. The energy available in a 500-nm photon in the visible region of the solar spectrum is 2.48 eV. For the reaction, H₂O + CO₂ → •OH + H⁺ + CO₂•[−], $E^\circ = -4.62 \text{ V}$ ($\Delta G^\circ = +4.62 \text{ eV}$) and, for the CO₂ splitting reaction in Eq. 7, $E^\circ = -1.35 \text{ V}$ ($\Delta G^\circ = +2.70 \text{ eV}$). The CO product in Eq. 7 is of interest as a component of syngas, a hydrogen/CO mixture for methanol synthesis (8, 9).



In order to carry out these reactions at or near the thermodynamic potentials for the separate half reactions requires catalysis and utilization of multielectron, multiproton transfer catalysis. This, in turn, requires the accumulation of multiple redox equivalents at single chemical sites or clusters and mechanistic pathways that avoid high-energy, 1e[−] intermediates. A key element in both is proton coupled electron transfer (PCET) and use of half reactions in which both protons and electrons are lost or gained to avoid charge buildup. A second is electron-proton transfer (EPT), in which concerted electron-proton transfer occurs to avoid high-energy intermediates (10–12).

Impressive advances have been made in catalytic water oxidation by transition metal complexes at single-site catalysts (13–25). Progress has also been made on catalytic reduction of CO₂ to CO (26–36). Both present a formidable challenge in chemical reactivity. Nonetheless, we report here that a single metal complex catalyst suffices for both half reactions and apply it for electrocatalytic CO₂ splitting.

Among the family of single-site Ru complex catalysts for water oxidation, [(tpy)(Mebim-py)Ru^{II}(S)]²⁺ **1** (tpy = 2, 2':6', 2''-terpyridine; Mebim-py = 3-methyl-1-pyridylbenzimidazol-2-ylidene; S = solvent. As [(tpy)(Mebim-py)Ru^{II}(OH₂)]²⁺ in water) is a robust example. It undergoes water oxidation by the mechan-

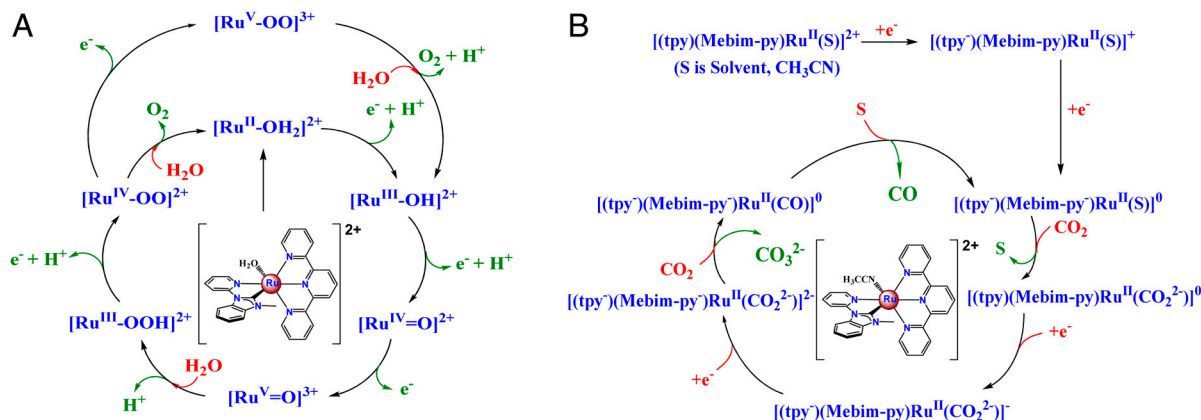
Author contributions: Z.C. and T.J.M. designed research; Z.C. performed research; J.J.C., M.K.B., P.K., M.R.N., and P.G.H. contributed new reagents/analytic tools; Z.C. and T.J.M. analyzed data; and Z.C. and T.J.M. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1203122109/-DCSupplemental.

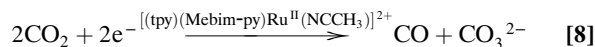


Scheme 1. (A) Mechanism for electrocatalytic single-site water oxidation by **1** as $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$ in water (21, 25). (B) Mechanism for electrocatalytic reduction of CO_2 to CO by **1** as $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{NCCH}_3)]^{2+}$ in CH_3CN (36).

ism shown in Scheme 1A (21, 25). In this mechanism, stepwise PCET oxidation and proton loss from $\text{Ru}^{\text{II}}\text{-OH}_2^{2+}$ provide access to $\text{Ru}^{\text{V}}=\text{O}^{3+}$. This high-oxidation state intermediate undergoes O-atom attack on water to give $\text{Ru}^{\text{III}}\text{-OOH}^{2+}$. Once formed, the peroxide intermediate undergoes further oxidation and O_2 loss and reenters the catalytic cycle as $\text{Ru}^{\text{III}}\text{-OH}^{2+}$. An important factor in the enhanced reactivity of the carbene complex compared to related complexes comes from the favorable driving force for the O—O bond forming step (24, 25).

Electrocatalyzed reduction of CO_2 by transition metal complexes, including polypyridyl complexes of Ru, is also well-known (26–36). Mechanistic insight has come from electrochemical and spectroscopic monitoring. A key element for polypyridyl catalysts is initial polypyridyl-based reduction with the reduced ligands acting as electron reservoirs for subsequent CO_2 reduction at the metal. For example, in Scheme 1B (36), **1** (as $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{NCCH}_3)]^{2+}$) is also a CO_2 reduction catalyst in CH_3CN . It undergoes two sequential $1e^-$ ligand-based reductions at

$E_{\text{p,c}} = -1.07$ V and -1.33 V vs. NHE ($E_{\text{p,c}}$ is the reductive peak potential) to give $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{NCCH}_3)]^0$. Ligand-based reduction is followed by rate limiting CO_2 coordination, $[(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{NCCH}_3)]^0 + \text{CO}_2 \rightarrow [(\text{tpy})(\text{Mebim-py})\text{Ru}^{\text{II}}(\text{CO}_2^{2-})]^0 + \text{CH}_3\text{CN}$. Once the metallocarboxylate intermediate is formed, it undergoes further reduction at the ligands to give CO and CO_3^{2-} (Eq. 8) as final products (36).



Water oxidation and CO_2 reduction by **1** in CH_3CN - H_2O mixtures were investigated. In the $\text{Ru}(\text{II})$ state, with 10% added CH_3CN (vol/vol), in 0.1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer (pH 7.45), aqua substitution by acetonitrile, $\text{Ru}^{\text{II}}\text{-OH}_2^{2+} + \text{CH}_3\text{CN} \rightarrow \text{Ru}^{\text{II}}\text{-NCCH}_3^{2+} + \text{H}_2\text{O}$, occurs and was complete in 10 min. This was shown by spectrophotometric monitoring, and the shift in λ_{max} for the dominant metal-to-ligand charge

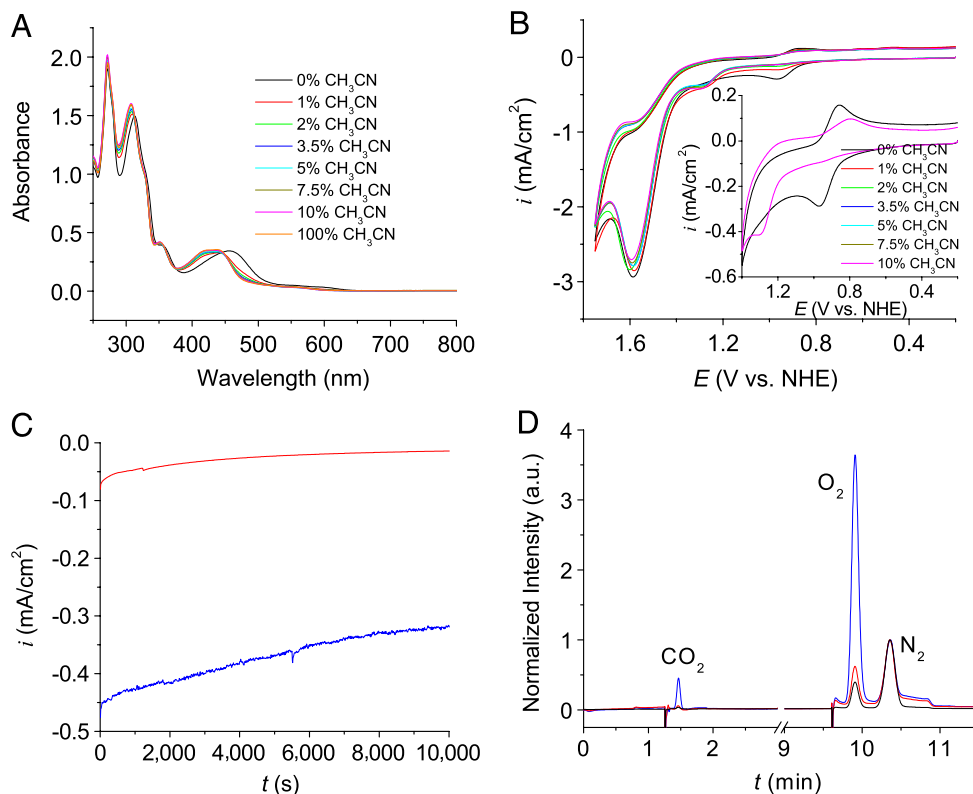


Fig. 1. (A) UV-visible spectra of 50 μM **1** in 0.1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer (pH 7.45) with increasing amounts of added CH_3CN . (B) CVs of 1 mM **1** in 0.1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer (pH 7.45) with increasing amounts of added CH_3CN . Electrode, glassy carbon (0.071 cm^2); scan rate, 100 mV/s. (Inset) Comparison of CVs with 0% (black) and 10% (magenta) added CH_3CN with potential scan reversal before water oxidation wave. The reference electrode used was the saturated calomel electrode (SCE) (0.244 V vs. NHE) with reported potentials converted to NHE. In A and B, the UV-visible and CV measurements were conducted after addition of CH_3CN for 10 min. (C) As in B, controlled potential electrolysis in the absence (red) or presence (blue) of 1 mM **1** with 10% added CH_3CN . Electrode, BDD/Si (approximately 0.85 cm^2); applied potential, 1.55 V vs. NHE. The solution was stirred during electrolysis. (D) As in C, showing corresponding gas chromatograms (thermal-conductivity detector, TCD) in the absence (red) or presence (blue) of catalyst after electrolysis. The black line represents the gas chromatogram before electrolysis. The chromatography response for O_2 was normalized to O_2/N_2 in air.

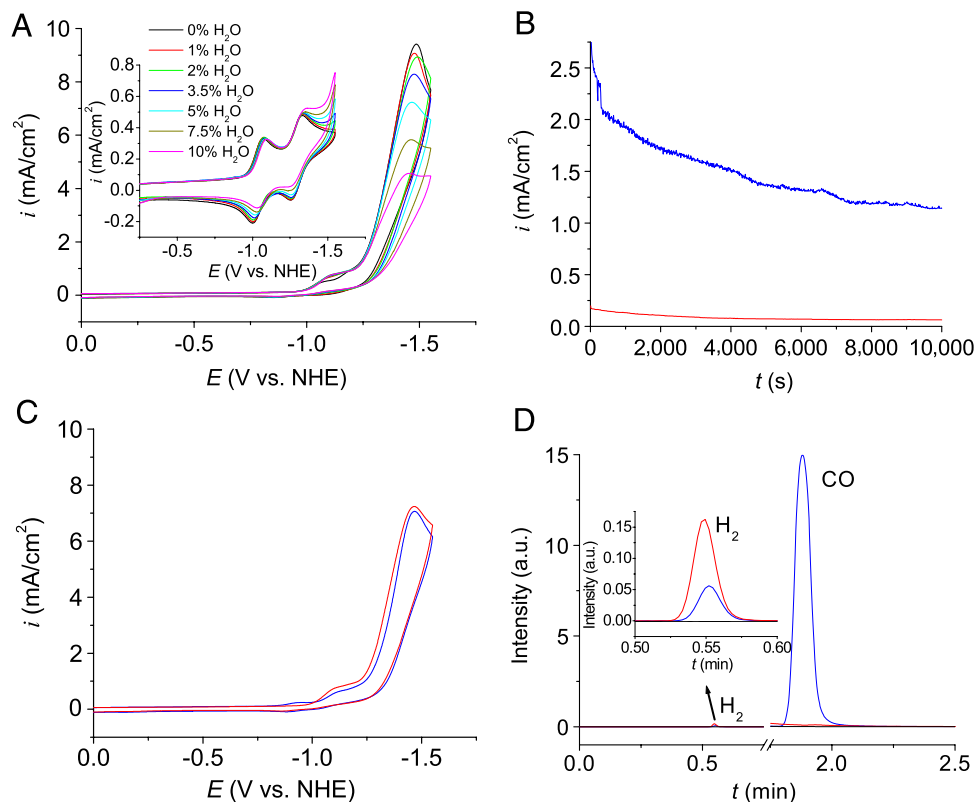


Fig. 2. (A) CVs of 1 mM **1** in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ under CO_2 with increasing amounts of added water. Electrode, glassy carbon (0.071 cm^2); scan rate, 100 mV/s . (Inset) As in the figure but under Ar. The reference electrode used was Ag/AgNO_3 (0.55 V vs. NHE) with reported potentials converted to NHE. (B) As in A, controlled potential electrolysis with 5% added water under Ar (red) and CO_2 (blue). Electrode, glassy carbon (0.071 cm^2); applied potential, -1.45 V vs. NHE . The solution was stirred during electrolysis. (C) As in B, CVs before (red) and after (blue) electrolysis under CO_2 at freshly polished glassy carbon electrodes. (D) As in B, showing corresponding gas chromatograms (pulsed discharge helium ionization detector, PDHID) in the absence (red) or presence (blue) of catalyst after electrolysis. The black line represents the gas chromatogram before electrolysis.

transfer (MLCT) absorption from 456 nm to $420\text{--}440\text{ nm}$ (Fig. 1A). Cyclic voltammetric (CV) measurements reinforce this observation. Addition of 10% CH_3CN , in $0.1\text{ M NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer ($\text{pH } 7.45$), causes the wave for $\text{Ru}^{\text{II}}\text{-OH}_2^{2+} \rightarrow \text{Ru}^{\text{III}}\text{-OH}_2^{2+}$ oxidation at $E_{\text{p,a}} = 0.96\text{ V vs. NHE}$ ($E_{\text{p,a}}$ is the oxidative peak potential) to diminish with appearance of a new wave at $E_{\text{p,a}} = 1.30\text{ V}$ for $\text{Ru}^{\text{II}}\text{-NCCH}_3^{2+} \rightarrow \text{Ru}^{\text{III}}\text{-NCCH}_3^{3+}$ oxidation (Fig. 1B). The sense of the substitution is reversed upon oxidation. As shown in the Fig. 1B, Inset, in reverse scans, a distorted wave for $\text{Ru}^{\text{III}}\text{-OH}_2^{2+} \rightarrow \text{Ru}^{\text{II}}\text{-OH}_2^{2+}$ reduction appears at $E_{\text{p,c}} = 0.80\text{ V}$ rather than a wave for $\text{Ru}^{\text{III}}\text{-NCCH}_3^{3+} \rightarrow \text{Ru}^{\text{II}}\text{-NCCH}_3^{2+}$ reduction. The reactions that occur in this sequence are shown in Eqs. 9–11. Re-aquation at $\text{Ru}(\text{III})$ allows the catalyst to enter the catalytic cycle in Scheme 1A as $\text{Ru}^{\text{III}}\text{-OH}_2^{2+}$ and water oxidation to proceed without interference from substitution.

In the cycle in Scheme 1A, water oxidation is triggered by oxidation of $\text{Ru}^{\text{IV}} = \text{O}^{2+}$ to $\text{Ru}^{\text{V}} = \text{O}^{3+}$ at an onset potential of approximately 1.4 V vs. NHE . Fig. 1C shows the results of a controlled potential electrolysis experiment at 1.55 V with 10% added CH_3CN at a polycrystalline silicon wafer coated with boron-doped diamond (BDD|Si). Electrode choice is important in these experiments with competitive surface oxidation occurring at conventional glassy carbon or other carbon electrodes. The catalytic current decreased initially, but was relatively stable over the 3 h electrolysis period. The current decrease appears to be due to slow catalyst decomposition by oxidation of the carbene ligand.* Analysis of the head space in the electrolysis cell by gas chromatography (Varian 450-GC) demonstrated oxygen production with a Faradaic efficiency of approximately 88% through approximately 5 catalyst turnovers (Fig. 1D).

*A small amount of CO_2 ($\text{O}_2:\text{CO}_2 = 20:1$, mol:mol) appeared in the gas chromatographic analysis in Fig. 1D, presumably due to slow decomposition of the carbene ligand in the catalyst.

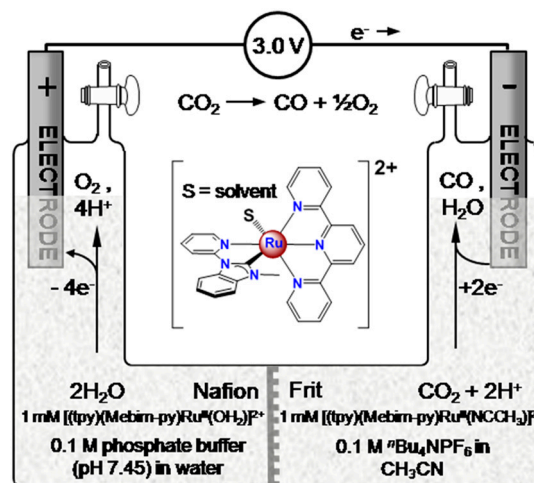
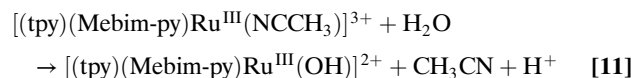
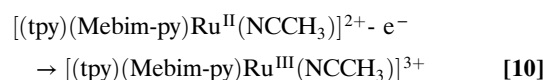
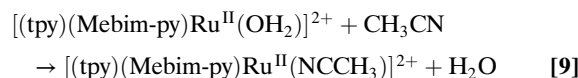


Fig. 3. Schematic diagram for the two-compartment, Nafion|Frit-separated electrochemical cell for CO_2 splitting. A three-electrode potentiostat was used to control the two-electrode cell with one electrode as the working electrode and the other acting as both counter and reference electrodes. The iR drop across the Nafion|Frit was not compensated.

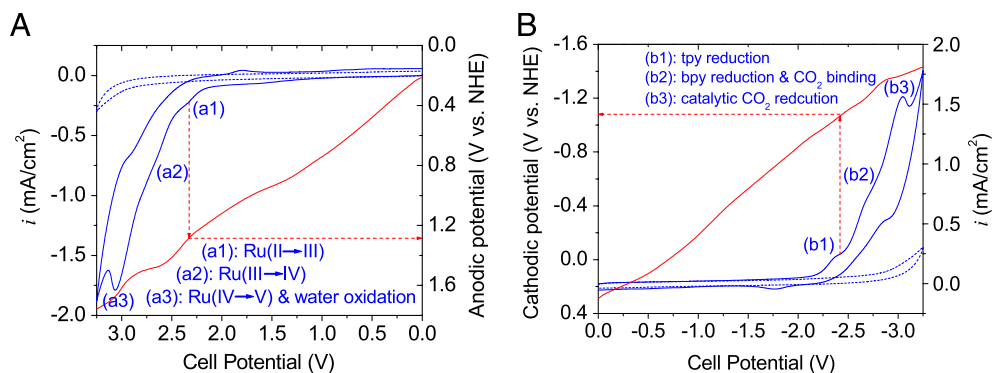
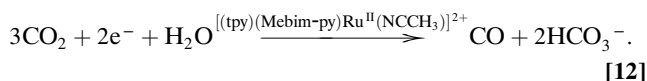


Fig. 4. Note Figs. S1 and S2. Blue lines: CVs at glassy carbon electrodes (0.071 cm²) with 10% CH₃CN and 5% H₂O added in the anode and cathode compartments, respectively: (A), anodic scan for water oxidation and (B), cathodic scan for CO₂ reduction. The dashed blue lines are the background without catalyst. Red lines: the applied potential (vs. NHE) at the working electrode during forward potential scans. As examples, the peak potentials for peaks a1 and b1, as determined by the intersecting red dashed lines, are shown in the figure. Scan rate, 100 mV/s.

Fig. 2A shows CVs of 1 atm CO₂-saturated solutions containing 1 mM **1** in 0.1 M ⁿBu₄NPF₆/CH₃CN (ⁿBu₄N⁺ = tetrabutylammonium cation) at a glassy carbon electrode with addition of increasing amounts of water. Peak currents for electrocatalytic CO₂ reduction decreased slightly with added water falling by 20% with 5% added water. Fig. 2B shows the results of a controlled potential electrolysis experiment at -1.45 V vs. NHE at a glassy carbon in a CO₂ saturated solution with 5% added water. The catalytic current was sustained for at least 3 h with a slow current decrease due to catalyst precipitation on the electrode surface.[†] The catalyst retained its activity as shown by CV measurements at fresh electrodes (Fig. 2C). Analysis of the head space in the electrolysis cell by gas chromatography showed formation of CO with a Faradaic efficiency of approximately 85% with 3.5 catalyst turnovers (Fig. 2D). A small amount of hydrogen was also detected in the head space with a Faradaic efficiency of <2% (Fig. 2D, *Inset*). There was no evidence for CH₃OH, HC(O)H, or HC(O)O⁻ in the liquid phase by gas chromatography (GC-2014, Shimadzu) and ¹H NMR (Bruker Avance-400 MHz). The reaction stoichiometry for the half reaction with added water is shown in Eq. 12 (36), as follows:



The ability of the single-site Ru carbene complex to act as an electrocatalyst for both water oxidation and CO₂ reduction provides a basis for the two compartment electrolysis cell for CO₂ splitting shown in Fig. 3. In the cell a Nafion cation exchange membrane cast on a glass frit (Nafion|Frit) was used to separate the compartments (37).[‡]

The i - E characteristics of the two-electrode electrochemical cell were examined by CV measurements (Fig. 4). In these experiments, the anode compartment contained the aqueous NaH₂PO₄/Na₂HPO₄ buffer (pH 7.45) with 10% added CH₃CN and the cathode 0.1 M ⁿBu₄NPF₆ in CO₂-saturated CH₃CN with 5% added H₂O. The potential applied at the working electrode was monitored by a second potentiostat (Figs. S1 and S2). Assignment of the current-potential features in Fig. 4 are based on comparisons with profiles for the separate catalytic water oxidation and CO₂ reduction half-reactions described here and previously (25, 36).

[†]Note figure S8 in the Supporting Information in ref. 36 which documents slow loss of catalytic current as HCO₃⁻/CO₃²⁻ build up in solution leading to precipitation of the catalyst as the HCO₃⁻/CO₃²⁻ salt.

[‡]Nafion is slowly permeable to both water and CH₃CN. Based on a control experiment in an unstirred solution, solvent (CH₃CN-H₂O) inter-permeability across the Nafion|Frit separator in Fig. 3, was <2% in 24 h.

In the current-potential traces, i - E features appear from +2.2 to +3.25 V in Fig. 4A and from -2.2 to -3.25 V in Fig. 4B. The former are associated with the metal-based oxidations which result in water oxidation in Scheme 1A, and the latter to the ligand-based reductions for electrocatalytic CO₂ reduction in Scheme 1B. As dictated by the potentials for Ru^{IV} = O²⁺ → Ru^V = O³⁺ oxidation at approximately +1.55 V for peak a3 in Fig. 4A, which triggers water oxidation to O₂, and [(tpy)⁻(Mebim-py)Ru^{II}(CO₂²⁻)]⁻ reduction at approximately -1.45 V for peak b3 in Fig. 4B, which triggers CO₂ reduction to CO, CO₂ splitting in Eq. 7, occurs at an applied cell potential of approximately 3.0 V [= +1.55 - (-1.45)], with an overpotential of approximately 1.65 V (=3.0 - 1.35). The current densities of both anodic and cathodic scans in Fig. 4 are equivalent with overall cell performance limited by the rate of water oxidation at the anode as was determined by the separate studies on the half reactions in Figs. 1 and 2.

Fig. 5 shows a current-time (i - t) profile obtained by controlled potential electrolysis (3.0 V) under the conditions in Fig. 3 with two BDD|Si electrodes (approximately 0.85 cm²). The physically separated gaseous products were collected in the head spaces of the separate electrode compartments for gas chromatographic analysis.

Based on the integrated i - t profiles in Fig. 5 and gas chromatographic analyses, coulombic efficiencies for formation of approximately 7.4 μmol of CO (approximately 5 TONs), approximately 0.5 μmol of H₂ (approximately 0.3 TONs), and approximately 2.9 μmol of O₂ (approximately 2 TONs) for a 3 h electrolysis period were approximately 76, 5, and 60%, respectively. CO and O₂ have a ratio of 2.5:1, close to the 2:1 expected for CO₂ split-

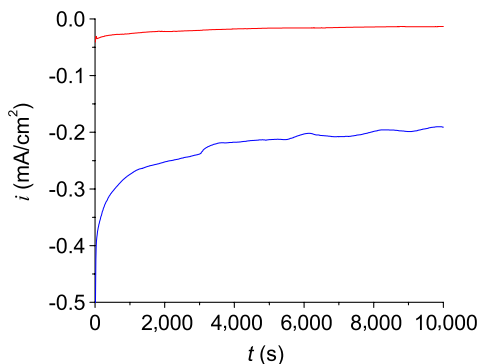


Fig. 5. Blue line: As in Fig. 3, controlled potential electrolysis at 3.0 V at two BDD|Si electrodes (approximately 0.85 cm²). Red line: Background current without added catalyst. The solution was unstirred during the electrolysis to minimize solution equilibration between cell compartments.

ting. For comparison, electrolysis under identical conditions but without catalyst resulted in <5% gaseous products.

The results described here illustrate the use of a single catalyst for CO₂ splitting, but this is only a first step. Under our conditions, electrocatalysis is limited by the rate of water oxidation at the anode. Long-term performance is further limited by slow carbene ligand oxidation at the anode* and catalyst precipitation at the cathode.† More efficient designs, based on ligand variations and surface attachment, are currently under investigation.

In its simplicity, the contrast with natural photosynthesis is striking. Photosynthesis in green plants involves thousands of atoms, five membrane-bound integrated assemblies, and the Calvin cycle and evolved over billions of years to achieve CO₂ splitting into oxygen and carbohydrates. In the electrochemical/photoelectrochemical approach, single catalysts or pairs of catalysts are combined with semiconductors, electrodes, wires, and membranes to connect the half reactions and exchange electrons and protons.

Materials and Methods

Chemicals. NaH₂PO₄ (≥99.5%), Na₂HPO₄ (≥99.5%), and tetrabutylammonium hexafluorophosphate (¹⁸Bu₄NPF₆) was obtained from Fluka. CO₂ gas was purchased from Airgas National Welders (medical grade, 99.999%). All other reagents were ACS grade and used as received. All aqueous solutions were prepared with Milli-Q ultrapure water (>18 MΩ), and all nonaqueous solutions were prepared with acetonitrile (CH₃CN) of HPLC grade unless stated otherwise.

Instrumentation. Electrochemical measurements were performed with the model CHI660D electrochemical workstation. The three-electrode system for half-reaction study consisted of a working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode (approximately 0.244 V vs. NHE) in aqueous solution or an Ag/AgNO₃ reference electrode (approximately 0.55 V vs. NHE) in nonaqueous solution. The two-electrode system for CO₂ splitting consisted of electrodes of the same materials, with one as the working electrode and the other acting as both counter and reference electrodes. In the two-electrode system, a second potentiostat was integrated to monitor the real potential applied at the working electrode by including an additional counter (Pt wire) and reference (SCE for aqueous solution or Ag/AgNO₃ for nonaqueous solution) electrodes to constitute a three-electrode system. Unless stated otherwise, all potentials were reported vs. NHE.

The gas product analysis in the headspace was conducted by gas chromatography (Varian 450-GC, molecular sieve column) with thermal-conductivity

detector (TCD) for the detection of O₂ in the anode compartment and pulsed discharge helium ionization detector (PDHID) for the detection of CO and H₂ in the cathode compartment. Calibration curves for O₂, CO, and H₂ were determined separately. HC(O)H or CH₃OH as possible products in the liquid phase were analyzed by gas chromatography with flame ionization detector (FID) (Shimadzu GC-2014, Agilent DB-Wax column) and HC(O)O[−] by ¹H NMR (Bruker Avance-400 MHz). For the latter, 30–50% CD₃CN was added to the electrolyzed solution prior to NMR measurement. All experiments were performed at room temperature 22 °C.

Synthesis. Synthesis of catalyst **1** was reported elsewhere (38). Briefly, it was obtained by reaction of the monocationic carbene precursor ligand with Ru(tpy)Cl₃ in ethylene glycol at 150 °C in the presence of NEt₃. In this case, the aqua complex is the product rather than the chloro analog due to the *trans*-labilizing effect of the carbene.

Other Procedures. Prior to the experiments, the glassy carbon disk electrode (0.071 cm²) was polished with 0.05 μm Al₂O₃ slurry to obtain a mirror surface followed by sonication in distilled water for 30 s to remove debris, and were thoroughly rinsed with Milli-Q ultrapure water.

The BDD|Si electrode (approximately 0.85 cm²) was fabricated by depositing boron-doped diamond films on polycrystalline silicon wafers by microwave plasma-enhanced chemical vapor deposition (MPCVD). The MPCVD was performed in a 915 MHz plasma at a growth pressure of approximately 80 Torr. A 3% methane/hydrogen source gas, doped with 100 ppm of diborane, was used during deposition at a temperature of approximately 800 °C. The films were approximately 1.56 microns in thickness, with a sheet resistance of approximately 110 Ω/sq. The BDD|Si electrode was used for electrolysis without further treatment.

The glass frit-supported Nafion film (Nafion|Frit) was prepared by carefully spreading 40 μL of 2 wt % Nafion perfluorinated ion-exchange resin solution (diluted by methyl alcohol) onto the frit surface on the anode side (Fig. 3), followed by drying at room temperature.

ACKNOWLEDGMENTS. We thank Professor John Newman (University of California, Berkeley, CA) for helpful comments on the paper and Dr. Brian R. Stoner (RTI International, NC) for generous donation of BDD|Si slides. This work was supported by the University of North Carolina Energy Frontier Research Center (EFRC): Center for Solar Fuels an EFRC funded by the Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Award DE-SC0001011 (to J.J.C., M.K.B., P.K., M.R.N., and P.G.H.). Support of electrochemical experiments by Z.-F.C. was provided by the same DOE BES EFRC Award DE-SC0001011. Support of product analysis by Z.-F.C. was provided by the Army Research Office through Grant W911NF-09-1-0426.

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