Enhanced Electrochemical CO₂ Reduction by a Series of Molecular Rhenium Catalysts Decorated with Second-Sphere Hydrogen-Bond Donors

Kallol Talukdar,^{†#} Sayontani Sinha Roy,^{†#} Eva Amatya,[†] Elizabeth A. Sleeper,[†] Pierre Le Magueres,[‡] and Jonah W. Jurss[†]*

† Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States

‡ Rigaku Americas Corporation, The Woodlands, Texas 77381, United States

K.T. and S.S.R. contributed equally.

*E-mail address: jwjurss@olemiss.edu

-Supporting Information-

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Materials and Methods. All synthetic manipulations were carried out under nitrogen atmosphere using an MBraun glovebox or standard Schlenk techniques. Freshly distilled 1,4-dioxane and acetonitrile (CH₃CN) were used for synthesis and electrochemistry. Dichloromethane and toluene were dried with a Pure Process Technology® solvent purification system. Water was purified with a Barnstead NANOpure Diamond water purification system.

Rhenium(I) pentacarbonylchloride purchased from Organics. was Acros Tetrakis(triphenylphosphine)palladium(0) was purchased from Chem-Impex International Inc. 3-Aminophenylboronic acid and 4-aminophenylboronic acid hydrochloride were obtained from Combi-Blocks Inc. 2-Aminophenylboronic acid pinacol ester was obtained from Boron Molecular. All other chemicals and solvents were reagent or ACS grade, purchased from commercial vendors, and used without further purification. ¹H and ¹³C NMR spectra were obtained using Bruker spectrometers operating at 300 or 400 MHz (¹H) and 75 or 100 MHz (¹³C). Spectra were calibrated versus residual protiated solvent peaks and chemical shifts are reported in parts per million (ppm). High-resolution electrospray ionization mass spectra (HR-MS) were obtained with a Waters SYNAPT HDMS Q-TOF mass spectrometer. Gas samples were analyzed by a custom Agilent 7890B Gas Chromatograph (Agilent PorapakQ column, 6 ft, 1/8 in. OD) with a dual detector system (TCD and FID). Ultra-High Purity (UHP) Nitrogen (nexAir LLC) was used as the carrier gas. Calibration curves for the observed gases were prepared from commercial standards of known concentration obtained from buycalgas.com. Elemental analyses of carbon, hydrogen, and nitrogen were conducted by Atlantic Microlab, Inc., Norcross, Georgia.

X-Ray Crystallography. A single crystal of 1-Re was coated with a trace of Fomblin oil and transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, and a Photon100 CMOS area detector. Likewise, a single crystal of 2-Re was secured to a fiber loop micromount using Paratone oil and transferred to the goniometer head of a Rigaku XtaLAB Synergy-S X-ray diffractometer equipped with a HyPix-6000HE hybrid photon counting (HPC) detector and a microfocused X-ray source. Both instruments were equipped with an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K (1-Re) or 100 K (2-Re). For 1-Re, data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.¹ The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs^{2,3} and refined by full matrix least squares against F² with all reflections using Shelxl2018^{4,5} using the graphical interface Shelxle.⁶ If not specified otherwise, H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic C-H moieties. Uiso(H) values were set to a multiple of U_{eq}(C) with 1.2 for C-H units. Data processing for 2-Re was performed with CrysAlis^{Pro.7} Using the SCALE3 ABSPACK scaling algorithm,⁸ empirical and numerical (Gaussian) absorption corrections, determined via faceindexing in CrysAlisPro, were applied to the data. The structure was solved via intrinsic phasing methods using ShelXT and refined using ShelXL in the Olex2 graphical user interface.^{5,9,10} The final structural refinements included anisotropic temperature factors on all non-hydrogen atoms. All hydrogen atoms were placed according to their electron density Q-peak and refined as free atoms for 2-Re.

Additional data collection and refinement details can be found in the Table S1. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1976889 (1-Re) and 1976890 (2-Re) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Measurements. All cyclic voltammetry experiments were performed with a three-electrode setup using a CH Instruments 600E Series potentiostat. Ohmic drop was compensated using the positive feedback compensation implemented via the potentiostat. The electrochemical cell was equipped with a glassy carbon disk working electrode (3 mm diameter, Bioanalytical Systems, Inc.), a platinum wire counter electrode, and a silver wire quasi-reference electrode. Acetonitrile solutions containing 0.1 M *n*-tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte were used in all studies as specified. Ferrocene was added at the end of experiments and served as an internal standard to reference the potential. Electrochemical cells were thoroughly degassed with N_2 or CO_2 for 10 to 20 minutes prior to each experiment. Solutions were freshly prepared before each experiment. Controlled potential electrolyses (CPE) were conducted in an airtight two-compartment cell with a glassy carbon rod working electrode (type 2, Alfa Aesar, 2 mm diameter), a silver wire quasi-reference electrode, and a high-surface area platinum mesh counter electrode. The platinum counter electrode was positioned inside a small isolation chamber with a fine frit. The isolation chamber contained the same solution, but without catalyst. The electrolysis solution in the working electrode compartment was continuously stirred during experiments. The headspace of the airtight cell was periodically sampled by taking aliquots using a sealable gastight syringe and injecting into the gas chromatograph. The electrolyzed solution was analyzed after the experiment for liquid and solvated products.

Infrared Spectroelectrochemical (IR-SEC) Measurements. IR-SEC measurements were performed using an Optically Transparent Thin-Layer Electrode (OTTLE) cell¹¹ purchased from Bio-Logic Science Instruments. The cell is comprised of CaF₂ windows, and an electrode assembly featuring Pt minigrid working and counter electrodes and a Pt wire pseudo-reference electrode. The OTTLE cell was filled with thoroughly degassed 2.5 mM catalyst solution in CH₃CN/0.1 M Bu₄NPF₆ under inert conditions, sealed from the atmosphere, and placed in a Bruker Tensor 27 FT-IR spectrometer. A potentiostat was used to perform cyclic voltammetry and bulk electrolyses in the cell, and the respective changes in solution were monitored by FT-IR spectroscopy. The reported spectra were obtained by performing short-term bulk electrolysis (> 60 sec) at different regions of the cyclic voltammogram.

UV-Vis Spectroelectrochemical (UV-Vis SEC) Measurements. UV-Vis SEC measurements were performed in a Honeycomb thin-layer spectroelectrochemical cell purchased from Pine Research Instrumentation. The cell consists of a thin-layer quartz cuvette, a honeycomb electrode card composed of onboard Au working and Pt counter electrodes, and a Ag wire quasi-reference electrode. The cell was filled with freshly made 0.5 mM catalyst solution in $CH_3CN / 0.1 M Bu_4NPF_6$, which was thoroughly purged with N₂ and sealed from atmosphere prior to each experiment. The cell was then placed in an Agilent Technologies Cary 8454 UV-Vis Spectrophotometer equipped with a diode-array detector. A potentiostat was connected to the cell to perform CVs and bulk electrolyses

while monitoring spectral changes in the solution by the UV-Vis spectrometer. The reported spectra were obtained by performing short-term bulk electrolyses (> 120 sec) at different potentials based on the cyclic voltammogram.

Synthesis of the Ligands. Ligand precursor 6-bromo-2,2'-bipyridine was synthesized according to literature procedures.¹² Ligands L1, L2, and L3 were prepared following modified literature procedures.^{13,14}



2-([2,2'-bipyridin]-6-yl)aniline, L1. A two-neck round bottom flask was equipped with a stir bar and a reflux condenser. 6-bromo-2,2'-bipyridine (0.250 g, 1.064 mmol), 2-aminophenylboronic acid pinacol ester (0.233 g, 1.064 mmol), K_2CO_3 (0.441 g, 3.192 mmol), and [Pd(PPh_3)_4] (0.062 g, 0.053 mmol) were added to the flask and it was evacuated and refilled with nitrogen three times. Deaerated dioxane (15 mL) and H₂O (1.2 mL) were added to the flask and the mixture was refluxed for 48 h. Then the reaction mixture was cooled to room temperature and poured on to 100 mL deionized water. The aqueous solution was extracted with dichloromethane (3 x 25 mL) and the organic fractions were combined, concentrated under vacuum, and purified by a deactivated silica column eluting with hexanes/ethyl acetate (4:1). The product was obtained as a light-yellow oil with 87% yield (0.231 g). ¹H NMR (CD₃CN, 300 MHz): δ 8.70 - 8.69 (m, 1H), 8.32 (br t, *J* = 7.74 Hz, 2H), 7.98 (t, *J* = 7.95 Hz, 1H), 7.91 (td, *J* = 1.68 Hz, *J* = 7.68 Hz, 1H), 7.75 (d, *J* = 7.89 Hz, 1H), 7.58 (dd, *J* = 1.35 Hz, *J* = 7.83 Hz, 1H), 7.43 - 7.39 (m, 1H), 7.21 - 7.15 (m, 1H), 6.82 (dd, *J* = 0.81 Hz, *J* = 8.08 Hz, 1H), 6.78 - 6.73 (m, 1H), 5.96 (br s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 158.93, 156.32, 154.60, 149.47, 146.42, 138.18, 137.11, 130.15, 129.78, 123.89, 122.70, 120.98, 118.68, 118.03, 117.37. HR-ESI-MS (M⁺) m/z calc. for [L1 + H]⁺, 248.1188, Found, 248.1173.

3-([2,2'-bipyridin]-6-yl)aniline, L2. A two-neck round bottom flask was equipped with a stir bar and a reflux condenser. 6-bromo-2,2'-bipyridine (0.250 g, 1.064 mmol), 3-aminophenylboronic acid (0.146 g, 1.064 mmol), K₂CO₃ (0.441 g, 3.192 mmol), and [Pd(PPh₃)₄] (0.062 g, 0.053 mmol) were added to the flask and it was evacuated and refilled with nitrogen three times. Deaerated dioxane (15 mL) and H₂O (1.2 mL) were added to the flask and

the mixture was refluxed for 48 h. Then the reaction mixture was cooled to room temperature and poured on to 100 mL deionized water. The aqueous solution was extracted with dichloromethane (3 x 25 mL) and the organic fractions were combined, concentrated under vacuum, and purified by silica gel chromatography eluting with hexanes/ethyl acetate (4:1). The product was obtained as a brown oil with 82% yield (0.216 g). ¹H NMR (CD₃CN, 300 MHz): δ 8.69 - 8.67 (m, 1H), 8.63 (br d, *J* = 7.98 Hz, 1H), 8.35 (dd, *J* = 0.78 Hz, *J* = 7.73, 1H), 7.96 - 7.90 (m, 2H), 7.83 (dd, *J* = 0.84 Hz, *J* = 7.86 Hz, 1H), 7.54 (t, *J* = 1.89 Hz, 1H), 7.45 - 7.38 (m, 2H), 7.24 (t, *J* = 7.83 Hz, 1H), 6.79 - 6.73 (m, 1H), 4.29 (br s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 156.67, 156.58, 155.74, 149.19, 146.97, 140.61, 137.73, 136.98, 129.78, 123.83, 121.49, 120.54, 119.45, 117.50, 116.02, 113.80. HR-ESI-MS (M⁺) m/z calc. for [L2 + H]⁺, 248.1188, Found, 248.1173.

4-([2,2'-bipyridin]-6-yl)aniline, L3. A two-neck round bottom flask was charged with 4-aminophenylboronic acid hydrochloride (0.185 g, 1.064 mmol), and NaOH (0.043 g, 1.064 mmol) before it was evacuated and refilled with nitrogen three times. Then deaerated dioxane (15 mL) and H₂O (1.2 mL) were added to the flask and the suspension was stirred for 20 minutes at room temperature. 6-bromo-2,2'-bipyridine (0.250 g, 1.064 mmol), K₂CO₃ (0.441 g, 3.192 mmol), and [Pd(PPh₃)4] (0.062 g, 0.053 mmol) were subsequently added to the flask against a positive pressure of nitrogen. The mixture was then stirred at reflux for 48 h. After completion of the reaction, the mixture was cooled to room temperature and poured on to 100 mL deionized water. The aqueous solution was extracted with dichloromethane (3 x 25 mL) and the organic fractions were combined, concentrated under vacuum, and purified by silica gel chromatography eluting with hexanes/ethyl acetate (1:1). The product was obtained as an off-white solid with 93% yield (0.244 g). ¹H NMR (CD₃CN, 300 MHz): δ 8.67 - 8.65 (m, 1H), 8.60 (br d, *J* = 7.98 Hz, 1H), 8.24 (dd, *J* = 0.78 Hz, *J* = 7.68, 1H), 8.01 - 7.96 (m, 2H), 7.94 - 7.83 (m, 2H), 7.75 (dd, *J* = 0.81 Hz, *J* = 7.11 Hz, 1H), 7.41 - 7.36 (m, 1H), 6.79 - 6.74 (m, 2H), 4.42 (br s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 156.78, 155.55, 149.14, 147.58, 137.63, 136.93, 129.93, 128.25, 123.71, 121.42, 119.22, 118.29, 115.21. HR-ESI-MS (M⁺) m/z calc. for [L3 + H]⁺, 248.1188, Found, 248.1174.

Synthesis of the Metal Complexes. Re(bpy)(CO)₃Cl was prepared according to a previously reported procedure.¹⁵

Common synthetic procedure. An equimolar amount of the ligand and Re(CO)₅Cl were added to an oven-dried two-neck round bottom flask connected to a reflux condenser. The flask was evacuated and refilled with nitrogen three times. Anhydrous toluene (12 mL) was added to the flask via a cannula and the suspension was refluxed for 12 h. The mixture was then cooled to room temperature and the yellow precipitate was filtered on a glass frit. The precipitate was washed with a small amount of hexanes and ice-cold dichloromethane, and dried under vacuum.

 $(2-([2,2'-bipyridin]-6-yl)aniline)Re(CO)_3Cl$, *1-Re*. The complex was prepared from ligand L1 (0.09 g, 0.364 mmol) and Re(CO)₅Cl (0.132 g, 0.364 mmol) following the common synthetic procedure. X-ray quality crystals were grown from a concentrated acetonitrile solution by slow diffusion of di-isopropyl ether at -20 °C. Yield = 83% (0.167 g). Elem. Anal. calc. for C₁₉H₁₃ClN₃O₃Re: C, 41.27; H, 2.37; N, 7.60. Found: C, 41.13; H, 2.27; N, 7.49. ¹H NMR (CD₃CN, 300 MHz): δ 9.07 - 9.05 (m, 1H), 8.47 - 8.42 (m, 2H), 8.23 - 8.16 (m, 2H), 7.64 - 7.58 (m, 2H),

7.32 - 7.22 (m, 1H), 7.13 - 7.10 (m, 1H), 6.89 - 6.77 (m, 2H), 4.12 (br s, 2H). HR-ESI-MS (M⁺) m/z calc. for [**1-Re** − Cl⁻]⁺, 518.0515, Found, 518.0478. FT-IR (KBr) *v*_{CO}: 2017, 1917 (br), and 1900 (sh) cm⁻¹.

 $(3-([2,2'-bipyridin]-6-yl)aniline)Re(CO)_3Cl, 2-Re.$ This complex was prepared from ligand L2 (0.100 g, 0.404 mmol) and Re(CO)_5Cl (0.146 g, 0.404 mmol) following the common synthetic procedure. X-ray quality crystals were grown from a concentrated DMF solution by slow diffusion of diethyl ether at 8 °C. Yield = 84% (0.187 g). Elem. Anal. calc. for C₁₉H₁₃ClN₃O₃Re•1.5H₂O: C, 39.35; H, 2.78; N, 7.24. Found: C, 39.48; H, 2.43; N, 6.83. ¹H NMR (CD₃CN, 300 MHz): δ 9.06 - 9.04 (m, 1H), 8.46 - 8.39 (m, 2H), 8.22 - 8.15 (m, 2H), 7.67 - 7.58 (m, 2H), 7.24 (t, *J* = 8.25 Hz, 1H), 6.86 - 6.80 (m, 3H), 4.36 (br s, 2H). HR-ESI-MS (M⁺) m/z calc. for [2-Re - Cl⁻]⁺, 518.0515, Found, 518.0558. FT-IR (KBr) v_{co} : 2018, 1909, and 1881 (br) cm⁻¹.

 $(4-([2,2'-bipyridin]-6-yl)aniline)Re(CO)_3Cl$, 3-Re. This complex was prepared from ligand L3 (0.050 g, 0.202 mmol) and Re(CO)₅Cl (0.073 g, 0.202 mmol) following the common synthetic procedure. Yield = 89% (0.099 g). Elem. Anal. calc. for C₁₉H₁₃ClN₃O₃Re: C, 41.27; H, 2.37; N, 7.60. Found: C, 41.19; H, 2.32; N, 7.44. ¹H NMR (CD₃CN, 300 MHz): δ 9.06 - 9.04 (m, 1H), 8.42 (d, *J* = 8.25 Hz, 1H), 8.35 - 8.32 (m, 1H), 8.22 - 8.11 (m, 2H), 7.67 - 7.58 (m, 2H), 7.39 - 7.36 (m, 2H), 6.78 - 6.75 (m, 2H), 4.53 (br s, 2H). HR-ESI-MS (M⁺) m/z calc. for [3-Re – Cl⁻]⁺, 518.0515, Found, 518.0515. FT-IR (KBr) *v*_{CO}: 2017, 1911, and 1868 cm⁻¹.

Table S1. Cry	/stal data and	structure refinement for	1-Re and 2-Re.
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Compound	1-Re	2-Re	
CCDC Deposition #	1976889	1976890	
Description	yellow rod	yellow plate	
Empirical Formula	C ₁₉ H ₁₃ CIN ₃ O ₃ Re	C ₂₂ H ₂₀ CIN ₄ O ₄ Re	
Formula Weight (g·mol ⁻¹)	552.97	626.07	
Temperature (K)	150	100	
Wavelength (Å)	0.71073	0.71073	
Crystal System	Orthorhombic	Monoclinic	
Space Group	P212121	P2 ₁ /n	
a (Å)	9.0747(6)	12.7139(4)	
b (Å)	10.5049(6)	10.7916(2)	
c (Å)	19.2694(12)	17.1505(4)	
α (°)	90	90	
β(°)	90	109.070(3)	
γ (°)	90	90	
Volume (Å ³)	1836.9(2)	2223.97(10)	
Ζ	4	4	
$\rho_{calc} (g \cdot cm^{-3})$	2.000	1.870	
μ (mm ⁻¹)	6.785	5.621	
F(000)	1056	1216	
Crystal Dimensions (mm)	0.060 x 0.070 x 0.190	0.02 x 0.068 x 0.111	
θ Range for Data Collection (°)	2.869 to 33.138°	2.417 to 26.368°	
Index Ranges	-13 ≤ h ≤ 11 -16 ≤ k ≤ 10 -24 ≤ l ≤ 22	-15 ≤ h ≤ 15 -12 ≤ k ≤ 13 -21 ≤ l ≤ 21	
Reflections Collected	19476	15717	
Unique Data	5885 [R _{int} = 0.0318]	4546 [R _{int} = 0.0252]	
Data / Restraints / Parameters	5885 / 2 / 251	4546 / 0 / 369	
Goodness of Fit on F ²	1.077	1.028	
Final R Factors, $[I > 2\sigma (I)]$	$R_1 = 0.0266$ $wR_2 = 0.0485$	$R_1 = 0.0167$ $wR_2 = 0.0351$	
Largest Residual Peak / Hole (e·Å-3)	2.978 / -1.094	0.832 / -0.462	



Figure S1. ¹H NMR spectrum of L1 (300 MHz, CD₃CN).



Figure S2. ¹³C NMR spectrum of L1 (75 MHz, CDCI₃).



Figure S3. ¹H NMR spectrum of L2 (300 MHz, CD₃CN).



Figure S4. ¹³C NMR spectrum of L2 (100 MHz, CDCl₃).



Figure S5. ¹H NMR spectrum of L3 (300 MHz, CD₃CN).



Figure S6. ¹³C NMR spectrum of L3 (100 MHz, CDCl₃).



Figure S7. ¹H NMR spectrum of 1-Re (300 MHz, CD₃CN).



Figure S8. ¹H NMR spectrum of 2-Re (300 MHz, CD₃CN).



Figure S9. ¹H NMR spectrum of 3-Re (300 MHz, CD₃CN).



Figure S10. FT-IR (KBr) spectrum of 1-Re in solid state.



Figure S11. FT-IR (KBr) spectrum of 2-Re in solid state.



Figure S12. FT-IR (KBr) spectrum of 3-Re in solid state.



Figure S13. Cyclic voltammograms of 0.5 mM **1-Re** at scan rates of 0.1 V/s and 1 V/s (specified in the figures) in $CH_3CN / 0.1 M Bu_4NPF_6$ solution under N_2 atmosphere.



Figure S14. Cyclic voltammograms of 0.5 mM **2-Re** at scan rates of 0.1 V/s and 1 V/s (specified in the figures) in $CH_3CN / 0.1 M Bu_4NPF_6$ solution under N_2 atmosphere.



Figure S15. Cyclic voltammograms of 0.5 mM **3-Re** at scan rates of 0.1 V/s and 1 V/s (specified in the figures) in $CH_3CN / 0.1 M Bu_4NPF_6$ solution under N₂ atmosphere.



Figure S16. (Left) Cyclic voltammograms of 0.5 mM **1-Re** in $CH_3CN / 0.1$ M Bu_4NPF_6 solution under N_2 atmosphere at different scan rates. (Right) Scan rate dependence: A plot of reductive peak currents vs the square root of the scan rate. The black linear fit corresponds to the first reduction and the red linear fit corresponds to the second reduction.



Figure S17. (Left) Cyclic voltammograms of 0.5 mM **2-Re** in $CH_3CN / 0.1$ M Bu_4NPF_6 solution under N_2 atmosphere at different scan rates. (Right) Scan rate dependence: A plot of reductive peak currents vs the square root of scan rate. The black linear fit corresponds to the first reduction and the red linear fit corresponds to the second reduction.



Figure S18. (Left) Cyclic voltammograms of 0.5 mM **3-Re** in $CH_3CN / 0.1$ M Bu_4NPF_6 solution under N_2 atmosphere at different scan rates. (Right) Scan rate dependence: A plot of reductive peak currents vs the square root of scan rate. The black linear fit corresponds to the first reduction and the red linear fit corresponds to the second reduction.



Figure S19. (Left) Cyclic voltammograms of 0.5 mM **ReBpy** in $CH_3CN / 0.1$ M Bu_4NPF_6 solution under N_2 atmosphere at different scan rates. (Right) Scan rate dependence: A plot of reductive peak currents vs the square root of scan rate. The black linear fit corresponds to the first reduction and the red linear fit corresponds to the second reduction.

Species	<i>v_{C0}</i> , cm ⁻¹	Solvent	Reference	
[Re(L1)(CO) ₃ Cl], (1-Re)	2023, 1919, 1895	CH ₃ CN		
[Re(L2)(CO) ₃ Cl], (2-Re)	2022, 1919, 1892	CH ₃ CN	This work	
[Re(bpy)(CO) ₃ Cl]	2020.5, 1914, 1897	CH ₃ CN	16	
[Re(bipy-tBu)(CO) ₃ Cl]	2023, 1916, 1898	CH ₃ CN	17	
[Re(pdbpy)(CO) ₃ Cl]	2023, 1918, 1901	CH ₃ CN	18	
[Re(dmb)(CO) ₃ Cl]	2021, 1914, 1898	CH ₃ CN	19	
(MesDABMe)Re(CO)3Br	2027, 1937, 1898	CH ₃ CN	20	
Re(MeCyIm)(CO) ₃ Cl	2021, 1911, 1899	CH ₃ CN	21	
[Re(L1)(CO) ₃ Cl]	2006, 1895, 1879	CH ₃ CN		
[Re(L2)(CO) ₃ Cl] ⁻	2000, 1889, 1863	CH ₃ CN	I his work	
[Re(bpy)(CO) ₃ Cl] ^{•-}	1998, 1885, 1867.5	CH ₃ CN	16	
[Re(bpy)(CO) ₃ Cl] ⁻	1998, 1880, 1866	CH ₃ CN	19	
[Re(bipy-tBu)(CO) ₃ Cl]	2005, 1895, 1878	CH ₃ CN	17	
[Re(pdbpy)(CO) ₃ Cl]	2002, 1891, 1871sh	CH ₃ CN	18	
[(^{Mes} DAB ^{Me})Re(CO) ₃ Br]	2010, 1896, 1884	CH ₃ CN	20	
[Re(MeCyIm)(CO) ₃ Cl] ⁻	2012, 1897, 1882	CH ₃ CN	21	
$[\text{Re}(\text{L2})(\text{CO})_3(\text{CH}_3\text{CN})]^{\bullet}$	2007, 1892, 1871	CH ₃ CN	This work	
[Re(bpy)(CO) ₃ (CH ₃ CN)] [•]	2011, 1895 (br)	CH ₃ CN	16	
[Re(pdbpy)(CO) ₃ MeCN] [•]	2017 (DFT: 2017, 1917, 1899)	CH ₃ CN	18	
[Re(bpy)(CO) ₃ (CH ₃ CN)] [•]	2017, 1902 (br)	CH ₃ CN	19	
[Re(dmb)(CO) ₃ (CH ₃ CN)] [•]	2012, 1904 (br)	CH ₃ CN	19	
[Re(L1)(CO) ₃]•	1984, 1865, 1853	CH ₃ CN	This moult	
[Re(L2)(CO) ₃]•	1986, 1868, 1848	CH ₃ CN	I his work	
[Re(bipy-tBu)(CO) ₃] [•]	1983, 1865, 1850	CH ₃ CN	17	
[Re(MeCyIm)(CO) ₃] [•]	1995, 1875, 1862	CH ₃ CN	21	
$[\text{Re}(\text{L1})(\text{CO})_3]^-$	1947, 1847 (br)	CH ₃ CN	This moult	
[Re(L2)(CO) ₃] ⁻	1946, 1848 (br)	CH ₃ CN	This work	
[Re(bpy)(CO) ₃] ⁻	1948, ~1846	CH ₃ CN	16	
[Re(bipy-tBu)(CO) ₃] ⁻	1938, 1834 (br)	CH ₃ CN	17	
[Re(bpy)(CO) ₃] [K(18-crown-6)]	1945, 1839	THF	22	
[Re(dmb)(CO) ₃] ⁻	1943, 1828	CH ₃ CN	19	
$[(^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}^0(\text{CO})_3]^-$	1951, 1840, 1829	CH ₃ CN	20	
[Re(MeCyIm)(CO) ₃] ⁻	1943, 1839	CH ₃ CN	21	
$[\text{Re}(\text{L2})(\text{CO})_3(\text{CH}_3\text{CN})]^-$	1992 (overlapped)	CH ₃ CN	This work	
[Re(bpy)(CO) ₃ (CH ₃ CN)] ⁻	1986, 1868, 1852	CH ₃ CN	16	
[Re(pdbpy)(CO) ₃ (CH ₃ CN)] ⁻	1993 (DFT: 1989, 1890, 1869)	CH ₃ CN	18	
[(^{Mes} DAB ^{Me})Re ^I (CO) ₃ (CH ₃ CN)]-	1984, 1875, 1865	CH ₃ CN	20	
[Re ^I (MeCyIm)(CO) ₃ (CH ₃ CN)] ⁻	1986, 1852	CH ₃ CN	21	
[Re(bpy)(CO) ₃] ₂	1991, 1951, 1885, 1862	THF	23	
[Re(bpy)(CO) ₃] ₂	1990, 1952, 1986, 1862	THF	22	
[Re(dmb)(CO) ₃] ₂	1982, 1943, 1876, 1843	CH ₃ CN	19	
[Re(bpy)(CO) ₃] ₂ [K(18-crown-6)]	1990, 1974, 1951, 1886, 1862, 1837	THF	22	

Table S2. Experimental v_{CO} frequencies of different intermediates detected by IR-SEC experiments on **1-Re** and **2-Re** and related Re(CO)₃ complexes.



Figure S20. Cyclic voltammograms of **1-Re**, **2-Re**, **3-Re**, and **ReBpy** at a scan rate of 10 mV/s with 0.5 mM catalyst concentrations in $CH_3CN / 0.1 \text{ M Bu}_4\text{NPF}_6$ solutions under N₂ (black) or CO₂ (red/green) atmospheres.



Figure S21. Cyclic voltammograms at different scan rates with 0.5 mM catalyst concentrations, A) **1-Re**, B) **2-Re**, C) **3-Re**, and D) **ReBpy** in CO₂-saturated CH₃CN / 0.1 M Bu₄NPF₆ solutions.



Figure S22. A plot of TOF (s⁻¹) vs scan rate (mV/s) for all of the catalysts studied here. TOFs were determined from CVs at different scan rates using equation 3 as described in the main text.



Figure S23. Foot-of-the-Wave Analysis (FOWA) and plots of the associated TOFs vs scan rate for A) **1-Re**, B) **2-Re**, and C) **3-Re**. TOFs were determined using equations 4 and 5 as described in the main text from linear sweep voltammograms obtained with 0.5 mM catalyst in CO₂-saturated CH₃CN / 0.1 M Bu_4NPF_6 solutions.



Figure S24. CVs of 0.5 mM **2-Re** at a scan rate of 100 mV/s in $CH_3CN / 0.1$ M Bu_4NPF_6 solutions under N₂ (black) or CO₂ (red) atmosphere in the presence of different proton sources (H₂O, methanol, and phenol as specified in the graphs), v = 100 mV/s.



Figure S25. Cyclic voltammograms at different scan rates of 0.5 mM catalyst, A) **1-Re**, B) **2-Re**, C) **3-Re**, and D) **ReBpy** in CO₂-saturated CH₃CN / 0.1 M Bu₄NPF₆ solutions containing 4% TFE.



Figure S26. A plot of TOF (s⁻¹) vs scan rate (mV/s) for all four catalysts in presence of 4% TFE. TOFs were determined from the CVs in Figure S27 using equation 3 as described in the main text.



Figure S27. Foot-of-the-Wave Analysis (FOWA) and plots of the associated TOFs vs scan rate for A) **1-Re**, B) **2-Re**, and C) **3-Re**. TOFs were determined using equations 4 and 5 as described in the main text from linear sweep voltammograms obtained with 0.5 mM catalyst in CO₂-saturated CH₃CN / 0.1 M Bu_4NPF_6 solutions containing 4% TFE.

We note that similar maximum TOFs for each catalyst were determined by FOWA for CO₂ reduction in anhydrous conditions and with 4% TFE added to solution. The data from CVs collected under anhydrous conditions were analyzed by FOWA using both $E_{p2,c}$ and $E_{cat/2}$ values (in separate plots) for the E_{cat} term in equation 4. Likewise, data from CVs collected in the presence of 4% TFE were analyzed by FOWA using both $E_{p1,c}$ and $E_{cat/2}$ values (in separate plots) for the E_{cat} term in equation 4. The reported FOWA plots use $E_{cat/2}$ for both anhydrous (Figure S23) and 4% TFE conditions (Figure S27), which gave more linear curves and more consistent trends in the calculated TOF values as a function of scan rate than the alternative.

Comparable TOF_{max} values for each catalyst were obtained by FOWA under anhydrous conditions when using either potential value ($E_{p2,c}$ or $E_{cat/2}$) for the E_{cat} term in equation 4, whereas lower TOF_{max} values were obtained for each catalyst under protic conditions when using $E_{p1,c}$ rather than $E_{cat/2}$ for the E_{cat} term. This is likely due to the presence of two catalytic regimes as the potential is scanned more negatively and begins to approach the second reduction (Figure 4). Importantly, the same relative activities for all four catalysts studied in this work were observed regardless of how the FOWA was done and none of the conclusions are affected. We have employed both the i_{cat}/i_p method and FOWA to calculate TOFs to facilitate comparison to the literature. The TOF values should be treated as estimates (*Inorg. Chem.* **2014**, *53*, 9983; *J. Am. Chem. Soc.* **2015**, *137*, 8564; *Inorg. Chem.* **2015**, *54*, 5285).



Figure S28. Concentration dependence of catalyst **2-Re**. (Left) Cyclic voltammograms of **2-Re** at different concentrations in CO₂-saturated CH₃CN / 0.1 M Bu₄NPF₆ solution, v = 100 mV/s. (Right) A plot of the peak catalytic current versus [**2-Re**].



Figure S29. Substrate concentration dependence of catalyst **2-Re**. (Left) Linear sweep voltammograms of **2-Re** with increasing concentrations of CO₂ in CH₃CN / 0.1 M Bu₄NPF₆ solution, v = 100 mV/s. (Right) A plot of the peak catalytic current versus [CO₂]^{1/2}.



Figure S30. Concentration dependence of added trifluoroethanol (TFE) as a proton source. Cyclic voltammograms of 0.5 mM catalyst A) **1-Re** and B) **2-Re** with increasing amounts of added TFE in CO₂-saturated CH₃CN / 0.1 M Bu₄NPF₆ solution, v = 100 mV/s. Then the peak catalytic current is plotted against the corresponding [TFE].



Figure S31. Representative charge versus time plots for controlled potential electrolyses of **1-Re** (green), **2-Re** (red), **3-Re** (blue), and **ReBpy** (black). *Conditions*: 0.5 mM catalyst in CO_2 -saturated anhydrous $CH_3CN / 0.1 M Bu_4NPF_6$ solution, glassy carbon rod working electrode. Background CPE was performed in the absence of catalyst.



Figure S32. Representative charge versus time plots for controlled potential electrolyses of **1-Re** (green), **2-Re** (red), **3-Re** (blue), and **ReBpy** (black). *Conditions*: 0.5 mM catalyst in CO₂-saturated CH₃CN / 0.1 M Bu₄NPF₆ solution containing 4% TFE, glassy carbon rod working electrode. Background CPE was performed in the absence of catalyst.



Figure S33. FT-IR spectra of solutions containing **1-Re** (left) and **2-Re** (right) before and after controlled potential electrolyses. The v_{co} bands in the 2050–1800 cm⁻¹ region show the presence of [Re(L)(CO)₃Cl] and [Re(L)(CO)₃Cl]⁻⁻ species in both of the solutions after the electrolyses. The peaks in the 1700–1600 cm⁻¹ region corresponds to HCO₃^{-/}/CO₃²⁻ species. Details are provided in the manuscript. *Conditions*: 2 mM catalyst in CO₂-saturated anhydrous CH₃CN / 0.1 M Bu₄NPF₆ solution, glassy carbon rod working electrode.



Figure S34. Crystal structure of **2-Re** showing co-crystallized outer-sphere DMF molecule. Thermal ellipsoids rendered at the 50% probability level.

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