Electrochemical Reduction of CO₂ Catalyzed by Re(pyridineoxazoline)(CO)₃Cl Complexes

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Supporting Information

ABSTRACT: A series of rhenium tricarbonyl complexes coordinated by asymmetric diimine ligands containing a pyridine moiety bound to an oxazoline ring were synthesized, structurally and electrochemically characterized, and screened for CO_2 reduction ability. The reported complexes are of the type $Re(N-N)(CO)_3Cl$, with N-N = 2-(pyridin-2-yl)-4,5-dihydrooxazole (1), 5-methyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (2), and 5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (3). The electrocatalytic reduction of CO_2 by these complexes was observed in a variety of solvents and proceeds more quickly in acetonitrile than in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The analysis of the catalytic cycle for electrochemical CO_2 reduction by 1 in acetonitrile using density functional theory (DFT) supports the C–O bond cleavage step



being the rate-determining step (RDS) ($\Delta G^{\ddagger} = 27.2 \text{ kcal mol}^{-1}$). The dependency of the turnover frequencies (TOFs) on the donor number (DN) of the solvent also supports that C–O bond cleavage is the rate-determining step. Moreover, the calculations using explicit solvent molecules indicate that the solvent dependence likely arises from a protonation-first mechanism. Unlike other complexes derived from *fac*-Re(bpy)(CO)₃Cl (I; bpy = 2,2'-bipyridine), in which one of the pyridyl moieties in the bpy ligand is replaced by another imine, no catalytic enhancement occurs during the first reduction potential. Remarkably, catalysts 1 and 2 display relative turnover frequencies, $(i_{cat}/i_p)^2$, up to 7 times larger than that of I.

INTRODUCTION

The concentration of carbon dioxide in the atmosphere has recently surpassed 400 ppm for the first time in recorded history, representing a significant accelerator of global climate change.¹ Extensive efforts have been directed toward climate change mitigation by developing new methodologies for chemical fixation of CO_2 . Despite the fact that CO_2 is thermodynamically stable, it has the potential to be an abundant C1 source for fuels and organic materials.^{2,3} CO₂ to fuel conversion could also help mitigate other global problems, including energy shortages, fuel resource depletion, and economic issues with global fuel trade. For the successful design of new routes capable of reducing CO₂, attention must be paid to the fact that the reductive conversion via oneelectron steps involves going through the high-energy radical anion intermediate $(CO_2^{\bullet-})$, demanding potentials as high as -1.90 V vs NHE at pH 7.⁴ Although the $CO_2^{\bullet-}$ radical can react with molecules such as olefins to produce carboxylate compounds, transition-metal catalysts capable of facile multielectron transformations offer an alternate pathway to circumvent this undesirable high-energy intermediate.^{5–15} Among the many chemical transformations of CO_2 catalyzed by transitionmetal catalysts, the reduction of CO_2 to carbon monoxide (CO), either electrochemically or photochemically, is a popular synthetic route because it can potentially lead to the generation of a range of fuels and chemicals via the Fischer–Tropsch reaction, hydroformylation, and similar technologies.

Mn, Re, and Ru carbonyl catalysts containing diimine ligands based on 2,2'-bipyridine (bpy) have been investigated extensively for their CO₂ reduction activity. The first catalyst of this family, *fac*-Re(bpy)(CO)₃Cl (I), was reported by Hawecker and co-workers in 1983.^{6,16} Since the discovery of **I** as an effective catalyst for CO₂ reduction,^{6,17} rhenium(I) complexes have been the focus of intense studies on multiple aspects of the catalytic process.^{18–29} The synthesis of

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Figure 1. Structural representation of compounds 1-3.

derivatives of I in combination with elegant mechanistic studies has provided valuable insights into the reaction mechanism. Synthetic efforts have also resulted in novel rhenium catalysts with enhanced properties (e.g., larger turnover number and lower overpotentials).³⁰ Early mechanistic studies reported that two independent pathways for the electrocatalytic reduction of CO₂ to CO by I exist: a one-electron pathway and a twoelectron pathway. In the one-electron pathway, a net twoelectron reduction of CO₂ is initiated by the nucleophilic attack of the Re(0) species $[Re^{0}(bpy)(CO)_{3}]$, which originates from the one-electron-reduced anion $fac-[Re(bpy^{\bullet-})(CO)_3Cl]^-$. Previous work on I and its derivatives has shown that the redox potential for the first reduction under nitrogen is relatively insensitive to the replacement of chloride by other ligands, supporting the fact that the reduction is ligand-based.³¹ Thus, the bpy ligand plays an important "noninnocent" role during CO₂ reduction by storing the first reducing equivalent in a $\operatorname{Re}^{I}(\operatorname{bpy}^{\bullet-})$ state, which facilitates CO_{2} binding through a low reorganization energy pathway. In the two-electron pathway, I is reduced by two electrons before it binds to CO2.¹⁷ The second reduction of I is assigned to a metal-based reduction, producing the anion $[\text{Re(bpy)(CO)}_3]^{-.32}$ In CO₂-saturated solutions, no catalytic enhancement is observed at the first reduction potential on standard cyclic voltammetry time scales, whereas a significant increase in current is observed at the potential of the second reduction, illustrating that the twoelectron pathway is much more rapid than the one-electron pathway. However, controlled-potential electrolysis at the first reduction potential still results in CO₂ reduction. Altogether, the data indicate that, under electrocatalytic reduction conditions, the two-electron-reduced species of I reduces CO_2 more efficiently than the one-electron-reduced species $[\text{Re}^{0}(\text{bpy})(\text{CO})_{3}]$. It is interesting to note that a recent report has shown that no CO₂ reduction electrocatalysis is observed for $\text{Re}_2(\text{CO})_{10}$ on the cyclic voltammetry time scale, as opposed to $M(CO)_6$ (M = Cr, Mo, W) precursors that are effective catalysts.³³ This fact highlights the importance of the role of the noninnocent bpy ligand for the efficient electrocatalytic reduction of CO₂ by I.

In this report, we explore changes in the nature of the diimine ligand in complexes of the type $\text{Re}(\text{diimine})(\text{CO})_3\text{Cl}$ in a combined experimental and computational effort. Specifically, we introduce rhenium complexes with the three pyridine-oxazoline ligands 2-(pyridin-2-yl)-4,5-dihydrooxazole, and 5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (Figure 1). Pyridine-oxazoline ligands are easily prepared, are resistant to reducing conditions, and offer great potential for derivatization in multiple sites. Metal complexes of pyridine-oxazoline ligands have been employed in a range of catalytic reactions; however, they have not been used in CO₂ activation reactions.³⁴ The pyridine moiety is in conjugation with the oxazoline C=N, and this is expected to provide storage of the redox equivalents

needed for the activation of CO₂, whereas the donating ability of oxazoline is anticipated to increase the nucleophilicity of the reduced rhenium complex. The substitution of one pyridyl in bpy at compounds derived from I has been previously investigated and has produced active electrocatalysts.³⁵ Stanton and co-workers studied the use of pyridyl Nheterocyclic carbenes (NHCs) derived from methylbenzimidazolium-pyridine and showed that the rhenium complex of this ligand was capable of binding and transforming CO₂ at the first reduction potential.³⁵ In another example of substitution of one pyridyl in bpy, Liyanage et al. examined several other pyridyl Nheterocyclic carbenes.³⁶ The rhenium complexes formed by these ligands can also efficiently reduce CO2 at the first reduction wave with $(i_{cat}/i_p)^2$ ranging from 1 to 3, with the tricarbonylbromorhenium(I) complex formed with the 3-(4trifluoromethylphenyl)-1-(2'-pyridyl)imidazolin-2-ylidene ligand showing the highest catalytic rate.³⁶ Herein, the syntheses, structural characterization, the electrocatalytic activity, and the step-by-step mechanism calculated using density functional theory (DFT) for CO_2 reduction by rhenium complexes with pyridine-oxazoline are presented. Unlike the aforementioned examples of substitution of one pyridyl in bpy, no catalytic enhancement occurs at the first reduction potential. Interestingly, two of our new catalysts display relative turnover frequencies, $(i_{cat}/i_p)^2$, up to 7 times larger than that of I.

EXPERIMENTAL DETAILS

Materials. Acetonitrile, ethanol, benzene, toluene, isobutyl chloroformate, 2-chloroethylamine hydrochloride, potassium hydroxide, sodium sulfate, sodium sulfite, pyridine-2-carboxylic acid, 2quinolinecarboxylic acid, 2-pyridinecarboxaldehyde, amino-2-propanol, sodium sulfite, sodium bicarbonate, 2-amino-1-phenylethanol, 2aminobenzaldehyde, 2-amino-3-pyridinecarboxaldehyde, 2-chloro-3quinolinecarboxaldehyde, ethylene glycol, acetamide, pentacarbonylchlororhenium(I), and sodium carbonate were purchased from Sigma-Aldrich. Chloroform, sodium chloride, magnesium sulfate, potassium carbonate, and ammonium chloride were purchased from J. T. Baker. Iodine, 2-acetylpyridine, and p-toluenesulfonic acid monohydrate were purchased from Acros Organics. Methanol, isopropyl alcohol, and triethylamine were purchased from Fisher Scientific. For the controlled-potential electrolysis, acetonitrile was purified using an Innovative Technology PureSolv system under N2, whereas TBAPF₆ was purchased from TCI and recrystallized from HPLC-grade methanol and then dried in a vacuum oven overnight prior to use.

Syntheses. The ligands 2-(pyridin-2-yl)-4,5-dihydrooxazole (pyroxa), 5-methyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (Me-pyroxa), and 5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (Ph-pyroxa) were prepared according to previously reported methods.³⁹

Re(pyroxa)(\overline{CO})₃*Cl* (1). In a 50 mL round-bottom flask, Re(CO)₅Cl (0.2 g, 0.6 mmol), pyroxa (0.08 g, 0.6 mmol), and toluene (30 mL) were added together and the resultant reaction mixture was heated to reflux. After 2.5 h, the reaction mixture was cooled and the solvent was evaporated under reduced pressure to afford a yellow solid (0.2 g, yield 80%). Recrystallization from C₆H₆ and hexanes afforded material suitable for single-crystal X-ray crystallography. ¹H NMR (δ , 400

MHz, DMSO- d_6): 9.04 (d, 1H), 8.35 (t, 1H), 8.15 (d, 1H), 7.89 (t, 1H), 5.02 (m, 2H), 4.31 (m, 1H), 4.11 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 196.87 (s), 195.70 (s), 188.03 (s), 171.89 (s), 154.32 (s), 144.49 (s), 139.61 (s), 129.70 (s), 126.39 (s), 73.11 (s), 55.14 (s). ESI-MS (CH₃CN): m/z 460.1 [M – Cl⁻ + CH₃CN]⁺. Anal. Found for C₁₁H₈N₂O₄ClRe·1/3C₆H₆: C, 32.50; H, 2.01; N, 5.80. Calcd: C, 32.53: H, 2.10; N, 5.84.

*Re(Me-pyroxa)(CO)*₃*Cl* (2). In a 50 mL round-bottom flask, Re(CO)₅Cl (0.7 g, 1.9 mmol), Me-pyroxa (0.31 g, 1.9 mmol). and methanol (30 mL) were added together and the resultant reaction mixture was heated to reflux. After 24 h, the reaction mixture was cooled and the solvent was evaporated under reduced pressure to afford a yellow solid (0.7 g, yield 79%). Recrystallization from C₆H₆ and hexanes afforded material suitable for single-crystal X-ray crystallography. ¹H NMR (δ , 400 MHz, CDCl₃): 8.99 (m, 1H), 8.06 (m, 1H), 7.90 (m, 1H), 7.63 (m, 1H), 5.36 (m, 1H), 4.39 (m, 1H), 3.86 (m, 1H), 1.63 (m, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 170.98 (s), 154.28 (s), 144.76 (s), 139.29 (s), 129.37 (s), 126.19 (s), 8.348 (s), 61.31 (s), 20.82 (s). ESI-MS (CH₃CN): *m/z* 474.1 [M – Cl⁻ + CH₃CN]⁺. Anal. Found for C₁₂H₁₀N₂O₄CIRe·H₂O: C, 29.76; H, 2.25; N, 5.36. Calcd: C, 29.66; H, 2.49; N, 5.77.

*Re(Ph-pyroxa)(CO)*₃*Cl* (3). In a 50 mL round-bottom flask, Re(CO)₅Cl (0.25 g, 0.7 mmol), Ph-pyroxa (0.15 g, 0.7 mmol), and methanol (30 mL) were added together and the resultant reaction mixture was heated to reflux. After 24 h, the reaction mixture was cooled and the solvent was evaporated under reduced pressure to afford a yellow solid (0.3 g, yield 86%). Recrystallization from C₆H₆ and hexanes afforded material suitable for single-crystal X-ray crystallography. ¹H NMR (δ , 400 MHz, CDCl₃): 9.00 (s, 1H), 8.07 (m, 1H), 7.91 (m, 1H), 7.65 (m, 1H), 7.44 (m, 5H), 6.11 (m, 1H), 4.67 (m, 1H), 4.30 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.12 (d), 148.49 (d), 138.81 (s), 133.60 (d), 130.79 (s), 124.55 (d), 121.79 (s), 120.63 (d), 81.72 (d), 56.05 (d). ESI-MS (CH₃CN): *m/z* 536.1 [M - Cl⁻ + CH₃CN]⁺. Anal. Found for C₁₇H₁₂N₂O₄ClRe·0.1C₆H₆: C, 39.55; H, 2.42; N, 5.32. Calcd: C, 39.27; H, 2.36; N, 5.21.

Methods. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE (300 MHz) or Bruker AVANCE III (400 MHz) system at ambient temperature and were referenced to residual solvent peaks. UV-vis spectra were recorded on a Cary 50 spectrophotometer. Solution IR spectra (CH₃CN) were carried on a Jasco FT/IR-6100 spectrometer. Elemental analyses were performed at Atlantic Microlab, Inc., in Norcross, GA. Cyclic voltammetry experiments were performed by using a Model 6012D electrochemical analyzer from CH Instruments, Inc. or DY2311 potentiostat from Digi-Ivy. Cyclic voltammetry experiments were performed under $N_2(g)$ or $CO_2(g)$ in a one-compartment cell with a glassy-carbon working electrode, a platinum-wire counter electrode, and a Ag/Ag⁺ (10 mM AgNO₃ in acetonitrile, DMF or DMSO) reference electrode with ferrocene as an external reference. Experiments were performed by using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) or tetrabutylammonium chloride (TBACl) as the supporting electrolyte as indicated, with acetonitrile, DMF, or DMSO as solvent, and with rhenium complexes at concentrations ranging from 0.5 to 1.0 mM. ESI-MS was performed on acetonitrile solutions of the complexes in a Quattro-II instrument (triple quadrupole mass spectrometer, Waters). Controlled-potential electrolyses were performed using an eDaq ER466 potentiostat with 25 mL of an acetonitrile/TBAPF₆ solution in a cell with a carbon-rod working electrode ($\sim 1.9 \text{ cm}^2$ submersed area), a silver-wire pseudoreference protected by a CoralPor frit, and a platinum-wire counter electrode separated from the solution by a medium-porosity frit. Gas chromatography analysis of the headspace was performed on an Agilent 7820 instrument equipped with a HP-Molesieve column and a gas sampling valve. A TCD detector was used with N₂ as the carrier gas. Calibration curves for carbon monoxide and hydrogen were created by injecting known quantities of CO or H₂ into the electrochemical cell and then sampling the headspace. IR of the bulk electrolysis solutions was obtained with an ABB FTLA2000 spectrometer using a Buck Scientific demountable liquid cell equipped with KBr windows and a 0.1 mm spacer.

X-ray Crystallography. X-ray diffraction data were collected on a Bruker APEX DUO CCD platform diffractometer (Mo K α (λ = 0.71073 Å)) at 125 K. Suitable crystals were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2008).⁴⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. A 2-fold disorder of the methyl group and part of the five-membered oxazole ring in complex **2** were modeled and refined with the help of similarity restraints on 1–2 and 1–3 distances and anisotropic displacement parameters (DELU).

Infrared Spectroelectrochemistry (IR-SEC). IR-SEC was performed using an optically transparent thin-layer electrochemical (OTTLE) cell purchased from Bio-Logic Inc. The demountable OTTLE cell was composed of CaF_2 windows and a Teflon spacer equipped with a platinum-mesh working electrode, a platinum-wire counter electrode, and a silver-wire pseudoreference. The potential was controlled using an eDaq ER466 potentiostat, and IR spectra were collected with a ABB FLTA2000 spectrometer. All species were at 2.5 mM in solution.

Computational Methods. Density Functional Theory. All geometries were fully optimized at the M06-L level of theory, with the SMD continuum solvation model⁴³ for acetonitrile as the solvent. The Stuttgart [8s7p6d2f | 6s5p3d2f] ECP60MWB contracted pseudopotential basis set⁴⁴ was used for Re and the 6-31G(d) basis set⁴⁵ for all other atoms. Nonanalytical integrals were evaluated using the *integral* = (grid = ultrafine) option and an automatically generated density-fitting basis set used within the resolution-of-the-identity approximation to speed the evaluation of Coulomb integrals, as implemented in Gaussian 09.⁴⁶ The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 cm⁻ replaced by 50 \mbox{cm}^{-1} when computing free energies), and for determination of the reactants and products associated with each transition-state structure (by following the normal modes associated with imaginary frequencies). Partition functions were used in the computation of thermal contributions to free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation at 298 K.47 Free energy contributions were added to single-point M06-L electronic energies computed with the SDD basis set on rhenium and the 6-311+G(2df,p) basis set on all other atoms to arrive at final, composite free energies.

Solvation and Standard Reduction Potentials. As mentioned above, solvation effects for acetonitrile were accounted for by using the SMD continuum solvation model.⁴³ A 1 M standard state was used for all species in solution. Thus, the free energy in solution is computed as the 1 atm gas-phase free energy, plus an adjustment for the 1 atm to 1 M standard-state concentration change of *RT* ln 24.5, or 1.9 kcal/mol, plus the 1 to 1 M transfer (solvation) free energy computed from the SMD model.

Standard reduction potentials were calculated for various possible redox couples to assess the energetic accessibility of different intermediates at various oxidation states. For a redox reaction of the form

$$O(\text{soln}) + ne^{-}(g) \to R(\text{soln})$$
(1)

where *O* and *R* denote the oxidized and reduced states of the redox couple, respectively, and *n* is the number of electrons involved in redox reaction, the reduction potential E_{OIR}° relative to SCE was computed as

$$E_{\rm O|R}^{\circ} = -\frac{\Delta G_{\rm O|R}^{\circ}}{nF} - \Delta E_{\rm ref}^{\circ}$$
⁽²⁾

where $\Delta G_{\text{OIR}}^{\circ}$ is the free energy change associated with eq 1 (using Boltzmann statistics for the electron) and $\Delta E_{\text{ref}}^{\circ}$ is taken as 0.141 V,²² which is required for the conversion of calculated E_{OIR}° versus the



Figure 2. (left) Thermal ellipsoid plot of 1 at 50% probability. Hydrogen atoms are omitted for clarity. (right) Selected geometrical features for 1 obtained via X-ray crystallography and DFT calculations at the M06-L level, with bond lengths in units of angstroms (Å) and bite angles in units of degrees.

normal hydrogen electrode (NHE) in aqueous solution ($E_{\rm NHE} = -4.281 \text{ V}$)⁴⁸ to $E_{\rm OIR}^{\circ}$ versus the saturated calomel electrode (SCE) in acetonitrile ($E_{\rm SCE} = -4.422 \text{ V}$).⁴⁸ We obtained reduction potentials referenced to the ferrocene/ferrocenium couple by using a shift of -0.384 V from $E_{\rm OIR}^{\circ}$ vs SCE.

Benchmark Calculations. Benchmark calculations at the M06-L, B3LYP,⁴⁹ M06,^{41,42,50} MP2, domain based local pair natural orbital (DLPNO) based single- and double-excitation coupled-cluster (DLPNO-CCSD),^{51,52} and DLPNO-CCSD with perturbative inclusion of triple excitations (DLPNO-CCSD(T))⁵² levels of theory were performed using the def2-TZVPP basis set⁵³ on all atoms and the COSMO continuum solvation model for acetonitrile as implemented in the ORCA program package.⁵⁴ Scalar relativistic effects were accounted for using the zeroth-order regular approximation (ZORA) Hamiltonian.^{55–58} Atom-pairwise dispersion correction to the DFT energies with Becke–Johnson damping has been applied for B3LYP density functional.⁵⁹ The activation energies were computed using the optimized geometries at the M06-L level of theory (see above for full description).

RESULTS

Syntheses and Characterization of the Re(I) Complexes. The synthesis of complex 1 was carried out by treating $Re(CO)_5CI$ with the corresponding ligand in refluxing toluene under N₂ for 2 h (Figure 1). Complexes 2 and 3 were synthesized in boiling methanol under an atmosphere of nitrogen for 24 h. The change in reaction conditions for compounds 2 and 3 are critical for their formation, as the reactions result in lower yields in toluene. The crude products were collected by filtration and purified by recrystallization to provide the Re(I) complexes in good yields (70–80%). Complexes 1–3 were characterized by ¹H and ¹³C NMR, mass spectrometry, and elemental analysis.

The molecular structures of 1-3 were determined by X-ray crystallography. Thermal ellipsoid plots of the three compounds are given in Figures 2-4. The three structures can be considered as distorted octahedral with three CO groups coordinated in a facial arrangement. The $Re-N_{\text{diimine}}$ distances range from 2.141(2) to 2.204(2) Å and resemble those of other rhenium diimine complexes. The rhenium complexes with pyridine-oxazoline ligands contain bite angles that vary in the range $74.12(8) - 74.47(6)^{\circ}$. These angles are also similar to those reported for other rhenium(I) complexes with similar chelating ligands.^{35,60} In compounds 1-3, the C–O bond lengths of the carbonyl trans to the diimine ligands are close in magnitude to each other and vary in the range 1.146(3)-1.157(3) Å. The small differences in bonding distances are likely due to effects arising from crystal packing, because the $\nu_{\rm CO}$ values for these compounds do not differ significantly from each other (see below). In addition, the C-Re-C angles for



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Figure 3. Thermal ellipsoid plot of 2 at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Re–N1 2.204(2), Re–N2 2.141(2), Re–Cl 2.4863(6), Re–Cl 1.912(4), Re–C2 1.927(3), Re–C3 1.908(3).



Figure 4. Thermal ellipsoid plot of 3 at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Re–N1 2.198(2), Re–N2 2.162(2), Re–Cl 2.4708(5), Re–Cl 1.915(3), Re–C2 1.926(2), Re–C3 1.926(3).

the three complexes range from 88.1 to 90.8° and are similar to the reported structures for other Re diimine complexes.⁶⁰ The geometrical features of structure of **1** optimized in acetonitrile at the M06-L level of theory are in very good agreement with X-ray data and are presented in Figure 2.

Carbonyl Vibrational Spectra. Three CO stretching bands are observed in the infrared spectra of the rhenium complexes 1-3 in a *fac* configuration. The force constants associated with CO stretching were calculated according to the

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Cotton-Kraihanzel method (Table 1).^{61,62} The interaction constants, k_i , for 1-3 are very similar to those calculated for I

Table 1. CO Vibrational Stretching Frequencies ν_{CO} (cm⁻¹) in Acetonitrile and Calculated Force Constants k (mdyn/Å) of Rhenium(I) Complexes^{*a*}

		$\nu_{\rm CO}$				
complex	$A'(1)^{b}$	$A'(2)^{b}$	Α″ ^b	k_1	k_2	$k_{ m i}$
1	2023	1917	1898	15.03	15.44	0.60
2	2023	1916	1898	15.04	15.43	0.60
3	2024	1918	1899	15.05	15.46	0.60
^{<i>a</i>} Cotton–Kraihanzel method. ^{<i>b</i>} Pseudo-C _s point group.						

($k_1 = 15.07$, $k_2 = 15.44$, and $k_i = 0.60$), indicating similar weak σ bonding between the α -diimine ligands and the tricarbonylrhenium fragments,⁶² in agreement with the similar Re–N_{diimine} distances observed by X-ray crystallography.

Absorption Spectra. The electronic absorption spectra of complexes 1-3 in acetonitrile exhibit metal to ligand charge transfer (MLCT) transitions at 369–375 nm for the lowest energy observed transition (Table 2).⁶³ This assignment is

Table 2. UV/Vis Data and Charge-Transfer Absorption Maxima $\nu_{\rm max}~({\rm cm}^{-1})$ of 1–3

		MLCT $\nu_{\rm max}$		
complex	$\lambda_{\mathrm{max}}~(arepsilon,~\mathrm{M}^{-1}~\mathrm{cm}^{-1})$	acetonitrile	toluene	${\Delta u_{ m max} \over (m cm^{-1})}$
1	255 (4800), 369 (1400)	26667	24938	1729
2	258 (5900), 375 (2500)	26833	24933	1950
3	258 (10400), 375 (3600)	26672	24933	1739

supported by the significant bathochromic shift on going from polar to less polar solvents ($\Delta \nu_{max}$ Table 2). The extent of MLCT solvatochromism can be correlated with the metal/ ligand orbital interaction. An increase of mixing of metal and ligand molecular orbitals results in a decrease of the solvatochromic effect due to the diminished polarity difference between ground and excited states.⁶⁴ In addition, the MLCT bands for compounds 1–3 are broad, with $\Delta \nu_{1/2} \approx 6900 \text{ cm}^{-1}$. Although a number of factors can influence the width of an absorption band, the broader MLCT bands observed for the rhenium pyridine-oxazoline complexes 1-3 likely originate from a more diverse population of MLCT vibrational states in their S1 excited state. The absorption bands observed at ~250 nm in compounds 1-3 can be assigned as arising from the ligands $\pi\pi^*$ LC transitions, as similar transitions are also observed in the spectra of the free ligands.

Electrochemical Studies of $\text{Re}(\text{L})(\text{CO})_3\text{Cl}$ Complexes. Table 3 presents a summary of the results of cyclic voltammetry studies of complexes 1–3. Representative voltammograms under an atmosphere of N₂ of solutions containing complexes 1–3 in 0.1 M TBAPF₆/acetonitrile at a scan rate of 100 mV/s are shown in Figure 5. For these complexes, $E_{1/2}$ values for the first reduction range from –1.73 to –1.85 V vs Fc^{+/0}, with the most negative potential corresponding to compound 2, possessing the ligand with a methyl substituent. The first one-electron reduction for complexes 1–3 seems irreversible at 0.1 V/s. At faster scan rates (up to 1 V/s), increasing reversibility is observed as the current ratio, i_c/i_{a^2} increases progressively with the scan rate (Figures S17 and S18 in the Supporting Information), indicating that an irreversible Table 3. First and Second Reduction Peak Potentials in the Absence of a Substrate (E_p) .^{*a*} Current Densities (j),^{*b*} Relative Turnover Frequencies $((i_{cat}/i_p)^2)$, and Overpotentials $(\eta)^c$ for the Reduction of CO₂ by 1–3

catalyst	1st reduction potential (V vs Fc ^{+/0})	2nd reduction potential (V vs Fc ^{+/0})	$j (mA/cm^2)$	$(i_{\rm cat}/i_{\rm p})^2$	η (V)
1	-1.75	-2.31	1.31	66	2.11
2	-1.85	-2.35	1.26	85	2.24
3	-1.73	-2.24	0.74	11	2.26
\mathbf{I}^d	-1.73	-2.11	0.50	12	

^{*a*}Cyclic voltammograms were recorded in acetonitrile solution (1.0 mM in catalyst) with 0.1 M [ⁿBu₄N]PF₆ supporting electrolyte, using a 3 mm glassy-carbon working electrode, Pt-wire counter electrode, Ag/Ag⁺ reference electrode (10 mM AgNO₃ in acetonitrile), and scan rate 0.1 V/s. ^{*b*}Current densities, *j*, and overpotentials were determined at the potential of $E_{cat/2}$. ^{*c*}Calculated as described in ref 66. ^{*d*}Reference 30.



Figure 5. Representative cyclic voltammograms of (A) 1 in acetonitrile (ACN), (B) 1 in DMF, (C) 2 in ACN, and (D) 3 in ACN at a scan rate of 0.1 V/s under N₂ (black) and under CO₂ (red). Conditions: 3 mm diameter glassy-carbon working electrode, platinum-wire counter electrode, 100 mV/s, 1 mM catalyst, 0.1 M TBAPF₆, room temperature.

chemical reaction follows a reversible electron transfer. It is quite common for rhenium complexes of the $Re(L)(CO)_3Cl$ type that Cl⁻ dissociation follows the electron transfer step. For this reason we investigated changes in the cyclic voltammetry response when tetrabutylammonium chloride served as the electrolyte. The presence of excess chloride, 0.1 M, shifts the equilibrium away from the dissociation of Cl- and results in increasingly reversible first reduction waves (Figure S19 in the Supporting Information). The first reduction wave is followed by a second irreversible one-electron reduction wave at more negative potential (ca. -2.4 V vs Fc^{+/0}) in comparison to I $(-2.2 \text{ vs Fc}^{+/0})$. Due to the similar potentials at which the first reduction wave appears for I and 1-3, it is likely that it represents a pyridine-based reduction of the starting complex to form the radical complex $[Re(pyroxa^{-})(CO)_3(CI)]^{-.65}$ Since the complexes undergo facile halide loss on reduction, an anodic peak appears at -1.6 V corresponding to the $[\text{Re}(\text{pyroxa})(\text{CO})_3(\text{solvent})]^{0/+}$ couple. This behavior is consistent with the ECE reduction behavior of I and similar rhenium species.

When the solutions containing complexes 1-3 are exposed to a CO₂ atmosphere, their cyclic voltammograms show an increase of the second cathodic peak (Figure 5). To compare the activity of these catalysts with others reported in the literature, the quantity $(i_{cat}/i_p)^2$, obtained from cyclic voltammetry, was used. It has been proposed that $(i_{cat}/i_p)^2$, being proportional to the turnover frequency (TOF), provides a useful quantity to compare relative TOFs.^{67,68} On the basis of such analysis, catalyst 1 shows a higher performance in comparison to I. Introducing the electron-donating methyl group to the oxazoline ring increases the activity of catalyst 2, whereas the electron-withdrawing phenyl moiety on catalyst 3 decreases its performance with respect to $(i_{cat}/i_p)^2$ quantity. The current densities for the three catalysts are higher than that of I; however, the required overpotentials are also higher. The catalytic activity of compounds 1-3 was also measured in DMF and DMSO. The relative TOFs and current densities in these solvents are smaller than those observed in acetonitrile (Table 3 and Table S1 in the Supporting Information).

In order to study the catalytic reduction of CO_2 , preparativescale electrolysis experiments were carried out with catalysts 1– 3. Controlled-potential electrolysis at -2.8 V (vs Fc^{+/0}) with a carbon-rod electrode under a CO_2 atmosphere led to formation of CO with Faradaic efficiencies ranging from 30% to 55%, as detected by gas chromatography (Table 4). IR spectroscopy did

Table 4. Results of Bulk Electrolysis in Acetonitrile^a

		Faradaic eff	Faradaic efficiency (%)		
compound	potential (V) vs Fc ^{+/0}	СО	H ₂		
1	-2.8	55	<3		
2	-2.8	55	<3		
3	-2.8	30	<3		
ac 1.0 1.1		. 1	1 1.		

^{*a*}Conditions: held at the potential for 30 min, carbon-rod working electrode, 1 mM complex, 0.1 M TBAPF₆ electrolyte.

not show evidence for carbonate, formate, or oxalate. Likewise, NMR showed no formation of formate. H₂ was detected with less than 3% efficiency for the three catalysts. Therefore, similar to the case for I, the reaction is likely to proceed as $CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$. We also performed a bulk electrolysis experiment at a lower potential for 1 (at -2.3 V vs Fc^{+/0}) and observed a similar Faradaic efficiency (61%) and TON = 2.5 for the formation of CO after 1 h. The low Faradaic efficiency is likely due to decomposition of the catalysts over time, which creates species that can be reduced but do not yield CO_2 reduction products (bulk electrolysis in the absence of CO_2 produced a trace amount of CO (1% Faradaic efficiency). Notably, solid formation was observed over the course of bulk electrolysis experiments under CO_2 , which supports this hypothesis.

We also performed a controlled-potential electrolysis of 1 in the presence of CO_2 with 1 M added water. CO was still observed, but at lower Faradaic efficiencies (27%) in comparison to hydrogen (33%). In addition, some formate was observed in solution (11%). Therefore, selectivity is lost with added water. However, the TON of CO after 1 h was still ca. 2, similar to the CO_2 reduction without water.

Electrochemical Behavior in the Presence of Brønsted Acids. We investigated the effect of the addition of weak Brønsted acids on the CO₂ reduction process. For complex 1 under N₂, addition of H₂O (0.55-2.75 M) resulted in a negligible effect on the first cathodic wave, but new cathodic waves appeared at more negative potentials. In addition, the second cathodic wave showed a large current increase, indicating that the complexes are able to reduce H⁺ ions to H_2 . Under CO_2 , reduction of CO_2 shifted to lower potentials, with a larger increase in current observed for the more acidic proton donor, methanol (Figure S21 in the Supporting Information). The addition of the more acidic proton donor phenol (pK_a values 9.95 and 18.0 in H₂O and DMSO, respectively) to the solution resulted in a shift of the first cathodic wave under N2, likely due to proton binding, and a large current enhancement at more negative potential indicative of H⁺ reduction. Similar to the behavior observed in the presence of methanol, the addition of phenol under CO₂ resulted in the CO₂ reduction process shifting toward more positive potentials (Figure S21). Compounds 2 and 3 showed similar behavior in the presence of water and methanol (Figures S22 and S23 in the Supporting Information).

Regeneration of the Catalyst after CO Formation. The complex $[Re(pyroxa)(CO)_4](OTf)$ (4) was synthesized similarly to a reported procedure for $[Re(bpy)(CO)_4](OTf)$.⁶⁹ Compound 4 was characterized by elemental analysis and FT-IR spectroscopy (Figure 6) as well as ¹H and ¹³C NMR



Figure 6. FT-IR spectra of $[Re(pyroxa)(CO)_4](OTf)$ (4) before (red) and after exposure to a substoichiometric amount of Na–Hg amalgam (0.1–0.2 equiv, blue) in acetonitrile.

spectroscopy. The cation is likely to be a product formed during the reduction of CO_2 under the conditions used in the electrochemical experiments. A solution of 4 can remain unchanged in solution for hours, as it is a very stable compound as determined by FT-IR experiments. On the basis of previous studies on $[Re(bpy)(CO)_4](OTf)$,⁶⁹ we hypothesized that the release of CO from $[Re(pyroxa)(CO)_4]^+$ requires additional reducing equivalents.^{69,70} When a solution of 4 in acetonitrile under an inert atmosphere was exposed to a substoichiometric amount of Na-Hg amalgam (0.1-0.2 equiv), it rapidly resulted in a new compound that upon exposure to air produced $[Re(pyroxa)(CO)_3(CH_3CN)]^+$ (Figure 6). This result indicates that CO loss from $[Re(pyroxa)(CO)_4]^+$ can be catalyzed by electron transfer, similarly to the dissociation reaction observed with $[Re(bpy)(CO)_4](OTf)$.⁶⁹

Infrared Spectroelectrochemistry. In order to examine the species formed upon reduction of complexes 1–3, IR-SEC of the complexes was performed. IR-SEC has previously been critical for elucidating the behavior of Re- and Mn-based CO_2 reduction catalysts.^{13,30,70–75} Upon sweeping the potential negative, several species were observed, corresponding to various complexes (Figure 7 and Table 5). The initial reduction of 1 resulted in a spectrum with a pattern similar to that of compound 1, but with signals shifted to lower wavenumbers by $13-20 \text{ cm}^{-1}$, consistent with a ligand reduction to form



Figure 7. Infrared spectrelectrochemistry spectra of the reduction of **1** in acetonitrile under Ar with 0.1 M TBAPF₆ as a supporting electrolyte. $[\text{Re}(\text{pyroxa})(\text{CO})_3\text{Cl}]^-$ is formed by the first reduction of the complex, with the electron density mostly localized on the pyridine moiety of the ligand. Upon Cl⁻ dissociation, $[\text{Re}(\text{pyroxa})(\text{CO})_3]^0$ forms. The second reduction of the complex leads to the five-coordinate anion $[\text{Re}(\text{pyroxa})(\text{CO})_3]^-$, which acts as the active catalyst species.

Table 5. Signals Observed in IR-SEC Spectra of Compound 1 in Acetonitrile under Ar with 0.1 M TBAPF₆ as a Supporting Electrolyte^{*a*}

compound	signal (cm ⁻¹)
1	2023, 1913, 1894
[Re(pyroxa)(CO) ₃ Cl] ⁻	2010, 1894, 1873
[Re(pyroxa)(CO) ₃] ⁰	1981, 1867, 1852
[Re(pyroxa)(CO) ₃] ⁻	1979, 1850

^{*a*}The behavior and IR-SEC spectra for complexes **2** and **3** were very similar to those of **1** (see the Supporting Information).

 $[\text{Re}(\text{pyroxa})(\text{CO})_3\text{CI}]^-$. Allowing this species to stand in solution without changing the potential results in a new species with signals that are 20–30 cm⁻¹ more negative. We attribute this to the loss of Cl⁻ and the charge transfer from the pyroxa ligand to the Re metal, analogous to Re(bpy-R) catalysts. The $[\text{Re}(\text{pyroxa})(\text{CO})_3]^0$ species can then be reduced by one more electron to the active anion $[\text{Re}(\text{pyroxa})(\text{CO})_3]^-$. The IR spectra for $[\text{Re}(\text{pyroxa})(\text{CO})_3]^-$ possesses signals that are similar to, but more positive than, those of the corresponding $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ species in acetonitrile,^{70,72} indicating that the reduced pyroxa ligand provides less back-donation to the metal carbonyl antibonding orbitals in comparison to the bpy ligand.

Theoretical Investigation of the CO₂ Reduction Mechanism. Density functional theory (DFT) calculations at the M06-L level of theory coupled with the SMD continuum solvation method were employed to study the reaction mechanism of CO₂ reduction by 1 (see Computational Methods for details), and the results are summarized in Scheme 1. The proposed mechanism starts with two consecutive one-electron-reduction steps along with chloride ion decoordination from the Re center to generate the pentacoordinate [Re]⁻ intermediate. The calculated potentials are -1.87 and -2.00 V vs Fc^{+/0}, respectively. The first reduction of 1 is ligand-based and results in the localization of the electron density on the pyridine ring of the diimine ligand (Figure S26 in the Supporting Information). After the first reduction, the decoordination of the chloride ligand is possible and proceeds with a computed free energy of activation (ΔG^{\ddagger}) of 9.1 kcal/mol. Following this step the reduction of pentacoordinate [Re] species (or the solvent-bound [Re-S]

species) will generate the pentacoordinate [Re]⁻ intermediate, consistent with an ECE pathway for the reduction of compound 1. Further results on other possible pathways other than those shown in Scheme 1 for the initial activation and reduction steps of the catalyst 1 along with catalysts 2 and 3 are reported in Scheme S1 and Table S5 in the Supporting Information. [Re]⁻ undergoes an electrophilic attack by CO₂ (Figure 8) with a free energy of activation (ΔG^{\ddagger}) of 12.5 kcal/ mol, generating the highly basic $[\text{Re-CO}_2]^-$ (pK_a^{calc} = 26.0), protonation of which results in the formation of the metallocarboxylic acid intermediate [Re-CO₂H] (Scheme 1). The following steps involve C-OH bond cleavage to evolve CO by either the protonation-first or reduction-first pathway (Scheme 1).²⁴ The initial step of the protonation-first pathway is the cleavage of the C-OH bond in [Re-CO₂H] with a Brønsted acid as the proton source (e.g., H_2O). The optimized transition state structure with H_2O (Figure 8) as the proton source features a ΔG^{\ddagger} value of 27.9 kcal/mol and is followed by a reduction step with an associated computed potential of E =-1.63 V vs Fc⁺⁷⁰ to generate [**Re-CO**]. On the other hand, the reduction-first pathway starts with the reduction of [Re-CO₂H] to $[\text{Re-CO}_2\text{H}]^-$ with a computed potential of E = -2.00 V vs Fc^{+/0}, followed by C–OH bond cleavage with $\Delta G^{\ddagger} = 27.2$ kcal/ mol with H₂O as the proton source. Both the protonation-first and reduction-first pathways results in the formation of the neutral tetracarbonyl species [Re-CO], from which the reduction with simultaneous evolution of CO requires a potential of E = -2.20 V vs Fc^{+/0} and regenerates the active catalyst $[Re]^-$ completing the catalytic cycle. For both pathways, cleavage of the C-OH bond is predicted to be rate-determining; therefore, this step was examined more closely at different levels of theory. First, the effect of inclusion of an additional water molecule or a cation (tetramethylammonium, Me₄N⁺, is used to model tetrabutylammonium cation available in reaction solutions) to stabilize the newly forming OH⁻ anion in the C-OH bond cleavage step is examined. The presence of an additional water molecule significantly reduces the activation free energy (\sim 3 kcal/mol) for the reduction-first pathway, but the presence of Me₄N⁺ did not result in any enhancement in the activation free energies (Tables S6 and S7 in the Supporting Information). We further tested these effects by reoptimizing selected structures at the M06 and B3LYP Scheme 1. Proposed Catalytic Cycle for Reduction of CO₂ to CO by Compound 1^a



^{*a*}Free energy changes are reported in kcal/mol and redox potential in V vs Fc^{+/0} couple.



Figure 8. Located transition state structures for (a) CO_2 binding to $[Re]^-$, (b) C–OH bond cleavage for $[Re-CO_2H]$, and (c) C–OH bond cleavage for $[Re-CO_2H]^-$. Color code: Re (cyan), C (gray), N (blue), O (red), H (white).

levels of theory and found very similar results (Tables S6 and S7). Finally, we performed benchmark calculations at the DLPNO-CCSD(T) level of theory for the ΔE^{\ddagger} values associated with the protonation-first pathway to assess the performance of a set of selected density functionals and found quantitatively the M06-L and B3LYP functionals to provide the best agreement with the DLPNO-CCSD(T) level of theory (Table S8 in the Supporting Information).

DISCUSSION

In comparison to the known compound I, compounds 1-3 with partially electron rich diimine ligands exhibit less reversible electron uptake due to more facile halide dissociation. After one-electron reduction of the new complexes, the corresponding anions may be best described as ligand-centered radical

species $[\text{Re}^{I}(\alpha\text{-diimine}^{\bullet-})(\text{CO})_{3}\text{CI}]^{-}$ and not as $[\text{Re}^{0}(\alpha\text{-diimine})(\text{CO})_{3}\text{CI}]^{-}$, similarly to $\mathbf{I}^{\bullet-}$ and other "18 + δ " rhenium complexes containing α -diimine ligands.³¹ The δ charge transmitted from the π SOMO of the reduced α -diimine labilizes the Re–Cl bond, the effect being stronger for larger δ . Upon chloride release, a ligand to metal charge transfer localizes the electron density mainly to the rhenium center, as shown by both the spectroelectrochemistry studies and the DFT calculations (Figure 7 and Figure S26 in the Supporting Information). Compounds 1–3 all undergo a second electrochemical reduction which is irreversible. The inspection of molecular orbitals and calculated unpaired spin densities for complexes 1–3 at the M06-L level of theory also confirm this analysis. The computed unpaired spin densities indicate that the reduction of $[\text{Re}^{I}(\alpha\text{-diimine})(\text{CO})_{3}\text{CI}]^{0}$ is ligand-centered

	rate constant $(M^{-1} s^{-1})$			$\Delta G^{\ddagger} \; (ext{kcal/mol})^{a}$		
compound	acetonitrile	DMF	DMSO	acetonitrile	DMF	DMSO
1	203 ± 6	5.3 ± 0.1	2 ± 0.3	11.9	14.0	14.6
2	157 ± 24	4.4 ± 0.1	3.3 ± 0.1	12.0	14.1	14.3
3	66 ± 10	12 ± 2	12 ± 2	12.5	13.5	13.5
^{<i>a</i>} Calculated assuming the pre-exponential factor $A = 10^{11}$ and using the rate constants from the reactions in acetonitrile, DMF, or DMSO. ⁷⁶						

and generates $[\text{Re}^{I}(\alpha \text{-diimine}^{\bullet-})(\text{CO})_{3}\text{Cl}]^{-}$ (Figures S26–S28 in the Supporting Information). However, the dissociation of chloride ion proceeds with a relatively low ΔG^{\ddagger} value (8–9 kcal/mol depending on the complex) and this results in negative charge transfer from the ligand to the metal center for the pentacoordinate $[\text{Re}^{I}(\alpha\text{-diimine}^{\bullet-})(\text{CO})_{3}]^{0}$ species. Further, the product of the second reduction could be assigned as $[\text{Re}^{0}(\alpha\text{-diimine}^{\bullet-})(\text{CO})_{3}]^{-}$ on the basis of the molecular orbital analysis (Figures S26-S28). As expected, the second irreversible reduction wave appears at more negative potentials for 1-3 in comparison to I, in which the additional electron resides in the more delocalized bipyridine system. In the rhenium pyroxa complexes, the substituents on the oxazoline ring are not close to the imines bound to the rhenium center; however, they do exert a small electronic effect on the reduction potentials.

When the Re compounds containing pyridine-oxazoline ligands are reduced in the presence of CO₂, they behave in a fashion similar to that for I. That is, the peak corresponding to the second reduction shows an increase in current. In acetonitrile, the relative TOFs, $(i_{cat}/i_p)^2$, are larger for 1 and 2 in comparison to I, whereas the corresponding quantity for 3 is smaller. The lower activity of 3 is not due to a steric factor, since the crystal structure of the complex shows that the phenyl substituent is not located near the reaction center. Thus, electronic factors seem to be the reason for the lower relative TOF for 3. Along with a lower relative TOF, complex 3 also shows a lower Faradaic efficiency. The measured $(i_{cat}/i_p)^2$ values for 1-3 decrease considerably when DMF and DMSO are used as solvents in the reaction. A similar behavior associated with I has not been observed, and we have corroborated this fact. Interestingly, DuBois and co-workers reported that CO₂ reduction with the Pd complex [Pd-(triphosphine) solvent)](BF₄)₂ also depends on the solvent, with reaction rate constants of 200 ± 100 , 50 ± 20 , and less than 1 M⁻¹ for the reactions in ACN, DMF, and DMSO, respectively.¹⁰ The origin of the low rate in DMSO was the competition for the active site; however, no explanation was put forward for the rate decrease in DMF.¹⁰

To obtain more information on the solvent dependence of the reactions catalyzed by 1-3, the second-order rate constant for the CO₂ reduction was calculated using eq 3.

$$i_{\rm c} = nFA[\operatorname{cat.}](Dk[\operatorname{CO}_2])^{1/2}$$
(3)

Terms include i_c for the catalytic current observed in the voltammograms, n for the number of electrons (2 for the reduction of CO₂ to CO; see Table 4), F for Faraday's constant, A for the area of the electrode surface, k for the rate constant, and D for the diffusion coefficient. The diffusion coefficients were determined by ¹H 2D-DOSY experiments. The diffusion coefficients for 1–3 using this method were similar to those determined using a rotating-disk electrode (Table S4 in the Supporting Information). The equation applies to these

systems since the catalytic current depends linearly on the concentration of the complex and the square root of the concentration of carbon dioxide (see Figures S15 and S16 in the Supporting Information).

Second-order rate constants ranging from 66 ± 10 to $203 \pm 6 \text{ M}^{-1} \text{ s}^{-1}$ were obtained for compounds 1–3 in ACN (Table 6). The rate constants do not parallel the variation in the dielectric constant (ACN 38.0, DMF 36.1, and DMSO 46.7) or acceptor number (ACN 18.9, DMF 16.0, and DMSO 19.3); however, they correlate with the solvent's donor number (DN, for ACN, DMF, and DMSO the DNs are 14.1, 26.6, and 29.8, respectively; Figure 9), a parameter known to relate to the



Figure 9. Second-order rate constants (*k*) measured for compounds 1-3 correlating with the donor number of the solvents: (a) 1 (red •); 2 (black \blacksquare); 3 (blue \blacktriangle). Donor numbers for acetonitrile, DMF, and DMSO are 14.1, 26.6, and 29.8, respectively.

Lewis basicity of the solvent.⁷⁷⁻⁷⁹ The Lewis base character of the solvent can exert important effects on the transition state(s) of the CO₂ reduction reaction (by either stabilizing or destabilizing them). As portrayed in Scheme 1, conversion of CO_2 by these rhenium complexes involves competing processes where the solvent can exert a different influence over each of these steps. The correlation of a composite quantity such as $\ln k$ with a single-parameter solvent scale is not to be expected unless one of the steps is dominant. If this correlation were to reflect strongly an associative chemical step involving the solvent, an increase in $\ln k$ with increasing solvent donor number would be anticipated. The negative slope suggests a dominant physical role, such as hydrogen bonding, by the solvent. A plausible explanation is that C-OH bond cleavage is the largest effective barrier in the reaction⁸⁰ so that either the solvent molecules participate with H bonding to C-OH bond cleavage or compete with the metallocarboxylate for the pool of available protons. Our DFT results show the largest effective barriers during C-OH bond cleavage from either the protonation-first or reduction-first pathway (Scheme 1). To further probe the mechanism, we examined the catalyst activation and C-OH bond cleavage steps for complex 1 in ACN, DMF, and DMSO solvents using the SMD continuum solvation method to account for bulk solvation effects. The

computed reduction potentials for activation of the catalyst from **[Re-Cl]** to **[Re]**⁻ was found to be quite similar in all three solvents with only small differences ($\Delta E \approx 0.10$ V) arising in potentials which involve solvent -coordinated species (Table S9 in the Supporting Information). Next, we considered C-OH bond cleavage steps from either the protonation-first or reduction-first pathway and found similar free energies of activation for the optimized transition state structures (Table S10 in the Supporting Information). The similarity in the geometric parameters of optimized structures and ΔG^{\ddagger} values indicate that the bulk solvation effects of ACN, DMF, and DMSO solvents accounted for by the SMD continuum model are quite similar and do not introduce significant changes in C-OH bond cleavage for either pathway. As a next step, we optimized C-OH bond cleavage TSs including one explicit solvent molecule hydrogen bonded to one of the H2O molecules in C-OH bond cleavage structures. In order to avoid errors that could arise from the computation of relative energies of reactant complexes in different solvents, here we only report the ΔG^{\ddagger} values from reactant complexes but ΔG^{\ddagger} values from separated reactants are also reported in Table S10. The computed ΔG^{\ddagger} values in the protonation-first pathway are 16.1, 17.6, and 19.0 kcal/mol for C-OH bond cleavage in ACN, DMF, and DMSO as solvents, respectively, whereas ΔG^{\ddagger} values in the reduction-first pathway are 15.3, 15.2, and 15.3 kcal/mol. These results should be interpreted with caution, given the complex nature of the reaction (e.g., proton transfer with concomitant C-OH bond cleavage, H bonding to solvent molecules, etc.) and associated issues with the computational modeling protocol. The computed ΔG^{\ddagger} values indicate that H bonding to solvent molecules has a significant effect on C-OH bond cleavage in the protonation-first pathway and coincides well with the experimental observations, whereas the effect is insignificant in the reduction-first pathway (Table S8 in the Supporting Information). This indicates that the H bonding of solvent molecules with proton sources (e.g., H₂O, MeOH, PhOH) and $[Re-CO_2H]$ (or $[Re-CO_2H]^-$) intermediate and competition in between those could at least partially be responsible in the CO₂ reduction activity trend in ACN, DMF, and DMSO.

Upon conversion of CO_2 to CO, a rhenium complex of the form $[Re(diimine)(CO)_4]^+$ is formed. These complexes are generally stable and can remain in solution unchanged for several hours. The DFT calculations indicate that upon one electron reduction of $[Re(diimine)(CO)_4]^+$ the CO ligand stays bound resulting in $[Re(diimine)(CO)_4]$. However, further reduction results in spontaneous dissociation of CO to generate the pentacoordinate $[Re(diimine)(CO)_3]^-$ species. Our experimental evidence corroborates that the reduction of the tetracarbonyl complex catalyzes the labilization of a carbonyl ligand, similar to the behavior of the analog $[Re(bpy)-(CO)_4]^{-,69}$ regenerating the active species.

In comparison with I and other analogues such as $\operatorname{Re}(^{t-\operatorname{Bu}}\operatorname{bpy})(\operatorname{CO})_3\operatorname{Cl}(^{t-\operatorname{Bu}}\operatorname{bpy} = 4,4'-\operatorname{di}-tert-\operatorname{butyl}-2,2'-\operatorname{bipyridine}),^{30}$ the rhenium pyridine-oxazoline complexes show similar electrochemical behavior under an inert atmosphere, as highlighted by the cyclic voltammetry and IR-SEC studies. However, their reactivity toward CO₂ present important differences that should be highlighted. $\operatorname{Re}(^{t-\operatorname{Bu}}\operatorname{bpy})(\operatorname{CO})_3\operatorname{Cl}$ is the fastest catalyst with a reported second-order rate constant of 650 M⁻¹ s⁻¹,³⁰ 3 times the rate constant of 1, the fastest catalyst in the series presented here. 1 is, nevertheless, more active than other $\operatorname{Re}(\operatorname{bpy})(\operatorname{CO})_3\operatorname{Cl}$ derivatives containing

electron-withdrawing substituents or electron-donating substituents on the 2,2'-bipyridine ligand, namely $-CO_2H$, $-CH_3$, and $-OCH_3$.³⁰ The better activity of Re(^{t-Bu}bpy)(CO)₃Cl in comparison to other analogues of 1 has been hypothesized to partially arise from the lower tendency to form a rhenium dimer containing a metal-metal bond which is less reactive toward CO₂ as compared to the reduced monomer. This does not seem to apply in the case of the pyridine-oxazoline rhenium complexes because 1 is probably more likely to form dimers than 2, since the latter contains a methyl substituent on the oxazoline moiety.

CONCLUSIONS

We have prepared and characterized a new family of mononuclear complexes of the general formula Re(pyridineoxazoline)(CO)₃Cl, which were demonstrated to electrocatalytically reduce CO₂ to form CO. Two of our new catalysts display relative turnover frequencies, $(i_{cat}/i_p)^2$, superior to that of the known Re(bpy)(CO)₃Cl (I). The faster reaction rates are due to the presence of the oxazoline ligand, which is a better σ donor than pyridine. These complexes, however, are less stable than I under reducing conditions and show decreased Faradaic efficiency. The reaction rates of the rhenium pyridineoxazoline complexes are affected by the solvent donor number. This behavior can be explained by postulating that the largest effective barrier corresponds to the C-OH bond cleavage step, in line with the computational results. DFT calculations provide detailed mechanistic information for the reaction cycle and predict the C-OH bond cleavage from metallocarboxylate intermediates as the rate-limiting step. Moreover, the computed ΔG^{\ddagger} values using explicit solvent molecules predict that the observed solvent dependence likely arises from the protonation-first pathway and not from the reduction-first pathway. However, the latter prediction requires further testing. Future work will focus on stabilizing the oxazoline ring and fully understanding the effect of the solvent and proton donors on the rate-determining transition state(s).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02384.

¹H NMR, ¹³C NMR, cyclic voltammograms, and computational data (PDF) Crystallographic data (CIF) Crystallographic data (CIF) Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) IPCC 2014: Climate Change 2014 Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; IPCC: Geneva, Switzerland, 2014.

(2) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO2 Fixation. *Chem. Rev.* **2013**, *113*, 6621–6658.

(3) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81.

(4) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. Thermodynamics and kinetics of CO_2 , CO, and H⁺ binding to the metal center of CO_2 reduction catalysts. *Chem. Soc. Rev.* **2012**, *41*, 2036–2051.

(5) Fisher, B. J.; Eisenberg, R. Electrocatalytic reduction of carbon dioxide by using macrocycles of nickel and cobalt. *J. Am. Chem. Soc.* **1980**, *102*, 7361–3.

(6) Hawecker, J.; Lehn, J.-M.; Ziessel, R. Efficient photochemical reduction of CO_2 to CO by visible light irradiation of systems containing $Re(bipy)(CO)_3X$ or $Ru(bipy)_3^{2+}-Co^{2+}$ combinations as homogeneous catalysts. J. Chem. Soc., Chem. Commun. **1983**, 536–538.

(7) Lieber, C. M.; Lewis, N. S. Catalytic reduction of carbon dioxide at carbon electrodes modified with cobalt phthalocyanine. *J. Am. Chem. Soc.* **1984**, *106*, 5033–4.

(8) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. Carbon dioxide activation: thermodynamics of carbon dioxide binding and the involvement of two cobalt centers in the reduction of carbon dioxide by a cobalt(I) macrocycle. *J. Am. Chem. Soc.* **1988**, *110*, 4870–4871.

(9) Aresta, M.; Quaranta, E.; Tommasi, I. Reduction of coordinated carbon dioxide to carbon monoxide via protonation by thiols and other Broensted acids promoted by nickel systems: a contribution to the understanding of the mode of action of the enzyme carbon monoxide dehydrogenase. *J. Chem. Soc., Chem. Commun.* **1988**, *0*, 450–452.

(10) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. Electrochemical reduction of carbon dioxide catalyzed by [Pd(triphosphine)(solvent)]- $(BF_4)_2$ complexes: synthetic and mechanistic studies. *J. Am. Chem. Soc.* **1991**, *113*, 8753–64.

(11) Schneider, J.; Jia, H.; Kobiro, K.; Cabelli, D. E.; Muckerman, J. T.; Fujita, E. Nickel(II) macrocycles: highly efficient electrocatalysts for the selective reduction of CO_2 to CO. *Energy Environ. Sci.* **2012**, *5*, 9502–9510.

(12) Costentin, C.; Drouet, S.; Robert, M.; Saveant, J.-M. A Local Proton Source Enhances CO_2 Electroreduction to CO by a Molecular Fe Catalyst. *Science* **2012**, 338, 90–94.

(13) Smieja, J. M.; Sampson, M. D.; Grice, K. A.; Benson, E. E.; Froehlich, J. D.; Kubiak, C. P. Manganese as a Substitute for Rhenium in CO_2 Reduction Catalysts: The Importance of Acids. *Inorg. Chem.* **2013**, *52*, 2484–2491.

(14) Taheri, A.; Berben, L. A. Tailoring Electrocatalysts for Selective CO_2 or H⁺ Reduction: Iron Carbonyl Clusters as a Case Study. *Inorg. Chem.* **2016**, *55*, 378–385.

(15) Manbeck, G. F.; Muckerman, J. T.; Szalda, D. J.; Himeda, Y.; Fujita, E. Push or Pull? Proton Responsive Ligand Effects in Rhenium Tricarbonyl CO_2 Reduction Catalysts. *J. Phys. Chem. B* **2015**, *119*, 7457–7466.

(16) Hawecker, J.; Lehn, J. M.; Ziessel, R. Photochemical and electrochemical reduction of carbon dioxide to carbon monoxide mediated by (2,2'-bipyridine)tricarbonylchlororhenium(I) and related complexes as homogeneous catalysts. *Helv. Chim. Acta* **1986**, *69*, 1990–2012.

(17) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. One- and two-electron pathways in the electrocatalytic reduction of CO_2 by fac-Re(bpy)(CO)₃Cl (bpy = 2,2[prime or minute]-bipyridine). *J. Chem. Soc., Chem. Commun.* **1985**, 1414–1416. (18) Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. CO_2 Capture by a Rhenium(I) Complex with the Aid of Triethanolamine. *J. Am. Chem. Soc.* **2013**, 135, 16825–16828.

(19) Sato, S.; Sekine, A.; Ohashi, Y.; Ishitani, O.; Blanco-Rodriguez, A. M.; Vlcek, A., Jr.; Unno, T.; Koike, K. Photochemical Ligand Substitution Reactions of fac- $[Re(bpy)(CO)_3Cl]$ and Derivatives. *Inorg. Chem.* **2007**, *46*, 3531–3540.

(20) Schneider, T. W.; Angeles-Boza, A. M. Competitive ${}^{13}C$ and ${}^{18}O$ kinetic isotope effects on CO₂ reduction catalyzed by Re(bpy)-(CO)₃Cl. *Dalton Trans.* **2015**, *44*, 8784–8787.

(21) Schneider, T.; Ertem, M. Z.; Muckerman, J. T.; Angeles-Boza, A. M. Mechanism of Photocatalytic Reduction of CO_2 by Re(bpy)-(CO)₃Cl from Differences in Carbon Isotope Discrimination. ACS Catal. **2016**, *6*, 5473–5481.

(22) Keith, J. A.; Grice, K. A.; Kubiak, C. P.; Carter, E. A. Elucidation of the selectivity of proton-dependent electrocatalytic CO_2 reduction by fac-Re(bpy)(CO)₃Cl. J. Am. Chem. Soc. **2013**, 135, 15823–15829. (23) Benson, E. E.; Sampson, M. D.; Grice, K. A.; Smieja, J. M.; Froehlich, J. D.; Friebel, D.; Keith, J. A.; Carter, E. A.; Nilsson, A.; Kubiak, C. P. The Electronic States of Rhenium Bipyridyl Electrocatalysts for CO_2 Reduction as Revealed by X-ray Absorption Spectroscopy and Computational Quantum Chemistry. Angew. Chem., Int. Ed. **2013**, 52, 4841–4844.

(24) Riplinger, C.; Sampson, M. D.; Ritzmann, A. M.; Kubiak, C. P.; Carter, E. A. Mechanistic Contrasts between Manganese and Rhenium Bipyridine Electrocatalysts for the Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **2014**, *136*, 16285–16298.

(25) Agarwal, J.; Johnson, R. P.; Li, G. Reduction of CO_2 on a Tricarbonyl Rhenium(I) Complex: Modeling a Catalytic Cycle. J. Phys. Chem. A **2011**, 115, 2877–2881.

(26) Agarwal, J.; Sanders, B. C.; Fujita, E.; Schaefer Iii, H. F.; Harrop, T. C.; Muckerman, J. T. Exploring the intermediates of photochemical CO_2 reduction: reaction of Re(dmb)(CO)₃ COOH with CO_2 . *Chem. Commun.* **2012**, *48*, 6797–6799.

(27) Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. Mechanisms for CO Production from CO₂ Using Reduced Rhenium Tricarbonyl Catalysts. J. Am. Chem. Soc. **2012**, 134, 5180–5186.

(28) Grice, K. A.; Kubiak, C. P. Recent studies of rhenium and manganese bipyridine carbonyl catalysts for the electrochemical reduction of CO₂. *Adv. Inorg. Chem.* **2014**, *66*, 163–188.

(29) Riplinger, C.; Carter, E. A. Influence of Weak Bronsted Acids on Electrocatalytic CO_2 Reduction by Manganese and Rhenium Bipyridine Catalysts. *ACS Catal.* **2015**, *5*, 900–908.

(30) Smieja, J. M.; Kubiak, C. P. Re(bipy-tBu)(CO)₃Cl-improved Catalytic Activity for Reduction of Carbon Dioxide: IR-Spectroelec-trochemical and Mechanistic Studies. *Inorg. Chem.* **2010**, *49*, 9283–9289.

(31) Klein, A.; Vogler, C.; Kaim, W. The δ in 18 + δ Electron Complexes: Importance of the Metal/Ligand Interface for the Substitutional Reactivity of "Re(0)" Complexes (α -diimine)-Re^I(CO)₃(X). Organometallics **1996**, 15, 236–44.

(32) Paolucci, F.; Marcaccio, M.; Paradisi, C.; Roffia, S.; Bignozzi, C. A.; Amatore, C. Dynamics of the Electrochemical Behavior of Diimine Tricarbonyl Rhenium(I) Complexes in Strictly Aprotic Media. *J. Phys. Chem. B* **1998**, *102*, 4759–4769.

(33) Grice, K. A.; Saucedo, C. Electrocatalytic Reduction of CO_2 by Group 6 $M(CO)_6$ Species without "Non-Innocent" Ligands. *Inorg. Chem.* **2016**, *55*, 6240–6246.

(34) McManus, H. A.; Guiry, P. J. Recent Developments in the Application of Oxazoline-Containing Ligands in Asymmetric Catalysis. *Chem. Rev.* **2004**, *104*, 4151–4202.

(35) Stanton, C. J., III; Machan, C. W.; Vandezande, J. E.; Jin, T.; Majetich, G. F.; Schaefer, H. F., III; Kubiak, C. P.; Li, G.; Agarwal, J. Re(I) NHC Complexes for Electrocatalytic Conversion of CO₂. *Inorg. Chem.* **2016**, *55*, 3136–3144.

(36) Liyanage, N. P.; Dulaney, H. A.; Huckaba, A. J.; Jurss, J. W.; Delcamp, J. H. Electrocatalytic Reduction of CO_2 to CO With Re-Pyridyl-NHCs: Proton Source Influence on Rates and Product Selectivities. *Inorg. Chem.* **2016**, *55*, 6085–6094.

(37) Machan, C. W.; Chabolla, S. A.; Kubiak, C. P. Reductive Disproportionation of Carbon Dioxide by an Alkyl-Functionalized Pyridine Monoimine Re(I) *fac*-Tricarbonyl Electrocatalyst. *Organometallics* **2015**, *34*, 4678–4683.

(38) Sinha, S.; Berdichevsky, E. K.; Warren, J. J. Electrocatalytic CO_2 reduction using rhenium(I) complexes with modified 2-(2-pyridyl)imidazole ligands. *Inorg. Chim. Acta* **2016**, DOI: 10.1016/ j.ica.2016.09.019.

(39) Stokes, B. J.; Opra, S. M.; Sigman, M. S. Palladium-catalyzed allylic cross-coupling reactions of primary and secondary homoallylic electrophiles. J. Am. Chem. Soc. 2012, 134, 11408–11.

(40) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8.

(41) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(42) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(43) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–96.

(44) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Energy-adjustedab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta* **1990**, *77*, 123–141.

(45) Hehre, W. J. AB INITIO Molecular Orbital Theory; Wiley: New York, 1986.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc., Wallingford, CT, USA, 2009.

(47) Cramer, C. J. Essentials of Computational Chemistry: Theories and Models; Wiley: Hoboken, NJ, 2013.

(48) Isse, A. A.; Gennaro, A. Absolute Potential of the Standard Hydrogen Electrode and the Problem of Interconversion of Potentials in Different Solvents. J. Phys. Chem. B 2010, 114, 7894–7899.

(49) Becke, A. D. Density-Functional Thermochemistry. The Role Of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(50) Zhao, Y.; Truhlar, D. G. The Minnesota Density Functionals and their Applications to Problems in Mineralogy and Geochemistry. *Rev. Mineral. Geochem.* **2010**, *71*, 19–37.

(51) Riplinger, C.; Neese, F. An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* **2013**, 138, 034106.

(52) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.

(53) Pantazis, D. A.; Chen, X. Y.; Landis, C. R.; Neese, F. All-electron scalar relativistic basis sets for third-row transition metal atoms. *J. Chem. Theory Comput.* **2008**, *4*, 908–919.

(54) Neese, F. The ORCA program system. Wires Comput. Mol. Sci. 2012, 2, 73–78.

(55) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Regular 2-Component Hamiltonians. *J. Chem. Phys.* **1993**, *99*, 4597– 4610.

(56) Vanlenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Total-Energy Using Regular Approximations. *J. Chem. Phys.* **1994**, *101*, 9783–9792.

(57) VanLenthe, E.; Snijders, J. G.; Baerends, E. J. The zero-order regular approximation for relativistic effects: The effect of spin-orbit coupling in closed shell molecules. *J. Chem. Phys.* **1996**, *105*, 6505–6516.

(58) van Wullen, C. Molecular density functional calculations in the regular relativistic approximation: Method, application to coinage metal diatomics, hydrides, fluorides and chlorides, and comparison with first-order relativistic calculations. *J. Chem. Phys.* **1998**, *109*, 392–399.

(59) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 2011, 32, 1456–1465.

(60) Hevia, E.; Perez, J.; Riera, V.; Miguel, D.; Kassel, S.; Rheingold, A. New synthetic routes to cationic rhenium tricarbonyl bipyridine complexes with labile ligands. *Inorg. Chem.* **2002**, *41*, 4673–9.

(61) Kraihanzel, C. S.; Cotton, F. A. Vibrational Spectra and Bonding in Metal Carbonyls. II. Infrared Spectra of Amine-Substituted Group VI Carbonyls in the CO Stretching Region. *Inorg. Chem.* **1963**, *2*, 533–540.

(62) Cotton, F. A. Vibrational Spectra and Bonding in Metal Carbonyls. III. Force Constants and Assignments of CO Stretching Modes in Various Molecules; Evaluation of CO Bond Orders. *Inorg. Chem.* **1964**, *3*, 702–711.

(63) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. Photophysical properties of polypyridyl carbonyl complexes of rhenium(I). *J. Chem. Soc., Dalton Trans.* **1991**, 849–858.

(64) Grupp, A.; Bubrin, M.; Ehret, F.; Kvapilova, H.; Zalis, S.; Kaim, W. Oxidation and reduction response of α -diimine complexes with tricarbonylrhenium halides and pseudohalides. *J. Organomet. Chem.* **2014**, 751, 678–685.

(65) Kaim, W.; Kohlmann, S. The nature of reduced and excited states of p-electron-deficient complexes between tricarbonylhalorhenium and diimine ligands. *Inorg. Chem.* **1990**, *29*, 2909–2914.

(66) Appel, A. M.; Helm, M. L. Determining the overpotential for a molecular electrocatalyst. *ACS Catal.* **2014**, *4*, 630–633.

(67) Saveant, J.-M. Molecular Catalysis of Electrochemical Reactions. Mechanistic Aspects. *Chem. Rev.* **2008**, *108*, 2348–2378.

(68) Rountree, E. S.; McCarthy, B. D.; Eisenhart, T. T.; Dempsey, J. L. Evaluation of Homogeneous Electrocatalysts by Cyclic Voltammetry. *Inorg. Chem.* **2014**, *53*, 9983–10002.

(69) Grice, K. A.; Gu, N. X.; Sampson, M. D.; Kubiak, C. P. Carbon monoxide release catalysed by electron transfer: electrochemical and spectroscopic investigations of $[Re(bpy-R)(CO)_4](OTf)$ complexes relevant to CO₂ reduction. *Dalton Trans.* **2013**, *42*, 8498–8503.

(70) Stor, G. J.; Hartl, F.; van Outersterp, J. W. M.; Stufkens, D. J. Spectroelectrochemical (IR, UV/Vis) Determination of the Reduction Pathways for a Series of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})L']^{0/+}$ (L' = Halide, OTf-, THF, MeCN, n-PrCN, PPh₃, P(OMe)₃) Complexes. Organometallics **1995**, *14*, 1115–1131.

(71) Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. An in situ infrared study of CO_2 reduction catalysed by rhenium tricarbonyl bipyridyl derivatives. *J. Chem. Soc., Dalton Trans.* **1992**, 1455–1463.

(72) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. Electrocatalytic Reduction of CO₂ Using the Complexes [Re(bpy)-(CO)₃L]n (n = + 1, L = P(OEt)₃, CH₃CN; n = 0, L = Cl-, OTF; bpy = 2,2'-Bipyridine; OTf- = CF₃SO₃) as Catalyst Precursors: Infrared Spectroelectrochemical Investigation. *Organometallics* **1996**, *15*, 3374–3387.

(73) Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. Manganese catalysts with bulky bipyridine ligands for the electrocatalytic reduction of carbon dioxide: Eliminating dimerization and altering catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 5460–5471.

(74) Zeng, Q.; Tory, J.; Hartl, F. í. Electrocatalytic Reduction of Carbon Dioxide with a Manganese(I) Tricarbonyl Complex Containing a Nonaromatic α -Diimine Ligand. *Organometallics* **2014**, 33, 5002–5008.

(75) Machan, C. W.; Sampson, M. D.; Chabolla, S. A.; Dang, T.; Kubiak, C. P. Developing a Mechanistic Understanding of Molecular Electrocatalysts for CO_2 Reduction using Infrared Spectroelectrochemistry. *Organometallics* **2014**, *33*, 4550–4559.

(76) Marcus, R. A.; Sutin, N. Electron transfers in chemistry and biology. *Biochim. Biophys. Acta, Rev. Bioenerg.* **1985**, *811*, 265–322.

(77) Fawcett, W. R. Acidity and basicity scales for polar solvents. J. Phys. Chem. 1993, 97, 9540–9546.

(78) Gutmann, V. The Donor-Acceptor Approach to Molecular Interactions; Plenum: New York, 1978.

(79) Gutmann, V.; Wychera, E. Coordination reactions in non aqueous solutions - The role of the donor strength. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257–260.

(80) Kozuch, S.; Martin, J. M. L. The Rate-Determining Step is Dead. Long Live the Rate-Determining State! *ChemPhysChem* **2011**, *12*, 1413–1418. Article